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Synthesis, Properties, and Guest−Host Systems of Triphenylamine-Based Oligo(arylenevinylene)s: Advanced Materials for LED Applications

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ABSTRACT: The synthesis of triphenylamine-based oligo(arylenevinylene)s was accomplished by Pd-catalyzed one-pot coupling of styrenes and tris(4-bromophenylamine). These oligo(arylenevinylene)s are characterized by temperature-induced crystallization in bulk but are amorphous in guest−host systems with polysulfone from which high-quality films for optical applications were obtained. The photoluminescence spectra of the oligo(arylenevinylene)s differed significantly in different solvents as well as in different polymer hosts which is of interest for multicolored LEDs.

Introduction

Electroluminescence of polymer organic devices has recently attracted considerable interest[1−13] since light-emitting diodes (LED) based on organic materials may have advantages over conventional semiconductor devices. Organic materials can be tailored with respect to their physical properties such as band gap, photoluminescence yield, and charge carrier capabilities. All colors, including the blue range, can be emitted by polymer organic LEDs. Poly(*p*-phenylenevinylene) (PPV) and its derivatives have been investigated for this purpose.

The insolubility and infusibility of PPV is a major drawback which limits its use for LEDs. Additionally, structural defects in the polymer backbone or impurities may be present which detoriate material properties, such as thermal and electrical stability, and quantum efficiency. Using oligo(arylenevinylene)s instead of polymers allows a better control of structure and purity. The disadvantages in film formation of oligo(arylenevinylene)s can be overcome by guest−host systems with amorphous polymers acting as binder for the oligo(arylenevinylene)s.[14,15] However, para-linked *trans*-oligo(phenylenevinylene)s have high melting points and limited solubilities in organic solvents at room temperature and are immiscible with polymeric guests.[15] The solubility and miscibility can be significantly improved by lateral substituents on the phenylene moieties. These materials are characterized by rather low glass transition temperatures and recrystallization from guest−host systems upon annealing above the glass transition temperature.[15]

The triphenylamine-based *trans*-oligo(arylenevinylene)s presented have been already used successfully for LED applications.[7,10, 11] These compounds can form radical cations which make them hole-carrying materials.[7,10] The triphenylamine-based oligo(arylenevinylene)s presented here combine improved hole injection from ITO, hole-transporting properties, and light-emitting properties which make these materials of special interest for LED applications.

We want to report the synthesis and properties of triphenylamine-based *trans*-oligo(arylenevinylene)s. Special focus is on the miscibility of the oligo(arylenevinylene)s with polysulfone which is important with respect to LED application and their optical properties.

Experimental Part

Measurements. DSC measurements were performed by means of a Perkin-Elmer DSC 7 in standard aluminum pans, with a heating rate of 20 °C/min. IR spectroscopy was performed on Perkin-Elmer type 1600, using KBr pellets. ^{1}H-NMR spectra were recorded with a Bruker AC 300 (300 MHz), as well as ^{13}C-NMR spectra (75 MHz). Wide angle X-ray scattering (WAXS) was performed using a WAXS diffractometer (Siemens D 5000, with a Ni filter). Absorption spectra were recorded with a Perkin-Elmer type Lambda 9. Photoluminescence spectra were recorded with a Shimadzu type 1509.

Calculations. Semiempirical quantum mechanical calculations (SEQM) were performed by MOPAC 6.0 with the Parametric Model 3.[16]

Reagents. DMF was distilled over 4,4′-methylenediphenyl isocyanate and catalytic amounts of dibutyltin dilaurate. Chloroform was purified by distillation and filtration. Triethylamine was distilled under an argon atmosphere over KOH. Palladium diacetate ($Pd(OAc)_2$) was used as received (Degussa). Tri-*o*-tolylphosphine (TOP) was synthesized by following the literature.[17] **1** (Aldrich) was recrystallized from ethanol. **2a**,**b**,**d** (Aldrich) were used as received. **2c** was prepared by following a published procedure.[18]

