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Poly(amide imides) and Poly(ether imides) Containing 1,3,4-Oxadiazole or Pyridine Rings: Characterizations and Optical Properties

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Two series of new aromatic polyimides were synthesized from 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole and 2,5-diamino-pyridine and various diamidedianhydrides and dietherdianhydride via high-temperature polycondensation in *N*-methyl-2-pyrrolidinone. The structures of polymers were characterized by means of FTIR, ^{1}H NMR spectroscopy, and elemental analysis; the results showed an agreement with the proposed structure. The polymers exhibited high glass-transition temperatures (T_g = 199−290 °C) and high thermal stability with decomposition temperatures (T_d) in the range of 437−510 °C. The optical properties, that is, absorption and photoluminescence (PL) of synthesized polymers, were investigated in solution and in solid state as a blend with inert poly(methyl methacrylate) (PMMA). The polymers in solution emitted violet-blue light in the range of 417−453 nm depending on the polymer structure. The polymers containing pyridine rings in the backbone emitted light at a longer wavelength than polymers with oxadiazole units. The effect of solvent polarity on polymer emission was found. Additionally, the photoluminescence properties of the polymers before and after protonation with HCl were tested.

Introduction

Polyimides (PIs) are a class of high-performance polymers that possess the cyclic imide and aromatic groups in the main chain. They are extensively used in microelectronics, photonics, optics, and aerospace industries because of their excellent thermal stability, good mechanical properties, low dielectric constant, low coefficient of thermal expansion, and high radiation resistance.[1,2] Significant effort has been expended to improve their properties further by chemical modification of the chain backbones and higher-order structure control.[3] The development of new technologies has generated a need for the preparation of polymeric materials with specific properties. Nowadays, the development of novel fluorescent materials is an area of intensive research. Photoluminescence (PL) is the most useful process for studying the fundamental behavior of luminescent materials because it allows the greatest control over the excitation conditions. Research has been carried out with the objective of chemically tuning the emission color of polymers and improving the quantum efficiency, stability, and lifetimes.[4] Among many investigated polymer systems such as polyacetylenes, poly(*p*-phenylenes), poly(*p*-phenylene-vinylenes), poly(pyridylene), poly(pyridylenevinylene), poly(oxadiazole), polytriazole, poly(triazine), polyquinoline, polyquinoxaline, poly(4-vinylpyridine), polyaniline, or polypyrrole, PIs are also studied as potential luminescent polymers.[5] Their high glass-transition temperatures and thermal and chemical stability are essential for many applications as emissive materials.[6,7] The PIs consist of two different kinds of chromophores, dianhydride and diamine units. In PIs, the charge at HOMO and LUMO is localized at the electron-donating aminophenyl fragment and the electron-accepting imide fragment.[8] The first approach was to measure the fluorescence spectra of several commercial PI films such as Kapton, Ultem, and Upilex.[1] A literature survey revealed that PIs with moieties such as perylene,[9−11] oxadiazole,[8,12,13] acridine,[14] furyl,[5,15] fluorene,[6,12,14] naphthalene,[11,16,17] antracene,[18] carbazole,[19] pyrene,[20] and triphenylamine[21,22] units were investigated as potential light-emitting materials.

Different strategies have been reported for tuning the emission color of polymers: changing the main-chain molecular structure,[23] changing the side-chain molecular structure,[24] blending a light-emitting polymer with another polymer[25] or with small organic[26] or inorganic molecules,[27] and using multiplayer architectures.[4,28] However, the use of nonconvalent interactions between molecules that possess the desired complementary structural elements is a crucial synthetic tool for obtaining structural variation and specifically physical properties of materials. Protonation is one of the important nonconvalent interactions that plays a fundamental role in polymer properties as well as in the design of new polymer architectures.[29−33]

To obtain the polymer with required properties, the understanding of the relationship between polymer structures and the relevant macroscopic properties is necessary. Therefore, fundamental studies are necessary to produce high-performance novel optofunctional PIs.

Our efforts have been focused on synthesizing specially designed new PIs and investigating the relationship between polymer structure and their optical properties.[34−36] In this study, synthesized polymers that bear 1,3,4-oxadiazole moieties or pyridine rings in the main chain constitute two kind of PIs, that is, poly(amide imides) and poly(ether imides). Compared with a benzene ring, pyridine and oxadiazole rings are electron-deficient aromatic heterocycles with a localized lone pair of electrons in the sp^2 orbital on nitrogen atom; consequently, the derived polymers have increased affinity to improve electron-transporting properties.[20] The presence of a heteroatom with a free electron pair, in this case, the nitrogen atom in oxadiazole

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and pyridine units, gives an opportunity for protonation that may modify optical properties. A protonation concept for tuning the polymer properties is often used for π-conjugated polymers such as polyketanils, polyazomethines, and polyaniline.[29,32] However, to the best of our knowledge, in only one article was protonation with HCl described for PIs.[21] In this Article, we present studies of optical properties, that is, absorption and emission of the PIs in solution and in solid state as a blend with nonemissive PMMA. The effect of excitation wavelength, solution polarity, and polymer concentration in blend on the PL was investigated. Additionally, the modification of the optical properties of PIs by doping with HCl was studied.

