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The Copolymer Route to New Luminescent Materials for LEDs

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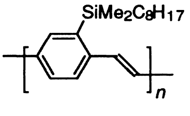
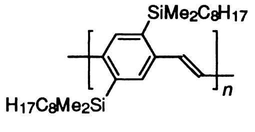
SUMMARY: The synthesis of the highly fluorescent mono- and bis-silylated poly(1,4-phenylene vinylene) derivatives **1** and **2** is reported. The Gilch dehydrohalogenation polycondensation and the Horner synthesis of strictly alternating copolymers have been used to prepare the copolymers **8-11** and **14, 16-18**, respectively, in which the tunability of various optoelectonic properties may be examined systematically.

Introduction

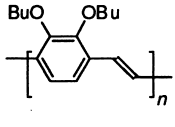
Over the past ten years a variety of conjugated polymers have been studied as the active emissive layer in thin film polymer light emitting devices.[1,2] Poly(1,4-arylene vinylene)s emerged as the early favored candidates for processing either through precursor polymers or in the fully conjugated form. More recently the tunability of the optoelectronic properties of copolymers has attracted considerable interest.[3]



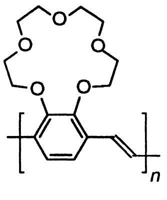
1 DMOS-PPV



2 BDMOS-PPV



3 DB-PPV



4 15C5-PPV

For example using up to three 1,4-bishalomethyl precursors, the Aventis-Covion-Philips group has developed statistical copolymeric poly(arylene vinylene)s exhibiting

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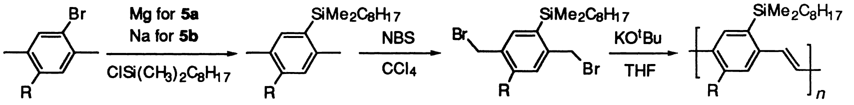
electroluminescence (EL) efficiencies in excess of 16 lm/W at realistic brightnesses (100 Cd m^{-2}).4)

Highly Luminescent Homopolymers

We have previously reported two homopolymers **1**5) and **3**6) which are highly efficient fluorescent materials emitting in the blue-green and green region of the visible spectrum, respectively. These were prepared by Gilch dehydrohalogenation condensation polymerization7) of the corresponding 1,4-bishalomethylbenzene derivatives. We now describe the synthesis of the analogous bis-silylated polymer BDMOS-PPV (**2**).8) The route to both **1** and **2** has much in common and is summarized in Scheme 1 below. One of the disadvantages of the use of *N*-bromosuccinimide for the preparation of dibromomethyl precursors is that the radical bromination step is always accompanied by side products such as monobromo compounds and ring halogenation products, and occasionally the yield of the required product can be modest (see **7b**). Therefore we are presently developing a completely new approach to this important class of compounds, which we shall report in due course. The polymers **1** and **2** are obtained in good yield and with high molecular weights by the Gilch method.

Scheme 1 Synthesis of Polymers **1** and **2**



5a R = H
5b R = Br

6a R = H (45 %)
6b R = $SiMe_2C_8H_{17}$ (60 %)

7a R = H (48 %)
7b R = $SiMe_2C_8H_{17}$ (25 %)

1 R = H (87 %)
2 R = $SiMe_2C_8H_{17}$ (76 %)

The relevant properties of the homopolymers **1**, **2** and **3** are summarized in Table 1. It is observed that all polymers emit either in the green (**1**, **2**) or blue green region of the spectrum with the 2,3-dialkoxy polymer **3** exhibiting the greatest blue shift, presumably as a result of steric and electronic effects. The silyl polymers show a significantly higher oxidation potential than **3** which suggests that lower turn-on voltages and improved efficiencies may be realized for statistical copolymers derived from combining the precursors **7a** and **7b** with monomers having the capability of lowering the oxidation potential.

Electroluminescent devices fabricated with the homopolymer BDMOS-PPV in the configuration ITO/BDMOS-PPV (100 nm)/Al showed light emission at a turn-on voltage of about 6 V in the forward bias direction, and preliminary results suggest that the device characteristics were strongly dependent on film morphology, with the best films arising from processing in toluene solution.8) Further work including the surface characterization of these devices is in hand.

