Final Report for 6709U0015-3C

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SYNTHESIS OF COMPOUNDS FOR LOS ALAMOS NATIONAL LABORATORY

As part of contract #6709U0015-3C, the compounds listed below were synthesized and transferred to LANL for evaluation. Work on these has resulted in several papers, manuscripts and talks bearing LANL and UTD coauthorship. In addition, parallel work at UTD has resulted in two additional published papers from UTD (included) which acknowledge support from LANL.

The detailed synthetic procedures are indicated in the following paragraphs and/or the attached manuscripts. Table I shows the chemical structure of mentioned compounds.

Synthetic procedures:

1. 2-Methoxy-5-(2'-ethylhexyloxy)-1,4-distyrylbenzene - see synthesis of compound **V** in the reference [1].

2. MEHPPV:

1.000 g 1,4-methoxyethylhexyloxy-2,5-dibromomethylbenzene + 0.0042 g (1 mol %) anthracene were dissolved in 35 ml dry THF and 1.0 M solution of *t*-BuOK in THF was added slowly during 60 min and stirred at room temperature for 20 hours. The red suspension was precipitated in 200 ml cold MeOH, the solid was filtered, washed by MeOH and dried in vacuum. The red-orange solid was extracted by boiling hexane for 24 hours. Insoluble in hexane red polymer was extracted by boiling xylene for 24 hours, soluble in xylene fraction was dissolved in THF and precipitated in MeOH. After filtration and drying in vacuum 0.220 g (36% yield) of red polymer with $M_w = 357000$ and absorption maximum at 496 nm (chloroform) was obtained.

3. 1,4-distyrylbenzene - see synthesis of compound **I** in the reference [1].

4. 1,4-Bis-(2',5'-dimethoxystyryl)-2-methoxy-5-(2'-ethylhexyloxy)benzene:

This compound was obtained in 51% yield according the general procedure for the Wittig reaction described in the reference [1] from 2-methoxy-5-(2'-ethylhexyloxy)-1,4-xylylene-bis(triphenylphosphonium chloride) and 2,5-dimethoxybenzaldehyde, m.p. 49-51°C.

5. Films of aromatic copolyamides with fragments of 9,10-bis(p-carboxyphenyl)anthracene and bis(m-aminophenyl)-9,10-anthracene - see synthesis of copolyamides **XXI** and **XXII** in the reference [2].

- 6,7. Films of the solid solution of 9,10-diphenylanthracene in poly(m-phenyleneisophthalamide) (PMPI) were obtained from the 5.0% solution of mixture 0.231 g PMPI and 0.0319 g 9,10-diphenylanthracene in N-MP at conditions described in the reference [2].
8. 2,5-Didodecyloxy-1,4-distyrylbenzene - see synthesis of compound **IV** in the reference [1].
9. 2,5- Dioctyloxy-1,4-distyrylbenzene - see synthesis of compound **III** in the reference [1].
10. 2,5-Dimethoxy-1,4-distyrylbenzene - see synthesis of compound **II** in the reference [1].
11. Films with the compositions of polystyrene (PS) + 2,5-didodecyloxy-1,4-distyrylbenzene (**8**) (40:60 w/w) and PS + 2,5-dioctyloxy-1,4-distyrylbenzene (**9**) (40:60 w/w) were obtained by evaporation of 10% solution of components in chloroform at room temperature.
12. FATs and other ω -substituted alkane thiols including -CN, -CHO, -OH, -NH₂.

REFERENCES

1. "Synthesis and optical properties of oligo- and poly(2,5-dialkoxy-1,4-*para*-phenylenevinylene)s", N. N. Barashkov, D. J. Guerrero, H. J. Olivos, and J. P. Ferraris, Synth. Met., **1995**, 75, 153.
2. "Synthesis and spectral-luminescence properties of aromatic polyamides and polyesters with chromophores in the polymer main chain", N. N. Barashkov, T. S. Novikova, D. J. Guerrero, and J. P. Ferraris, Synth. Met., **1995**, 75, 241.

Table I

Compound(s)	Amount	Date shipped
1	0.15 gm	5/95
	0.66 gm	6/95
	0.47 gm	9/95
2	0.25 gm (NBII-27)	7/95
	0.22 gm (NBII-35)	8/95
	0.25 gm (NBII-37)	8/95
3	0.12 gm	2/95
4	0.20 gm	1/95
5	0.13 gm	2/95
6	0.28 gm	2/95
7	0.30 gm	2/95
8	0.15 gm	2/95
9	0.15 gm	2/95
10	0.30 gm	3/95
11	0.1 gm ea	3/95
12	various	1995

Structures of compounds in Table I:

1 (MEH-DSB)

2 (MEH-PPV)

3 (DSB)

4

5

6

0.9 mol

0.1 mol

7

8: $R = C_{12}H_{25}$

9: $R = C_8H_{17}$

10: $R = CH_3$

$X-(CH_2)_n-SH$

$X = -CN, -CHO, -OH, -NH_2$

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Synthesis and optical properties of oligo- and poly(2,5-dialkoxy-1,4-*para*-phenylenevinylene)s

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Synthesis and optical properties of oligo- and poly(2,5-dialkoxy-1,4-*para*-phenylenevinylene)s

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Abstract

Model compounds based on 1,4-distyrylbenzene and its 2,5-dialkoxy derivatives were synthesized by the Wittig and Wittig–Horner methods. Corresponding poly(2,5-dialkoxy-1,4-*para*-phenylenevinylene)s (DAPPVs) were obtained from their 2,5-bis(chloromethyl)benzene monomers. The photophysical behavior of the model compounds and DAPPVs was investigated through absorbance, excitation and fluorescence spectroscopy. The absorbance and fluorescence spectra of DAPPVs are red shifted in comparison to the corresponding three- and five-ring model compounds by 4600 and 7000 cm⁻¹, respectively. We also report the fluorescence excitation and emission spectra of the model compounds deposited as solid films on quartz and as solid solutions in poly(methyl methacrylate) (PMMA). The photophysical properties of these materials are interpreted from their capacity to form excimer-like molecular dimers. The fluorescence excitation spectra of DAPPV solutions are concentration dependent. We show evidence for the existence of fluorescent aggregates in the solid state.

Keywords: Synthesis; Optical properties; Poly(2,5-dialkoxy-1,4-*para*-phenylenevinylene); Oligo(2,5-dialkoxy-1,4-*para*-phenylenevinylene)

1. Introduction

Conjugated polymers, such as poly(phenylenevinylene) (PPV), are receiving considerable attention due to their potential use in light-emitting diodes (LEDs) [1–4] and nonlinear optical applications [5,6]. This interest stems in large part from the changes in electronic and mechanical properties that can be effected by the introduction of substituents [7]. For example, substitution on the phenyl ring of PPV with two alkoxy groups reduces the HOMO–LUMO energy gap by about 0.3–0.4 eV compared to that of the parent [8,9], and affords solubility and film-forming properties to the polymer.