Experimental Section

Materials. Trimellitic anhydride acid chloride (TMACl), 4,4′-(1,3-phenylenedioxy)dianiline, 4,4′-methylenebis(2,6-dimethylaniline), 4,4′-(9-fluorenylidene)dianiline, 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole, 2,5-diamino-pyridine, and 4,4′-(4,4′-isopropylidene-diphenoxy)bis(phtalic anhydride), *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO), and other necessary starting chemicals were purchased from Aldrich Chemical and were used as received. Pyridine (Py), *m*-cresol, and tetrahydrofuran (THF) were purified by distillation in the usual manner. Diaminedianhydrides were synthesized on the basis of references.[37−39]

Polymer Synthesis. The synthesis of the polymers was carried out according to the procedure described for other PIs.[40] A solution of equimolar amounts of dianhydride and diamine in a mixture of solvents NMP and 1,2-dichlorobenzne (80/20 v/v, 20% of the total monomer concentration) was stirred at 175 °C for 3.5 h. The solution was poured in methanol. The precipitated polymer was filtered, washed with methanol, and dried. **PI 1**: ^{1}H NMR (DMSO-d_6, δ): 6.45 (d, ArH, 2H); 6.58 (dd, ArH, 2H); 6.72 (d, ArH, 1H); 7.08 (d, ArH, 4H); 7.35(d, ArH, 2H); 7.68 (dd, ArH, 2H); 7.83 (d, ArH, 1H); 8.10 (d, ArH, 4H); 8.25 (d, ArH, 4H); 8.43 (d, ArH, 4H); 10.64 (s, NH, 2H). FTIR (KBr, cm^{-1}): 1780, 1724 (C=O in imide), 1666 (C=O in amide), 1366 (C−N stretching), 740 (C=O bending). Anal. Calcd for $C_{50}H_{28}N_6O_9$: C, 70.09; H, 3.29; N, 9.80. Found: C, 68.31; H, 3.59; N, 9.54. η_{red} (reduced viscosity) = 0.7 dl/g (concentration = 0.2 g per 100 mL of NMP). **PI 2**: ^{1}H NMR (DMSO-d_6, δ): 7.16 (d, ArH, 2H); 7.34 (dd, ArH, 2H); 7.42 (d, ArH, 4H); 7.70−7.76 (m, ArH, 8H); 7.79 (dd, ArH, 2H); 8.14 (dd, ArH, 2H); 8.31 (dd, ArH, 2H); 8.45 (dd, ArH, 2H); 8.53 (dd, ArH, 4H), 10.65 (s, NH, 2H). FTIR (KBr, cm $^{-1}$): 1780, 1724 (C=O in imide), 1666 (C=O in amide), 1366 (C−N stretching), 748 (C=O bending). Anal. Calcd for $C_{57}H_{32}N_6O_7$: C, 74.99; H, 3.53; N, 9.20. Found: C, 71.21; H, 4.10; N, 8.87. η_{red} = 0.59 dl/g (concentration = 0.2 g per 100 mL of NMP). **PI 3**: ^{1}H NMR (DMSO-d_6, δ): 2.19 (s, CH_3, 12H); 3.83 (s, CH_2, 2H); 7.02 (d, ArH, 4H); 7.81 (d, ArH, 2H); 8.33 (dd, ArH, 2H); 8.36 (d, ArH, 4H); 8.49 (d, ArH, 2H); 8.55 (d, ArH, 4H), 10.14 (s, NH, 2H). FTIR (KBr, cm $^{-1}$): 1780, 1721 (C=O in imide), 1666 (C=O in amide), 1365 (C−N stretching), 724 (C=O bending). Anal. Calcd for $C_{49}H_{34}N_6O_7$: C, 71.87; H, 4.19; N, 10.26. Found: C, 68.44; H, 4.45; N, 9.79. **PI 4**: ^{1}H NMR (DMSO-d_6, δ): 2.17 (s, CH_3, 12H); 3.82 (s, CH_2, 2H); 7.01 (d, ArH, 4H); 7.75 (d, ArH, 2H); 8.15 (dd, ArH, 2H); 8.30 (t, ArH, 1H); 8.49 (d, ArH, 2H); 8.54 (d, ArH, 2H), 10.14 (s, NH, 2H). FTIR (KBr, cm $^{-1}$): 1784, 1730 (C=O in imide), 1654 (C=O in amide), 1355 (C−N stretching), 727 (C=O bending). η_{red} = 0.15 dl/g (concentration = 0.2 g per 100 mL of NMP). **PI 5**: ^{1}H NMR (DMSO-d_6, δ): 1.72 (s, CH_3, 6H); 7.12 (d, ArH, 4H); 7.38 (d, ArH, 2H); 7.42 (dd, ArH, 2H); 7.75 (d, ArH, 4H); 7.80 (d, ArH, 2H); 8.00 (d, ArH, 4H), 8.27 (d, ArH, 4H). FTIR (KBr, cm $^{-1}$): 1779, 1724 (C=O in imide), 1364 (C−N stretching), 748 (C=O bending), 1240 (C−O−C in ether group). **PI 6**: ^{1}H NMR (DMSO-d_6, δ): 1.68 (s, CH_3, 6H); 7.10 (d, ArH, 4H); 7.36 (d, ArH, 2H); 7.65 (dd, ArH, 2H); 7.80 (t, ArH, 1H); 7.85 (d, ArH, 2H); 7.96 (d, ArH, 4H), 8.26 (d, ArH, 2H). FTIR (KBr, cm $^{-1}$): 1783, 1730 (C=O in imide), 1374 (C−N stretching), 745 (C=O bending), 1238 (C−O−C in ether group). Anal. Calcd for $C_{36}H_{23}N_3O_6$: C, 72.84; H, 3.90; N, 7.08. Found: C, 69.87; H, 4.10; N, 6.44. η_{red} = 0.13 dl/g (concentration = 0.2 g per 100 mL of NMP).

Preparation of Blends. Polymer blends were obtained by dissolving the desired amount of polymers and PMMA in DMA to form a homogeneous solution. Films cast on glass were dried in a vacuum oven at 90 °C for over 8 h.

Measurements. ^{1}H NMR spectra were recorded on a Varian UNITY Inova 300 spectrometer (DMSO-d_6 solvent with TMS as an internal reference). FTIR spectra were taken with BIO-RAD FTS 40 A spectrometer as KBr pressed pellets. Elemental analysis was determined by a Vario EL III Elementar analyzer. Differential scanning calorimetry (DSC) was performed with a DSC 822^e Mettler Toledo apparatus under nitrogen using a heating/cooling rate of 20 °C$\cdot$min^{-1}. Thermogravimetric analysis (TGA) was done with a TGA/SDTA 851^e Mettler Toledo apparatus with a heating rate of 20 °C$\cdot$min^{-1} under a nitrogen atmosphere. The reduced viscosity was measured in NMP at 25 °C using an Ubbelohde viscometer. UV−vis spectra were recorded using a Jasco V570 UV−V−NIR spectrometer. The PL spectra of polymers in solution, in blends and free-standing film, were monitored on a Hitachi F-2500 spectrometer.