Table 1. Characteristics of DMOS-PPV **1**, BDMOS-PPV **2** and DB-PPV **3**

	DMOS-PPV **1**	BDMOS-PPV **2**	DB-PPV **3**
UV/VIS λ_{max} (nm) ($CHCl_3$)	420	435	444
UV/VIS λ_{max} (nm) (film)	414	438	454
Molecular weight (*Mn*) (GPC)	152,800	173,000	108,000
Polymer yield (%)	87	76	71
PL emission λ_{max} (nm) (film)	523	513	519
PL quantum efficiency (%)	60	60	40
HOMO-LUMO from UV/VIS film (eV)	2.58	2.50	2.4
Oxidation onset potential[a] (V)	1.33[a,b]	1.28[a,b]	1.0[a,b]

[a] Measured as films on a Pt disc electrode in CH_3CN at a scan rate of 20 mV s^{-1} with Pt counter electrode and *n*-Bu_4NClO_4 as electrolyte

[b] Ag/AgCl reference electrode referenced against ferrocene (Fc/Fc^+ 0.43 V)

Copolymers by Gilch Dehydrohalogenation Polymerization

In view of the interesting effects of 2,3-dialkoxy substitution on the properties of poly(1,4-phenylene vinylene) homopolymers we prepared the analogous fused crown ether analog **4** of DB-PPV **3**. This was related to our objective of studying potential emissive materials for applications in light-emitting electrochemical cells where polyelectrolyte supporting side chains may improve device performance.[9)]

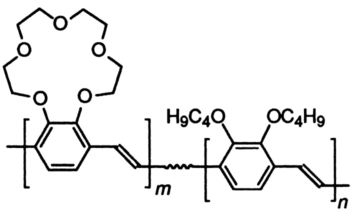
Table 2. Characterization of the homopolymer **4** and copolymers **8-11**

Polymer	Actual polymer composition (m:n)[a]	*Mn*[b] (x 10^3)	PDI	Yield (%)
15C5-PPV (**4**)	-	126	84[c]	58
15C5-DB-PPV (**8**)	2:3	14	9.7	35
15C5-DMOS-PPV (**9**)	2:3	37	7.7	76
15C5-DO-PPV (**10**)	1:2	29	17.9	50
15C5-BDMOS-PPV (**11**)	2:5	77	3.1	15

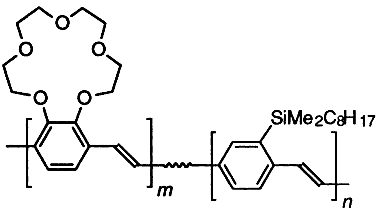
[a] Composition determined from ^1H NMR spectroscopy

[b] GPC in $CHCl_3$ using polystyrene standards

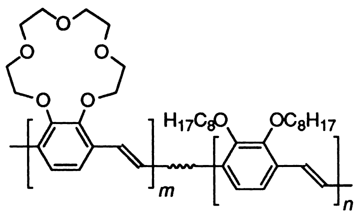
[c] High polydispersity owing to low solubility of polymer



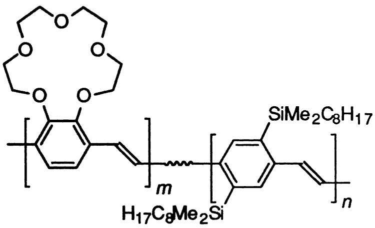
8 15C5-DB-PPV (m:n = 2:3)



9 15C5-DMOS-PPV (m:n = 2:3)



10 15C5-DO-PPV (m:n = 1:2)



11 15C5-BDMOS-PPV (m:n = 2:5)

Various applications of crown ethers in conjunction with electroactive polymers have appeared in the literature.10-12) Our interest was in the crown ether monomer and homopolymers and copolymers arising from it. The copolymers **8-11** were then prepared from the relevant monomeric precursors by statistical copolymerization. The properties are summarized in Table 2.

The optoelectronic properties of these polymers are displayed in Table 3. The overall photoluminescence efficiencies of the copolymers are lower than those of the corresponding parent homopolymers, but reasonable device efficiencies were realized in some circumstances, and the advantage of the copolymers is that oxidation potentials can be lowered. Single layer devices prepared with Al cathodes exhibited similar or higher EL efficiencies compared with devices made with Ca cathodes. The color of the emission varied according to the nature and proportion of each building block. Device characteristics were affected by processing conditions, and it is possible that the crown ether groups may have influenced polymer aggregation.