The ability to alter the polymer's π – π^* energy gap through changes in the molecular structure enables the adjustment of its fluorescence wavelength and color [9–11] throughout the visible (and into the NIR) spectrum. A polymer emitting blue light with high efficiency is particularly desirable as an active material in flat LEDs [12,13] and electroluminescent devices. Approaches for obtaining blue-emitting PPV-based polymers and copolymers include use of poly(*p*-phenylphenylenevinylene) itself, despite difficulties in processability

[13], polyethers incorporating residues of dimethoxy-substituted 1,4-distyrylbenzene [14] and polyesters with bina-*phthyl*-4,4'-ylene vinylene groups [15]. It is also known [14] that shortening the effective conjugation length of PPV is an alternative means of shifting the emission spectrum from green to blue.

However, relatively broad molecular weight distributions and the possible presence of blocks with different effective conjugation lengths can complicate the investigation of the optical properties of dialkoxy-substituted PPVs. Therefore, we chose to study the spectral properties of well-defined oligomeric model systems based on derivatives of 1,4-(distyryl)benzene (I, DSB). Recently, it was shown [16] that the luminescence intensity of compound I in the solid state can be significantly influenced by charge transfer complexation with distyrylbenzene-4,4'-dicarboxaldehyde. It is also known [17,18] that many aromatic hydrocarbons like DSB can produce complexes which exist only in the excited state (excimers) or can exist as dimers which are stable in the ground state, but exhibit the spectroscopic properties of excimers. In various studies, the latter have been designated as sandwich dimers [19,20] and associated dimers [21–25] and represent another form of aggregation of excimer-forming molecules. An analysis of the published data concerning the formation of excimer-like molecular dimers in films obtained

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Scheme 1. I: $R_1 = R_2 = H$; II: $R_1 = R_2 = OCH_3$; III: $R_1 = R_2 = OC_8H_{17}$; IV: $R_1 = R_2 = OC_{12}H_{25}$; V: $R_1 = OCH_3$, $R_2 = 2$ -ethylhexyloxy; VI: $R_1 = OCH_3$, $R_2 = 2$ -ethylhexyloxy; VII: $R_1 = OCH_3$, $R_2 = 2$ -ethylhexyloxy; VIII: $R_1 = R_2 = OC_8H_{17}$; IX: $R_1 = R_2 = OC_{12}H_{25}$; X: $R_1 = OC_8H_{17}$, $R_2 = OC_{12}H_{25}$.

by depositing the chromophore onto a substrate [26–28] and in polymer media [29–34] shows that information on the optical properties of such aggregates in DBS-based systems is very limited. In recent publications [35,36] possible aggregations of tert-butyl-substituted DSB in a polystyrene matrix (solid solution) and phosphonate-substituted DSB in a dimethylsulfoxide solution were discussed.

In this work, we report the absorbance, excitation and fluorescence spectra of oligomeric systems I–VI and compare these with spectra of MEHPPV (VII) and the dialkoxy PPVs (VIII–X) (Scheme 1). The capacity to form excimer-like molecular dimers for some of these compounds was also determined.

2. Experimental

Commercially available solvents were purified according to standard procedures. The instrumentation used was: IR spectra, Mattson Instruments Galaxy Series FT-IR 2025 spectrometer; UV–Vis spectra, Perkin-Elmer Lambda 9 spectrometer using SpectraCalc software (Galactic); fluorescence spectra, Jobin Yvon/Spex Fluorolog equipped with model 1680 double monochrometers for excitation and emission. Data were acquired using Datamax software; 1H NMR spectra, Jeol JNM-FX270 ($CDCl_3$, 270 MHz); gel permeation chromatography (GPC, polystyrene standards, THF), Varian VISTA 5500 chromatograph using PE Nelson software; elemental analyses were performed by Oneida Research Services, Whitesboro, New York.

Compounds I and II were synthesized by the Wittig–Horner method according to literature procedures [37], using

tetrahydrofuran (THF) and dimethylformamide (DMF), respectively. The reaction mixtures were quenched with methanol (10 ml) and concentrated to a small volume (20–30 ml). The concentrated mixtures were poured into cold water (100 ml) and the white–yellow precipitates were filtered, washed with water and methanol, and dried under vacuum. The crude products were converted to the *trans* isomer by heating in boiling toluene with a catalytic amount of iodine. The resulting colorless products were purified by recrystallization from toluene (compound I) or by column chromatography on silica gel (70–230 mesh) and eluted with toluene/hexane (1:1) (compound II).

2.1. 1,4-Distyrylbenzene (I)

Compound I was synthesized in 35% yield from diethylbenzylphosphonate (2.283 g, 10 mmol) and terephthalaldehyde (0.670 g, 5 mmol). M.p. 264–266 °C; lit. [37] 266–268 °C. 1H NMR (270 MHz, $CDCl_3$) δ : 6.75–7.97 (m).

2.2. 2,5-Dimethoxy-1,4-distyrylbenzene (II)

Compound II was synthesized in 47% yield from diethylbenzylphosphonate (2.283 g, 10 mmol) and 2,5-dimethoxyterephthalaldehyde (0.970 g, 5 mmol). M.p. 165–166 °C. 1H NMR (270 MHz, $CDCl_3$) δ : 6.79–7.65 (m, 16H), 3.91 (s, 6H, OCH_3). Anal. Calc.: C, 84.21; H, 6.43. Found: C, 84.72; H, 6.44%. FT-IR (KBr, cm^{-1}): 697, 757, 961, 1054, 1212, 1404, 1503, 2996, 3062.

2.3. General procedure for the Wittig reaction for the preparation of compounds III–VI

The Wittig reactions [38] were carried out in a three-neck flask equipped with a stirrer, a gas inlet tube and an addition funnel. In the flask, the monophosphonium salts (2 mmol) and dialdehyde (1 mmol) (compounds III and IV) or diphosphonium salts (1 mmol) and monoaldehyde (2 mmol) (compounds V and VI) were dissolved or suspended in DMF (15 ml). A freshly prepared 0.4 M solution of potassium tert-butoxide (2 mmol) in THF was added dropwise to this mixture. The mixture was stirred overnight at room temperature and poured into water (100 ml). The mixture was extracted three times with dichloromethane, the extracts were washed several times with water, dried over magnesium sulfate, and the solvent was removed in vacuo. The crude products were converted to the *trans* isomer by heating in boiling toluene with a catalytic amount of iodine. The resulting colorless products were separated by column chromatography on silica gel (70–230 mesh) and eluted with toluene/hexane (3:1).

2.3.1. 2,5-Dioctyloxy-1,4-distyrylbenzene (III)

Compound III was synthesized in 53% yield from benzyltriphenylphosphonium chloride (0.776 g, 2 mmol) and 2,5-dioctyloxyterephthalaldehyde (0.390 g, 1 mmol). M.p. 97–99 °C. 1H NMR (270 MHz, $CDCl_3$) δ : 6.88–7.90 (m,

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16H), 3.98 (t, 4H, OCH₂), 1.8–0.9 (m, 30H). *Anal. Calc.*: C, 84.76; H, 9.29. *Found*: C, 84.48; H, 9.11%. FT-IR (KBr, cm⁻¹): 684, 961, 1074, 1206, 1424, 1470, 2929, 3068.