Results and Discussion

In this work, poly(ester imides) and poly(amide imides) with 1,3,4-oxadiazole or pyridine rings were synthesized and characterized. The main goal of this Article was to investigate optical properties, that is, absorption and PL of new PIs with respect to their chemical structures. These polymers were synthesized by direct polycondensation of 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole and 2,5-diamino-pyridine with various prepared diamidedianhydrides having in the structure 1,3-phenylenedioxy, (9,9-fluorenylidene)diphenyl, and methylenebis(2,6-dimethyphenyl) units (**PI 1**−**PI 4**), and with commercial 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride) (**PI 5** and **PI 6**). The chemical structures of the polymers synthesized in this study are presented in Figure 1.

The polymers **PI 1**−**PI 4** and **PI 6** are new compounds, whereas, the poly(ether imide) **PI 5** was described in the literature.[8]

Polymer Characterization. Instrumental techniques including FTIR and ^{1}H NMR spectroscopies were performed for the characterization of the polymer molecular structure. Additionally, the structure of the resulting polymers was characterized by elemental analysis. Because all polymers in this study were prepared by the same polycondensation reaction conditions and because their structures are similar, only four selected polymers (mainly poly(amide imides)) were characterized by elemental analysis. The FTIR spectra of all polymers clearly showed the characteristic absorption bands due to the asymmetric and symmetric stretches of carbonyl group in imide ring at ~ 1784 and ~1724 cm^{-1}, whereas the absorption band at about 1364 cm^{-1} corresponds to the C−N stretching, and that around 740 cm^{-1} corresponds to the imide ring deformation vibration. In FTIR spectra of the poly(amide imides), the absorption band

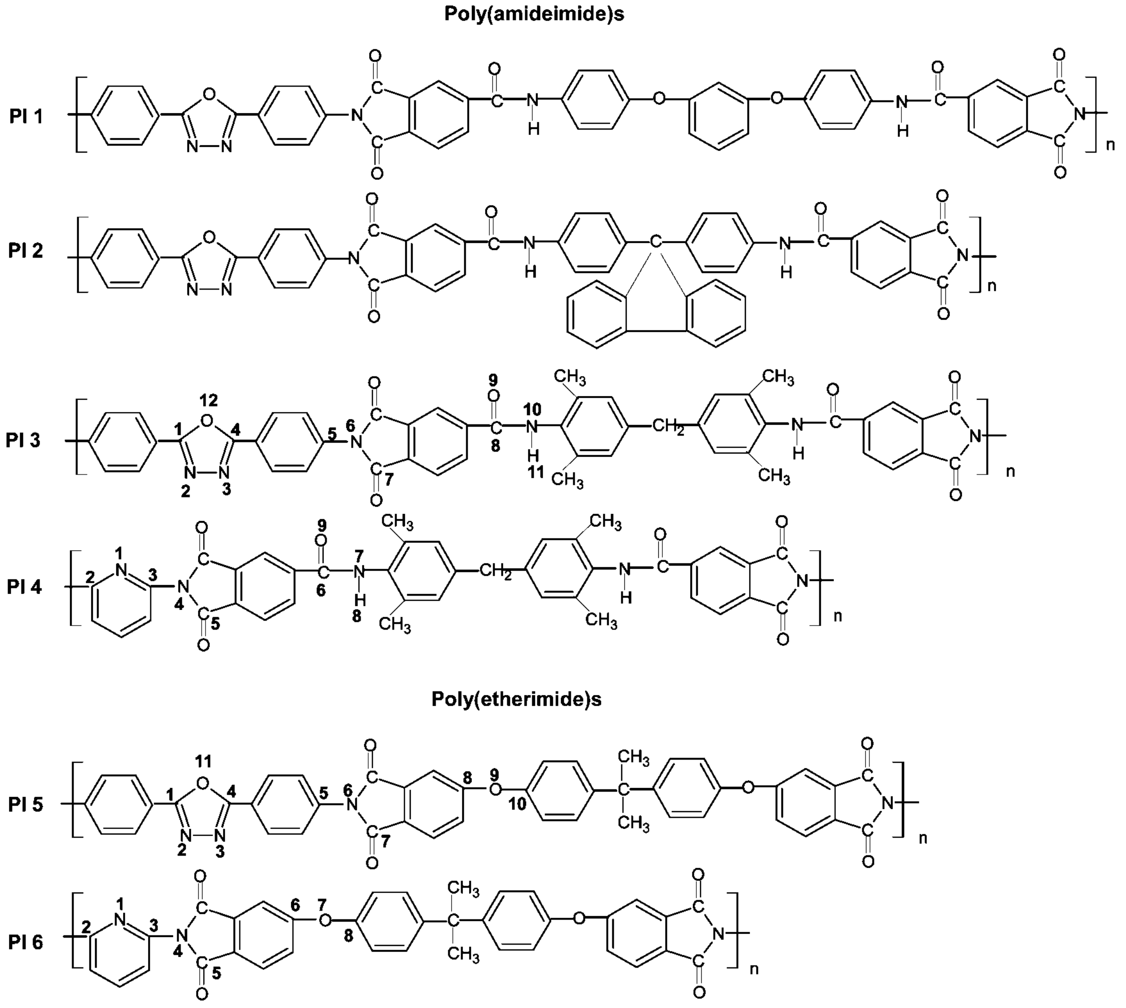

Figure 1. Chemical Structure of the Investigated Polymers.