Table 3. Optical and electrical properties of crown ether polymers **4** and **8-11**

Polymers	15C5-PPV (**4**)	15C5-DB-PPV (**8**)	15C5-DMOS-PPV (**9**)	15C5-DO-PPV (**10**)	15C5-BDMOS PPV (**11**)
Abs. max^a (nm)	442	445	432	446	440
Abs. onset^a (nm)	515	514	507	512	509
HOMO-LUMO (eV)	2.41	2.41	2.45	2.42	2.44
PL emiss. max^a (nm)	553	553	553	549	549 (526)
PL efficiency (%)	9	38	48	52	28
Oxidation onset potential E^{ox}_{onset} (V)	0.7^{a,b}	0.8^{a,b}	0.8^{a,b}	-	-
Reduction onset potential E^{red}_{onset} (V)	-1.4^{a,b}	-1.6^{a,b}	-1.5^{a,b}	-	-
HOMO	-5.1	-5.2	-5.2	-	-
LUMO	-3.0	-2.8	-2.9	-	-
$E_{ec}{}^c$ (eV)	2.1	2.4	2.3	-	-

[a] Measurements on polymer thin films

[b] CV measurements using Ag/AgCl as the reference electrode - values are corrected against ferrocene (Fc/Fc$^+$ 0.43 V), scan rate 166 mVs^{-1}

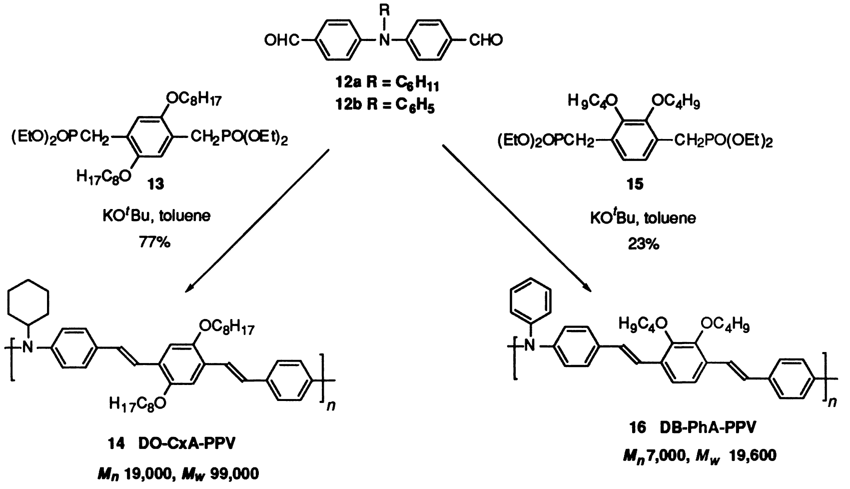
[c] E_{ec} = electrochemical band gap = $E^{ox}_{onset} - E^{red}_{onset}$.

Strictly Alternating Copolymers by Horner Polyolefination

The second family of copolymers to be described are novel hole transport materials based on in-chain tertiary amino groups. Such materials have shown considerable promise in modifying the charge transport properties of luminescent polymers for light emitting devices.$^{13-16)}$

The polyconjugated poly(arylene vinylene) backbone is segmented into distyrylbenzene (DSB) units which are connected by alkylamino and phenylamino groups, respectively. They are prepared by Horner-type polycondensation of arylamine dialdehydes and alkoxy-substituted xylylene bisphosphonates.$^{13)}$ These electron donating substituents lead to a significant decrease in the oxidation potential of the polymers (< 0.66 V *vs.* Ag/AgCl) compared to PPV homopolymers containing only dialkoxy side chains. Owing to their low and reversible oxidation potentials and the high hole mobility, these polymers show favorable properties in low voltage single and multilayer LED devices.

Scheme 2 Synthesis of the strictly alternating copolymers **14** and **16** containing dialkoxybenzene and arylamine groups



Horner polycondensation of the diphenylcyclohexylamino dialdehyde **12a** with the bis-phosphonate **13** in the presence of potassium *t*-butoxide in refluxing toluene afforded the polymer **14** in good yield. The corresponding reaction of the triphenylamino dialdehyde **12b** with the bis-phosphonate **15** afforded modest yields of the polymer **16**. The optical properties of the copolymers **14** and **16** are listed in Table 4. The PL efficiencies in the solid state are much lower than DB-PPV **3**, but are approximately in the same range as arylamine-2,5-dialkoxy PPV copolymers.[13] In contrast, the PL efficiencies in solution were very high (see Table 4).