2.3.2. 2,5-Didodecyloxy-1,4-distyrylbenzene (IV)

Compound IV was synthesized in 62% yield from benzyl-triphenylphosphonium chloride (0.776 g, 2 mmol) and 2,5-didodecyloxyterephthaldehyde (0.502 g, 1 mmol). M.p. 81–82 °C. ¹H NMR (270 MHz, CDCl₃) δ: 7.0–7.8 (m, 16H), 3.98 (t, 4H, OCH₂), 1.8–0.9 (m, 46H). *Anal. Calc.*: C, 84.92; H, 10.15. *Found*: C, 84.62; H, 8.97%. FT-IR (KBr, cm⁻¹): 690, 750, 968, 1067, 1212, 1431, 1476, 2857, 3056.

2.3.3. 2-Methoxy-5-(2'-ethylhexyloxy)-1,4-distyrylbenzene (V)

Compound V was obtained as a waxy solid in 32% yield from 2-methoxy-5-(2'-ethylhexyloxy)-1,4-xylylenebis(triphenylphosphonium chloride) (0.857 g, 1 mmol) and benzaldehyde (0.2120 g, 2 mmol). ¹H NMR (270 MHz, CDCl₃) δ: 7.0–7.8 (m, 16H), 3.85 (m, 5H, OCH₂, OCH₃), 2.0–0.9 (m, 15H). *Anal. Calc.*: C, 85.34; H, 7.76. *Found*: C, 85.79; H, 7.69%. FT-IR (KBr, cm⁻¹): 539, 692, 961, 1206, 1462, 1496, 2930, 3056.

2.3.4. 2-Methoxy-5-(2'-ethylhexyloxy)-1,4-distilbylbenzene (VI)

Compound VI was synthesized in 57% yield from 2-methoxy-5-(2'-ethylhexyloxy)-1,4-xylylenebis(triphenylphosphonium chloride) (0.857 g, 1 mmol) and 4-stilbenealdehyde (0.416 g, 2 mmol). M.p. 195–196 °C. ¹H NMR (270 MHz, CDCl₃) δ: 6.82–8.07 (m, 28H), 3.85 (m, 5H, OCH₂, OCH₃), 2.0–0.9 (m, 15H). *Anal. Calc.*: C, 87.57; H, 7.45. *Found*: C, 87.34; H, 7.41%. FT-IR (KBr, cm⁻¹): 545, 690, 810, 968, 1212, 1463, 1489, 2923, 3058.

2.4. Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEHPPV, VII)

Compound VII was synthesized by the following method: A solution of potassium tert-butoxide (2.073 g, 18.5 mmol) in THF (15 ml) was added over 40 min at room temperature to a stirred solution of 2-methoxy-5-(2'-ethylhexyloxy)-1,4-(dichloromethyl)benzene (1.00 g, 3.0 mmol) and anthracene (0.0267 g, 0.15 mmol) in THF (45 ml) under nitrogen atmosphere. The reaction mixture was stirred for 18 h and then filtered. The red solution was concentrated (to about 20 ml), added dropwise to stirred cold methanol (500 ml), and stirred for 1 h. After filtration the solid was washed with methanol, dried under vacuum overnight, then redissolved in THF (30 ml) and precipitated once again into methanol (400 ml). The collected red polymer (0.300 g, 38%) was dried under vacuum (*M_w* = 289 000 and *M_n* = 208 200, degree of polymerization, *DP* = 1110).

2.5. General procedure [39] for synthesis of poly(2,5-dialkoxy-1,4-*p*-phenylenevinylene)s (VIII–X)

A solution of potassium tert-butoxide in tert-butanol was quickly added at room temperature under nitrogen atmosphere to a stirring solution of 2,5-bis(chloromethyl)-1,4-dialkoxybenzene (4:1, base:monomer) (polymers VIII–IX) or a mixture of 2,5-bis(chloromethyl)-1,4-di(dodecyloxy)benzene and 2,5-bis(chloromethyl)-1,4-di(octyloxy)benzene (4:1, base:monomer) (polymer X) in *p*-xylene/tert-butanol. The reaction mixture was refluxed for 22 h, filtered at room temperature and rinsed with additional *p*-xylene. The red solution was concentrated (to about 25–30 ml) and poured into cold methanol (300 ml). After filtration, the solid was washed with methanol and dried under vacuum at room temperature.

2.5.1. Poly(2,5-dioctyloxy-1,4-phenylenevinylene) (VIII)

Compound VIII was prepared in 11% yield from 2,5-bis(chloromethyl)-1,4-dioctyloxybenzene (0.99 g, 2.3 mmol) in tert-butanol/*p*-xylene (1:2). *M_w* = 78 000, *M_n* = 64 600, *DP* = 217. *Anal. Calc.*: C, 80.44; H, 10.61. *Found*: C, 78.56; H, 10.26; Cl, 0.66%. FT-IR (KBr, cm⁻¹): 3057, 2924, 2855, 1504, 1468, 1420, 1386, 1354, 1252, 1202, 1044, 970, 854, 721, 702.

2.5.2. Poly(2,5-didodecyloxy-1,4-phenylenevinylene) (IX)

Compound IX was prepared in 33% yield from 2,5-bis(chloromethyl)-1,4-didodecyloxybenzene (1.0 g, 1.84 mmol) in tert-butanol/*p*-xylene (1:1). *M_w* = 57 000, *M_n* = 49 000, *DP* = 121. *Anal. Calc.*: C, 81.70; H, 11.49. *Found*: C, 80.14; H, 11.05; Cl, 0.17%. FT-IR (KBr, cm⁻¹): 3057, 2924, 2853, 1504, 1466, 1420, 1387, 1354, 1252, 1203, 1047, 970, 854, 721, 702.

2.5.3. Poly(2,5-dioctyloxy-1,4-phenylenevinylene)-co-(2,5-didodecyloxy-1,4-phenylenevinylene) (X)

Compound X was prepared in 20% yield from 2,5-bis(chloromethyl)-1,4-dioctyloxybenzene (0.39 g, 0.9 mmol) and 2,5-bis(chloromethyl)-1,4-didodecyloxybenzene (0.51 g, 0.9 mmol) in tert-butanol/*p*-xylene (1:1). *M_w* = 78 000, *M_n* = 34 000, *DP* = 188. *Anal. Calc.*: C, 81.16; H, 11.11. *Found*: C, 79.23; H, 10.53; Cl, 0.13%. FT-IR (KBr, cm⁻¹): 3057, 2924, 2855, 1504, 1468, 1420, 1387, 1354, 1252, 1204, 1047, 970, 856, 721.

3. Results and discussion

Figs. 1 and 2 show the absorbance, fluorescence and excitation spectra of oligomers I and III. The positions of maxima in the absorbance and fluorescence spectra of oligomers I–VI, as well as the extinction coefficients of the absorptions are shown in Table 1.

Fig. 1. Absorbance (1), fluorescence (2) and excitation (3, monitored at 422 nm) spectra of DSB (I) in chloroform.

Fig. 2. Absorbance (1), fluorescence (2) and excitation (3, monitored at 444 nm) spectra of oligomer III in chloroform.