General Procedure for the Synthesis of Compounds 3. A 100 mL flame-dried flask was charged with 24.1 g (50.0 mmol) of **1**, 170 mmol of **2**, 0.337 g (1.5 mmol) of $Pd(OAc)_2$, 2.7 g (9 mmol) of TOP, 18.2 g (179 mmol) of triethylamine, and 200 mL of DMF under an argon atmosphere. This mixture was heated with stirring for 48 h at 80 °C, for 48 h to 90 °C, and for 24 h to 100 °C. After cooling, the reaction mixture was poured into 1500 mL of methanol. The crude solid product was filtered off and purified by chromatography with basic aluminum oxide as the stationary phase (removal of Pd residues) followed by recrystallization.

Tris(4-styrylphenyl)amine (TSA, 3a). Yield: 25.7 g (93.2%). T_g: 74 °C (DSC). Mp: 291 °C (DSC). Anal. Calcd for $C_{42}H_{33}N$ (551.73): C, 91.47; H, 5.99; N, 2.54. Found: C, 90.55; H, 5.97; N, 2.56. IR (KBr): 3026, 1592, 1506, 1317, 1284, 1179, 961, 818, 751, 691 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.0−7.55 (m, 33 H). ^{13}C-NMR ($CDCl_3$): δ (ppm) = 124.2, 126.3, 127.3, 127.4, 128.6, 128.8, 132.1, 137.5, 146.6. MS (70 eV): *m*/*e* 551 (M$^+$, 100%), 450 (6.75%), 276 (21.48%). Absorption spectra λ_{max} (THF): 384 nm. Photoluminescence spectra λ_{max} (THF, λ_{exc} = 375 nm): 455 nm.

Tris[4-(4-methoxystyryl)phenyl]amine (MSA, 3b). Yield: 25.66 g (80%). T_g: 78 °C (DSC). Mp 201 °C (DSC). Anal. Calcd for $C_{45}H_{39}NO_3$ (641.80): C, 84.21; H, 6.12; N, 2.18; O, 7.49. Found: C, 84.41; H, 6.09; N, 2.28; O, not determined.

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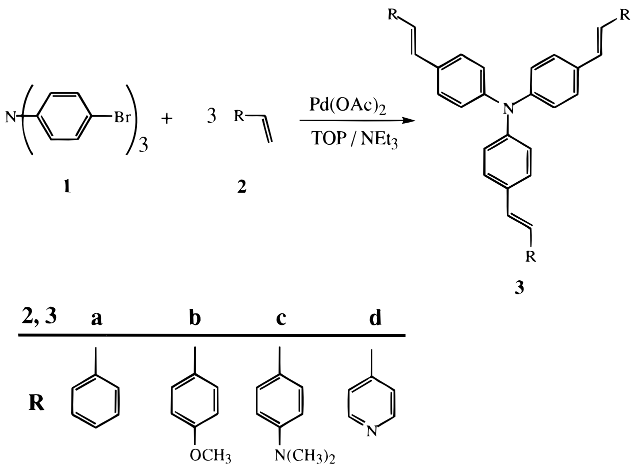
Scheme 1



IR (KBr): 3025, 1606, 1511, 1249, 1174, 1032, 962, 829 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ (ppm) = 3.84 (s, 9H), 6.95−6.97 (m, 6H), 6.90/7.45 (AB, J = 8.8 Hz, 12H), 7.10/7.40 (AB, J = 8.6 Hz, 10H). ^{13}C-NMR (CDCl$_3$): δ (ppm) = 55.26, 114.1, 124.2, 126.0, 126.9, 127.1, 127.5, 130.4, 132.4, 146.4, 159.1. MS (70 eV): *m*/*e* 641 (M$^+$, 100%), 510 (13.4%), 509 (26.3%). Absorption spectra λ_{max} (THF): 390 nm. Photoluminescence spectra λ_{max} (THF, λ_{exc} = 376 nm): 447 nm.