around 1666 cm^{-1} is assigned to the stretching vibration of carbonyl groups of amide linkages. In the case of poly(ether imides), the peak at about 1240 cm^{-1} appeared because of absorption of ether linkages. The absorption bands at nearly 960 and 1016 cm^{-1} were assigned to oxadiazole rings. In the spectra of polymers **PI 3**−**PI 6**, absorption peaks at 2919 and 2967 cm^{-1} are characteristic of vibration of aliphatic groups. In FTIR spectra of PIs with ether groups (**PI 5** and **PI 6**), no absorption peak characteristic of carbonyl in amide group was observed. The structure of the resulting polymers was also verified by ^{1}H NMR spectroscopy, and all peaks are assigned to the hydrogen atoms of the recurring unit. The singlet at about 10 ppm is assigned to the proton of amide groups. In the case of poly(ether imides) in ^{1}H NMR spectra, no signals corresponding to poly(amic acid) and the carboxylic acid group were observed. The absence of characteristic peaks for poly(amic acid) in FTIR and ^{1}H NMR spectra of poly(ether imides) confirmed the complete imidization to PI. In the case of polymers with amide linkages in the main chain, the ^{1}H NMR and FTIR spectroscopies are not sufficient to confirm the complete imidization. Full imidization in poly(amide imides) was confirmed by elemental analysis. Compared with the calculated content of nitrogen and hydrogen in the proposed structures, the elemental analyses show good agreement. However, a deficiency in carbon content of 1.78−3.78% was observed, and this is likely a result of the difficulties in burning these high-temperature polymers, which was also observed for other thermostable polymers.[41] The obtained results for the polymers are in accordance with the proposed structures.

TABLE 1: Thermal Properties of the Investigated Polyimides

code	T_d (°C)[a]	$T_{10\%}$ (°C)	$T_{15\%}$ (°C)	$T_{20\%}$ (°C)	residue at 800 °C (%)	T_g (°C)
PI 1	477	494	507	519	47	242
PI 2	475	499	514	528	50	290
PI 3	437	464	475	487	50	nd
PI 4	444	478	522	564	55	199
PI 5	505 (514)[b]	516	525	531	43	231 (257)[b]
PI 6	510	521	528	535	57	202

[a] Decomposition temperature based on 5% weight loss. [b] ref 8; nd: not detected.

The polymers were soluble in polar solvents, such as DMF, DMA, NMP, and DMSO, at room temperature and in *m*-cresol and pyridine upon heating.

Thermal Properties. The thermal behavior of polymers was evaluated by TGA under a nitrogen atmosphere and by DSC, and the results are summarized in Table 1.

All poly(ether imides) exhibited a similar TGA pattern in which decomposition proceeded through one step. The decomposition temperature (T_d) (based on 5% weight loss) and 10% weight loss temperatures ($T_{10\%}$), which were usually considered to be the criterion in determining the thermal stability of high-temperature polymers, were in the ranges of 437−510 and 464−521 °C, respectively. Furthermore, the residual weight at

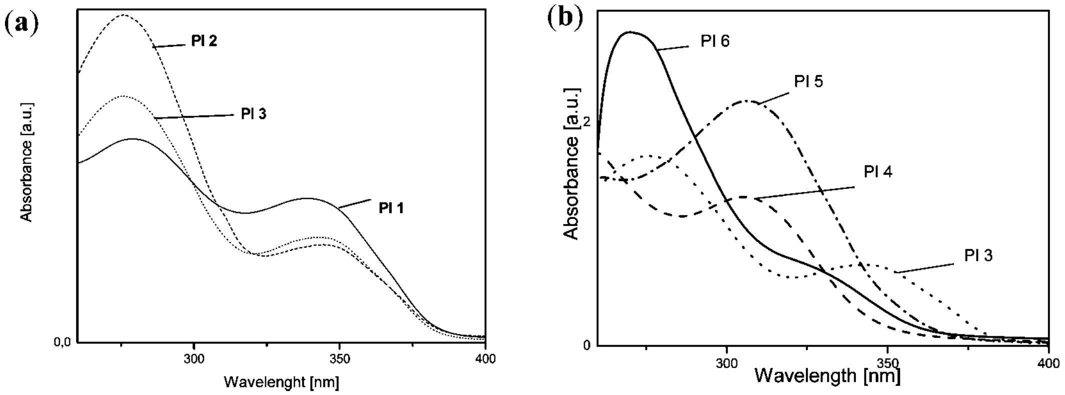

Figure 2. UV−vis absorption spectra of polymers containing oxadiazole rings (a) **PI 1**−**PI 3** and (b) **PI 5** and polymers with pyridine units, **PI 4** and **PI 6**, compared with oxadiazole group **PI 3**.

800 °C in nitrogen was in the range of 43−57%. The effect of the polymer backbone structure on polymer thermal behavior was detected. The polymers containing ether linkages (**PI 5** and **PI 6**) exhibited higher thermal stability in comparison with polymers possessing amide linkages (**PI 1**−**PI 4**). The same influence of ether groups on increasing the temperature of weight loss was also observed in the group of poly(amide imides) with oxadiazole rings; that is, the highest T_d showed the polymer with two ether linkages, **PI 1**. The lower T_d was observed for polymers with oxadiazole rings in comparison with PIs with pyridine units. Taking into account the amount of carbonized residue, this dependency was also pronounced; that is, char yield percent at 800 °C was lower in the polymer with pyridine rings than in the polymer with oxadiazole units. All results indicated that the obtained polymers exhibited high thermal stability.

All synthesized polymers gave similar DSC profiles with no melting endotherms and a clear T_g. These findings clearly indicated their amorphous nature. The DSC curves recorded with repeated heating−cooling cycles allowed the evaluation of T_g values of the investigated polymers in the range of 199−290 °C. It is obvious that they depend on the structure of the polymers. Taking into account the polymer backbone microstructure, it was found that fluorenylidene diphenyl units in poly(amide imides) (**PI 2**) significantly increased the value of T_g. However, the introduction of pyridine rings to the polymer backbone caused a decrease in the T_g value in comparison with the T_g of polymers with oxadiazole units.

Optical Properties. The optical properties of the studied polymers were analyzed by UV−vis and PL spectroscopies. The solvatochromic behavior of the polymers in various solvents with a different dipole moment and consequently with a different polarity was studied. For a chosen polymer, the effect of excitation wavelength on PL properties was also examined. Optical properties of the polymers in the solid state as a blend with nonemissive poly(methyl methacrylate) (PMMA) were investigated as well. Additionally, the UV−vis and PL properties of the PIs before and after protonation with HCl were tested.