The absorbance spectra in solution² of oligomers with three aromatic rings have the vibronic structure which is typical for DSB and its derivatives [40–43]. The energy of the long-wavelength electronic transition of DSB is 4000 cm^{-1} below that of stilbene. The addition of two strongly electron-donating alkoxy groups provides an additional red shift in the absorbance of approximately 2000–2200 cm^{-1} . The addition of two more benzene rings (oligomer VI) further red shifts this absorption by approximately 2400 cm^{-1} (compare with oligomer V). The shift is consistent with a decrease in transition energy as the length of conjugation is increased. The intensity of the band at long wavelength (for V and VI) is increased by a factor of 1.7, which is comparable to the increase observed upon the introduction of two benzene rings to a molecule of DSB [40].

The fluorescence spectrum of compound I compares to literature data [40]. In chloroform and ethanol no dependence of fluorescence upon excitation wavelength has been observed, indicating that the fluorescence transition is not influenced by selective photoexcitation of rotamers. The fluorescence maxima of oligomers II–IV are bathochromatically shifted relative to the maximum of compound I. This shift is relatively insensitive to the length of the alkoxy group in the 2,5-positions in the central benzene ring, suggesting that, if secondary ordering effects occur as a result of intramolecular van der Waals interaction between long alkyl chains, they must be small.

All model compounds have structured emission spectra at room temperature, which agree with data [42] obtained for fluorescence spectra of tert-butyl-substituted DSB. The emission spectra shift by nearly 1900 cm^{-1} in going from three rings (compound V) to five rings (compound VI). This shift is considerably smaller than the shift observed (3000 cm^{-1})

² All liquid solution spectra were taken in chloroform.

Table 1
Absorbance and fluorescence data for compounds I–X

Compound	Peak maxima (nm)	
	Absorbance ϵ ($\times 10^{-4} \text{ l mol}^{-1} \text{ cm}^{-1}$)	Fluorescence
I	342 (sh) ^b (7.69), 358 (8.68), 375 (5.52)	395 (sh), 422, 450, 470 (sh)
II	320 (3.23), 388 (4.79)	430, 465, 490 (sh)
III	325 (3.04), 389 (3.75)	444, 468, 500 (sh)
IV	325 (2.89), 389 (3.75)	446, 470, 505 (sh)
V	325 (4.20), 384 (5.39)	443, 467, 505 (sh)
VI	352 (4.36), 425 (9.26)	482, 512, 555 (sh)
VII solution ^a	497 (28.08)	592, 630 (sh)
VII solid	499	610, 640 (sh)
VIII solution	473 (14.51)	550, 593 (sh)
VIII solid	471	580, 621 (sh)
IX solution	470 (16.39)	545, 586 (sh)
IX solid	477	580, 621 (sh)
X solution	475 (15.96)	550, 591 (sh)
X solid	479	579, 620 (sh)

^a Chloroform solution.

^b Shoulder.

Fig. 3. Fluorescence (1) and excitation spectra (2–5) of a DSB (I) film prepared by thermal vacuum deposition on quartz monitored at the 416 (2), 450 (3), 500 (4) and 550 (5) nm emission maxima, respectively.

Fig. 4. Fluorescence (1) and excitation spectra (2,3) of a DSB (I) in PMMA 49% solid solution monitored at the 420 (2) and 508 (3) nm emission maxima, respectively.

Fig. 5. Fluorescence (1) and excitation spectra (2) of a DSB (I) in PMMA 0.9% solid solution.

in the emission spectra of a five-ring phosphonate-substituted oligo(phenylenevinylene) ((*E,E,E,E*)-tetraethyl-1,4-phenylbis(1,2-ethenyl-4-phenyl-1,2-ethenyl-4-phenylphosphonate)) when compared to the phosphonate-substituted DSB ((*E,E*)-tetraethyl-1,4-phenylbis(1,2-ethenyl-4-phenylphosphonate)) [36]. This difference in behavior has been observed before where substituents on the *para*-position of

phenyl radicals of DSB, regardless of their electronic structure, cause a more significant bathochromic shift in the spectrum than substituents in *meta*- or *ortho*-positions [41]. The excitation spectra of compounds I–VI in solution coincide with their absorption spectra, as has been similarly observed in other systems [35,36].

Figs. 3–5 show the fluorescence, excitation and emission spectra for films of DSB on quartz prepared by thermal vacuum deposition, as well as spectra of solid solutions of DSB in PMMA with concentrations of 49 and 0.9%, respectively. The data reveal differences in the fluorescence properties of the samples. The emission spectrum of a solid solution of 0.9% DSB in PMMA (Fig. 5) shows no significant differences from the liquid solution emission spectrum (Fig. 1). Most importantly, the features of the fluorescence excitation spectra of this sample are very similar to the features of the absorbance spectra of a liquid solution of DSB. However, in the emission spectra of a pure DSB film on quartz and the solid solution of 49% DSB in PMMA, a new band with maximum at 505–508 nm appears. The features of the fluorescence spectra of pure DSB depend on the film thickness. At the film thickness used here (0.6–5 μm), a new band is observed in the form of the shoulder at 550 nm. This film had an optical density of 1.0–1.2 at 350 nm.

There are important differences between the excitation spectra of solid solutions of 49% DSB in PMMA measured at various fluorescence maxima. The excitation curves monitored at 441, 472 and 508 nm were structureless and had a unique maxima at 390 nm. In contrast, the excitation spectra monitored at 393 and 420 nm were structured. Two maxima also appear in the excitation spectra of pure DSB films (340 and 390 nm). Table 2 lists the intensity ratios determined from the excitation spectra at various emission maxima for solid solutions at different concentrations and pure DSB.

These data demonstrate the presence of additional absorbing centers for samples with high concentration of DSB. Such centers could be fluorescent dimers or other aggregates with different degrees of overlap between the monomers. The ratio between the intensities at 390 and 340 nm (390/340) in the excitation spectra can be used to estimate the relative concentration of excimer-like components of fluorescence. The sharp decrease of this ratio upon reduction of the DSB concentration in solid solutions is analogous to the behavior of the fluorescence of pyrene and naphthalene, adsorbed as dimers (stable in the ground state), on a silica gel surface [26]. In this case fluorescence was ascribed to the excimeric state. Although the dimeric centers also absorb, there is no energy transfer to the dimeric form during the lifetime of the monomer excited state. A dependence between the dimer and monomer fluorescence intensity ratio and the chromophore concentration was also observed.

We also investigated whether fluorescent aggregates are present in pure solid films and solid solutions of compound III, a substituted DSB, in PMMA (0.9, 20 and 49%). The emission spectra of a film of pure III on quartz (Fig. 6), and of solid solutions in PMMA (49%, Fig. 7) exhibit intensities

Table 2

Intensity ratios of the 390 to 340 nm peaks in the excitation spectra of solid DSB (I) films and solid solutions of I in PMMA at different concentrations

Position of maxima in fluorescence spectra (nm)	Intensity ratio 390/340			
	Pure I	Concentration of I in PMMA (%)		
		49	20	0.9
508	0.86	0.55	0.53	
472	0.84	0.54	0.51	0.13
441	0.83	0.50	0.48	0.11
420	0.50	0.34	0.14	0.10

Fig. 6. Fluorescence (1) and excitation spectra (2,3) of oligomer III film prepared from chloroform solution on quartz monitored at the 483 (2) and 508 (3) nm emission maxima, respectively.