Tris[4-(4-(*N*,*N*-dimethylamino)styryl)phenyl]amine (DSA, 3c). Yield: 25.18 g (74%). T_g: 125 °C (DSC). Mp 258 °C (DSC). Calcd for $C_{48}H_{48}N_4$ (680.90): C, 84.67; H, 7.10; N, 8.23. Found: C, 84.88; H, 7.04; N, 7.96. IR (KBr): 2978, 1607, 1521, 1504, 1442, 1353, 1320, 1286, 1216, 1165, 963, 824 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ (ppm) = 2.97 (s, 18H), 6.96 + 6.87 (d, 6H), 7.41 + 7.06 (m, 12H), 7.36 + 6.81 (m, 12H). ^{13}C-NMR (CDCl$_3$): δ (ppm) = 40.5, 112.6, 124.0, 124.2, 126.8, 127.4, 132.8, 146.1, 149.9. MS (70 eV): *m*/*e* 683 (M$^+$, 6.4%), 682 (16.0%), 680 (100%). Absorption spectra λ_{max} (THF): 401 nm. Photoluminescence spectra λ_{max} (THF, λ_{exc} = 398 nm): 449 nm.

Tris[4-(pyridin-4-ylethyl)phenyl]amine)] (PSA, 3d). Yield: 13.58 g (49%). T_g: 118 °C (DSC). Mp 265 °C (DSC). Anal. Calcd for $C_{39}H_{30}N_4$ (554.66): C, 84.48; H, 5.42; N, 10.10. Found: C, 84.22; H, 5.27; N, 10.16. IR (KBr): 3028, 1589, 1415, 1324, 1289, 1179, 966, 827 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ (ppm) = 6.94 (d, 3H), 7.14 (d, 6H), 7.28 (d, 3H), 7.35 (d, 6H), 7.47 (d, 6H), 8.57 (d, 6H). ^{13}C-NMR (CDCl$_3$): δ (ppm) = 120.7, 124.4, 124.9, 128.2, 131.4, 132.3, 144.7, 147.3, 150.2. MS (70 eV): *m*/*e* 556 (9.8%), 555 (41.4%), 554 (M$^+$, 100%), 451 (12.0%), 452 (5.2%). Absorption spectra λ_{max} (THF): 403 nm. Photoluminescence spectra λ_{max} (THF, λ_{exc} = 403 nm): 479 nm.

Preparation of the Guest−Host Systems. Guest−host systems of **3** and polysulfone (PSu, based on 4,4′-dihydroxydiphenyl sulfone and 4,4′-isopropylidenediphenol) were prepared by dissolution of polysulfone in chloroform and addition of the desired amount of compound **3**. Films were obtained by film casting and drying in vacuum for 5 h at 45 °C. Guest−host systems with polystyrene (PS) and polycarbonate (PC, based on 4,4′-isopropylidenediphenol) were prepared analogously.

Results and Discussion

Synthesis of Triphenylamine-based Oligo(arylenevinylene)s, Thermal Properties, and Miscibility. Triphenylamine-based oligo(arylenevinylene)s were obtained in good yields by one-step Pd-catalyzed coupling reactions of styrenes and tris(4-bromophenyl)amine, which is known as the Heck reaction[19] (Scheme 1). The structures of TSA (**3a**), MSA (**3b**), DSA (**3c**), and PSA (**3d**) were verified by elemental analysis and IR, ^{1}H-NMR, ^{13}C-NMR, mass, absorption, and photoluminescence spectroscopy. It is evident from IR spectra that the vinylene moieties of compounds **3** are trans substituted, which is consistent with literature concerning the Heck reaction. Unlike many other linear para-linked *trans*-oligo(arylenevinylene)s, compounds **3** are easily soluble at room temperature in many organic solvents like THF or chloroform. DSC traces of compounds **3** show high glass transition temperatures (Table 1) in comparison to linear para-linked *trans*-oligo(arylenevinylene)s,[15] which is advantageous for the thermomechanical stability of homogeneous guest−host systems.