Ultraviolet−Visible Investigations. The UV−vis spectra of the investigated polymers in NMP solution are given in Figure 2.

Electronic spectra of the studied polymers exhibited similar characteristics with two absorption bands. The absorption band at lower energy is due to π-π^* transition in the polymer chain.[1] Polymers differ in the position of absorption maxima in relation to the backbone structure. The UV−vis spectra of poly(amide imides) obtained from different dianhydrides and the same diamine were similar (cf. Figure 2a). However, the differences in the intensity of their π-π^* bands were seen. It was observed that the structure of diamine applied to polymer synthesis exhibited basic influence on the position of absorption bands. Absorption spectra of the polymers prepared from 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole (**PI 3** and **PI 5**) and 2,5-diaminopyridine (**PI 4** and **PI 6**) were different (cf. Figure 2b). Absorption spectral data of studied polymers are summarized in Table 2.

TABLE 2: UV−Vis Absorption Characterization of the Polymers in NMP Solution

	UV−vis			
	before protonation		after protonation with HCl	
code	λ_{max} (nm)	ε_{max} (L·mol^{-1}·cm^{-1})[a]	λ_{max} (nm)	ε_{max} (L·mol^{-1}·cm^{-1})[a]
PI 1	279, 338	14.1, 9.9		
PI 2	276, 344	22.6, 6.8		
PI 3	276, 342	16.9, 7.2	324	5.4
PI 4	262, 306	3.4, 2.6	271, 297	1.8, 2.1
PI 5	261, 306	3.0, 4.4	274, 325	3.2, 5.2
PI 6	270, 330	5.6, 1.3	268, 297	3.0, 3.1

[a] Extinction coefficient × 10^{-4} at absorption maxima.

The smallest and the largest differences in the values of the molecular extinction coefficients between two absorption bands are observed for polymers **PI 4** and **PI 2**. The blue shift (24 nm) of the second band of the absorption maximum (λ_{max}) occurred between the poly(ether imide) containing pyridine units (**PI 6**) and the polymer with oxadiazole rings (**PI 5**). Whereas in the case of poly(amide imides), the opposite situation took place; that is, the polymer with pyridine units (**PI 4**) exhibited a red shift (37 nm) of the λ_{max} position in comparison with the polymer containing oxadiazole moieties (**PI 3**). The observed changes in the optical absorption spectra when the backbone structure is varied can be attributed to the modification of the polymer chain planarity.

The solvatochromic behavior of exemplary polymer, that is, **PI 5** in various solvents with a different dielectric constant (ε) and consequently with a different polarity, was investigated. UV−vis spectra of **PI 5** in following solvents were recorded: NMP ($\varepsilon = 33.0$), DMSO ($\varepsilon = 46.7$), THF ($\varepsilon = 7.58$), pyridine ($\varepsilon = 12.4$), and *m*-cresol ($\varepsilon = 11.8$). The spectral range of UV−vis measurements was limited by the transparency of the used solvents.

Taking into consideration the obtained results that are demonstrated in Figure 3, despite the different polarity of applied solvents, the spectra showed a λ_{max} position at almost the same of wavelength. Therefore, the solvatochromic effect was not observed in the studied polymer.

Photoluminescence Investigations. Many factors can influence the PL: the polymer chain architecture, the various chain

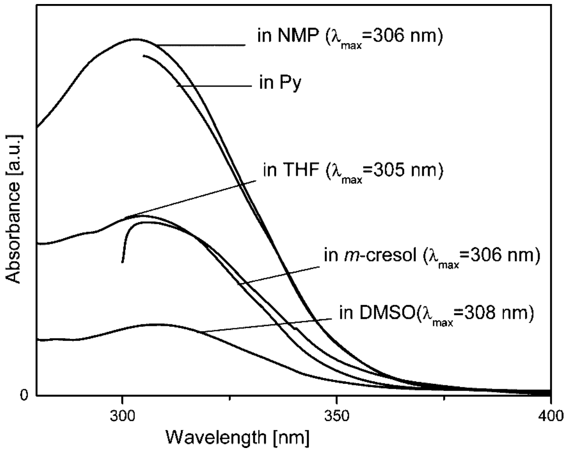

Figure 3. UV−vis spectra of **PI 5** recorded in various solvents.

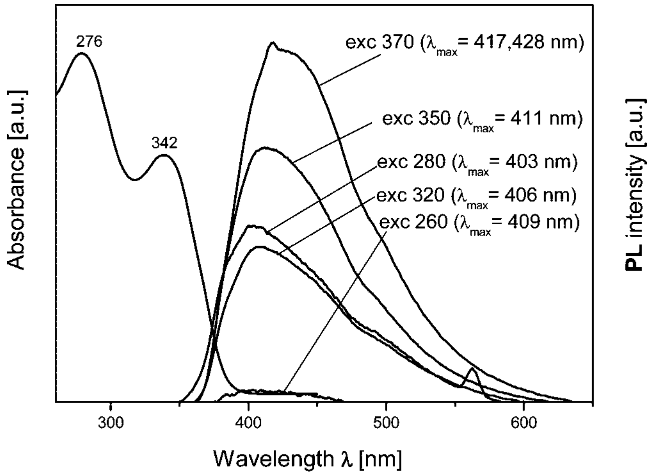

Figure 4. Emission spectra of the polymer **PI 3** under various excitation wavelength.

conformations, and possibilities of interaction with surroundings as solvents, dopands, or blending polymers. In this work, emission spectra were considered from the following main points of view: (i) changing the main-chain molecular structure, (ii) blending a light-emitting polymer with another nonemissive polymer, and (iii) doping. Moreover, for chosen polymers, the influence of excitation wavelength and the kind of solvent on the fluorescence was investigated. Additionally, the emission properties of one polymer with different concentration in blend were compared with Pl spectrum of free-standing film.