Fig. 7. Fluorescence (1) and excitation spectra (2,3) of oligomer III in PMMA 49% solid solution at the 475 (2) and 508 (3) nm emission maxima, respectively.

of the 508 nm shoulder that are higher than in the emission spectrum of the 0.9% solid solution (Fig. 8). The fluorescence excitation spectrum depends significantly on the wavelength of emission and does not coincide with the absorption spectrum. The curves representing fluorescence excitation at 508 nm have two additional maxima, at 428 and 458 nm, which may correspond to emission from fluorescent dimers (Fig. 6). We have previously shown [33] that multiple bands are indicative of dimer formation in pyrene in a PMMA

matrix. The concentration behavior of the 458/360 intensity ratio in the excitation spectra of pure III and solid solutions of III in PMMA (Table 3) suggests that, at comparatively low concentration (0.9 and 20%), the introduction of alkoxy groups in the DSB structure prevents aggregation into fluorescence dimers.

Fig. 9 shows the absorbance, fluorescence and excitation spectra of poly[2,5-di(octyloxy)-*p*-phenylenevinylene] (VIII) in the solid state and in chloroform. The long-wavelength part of the absorbance spectrum of VIII in solution is a broad structureless band beginning at 560 nm, peaking at 470 nm, and having a full width at half-maximum of 6700 cm^{-1} . Peak wavelengths for the film and solution spectra agree with each other, while the bandwidth for the solution is narrower than that for the film (a full width at half-maximum of 7800 cm^{-1}). This is also true for MEHPPV (Fig. 10). Similar behavior has been observed for a series of different dialkoxy PPVs [39]; the results were taken as evidence that conformational differences alter the effective conjugation lengths and, hence, the spectral characteristics of the polymers. The solution absorbance spectrum of polymer VIII is red shifted about 4600 cm^{-1} , compared to model compound III, as expected for an increase in conjugation length and the number of alkoxy substituents. However, the spectrum of VIII is significantly broader, most likely due to a distribution of effective conjugation lengths.

The intensities of the absorbance bands for compounds VII–IX show that the MEHPPV has the highest molar extinc-

Fig. 8. Fluorescence (1) and excitation (2) spectra of oligomer III in PMMA 0.9% solid solution.

Table 3

Intensity ratios of the 458 to 360 nm peaks in the excitation spectra of solid **III** films and solid solutions of **III** in PMMA at different concentrations

Position of maxima in fluorescence spectra (nm)	Intensity ratio 458/360			
	Pure III	Concentration of III in PMMA (%)		
		49	20	0.9
508	1.31	0.33	0.04	0.02
483	1.14	0.21	0.02	0
467		0.02	0	0

Fig. 9. Absorbance (1,2), fluorescence (3,4) and excitation (5,6) spectra of polymer **VIII** in chloroform with concentrations 10^{-3} g l^{-1} (1,3,5) or 10^{-1} g l^{-1} (6), and film on quartz (2,4). The ordinate axis is the actual value for curve 1 only.

Fig. 10. Absorbance (1,2) and fluorescence (3,4) spectra of MEHPPV (**VII**) in chloroform (1,3) and film on quartz (2,4). The ordinate axis is the actual value for curve 1 only.

tion coefficient (Table 1). Since the symmetry of the aromatic ring is reduced by addition of two different groups in MEHPPV, the symmetry-forbidden constraint of the transition is relaxed and the value of the molar extinction coefficient is increased [44].

The emission spectra of solutions and films of polymers **VII** and **VIII** agree with literature data [39] and are significantly red shifted compared to PPV spectra [45]. For liquid solutions of oligomers **III** and **V** and polymers **VII** and **VIII**, the fluorescence excitation spectra coincide with the absorbance spectra. However, for solutions of polymers with higher concentration (about 10^{-1} g l^{-1}) an additional band appears

in the excitation spectra at 520–524 nm. The ratio between the intensity of this band and the band corresponding to the absorbance spectra maxima (at 460–475 nm) depends significantly on the emission wavelength (Fig. 9). On the other hand, the emission spectra of the more concentrated solutions of polymer **VIII** depend only slightly on the excitation wavelength (decrease of full width at half-maximum from 2300 to 2100 cm^{-1} upon increasing the excitation wavelength from 355 to 470 nm). The results could be explained by either of two phenomena: (a) the existence of fluorescent aggregates and/or (b) excitation energy transfer from the absorbing segment of the polymer to the longest and therefore energetically lowest segment on each chain prior to emission. The second mechanism has been used [35] to explain the dependence of the fluorescence excitation spectra on the wavelength of emission for solutions of poly(*p*-phenylphenylenevinylene) in toluene. The red shift of the emission maximum for films of polymers **VII** and **VIII** in comparison with the emission maximum for solutions of these polymers may be attributed to a more efficient energy transfer processes in the films.

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Synthesis and spectral-luminescence properties of aromatic polyamides and polyesters with chromophores in the polymer main chain

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Synthesis and spectral-luminescence properties of aromatic polyamides and polyesters with chromophores in the polymer main chain

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Abstract

We report copolycondensation reactions of several benzimidazole-, benzoxazole- and diphenylanthracenyl-containing chromophores with *m*-phenylenediamine (MPD), isophthaloyl chloride (IPC) and bisphenol A (BPA) to form polyamides and polyesters. The absorbance and fluorescence spectra of the polymers were measured and the actual molar ratios of luminophoric and nonluminophoric moieties in their structures were determined by comparison to model compounds. Most copolymers showed intense blue fluorescence, from solution and film, with a maximum in the 410–515 nm range. The present results demonstrate that non-conjugated luminescent polymers, which are potentially useful for light-emitting diode applications, may be obtained by a one-stage copolycondensation technique.

Keywords: Synthesis; Luminescence; Aromatic polyamide; Polyester; Chromophore

1. Introduction

Aromatic polyamides, such as poly(*m*-phenyleneisophthalamide) (PMPI), have found wide application over the last 20–30 years due to their superior mechanical and dielectric properties coupled with their satisfactory heat resistance [1]. The possibility of obtaining colored and fluorescent copolyamides and copolyesters by introducing chromophore molecules into the polymer chain has been investigated [2–12]. In the case of aromatic copolyamides, polymers with acridine [2,3], stilbene [2,3], rhodamine [4], benzantrone [4,5], diphenylanthracene [3–5], phenylbenzimidazole [6] and anthraquinone [3,11] units have been examined. Recently [12], aromatic copolyesters containing binaphthyl-4,4'-ylene vinylene groups have been studied as potential materials for light-emitting diode applications.

The possibility of obtaining fluorescent copolyamides and copolyesters by a one-stage copolycondensation technique has also been raised [8–12]. The main problem in using this technique lies with the different reactivity ratios of the monomers (for PMPI: *m*-phenylenediamine (MPD) and iso-

phthaloyl chloride (IPC); for polyesters: bisphenol A (BPA) and IPC) and chromophore comonomers (diamine, diacid chlorides). If the chromophore comonomer has a lower reactivity than the base monomer, the former will not be significantly present in the polymer chain. In some cases, the comonomers do not participate in the reaction or only one functional group reacts. As a result the molar ratio of diamine–diacid chloride or diol–diacid chloride components in the polymer backbone is unbalanced and the polymer molecular weight drops. Also, the concentration of chromophores in the polymer chain is often not representative of the chromophore comonomer and base monomer feed ratio used in the polycondensation.