Table 4 Optical properties of the copolymers **14** and **16**

Polymer	Absorption (film) nm (eV)		PL_{max} in dioxane[a] nm (eV)	PL_{max}[b] (film) nm (eV)	PL efficiency in dioxane[a] (%)	PL efficiency[b] (film) %
	λ_{max}	Band edge				
DO-CxA-PPV (14)	428 (2.90)	500 (2.48)	489 (2.54)	534 (2.32)	78	15
DB-PhA-PPV (16)	434 (2.86)	500 (2.48)	477 (2.60)	525 (2.36)	70	10

[a] Measured using Perkin Elmer LS 50, PL quantum yields were determined from corrected spectra against quinine sulphate as standard (55% quantum yield)
[b] Measured using integrating sphere[17]

Table 5 Redox potentials for DB-amino-PPVs **14, 16-18**

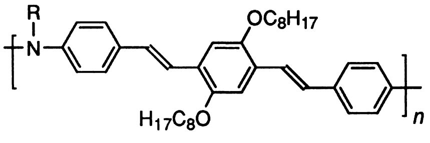
Polymer	Absorption onset[b] (= optical bandgap) nm (eV)	E^{ox}_{peak}[a] *vs.* Ag/AgCl (V)	HOMO level[c] (eV)
DB-CxA-PPV **(14)**	500 (2.48)	0.65	-4.91
DB-PhA-PPV **(16)**	500 (2.48)	0.82	-5.19
DO-MeA-PPV **(17)**	518 (2.39)	0.61	-4.98
DO-PhA-PPV **(18)**	512 (2.42)	0.66	-5.03

[a] Peak potentials obtained from DPP measurements; oxidation processes were fully reversible; Fc/Fc^+ *vs.* Ag/AgCl = 0.43 V

[b] Absorption measurements on polymer films

[c] HOMO level determined using -4.8 eV as the HOMO level for ferrocene *vs.* zero vacuum level

The polymers also showed potential as hole transporting materials by virtue of their acceptably low oxidation potentials. These are illustrated in Table 5. The availability of other 2,5-dialkoxy-methylphenylamino copolymers **17** and **18** provided an opportunity for comparison of properties between two differently substituted polymers. The influence of the connecting amine moiety as the electron-donating functionality is obvious with significant reductions in the oxidation compared with other PPV derivatives such as MEH-PPV. The polymers **14** and **16** showed reversible oxidations.



17 R = Me (DO-MeA-PPV)
18 R = Ph (DO-PhA-PPV)

It can be seen from these results that these copolymers do indeed behave as potential hole-transport materials. Preliminary investigation into their use in double-layer LEDs (with a layer of PSS-doped PEDOT at the ITO electrode) with aluminum and calcium cathodes indicated that they do not exhibit high efficiency EL emission properties. The turn-on voltages however, were low, in the range of 2.4-2.8 V for **16**. The device efficiency for **16** was 0.001 Cd/A with Al as cathode, while the use of a Ca cathode increased the efficiency by an order of magnitude. Future work with these polymers will involve evaluation of their hole-transport capabilities in multilayer devices.

The level of the charge injection barrier with respect to the anode (ITO) and cathode (such as Al and Ca) was estimated from the HOMO values of the materials which can be determined from the cyclic voltammetry/differential pulse polarography measurements. Taking the HOMO level of ferrocene standard as –4.8 eV with respect to zero vacuum level,18) the HOMO levels of these copolymers can be determined (Table 5). The reduction behavior of the polymers was not studied in this research, thus the LUMO levels are estimated from their optical bandgaps. These polymers are predicted to possess high LUMO values (>-2.4 eV), enabling them to act as good electron blocking materials.14-16)

Experimental Section

4,4'-Diformyl-*N*-cyclohexyldiphenylamine 12a

N-Cyclohexyldiphenylamine17) (13.0 g, 0.05 mol), dimethylformamide (15.2 g, 0.2 mole) and $POCl_3$ (31.8 g, 0.2 mole) were heated for 10 h at 70 °C. The reaction mixture was poured onto ice and the aqueous phase was neutralized with NaOH. After extraction of the aqueous layer with $CHCl_3$ the combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was chromatographed over silica gel and eluted with toluene to give the title compound (10.0 g, 63 %) as green-yellow crystals (m.p. 40 °C). ^{1}H NMR ($CDCl_3$) δ 9.9 (2H, s), 7.8 (4H, d *J* 10 Hz), 6,9 (4H, d, *J* 10 Hz), 4.0 (m, 1H), 2.1 - 1.0 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 190.6, 150.4, 131.4, 130.9, 122.6, 57.7, 31.7, 26.0, 25.4.