In the first step of investigation, some of the polymers **PI 3**−**PI 6** in NMP solution were excited with a different wavelength to establish conditions that provide the best fluorescence spectrum. In most cases, excited wavelength was equal to the maximum of absorption, which provides the best fluorescence spectrum.[4,42] Figure 4 presents the emission spectra of the exemplary polymer **PI 3** under various excitation wavelength.

Taking into account the relative emission intensity, the fluorescence spectrum with the highest emissions was obtained; then, the polymer solution was excited at 350 and 370 nm. The excited wavelength at 350 nm is almost equal to maximum absorption, which should give the best PL spectrum. In the case of studied polymers, the highest PL intensity was observed under excitation at 370 nm, laying at the slope of absorption band. However, when excitation at longer wavelength was used, the emission spectrum of **PI 3** was resolved into two peaks, which may be a vibronic structure instead of two separate peaks.[4] With an increase in the excitation wavelength, the PL spectra showed a red shift that can be attributed to a strong correspondence between excitation energy and the vibronic structure of the emission spectra.[4] With respect to obtained results, all polymers were excited at 350 and 370 nm. The PL properties of the investigated polymers in NMP solution are collected in Table 3.

In general, the PL spectra of the most-investigated polymers in NMP solution dominated double emission peaks. The shape of the band was not symmetrical, and a broad "tail" toward a longer wavelength was observed. Polymers emitted light at longer wavelength under shorter excitation wavelength. Both poly(amide imides) and poly(ether imides), which contain pyridine units in the polymer backbone, emitted a longer wavelength than did polymers with oxadiazole rings. In most cases, the polymer solutions emitted violet-blue light (exc. 370 nm). The group of poly(amide imides) obtained from 2,5-bis(4-aminophenyl)-1,3,4-oxadiazole polymer having in their structure 1,3-phenylenedioxy units (**PI 1**) emitted light at the longest wavelengths. The polymers that contained pyridine rings emitted blue light.

The Stokes shift is generated by electronic or geometrical structure relaxation of the photoexcited molecule,[43] which is induced by the intramolecular charge transfer process.[1] This information suggests a significant conformational difference between an absorbing ground state (S_0) and the emitting excited state (S_1).[19] However, from a practical point of view, if the Stokes shift is too small, then the emitted light will be self-absorbed and the luminescence efficiency will decrease in devices.[13] All studied polymers exhibited large Stokes shifts. The calculated Stokes shift values for the investigated polymers (Table 3) indicated significant differences in the energy loss, which occurred during the transition from S_0 to S_1.The highest values were observed for the poly(amide imide) with pyridine rings (**PI 4**) relative to the other polymers.

The effect of solution on the PL properties of the polymer **PI 2** was investigated in solvents that differed in polarity. The emission spectra of **PI 2** in the following solvents were recorded: DMSO, NMP, pyridine, and *m*-cresol. The emission intensity decreased as the medium changed from DMSO to *m*-cresol. It is expected that the relative PL intensity will increase as we change from a less polar to highly polar solvent.[18] By increasing the dielectric constant (ε) of the solvent, the shield between molecules increases, and consequently, PL self-quenching between neighboring polymer molecules diminishes.[18] According to this assumption, the relative PL intensity should follow the trend based on the dielectric constant (ε) series of solvents; that is, DMSO ($\varepsilon = 46.7$) > NMP ($\varepsilon = 33.0$) > pyridine ($\varepsilon = 12.4$) > *m*-cresol ($\varepsilon = 11.8$). The fluorescence band maxima of the polymer **PI 2** in different solvents were in a similar range.

The fluorescence characteristics of some polymers (**PI 1**, **PI 2**, **PI 4**, and **PI 6**) in solid state in the form of blends with PMMA and as a solid free-standing film (**PI 1**) were studied. The maxima of emission in blends containing 1% of polymer are presented in Table 3.

The PL spectra of the polymers in blends changed heavily compared with their spectra in solution. In comparison with the polymer solution, the emission of blends was more intensive because of the dilution effect. The PL maxima of polymer blends were red-shifted relative to those of solutions and become broad. It is very probable that the large bathochromic shifts of the emission maximum in the conjugated polymer in the solid state compared with that in solution might be explained by considering molecular packing. In blends, chains are able to achieve en

TABLE 3: Photoluminescence Properties of the Investigated Polymer[a]

	in blend with PMMA (1% w/w)		in NMP							
			pristine				HCl doped			
	exc = 350 nm	exc = 370 nm	exc = 350 nm		exc = 370 nm		exc = 350 nm		exc = 370 nm	
code	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)	$\Delta\nu$ (cm^{-1})[b]	λ_{max} (nm)	$\Delta\nu$ (cm^{-1})[b]	λ_{max} (nm)	$\Delta\nu$ (cm^{-1})[b]	λ_{max} (nm)	$\Delta\nu$ (cm^{-1})[b]
PI 1	468, **493**	468, **493**			417, **445**	7114				
PI 2	**417**	**445**, 495			417, **436**	6135				
PI 3			**411**	4909	417, **428**	5875	**407**	6294	**418**	6941
PI 4	407, 493	435, 495	391, **440**	9952	417, **450**	10458	**397**	8482	**407**	9100
PI 5			393, **406**	8049	417, **435**	9691	385, **405**	6078	417, **435**	7781
PI 6	**451**, 495	**450,** 495	392, **406**	5672	417, **453**	8228	**394**	8290	**410**	9280

[a] Bold data indicate the main peak. [b] Stokes shift calculated for main peaks according to the equation $\Delta\nu_{abs} - \nu_{emis} = (1/\lambda_{abs} - 1/\lambda_{emis}) \times 10^7$ (cm^{-1}).

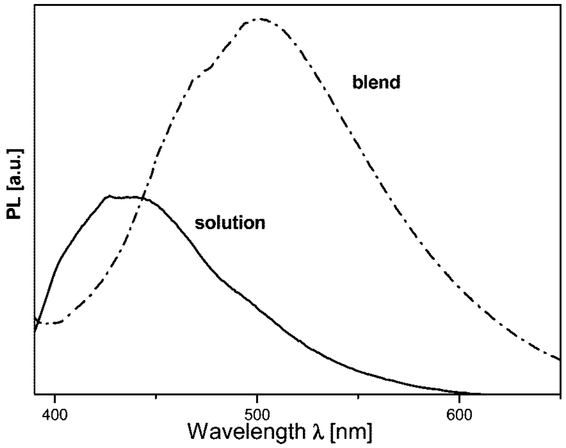

Figure 5. Emission spectra of the polymer **PI 2** in solution and in blend.