Since the copolymer molecular weight depends on the degree of participation of the functional groups during polycondensation, it is desirable to use comonomers with similar reactivities in order to obtain high molecular weight polymer. It is known that benzimidazole- and benzoxazole-containing aromatic diamines have similar reactivities to base diamines traditionally used for the preparation of polyamides [7,8]. We have previously found [9] that diacid chlorides derived from 9,10-diphenylanthracene have the same reactivity as IPC.

In this work we report the ability of seven chromophore comonomers (Fig. 1) to participate in copolycondensation reactions with the formation of aromatic polyamides and

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Fig. 1. Structures of chromophore comonomers used.

polyesters. The absorbance and fluorescence spectra were measured and the actual molar ratios of luminophoric and nonluminophoric moieties in the polymer were determined by comparison to model compounds.

Many of the starting luminophore diamines (I–V) have been used before for the synthesis of aromatic polyamides [7,10], but the essential goal of those syntheses was the generation of polymers with high heat resistance. As a result, the resulting polyamides did not fluoresce or did so only weakly due to effective concentration quenching [4]. We have previously shown [5] that, in cases where the polymers are prepared using two diamines and one diacid chloride monomer, the maximum fluorescence intensity can be obtained at an initial diamine/luminophore-diamine molar feed ratio of 0.85–0.95/0.15–0.05, respectively. In the present study, the initial molar feed ratio of *m*-phenylenediamine/luminophore-diamine was 0.9/0.1. In the case of polymers XXI–XXIII (see Table 2), one diamine (or diol) and two diacids were used and the initial diacid/luminophore-diacid molar feed ratio was 0.9/0.1.

2. Experimental

N-Methylpyrrolidone (NMP, Aldrich) was purified by vacuum distillation from calcium hydride. IR spectra were obtained on a Mattson Instruments Galaxy Series FT-IR 2025 spectrometer, UV–Vis spectra on a Perkin-Elmer Lambda 9 spectrometer and fluorescence and excitation spectra on a Jobin Yvon/Spex Fluorolog spectrometer. Gel permeation chromatography (GPC, polystyrene standards, NMP) was performed on a Varian VISTA 5500 chromatograph and the data were analyzed using PE Nelson software. The starting compounds, MPD, BPA, phenolphthalein and IPC, were used as received from Aldrich.

2,2'-Bis(4-aminophenyl)-5,5'-dibenzimidazol (I) was synthesized using a published method [7,13] by treatment of 3,3',4,4'-tetraaminodiphenyl with 4-aminobenzoic acid in a polyphosphoric acid solution. Melting points of I–VII are in agreement with literature data.

1,4-Bis[6-aminobenzimidazolyl-2-]benzene (II) was synthesized using a published method [7,13] by treatment of 1,2,4-triaminobenzene with terephthalic acid in a polyphosphoric acid solution.

4,4'-Bis[6-aminobenzimidazolyl-2-]diphenyl (III) was synthesized using a published method [7,13] by treatment of 1,2,4-triaminobenzene with 4,4'-dicarboxydiphenyl in a polyphosphoric acid solution.

7-Amino-2-(4'-aminophenyl)-4-phenylquinoline (IV) was synthesized using a published method [13] by treatment of 4-nitrobenzanilide with 4-nitroacetophenone in a polyphosphoric acid solution with subsequent reduction of the dinitro derivative.

7-Amino-2-(4'-amino-2'-hydroxyphenyl)benzoxazole (V) was synthesized using a published method [13] by treatment of 1,5-diaminophenol with 5-aminosalicylic acid in a polyphosphoric acid solution.

Diacid chloride of 9,10-bis(*p*-carboxyphenyl)anthracene (VI) was synthesized using a published method [4] by treatment of anthracene with *p*-aminobenzoic acid. The resulting dicarboxylic acid derivative was subsequently reacted with thionyl chloride.

Bis(*m*-aminophenyl)-9,10-anthracene (VII) was synthesized using a published method [14] by treatment of anthracene with *m*-nitroaniline with subsequent reduction of the dinitro derivative.

2.1. General procedure for the preparation of model compounds VIII–XIII

These reactions were carried out using NMP as solvent in a three-necked flask equipped with a stirrer and a nitrogen gas inlet. The diamine (1 mmol) and phthalic anhydride (2 mmol) were dissolved in NMP (15 ml) and the mixture was stirred overnight at room temperature. The resulting product was precipitated into toluene (100 ml), filtered and rinsed several times with hot toluene. Further purification was carried out by repeated recrystallization from ethanol and drying under vacuum at room temperature. The structures of compounds VIII–XIII were confirmed by IR spectroscopy and their purity was checked by a luminescence method [11]. Model compound XIV was prepared according to a literature procedure from anthracene and *p*-aminobenzoic acid [4].

2.2. General procedure for the preparation of polyamides XV–XX

The procedure used was modified from [11]. Solid IPC (1 mmol) was added slowly (10 min) to a solution of MPD (0.9 mmol) and diamine I–V or VII (0.1 mmol) in NMP (5 ml) under a nitrogen atmosphere. During the addition the temperature was maintained at 0–5 °C using an ice bath. The reaction was stirred at room temperature for 2 h and the resulting polymers were precipitated into water (100 ml). After filtration and rinsing with water, the polymer was Soxhlet extracted with methanol for complete removal of

low-mol vacuum

2.3. Ge. XXI and

A soli VI (0.1 MPD (1 in NMP addition ice bath. ature and was pou: with wat and then amide th propertie substrate film by h same cor films on XXI and IR spect actual lu copolym niques [

3. Resu

Table VIII–XI maxima, shows th concentr their mo and fluo absorbar respondi the natur pounds i values of *m* and *n* spectro nophore below th feed rati chloride: sation. F determin respectiv crepancy copolyar (compar

low-molecular fluorescent compounds and then dried under vacuum at room temperature.

2.3. General procedure for the preparation of polyamide XXI and polyesters XXII and XXIII

A solid mixture of IPC (0.9 mmol) and the diacid chloride VI (0.1 mmol) was added slowly (10 min) to a solution of MPD (1 mmol) or diol (BPA or phenolphthalein, 1 mmol) in NMP (10 ml) under a nitrogen atmosphere. During the addition the temperature was maintained at 0–5 °C using an ice bath. The suspension was stirred for 2 h at room temperature and 3 h at 45–50 °C. The slightly yellow viscous solution was poured into water (100 ml). After filtration and rinsing with water, the polymer was Soxhlet extracted with methanol and then dried under vacuum at room temperature. Copolyamide thin films (10 to 100 μm) with good mechanical properties were cast from 3–5% NMP solutions onto glass substrates at 60 °C. Residual solvent was removed from the film by heating it at 100 °C for 6 h under vacuum. Under the same conditions, copolyesters XXII and XXIII formed brittle films on glass substrates. The structures of polyamides XV–XXI and polyesters XXII and XXIII were characterized by IR spectroscopy, optical spectra and GPC (see Table 2). The actual luminophore and nonluminophore molar ratios in the copolymers were determined by spectrophotometric techniques [4] (see Table 2).