Table 1. Glass Transition Temperatures, Melting Points, and λ_{max} of Absorption Spectra of 3

compd	T_g^{a}/°C	mp^b/°C	AB λ_{max}^{c}/nm
3a	74	291	384
3b	78	201	390
3c	125	258	401
3d	118	265	403

[a] Measured by DSC (2. heating run, heating rate 20 °C/min). [b] Measured by DSC (1. heating run, heating rate 20 °C/min). [c] Measured in THF at 20 °C.

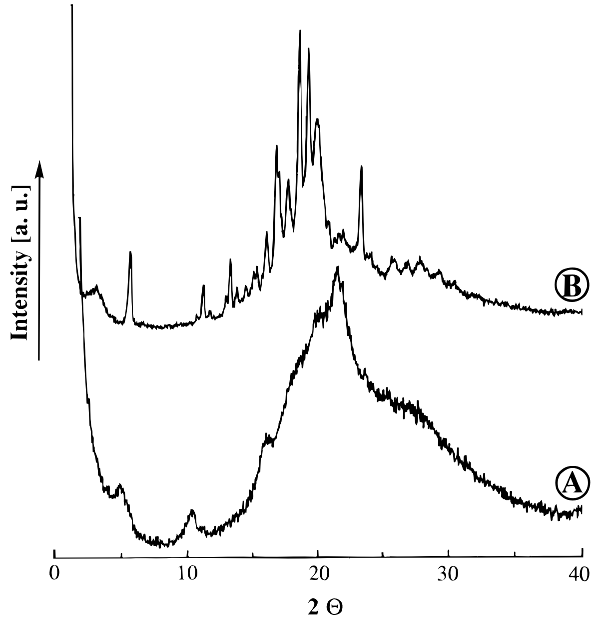


Figure 1. WAXS of **3b** as obtained from solution (dried in vacuum at 50 °C for 2 h) (curve A) and after annealing for 2 h at 97 °C (curve B).

The DSC traces of **3a**−**d** showed endotherms in the first heating runs which represent the melting points of **3** (Table 1). Glass transition temperatures were observed in the DSC traces of **3a**−**d** of the second heating runs, indicating amorphous materials. In the DSC traces of the first heating runs crystallization exotherms precede the melting endotherms of **3a** and **3b**. Temperature-induced crystallization can be crucial for LED cells since this can cause cell failure. Compounds **3** are crystalline or semicrystalline materials, as proved by wide angle X-ray scattering (WAXS). The WAXS of **3b** indicates semicrystallinity (Figure 1, curve A). The degree of crystallinity of **3b** is raised by annealing at 97 °C for 2 h (Figure 1, curve B).

Compounds **3a**−**d** do not form films from solution qualified for optical experiments, which is presumably due to their crystallinity, but high-quality films were obtained by guest−host systems with compounds **3** and polysulfone (Figure 2). Concentrations of 20−50% (w/w) of compounds **3a**−**d** in polysulfone cover the typical composition range for LED applications and were therefore investigated by WAXS in order to evaluate the miscibility of polysulfone and **3a**−**d**. WAXS clearly indicates that guest−host systems with 50% of **3a**−**d**

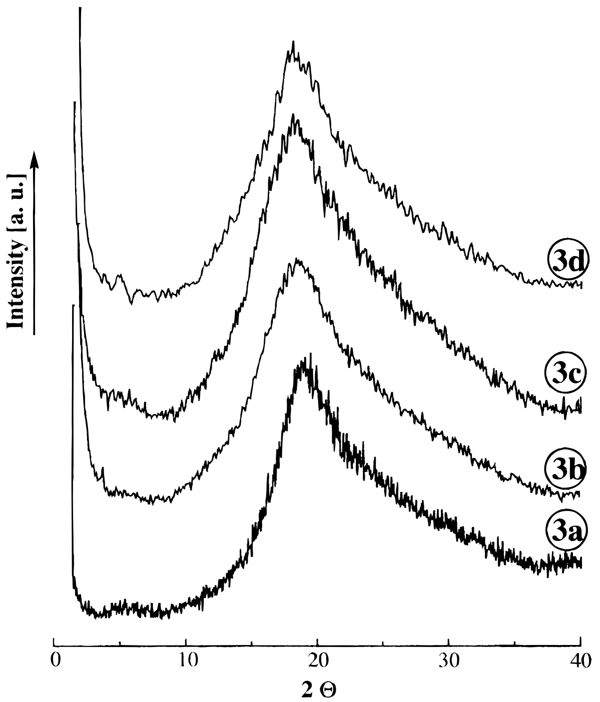


Figure 2. WAXS of mixtures of polysulfone (50% w/w) and **3** (50% w/w) annealed for 2 h at 100 °C.