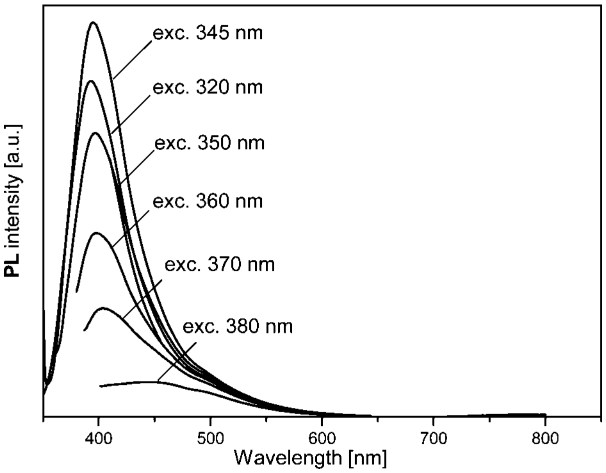

Figure 6. PL spectra of the polymer **PI 3** in blend with PMMA (1% polymer concentration) under various excitation wavelength.

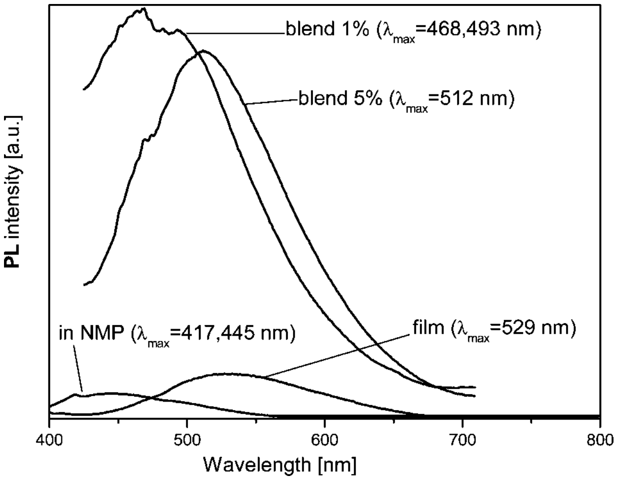

Figure 7. PL spectra of polymer **PI 1** in NMP solution, in blends (1 and 5% polymer concentration), and in free-standing film.

equilibrium morphology, adopting under photoexcitation energetically more favorable conformation and transforming into lower energy states.[4] A typical PL spectrum of exemplary polymer **PI 2** in NMP solution and in blends with PMMA is presented in Figure 5.

The influence of excitation wavelength on PL properties of bends was investigated. The polymer **PI 3** in blend with PMMA (1% polymer concentration) was excited with a different wavelength (Figure 6).

Taking into account the relative emission intensity, the fluorescence spectrum with the highest emissions was obtained; then, the blend was excited at 345 nm. The increase in the excitation wavelength caused a significant decrease in PL intensity.

The influence of polymer concentration in blend on PL spectra was examined as well. The emission spectra of blends containing 1 and 5% of the polymer **PI 1** were recorded. Additionally, the PL spectrum of the polymer **PI 1** as a free-standing film was acquired. The results are compared in Figure 7. The free-standing film was obtained by casting of the polymer **PI 1** in NMP solution (concentration 10%) on glass substrate and sequential heating to 180 °C during 8 h in vacuum. The thickness of the free-standing film was about 20 μm.

The position and intensity of the emission band were significantly different in relation to the polymer form (blend, film, or solution). Figure 7 shows that the emission spectra of polymer **PI 1** were red shifted from that of the polymer in solution, indicating that a stronger intermolecular interaction occurred in the solid state. In addition, the vibronic structures observed in the solution PL spectrum disappeared in the free-standing film spectrum. Polymer blends exhibited the highest intensity of emission in relation to solution and free-standing film because of the dilution effect. It is understood that the excitons are confined in isolated chain segments within the blend, and the chances for exciton quenching by migration to quenching sites are reduced.[5]

Protonation of Polymers. The optical properties of the polyimides **PI 3**−**PI 6** doped with HCl were investigated. Protonation of the polymers with HCl was carried out at room temperature in NMP solution. In the case of polymers with pyridine rings, the molar ratio of the dopant to the mer unit of

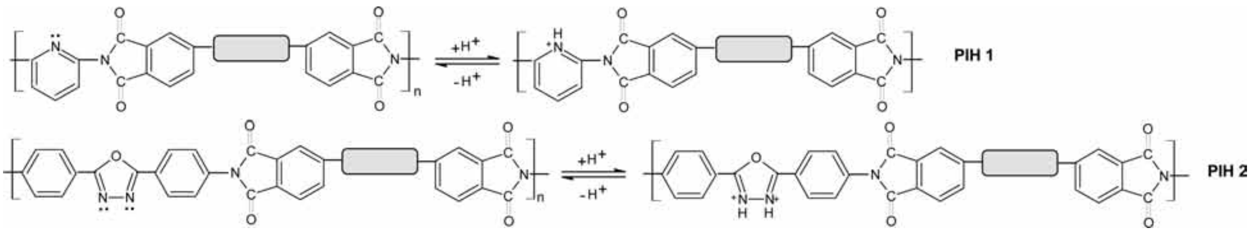

Figure 8. Proposed protonation of the polyimides.