3. Results and discussion

Table 1 shows the chemical structure of model compounds VIII–XIV, the positions of the absorbance and fluorescence maxima, and the absorbance extinction coefficients. Table 2 shows the general formula of copolymers XV–XXIII, the concentration of chromophore units in the polymer chain, their molecular weights and the positions of the absorbance and fluorescence spectra maxima. The wavelengths of the absorbance maxima of the model compounds and their corresponding copolymers agree with each other, indicating that the nature of the chromophore groups in both types of compounds is the same. Using the molar extinction coefficient values of the model compounds we were able to estimate the m and n values in the copolymers. As seen in Table 2, the spectrophotometrically determined concentration of luminophore groups (n) in the copolyamides is 1.1–1.7 times below the value calculated on the basis of the initial molar feed ratio of diamines (copolyamides XV–XX) or diacid chlorides (copolyamide XXI) used during the polycondensation. For copolyesters XXII and XXIII the calculated/determined molar ratios of luminophores are 3.3 and 2.5, respectively. We have previously found [4] a similar discrepancy for acridine- and stilbene-containing aromatic copolyamides which can be ascribed to a lower reactivity (compared to MPD) of the initial luminophore diamine.

For copolymers XXI–XXIII, another factor that explains the lower amount of luminophore found in the polymer is the limited solubility of the diacid chloride VI in NMP at room temperature. In order to increase its solubility the reaction temperature was maintained at 45–50 °C during copolycondensation. However, it is known [15] that at these temperatures it is possible to increase the yield of byproducts from a secondary reaction between the aromatic diacid chloride and NMP. As a result, one would expect the molecular weight of the obtained copolymer to be relatively lower. Indeed, we found a direct correlation between polymer luminophore content and its molecular weight. Table 2 shows that the lower the luminophore mole fraction (n , determined spectrophotometrically) the lower the molecular weight of the polymer (XV–XXI). Nonluminophore-containing PMPI had the highest molecular weight ($M_w = 852\,000$).

The bandwidth in the absorbance spectra for most copolymers is broader than for the corresponding model compounds. A similar effect has been observed [6] for the absorbance spectrum of an aromatic polyamide derived from 6,4'-diamino-2-phenylbenzimidazole and terephthaloylchloride as compared to the spectrum of model 6,4'-dibenzoylamino-2-phenylbenzimidazole.

Most of copolymers obtained have intense blue fluorescence in NMP solution with a maximum from 410 to 495 nm (Table 2). There is a red shift in the emission maximum for polymer films compared to their solution emission. This may be attributed to more efficient energy transfer processes in the films, possibly due to a significant contribution of non-radiative energy transfer in the solid state (film) [4]. The fluorescence spectra of model compounds VIII–XI are significantly bathochromically shifted with respect to the spectra of the corresponding copolyamides XV–XVIII. We have previously shown [4] that the introduction of carboxy groups in the acid component of aromatic copolyamides, with acridine fragments in the chain, causes a significant (25–30 nm) red shift in their fluorescence spectra. The red shift is likely due to hydrogen bond formation between the basic units and the carboxy groups.

Fig. 2 shows the absorbance and fluorescence spectra of diamine I, model compound VIII and corresponding copolyamide XV. The absorbance spectra of compounds I and VIII have broad bands with maxima at 355 and 350 nm, respectively. The shorter-wavelength position in the absorbance band of the dibenzoylamino derivative (VIII) reflects the fact that the $-\text{NHCOPh}$ group has weaker electron-donating properties than the amino group in I. It should be noted that the intensity of the absorbance band for model compound VIII ($\epsilon = 2.13 \times 10^5$) is higher than for compound I ($\epsilon = 1.77 \times 10^5$). This can be attributed to the special features found in the electronic structure of the chromophoric groups of these compounds. The long-wavelength transition in compound I involves an electronic system which includes the π -system in diphenylbis(phenylbenzimidazole) and the l -electrons of the nitrogen atoms from both amino groups. Because of the inclusion of the l -electrons in the overall π -

Table 1
Structure and spectral properties of model compounds VIII–XIV

No.	Structure	Absorbance		Fluorescence $\lambda_{\max}$ (nm)
		$\lambda_{\max}$ (nm)	$\epsilon (\times 10^{-4} \text{ l mol}^{-1} \text{ cm}^{-1})$	
VIII		350	21.3	415, 475 sh
IX		387	5.96	513
X		397	21.50	553
XI		383	1.48	529
XII		382	1.75	497
XIII		358 377 397	2.09 3.11 2.96	421 435 sh 454 sh 547
XIV		358 378 397	0.63 0.86 0.83	423 437 467

system the energy of the $S_1^* \rightarrow S_0$ transition in compound I is 4000 cm^{-1} lower than in unsubstituted diphenyl-bis(2-phenylbenzimidazole) [6]. We know that the l orbital of the nitrogen atoms in the amino groups is not parallel to the p_π orbitals of the benzene rings, but lies at a finite angle to it [16]. As a consequence, the intensity of the $(\pi, l) \rightarrow \pi^*$ transition in these systems is lower than in the case where there is a parallel orientation of the l and p_π orbital axes. Evidently, this stereochemical factor is less marked in model compound VIII where the amide functionality and the nitrogen atom l orbital are almost parallel to the p_π orbital.

The identification of chromophoric groups in copolyamide XV is based on the normal spectroscopic rule [6]. In this

rule, the long-wavelength transition in unsaturated molecules with a chain structure containing $-\text{O}-$, $-\text{NH}-$ and $-\text{NH}-\text{CO}-$ bridges is associated with the excitation of the system of conjugated bonds. However, the bridges confine this system of bonds and affect the electronic transition in the same way as substituents of the $-\text{OR}-$, $-\text{NR}-$, etc., type.

These considerations on the nature of the chromophore group in XV are confirmed by data on the effect of hydrochloric acid on the absorbance spectra of the polymer and of model compound VIII. The addition of acid to solutions of these compounds produces the following spectral effects. The absorbance band of a solution of VIII in NMP containing $10^{-4} \text{ mol l}^{-1} \text{ HCl}$ is bathochromically shifted with respect

Table 2
Structure

No.

XV

XVI

XVII

XVIII

XIX

XX

XXI

XXII

XXIII

a Determin

Table 2
Structure and spectral properties of the copolymers studied

No.	Structure	$m:n^a$	Absorbance $\lambda_{\max}$ (nm)	Fluorescence $\lambda_{\max}$ (nm)		Molecular weight	
				Solution	Solid	M_w	M_n
XV		0.92:0.08	358	414 475 sh	485	492000	179000
XVI		0.91:0.09	376 395 sh	424 450 sh	430 sh 470	732000	705000
XVII		0.92:0.08	389	431	490	466000	219000
XVIII		0.94:0.06	382	470	482	229000	146000
XIX		0.93:0.07	375	495	514	313000	158000
XX		0.90:0.10	357 377 369	420 437 459	435 465 sh	843000	703000
XXI		0.94:0.06	358 377 396	427 465 sh	454	239000	124000
XXII		0.97:0.03	356 375 395	425 460 sh	458	11500	5760
XXIII		0.96:0.04	355 376 397	426 463 sh	459	32000	14000

^a Determined spectroscopically.