Poly(cyclohexylimino-2,5-dioctyloxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene) 14

4,4'-Diformyl-*N*-cyclohexyldiphenylamine **12a** (2.5 g, 8.1 mmol) and 2,5-dioctyloxy-1,4-xylylene-bis(diethylphosphonate) **13** (5.2 g, 8.1 mmol) were dissolved in toluene (100 mL) whilst being stirred under argon with heating to reflux. To this solution was added solid KO^{t}Bu (2.8 g,24 mmol) in one portion. After 3 h at reflux the reaction mixture was quenched with aqueous HCl (50 ml). The organic layer was then separated, washed several times with distilled water and dried in a Dean-Stark-apparatus. The resulting toluene solution was filtered, reduced to a minimum and precipitated into methanol. The polymer was extracted with methanol for 4 h and filtered to give a light yellow powder (4.0 g, 77 %). The glass transition temperature was found to be 65 °C (DSC). M_n 19,000 (GPC) M_w 99,600 (GPC) IR film/cm^{-1} 3032 2927, 2853, 1594, 1508, 1204, 963; ^{1}H NMR ($CDCl_3$) δ 7.5 - 7.4 (6H, m), 7.1 (4H, d *J* 10 Hz), 6.9 (4H, d, *J* 10 Hz), 4.1 (4H, m), 3.9 (1H, m), 2.0 - 0.9 (40H, m) ^{13}C NMR ($CDCl_3$) δ 151.0, 145.6, 131.6, 128.1, 127.4, 126.9, 122.8, 121.5, 110.4, 69.6, 57.1, 31.8, 29.3, 29.4, 29.3, 26.3, 26.2, 25.8, 22.7, 14.1. Anal. C, 81.4; H, 9.8; N, 2.1. Calcd. for $C_{44}H_{59}NO_2$ C, 83.36; H, 9.38; N, 2.21.

Poly(phenylimino-1,4-phenylene-1,2-ethenylene-2,3-dibutoxy-1,4-phenylene-1,2-ethenylene-1,4-phenylene) 16

KO^{t}Bu (1.02 g, 9.0 mmol) was added all at once into a hot mixture of 4,4'-diformyl-*N*-phenyldiphenylamine **12b** (0.9 g, 3.0 mmol) and 2,3-dibutoxy-1,4-xylylene-bis(diethylphosphonate) **15** (1.6 g, 3.0 mmol) in toluene (30 cm^3) resulting in a color change to orange-yellow. The mixture was then heated at reflux for 4 h. Upon cooling to room temperature toluene (30 mL) was added. The mixture was then subjected to work-up as described above to give the polymer **16** as a bright yellow powder (0.35 g, 23%); Anal. C, 81.8; H, 7.2; N, 2.75, P, 0.4. Calcd. for $[C_{36}H_{37}NO_2]_n$ C, 83.9; H, 7.2; N, 2.7; P, 0; IR (film)/cm^{-1} 2958 (C-H), 2871 (C-H), 1507 (s), 1430 (Ar), 1324, 1281 (s), 1069 (C-O), 969 (*trans*-vinylene); ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.44-7.04 (19H, m, Ar-*H* and C*H*=C*H*), 4.04-4.01 (4H, m, ArOCH_2), 1.85-1.80 (4H, m, CH_2), 1.62-1.52 (4H, m, CH_2), 1.02-0.98 (6H, m, CH_3); ^{13}C NMR 100 MHz; APT, $CDCl_3$) δ 150.4, 147.2, 146.9 (C, Ar), 132.3, 131.2, 129.3, 128.4, 127.4, 124.8, 124.5, 131.2, 124.0, 121.4, 120.5, (CH, Ar), 73.6 (OCH_2), 32.4 (CH_2), 19.4 (CH_2), 14.0 (CH_3); GPC assay in THF revealed M_w 19.6 x 10^5, M_n 7.7 x 10^4, M_w/M_n 2.5; λ_{max} ($CHCl_3$/nm) 446; λ_{max} (film/nm) 434; PL emission (max)/nm 525; PL efficiency 10%.

Acknowledgements

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