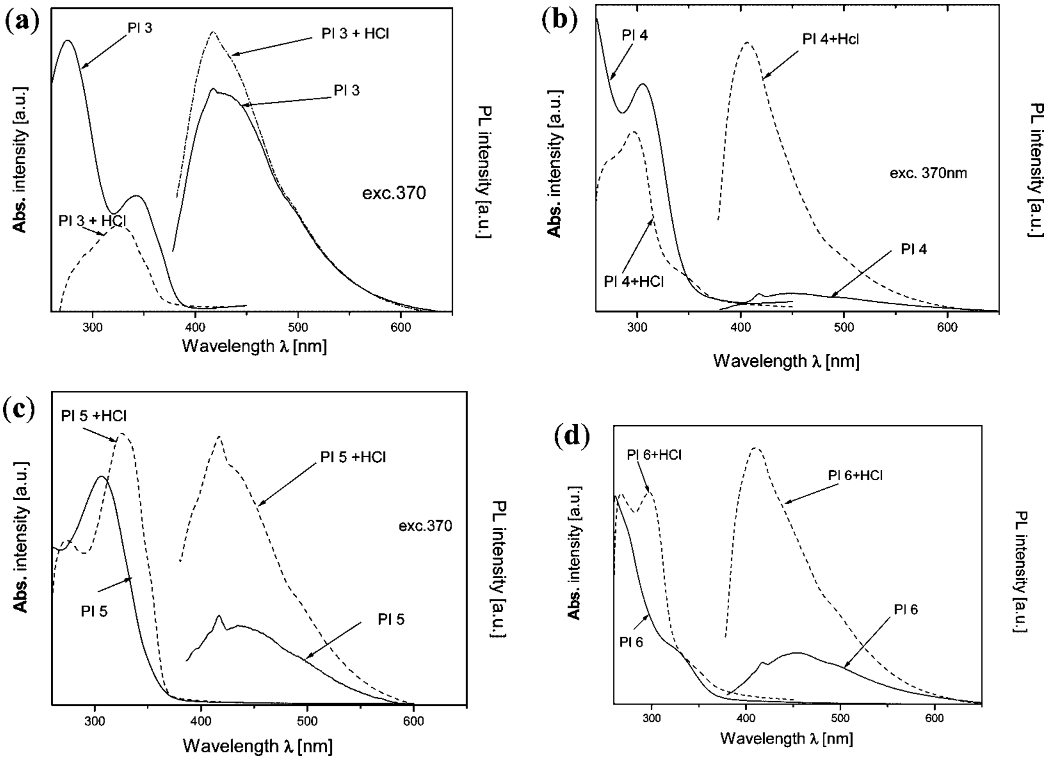

Figure 9. UV−vis spectra (concn 10^{-5} mol·L^{-1}) along with the PL spectra (concn 10^{-4} mol·L^{-1}) for undoped and doped with HCl (a) **PI 3**, (b) **PI 4**, (c) **PI 5**, and (d) **PI 6** in NMP solution.

the polymers was 1:1, whereas, for the polymers with oxadiazole units, it was 1:2. The proposed protonation of these polymers is shown in Figure 8.

The lone pair electrons of the nitrogen on pyridine and on oxadiazole was quaternated by protic acid to form quaternated polymers **PIH 1** and **PIH 2**.[21]

The UV−vis spectra of the investigated polymers were recorded in NMP solution (concn 10^{-5} mol·L^{-1}) before and after protonation with HCl. The UV−vis data of doped and undoped polymers are listed in Table 2, and obtained spectra are compared in Figure 9.

UV−vis spectra of the doped polymers showed well-defined spectral changes in the position and shape of the absorption band after protonation with HCl. Protonation of **PI 6**, **PI 3**, and **PI 4** caused a blue shift in both bands in comparison with the undoped polymer (cf. Figure 9). Additionally, it should be stressed that the second absorption band of the protonated poly(ether imides) **PI 5** and **PI 6** exhibited higher intensity than the undoped one. Taking into account the structure of diamine units, a bathochromic shift for polymers with oxadiazole rings in comparison with polymers containing pyridine units was found. (Compare **PI 3** and **PI 4** and **PI 5** and **PI 6** in Figure 9.) The observed changes in the spectroscopic properties of the protonated polymers can be attributed to the modification of the electronic structures of the polymer chain due to the interaction between the nitrogen in pyridine and oxadiazole rings with the proton of HCl.

The effect of the protonation of nitrogen in oxadiazole and pyridine rings on the emission properties of the polymers **PI 3**−**PI 6** was studied. To investigate the influence of protonation, the PIs with HCl were dissolved in NMP (concn 10^{-4} mol·L^{-1}), and the PL spectra were recorded. The PL peak wavelengths of undoped and doped PIs are listed in Table 3, and obtained PL spectra are compared in Figure 9. The Stokes shift value was found to be higher for the polymers (**PI 3**, **PI 6**) in protonated solution in comparison with those in pristine polymer solution, which illustrates that more energy loss occurred during the transition from S_0 to S_1 in the doped state. Protonation of the polymers in NMP solution under 350 and 370 nm excitation wavelength caused a blue shift in the PL band in comparison with undoped polymers. Hipsochromic shift of the emission wavelength indicated the shorter conjugation units in the polymer chain.[44] A higher value of blue shift between pristine and doped polymers was found for polymers with pyridine rings than for polymers with oxadiazole units. (See Table 3.) Protonation influenced a significant increase in the PL intensity; similar results were observed for PIs containing pyridine and triphenylamine groups.[21] In our case, the highest increase in PL intensity for polymers containing the pyridine rings (**PI 4** and **PI 6**) was observed.

Conclusions

A series of novel PIs with pyridine and oxadiazole units were obtained. The presence of these units containing a nitrogen atom available for nonconvalent interaction with Brønsted acids gave the opportunity for modification of polymer optical properties. Protonation with HCl applied as a dopant caused a significant increase in PL intensity. The polymers emitted violet-blue light in solution. Absorption and emission spectroscopies showed the influence of the diamines structures on the properties of these polymers. Polymers with pyridine rings emitted light at longer wavelengths than polymers with oxadiazole units. Emission of polymers in blend greatly differed in comparison with those detected in NMP solution. A significant bathochromic shift in the emission band between solution and blend was observed. PL intensity of the polymer blend was much higher than that of the polymer solution. The polymer solution and blend aid the separation of PL output from absorption, thereby alleviating self-absorption.

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