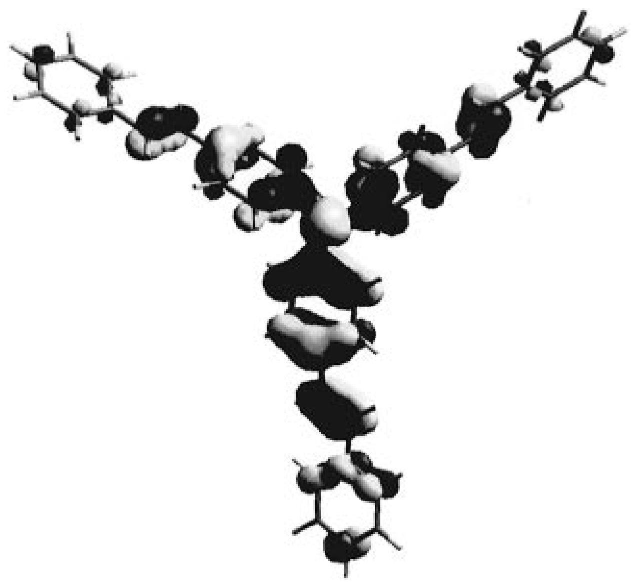


Figure 3. Calculation of the highest occupied molecular orbital (HOMO) of **3a** by SEQM.

in polysulfone are amorphous (Figure 2). However, it cannot be ruled out that extensive annealing at temperatures higher than 100 °C (preferably in the range of the glass transition temperature of the mixture) could cause crystallization-induced phase separation.

Optical Properties of Triphenylamine-Based Oligo(arylenevinylene)s. The π-conjugation of the triphenylamine-based oligo(arylenevinylene)s **3** is not interrupted by the central nitrogen atom. Evidence for this is the absorption spectra of **3a** (λ_{max} = 384 nm) which shows a bathochrome shift in comparison to 4-(*N*,*N*-dialkylamino)stilbene (λ_{max} = 350 nm) which is a structural analogue to **3a** but with only one conjugated branch. This was also confirmed by SEQM calculation of **3a** (Figure 3). It is evident from this calculation that the conjugation passes over the central nitrogen atom, resulting in an extended conjugated system.

Table 2. Dielectric Constants of Different Solvents and Photoluminescence Maxima of 3 in Different Solvents

		PL λ_{max}			
solvent	dielectric constant	TSA, **3a**	MSA, **3d**	DSA, **3c**	PSA, **3d**
ligroin	1.88	417	415	429	426
diethyl ether	4.34	438	431	439	456
THF	7.58	455	447	449	479
acetone	20.70	469	460	468	506
propylene carbonate	65.10	487	475	486	529

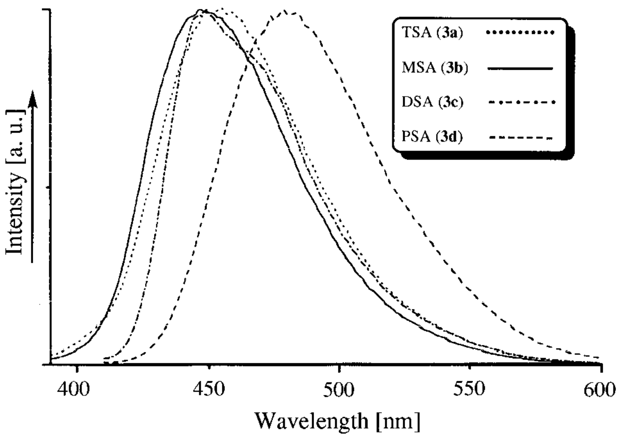


Figure 4. Photoluminescence spectra of compounds **3** in THF.