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Fig. 2. Absorbance (1–3) and fluorescence (4–7) spectra of solutions of diamine I (1, 4), model compound VIII (2, 5), copolyamide XV (3, 6) and film of XV (7).

to the band of the non-acidified solution, and has a maximum at 381 nm and higher intensity ($\epsilon = 2.24 \times 10^5$). At higher acid concentrations (0.1 mol l^{-1}) the position of the band is unchanged but its intensity is slightly higher ($\epsilon = 2.46 \times 10^5$). The spectrum of a solution of XV behaves similarly by having its band maximum shifting from 352 to 361 nm. The reason for the bathochromic shift of the absorbance bands for compounds VIII and XV is probably the same as that previously shown for 6,4'-diamino-2-phenylbenzimidazole (DAPBI) [17]. The effect is due to the protonation of the imidazole ring at the sp^2 hybridized nitrogen. The cationic form of all three compounds shows a lower energy for the electronic transition at the longer wavelengths. The special feature of compounds VIII and XV is that further additions of acid to their solutions do not produce the hypsochromic shift found in DAPBI, which is attributed to additional protonation at the amino groups (as a result of which the l electrons of the nitrogen atoms can no longer be released into the π -system). The absence of this effect in solutions of compounds VIII and XV is consistent with the reduced basicity of the nitrogen atoms of the benzoylamino group compared to those of the amino groups.

Model compound XII received additional attention in our investigation due to the presence of a hydroxy group in the *ortho*-position to the nitrogen atom of the benzoxazole ring. After absorption of a light quantum this molecule, as other internally H-bonded molecules, undergoes a number of changes corresponding to a new distribution of electron density, and finds itself at another lower excited level [18]. After emission of a photon, it again undergoes a number of changes, this time in the opposite direction. The following model [19] can be used for the description of the excited-state proton transfer in molecules, such as 2-(2'-hydroxyphenyl)-benzothiazole and 2-(2'-hydroxyphenyl)benzoxazole and their derivatives (Scheme 1).

According to this model, the proton remains predominantly on the phenol oxygen while in the ground state (enol form). Upon UV excitation, in the first excited singlet state, the

Scheme 1.

Fig. 3. Absorbance (1, 2) and fluorescence (3–5) spectra of solutions of model compound XII (1, 3), copolyamide XIX (2, 4) and film of XIX (5). Y scale represents the actual value for curve 1 only.

phenol is a considerably stronger acid and the nitrogen is a stronger base. Thus, the proton is transferred from the oxygen site to the nitrogen site, and the isomer formed ($S_1'^*$) is more stable than the isomer before proton transfer (S_1^*). $S_1'^*$ can then be regarded as a vibrationally excited form of S_1^* . Then the molecule de-excites to the ground state, emitting a photon. In the ground state the enol form is again the more stable form and the proton will then transfer back to the oxygen. S_0' is also a vibrationally excited state of S_0 . Because of this process the absorption and fluorescence spectra of model compound XII and copolyamide XIX do not intersect (Fig. 3) and the value of Stokes shift is about 6050 cm^{-1} .

A different explanation should be used for the red shift at the long-wavelength part of the fluorescence spectrum for a solution of model XIII (Fig. 4). Figs. 4 and 5 show the absorbance, fluorescence and excitation spectra of model compound XIII and copolyamide XX in NMP. Peak wavelengths for the absorbance spectra of both compounds agree with each other, while the fluorescence spectra are quite different. The short-wavelength band with a maximum at 421 nm is the same for the polymer and the model compound. The typical fluorescence vibronic structure in the spectral

Fig. 4. Absorbance and fluorescence spectra of solutions of model compound XIII ($1.7 \times 10^{-6} \text{ mol l}^{-1}$) (3).

Fig. 5. Absorbance and fluorescence spectra of solutions of copolyamide XX ($1.7 \times 10^{-6} \text{ mol l}^{-1}$) (3).

region from 420 to 580 nm is very similar to the emission from the polymer (Fig. 5). The fluorescence maximum of model XIII ($10^{-5} \text{ mol l}^{-1}$) is at 421 nm, peak maximum of the fluorescence of the copolyamide is at 421 nm (concentration of $10^{-5} \text{ mol l}^{-1}$) to the important to the excitation spectra of the absorbance spectra of the length of emission of the fluorescent chromophore literature data the quantum yield of chromophore to 580 nm

Fig. 4. Absorbance (1), fluorescence (2–5) and excitation (6) spectra of solutions of model compound **XIII** at concentrations 0.4×10^{-6} (1, 2, 6), 1.7×10^{-6} (3), 6.5×10^{-6} (4) and 1.6×10^{-5} mol/l (5).

a of solutions of film of **XIX** (5).

Fig. 5. Absorbance (1), fluorescence (2, 3) and excitation (4) spectra of solutions of copolyamide **XX** (1, 2, 4) and film of **XX** (3).

nitrogen is a m the oxygen S_1^* is more S_1^* . S_1^* can of S_1^* . Then ting a photon. more stable e oxygen. S_0 cause of this tra of model not intersect 5050 cm^{-1} . ie red shift at spectrum for a l 5 show the tra of model . Peak wave- pounds agree are quite dif- imum at 421 :l compound. the spectral

region from 410 to 460 nm can be attributed to the monomer emission from the diphenylanthracene chromophore group (Fig. 5). However, even for diluted solutions of compound **XIII** (10^{-5} – 10^{-6} mol l^{-1}) the long-wavelength part of the fluorescence spectra is broad and structureless beginning at 650 nm, peaking at 547 nm, and having a full width at half-maximum of 4500 – 5000 cm^{-1} . The ratio between intensities of the fluorescence at 547 and 421 nm depends on the concentration of the solution and varies from 5.5 ($C = 2 \times 10^{-5}$ mol l^{-1}) to 0.6 ($C = 0.4 \times 10^{-6}$ mol l^{-1}) (Fig. 4). It is important to notice that the features of the fluorescence excitation spectra of these solutions are very similar to the features of the absorbance spectra and do not depend on the wavelength of emission. We assumed that these spectral transformations could be explained by the formation of a set of fluorescent excimers with participation of the diphenylanthracene chromophore groups. Our results agree with the literature data [20,21] concerning a significant increase in the quantum yield of excimer fluorescence with the increase of chromophore concentration. The spectral region from 510 to 580 nm (Fig. 4) is a common spectral manifestation of

excimer fluorescence for 9,10-disubstituted anthracenes [22,23]. The absence of excimer fluorescence in solutions and films of copolyamide **XX** could be explained by a reduced flexibility of aromatic polyamides which prevents effective intermolecular energy transfer and decreases the probability of excimeric center formation.

4. Conclusions

Intense blue-light emission is observed from the solutions and films of aromatic polyamides and polyesters containing isolated chromophore units. The present results demonstrate that non-conjugated luminescent polymers, obtained by the one-stage copolymerization technique, give materials potentially useful for light-emitting diode applications. This approach provides films with a peak emission wavelength in the spectral region of 430–460 nm, which has a significant blue shift compared with the emission of other known non-conjugated polymers containing isolated chromophore units (485 nm) [12].

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