The absorption spectra show a bathochromic shift in the order **3a**, **3b**, **3c**, and **3d** (Table 1). The photoluminescence spectrum of **3d** in THF was detected at significantly lower energies in comparison to **3a**,**b**,**c**. The λ_{max} values of the photoluminescence spectra of compounds **3** in different solvents differ significantly, which is not unexpected according to the literature.[20] The magnitude of the shift of λ_{max} of the photoluminescence for compounds **3** in different solvents correlates linearly with the dielectric constant of the solvent (Table 2). Surprisingly, a shift of λ_{max} of the photoluminescence of **3d** was also observed in guest–host systems with different polymers which can be regarded as solidified solutions. In contrast to compounds **3a**–**c** the values for λ_{max} of the photoluminescence spectra of **3d** differed significantly in polystyrene, polycarbonate, and polysulfone. However, previous observations did not show a correlation of the photoluminescence spectra of **3d** with the polarity of the host when **3d** was mixed with polystyrene and poly(3,5-bis(trifluoromethyl)styrene).[21] The dipole moments of these polymer hosts differ significantly, but the photoluminescence spectra of **3d** did not. The λ_{max} values of the photoluminescence spectra of **3d** in polystyrene were 478 nm, in polysulfone 492 nm, and in polycarbonate 499 nm (Figure 5). We do not know the reason for this observation, but according to the literature a shift of λ_{max} of the photoluminescence depending on the nature of the matrix should not be observed in the solid state.[20] Regardless of the explanation for the reasons of the shift of λ_{max} of the photoluminescence of compounds **3** in different polymer hosts, this opens interesting perspectives for the design of LEDs. With this concept, multicolored LED devices were realized just by mixing **3d** and two immiscible polymers.[21] The promising potential is the color tuning by control of the host system with the same light-emitting material.

Conclusions

Triphenylamine-based *trans*-oligo(arylenevinylene)s can be prepared by a one-step Heck reaction from

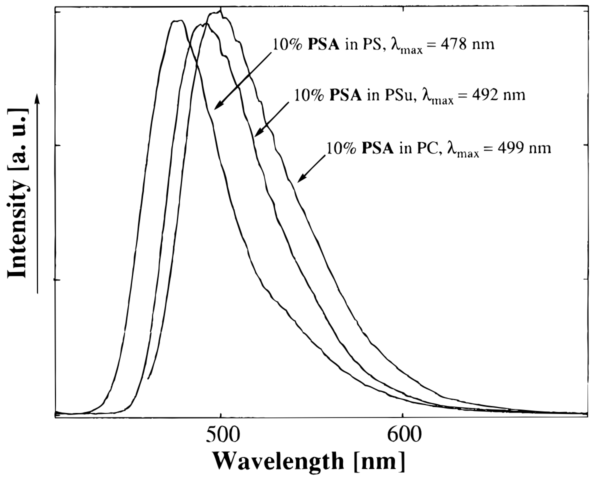


Figure 5. Photoluminescence spectra of **3d** in different polymer hosts (10% w/w of **3d**).

styrenes and tris(4-bromphenyl)amine. The glass transition temperatures of compounds **3** are higher in comparison to glass transition temperatures of known linear para-linked *trans*-oligo(arylenevinylene)s. The central nitrogen atom does not interrupt the π-conjugation, which leads to extended π-conjugation of the branches via the central nitrogen. The film-forming properties of bulk **3** are poor due to the presence of crystallites. High-quality films for optical applications can be obtained by mixing **3** and polysulfone. These guest−host systems form homogeneous transparent films. The triphenylamine-based oligo(arylenevinylene)s are not just another class of electroluminescent materials since they are characterized by a bunch of properties of great interest for LED applications: blue photoluminescence, superior hole carrier capabilities, and very good film-forming properties of mixtures of polysulfone and compounds **3**. Additionally, the choice of the polymer host allows the control of the emission properties, which offers a great potentential for multicolored LEDs.

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