Heteroatom Chemistry
Volume 16, Number 7, 2005

Organoselenium-Substituted Poly(*p*-phenylenevinylene)

Nicolai Stuhr-Hansen,[1] Edwin H. A. Beckers,[2] Lars Engman,[3] and René A. J. Janssen[2]

[1]*Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Denmark*

[2]*Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*

[3]*Uppsala University, Department of Chemistry, Organic Chemistry, Box 599, BMC, S-751 24 Uppsala, Sweden*

Received 2 February 2005; revised 9 August 2005

ABSTRACT: *A new type of conjugated polymer, organoselenium substituted poly(p-phenylenevinylene) (PPV), was synthesized from the corresponding alkylselenenyl p-xylylene dibromide via a Gilch route using potassium tert-butoxide in THF. The p-xylylene dibromide precursors were synthesized by reacting lithiated bis(methoxymethyl)benzenes with elemental selenium, followed by alkylation of the generated selenolates. As a final demasking step, the bromomethyl functions were liberated by ether cleavage using boron tribromide. Bis-alkylselenenyl PPV was obtained with an average molecular weight M_w of approximately 300,000 g/mol and with polydispersity $M_w/M_n = 2$. Due to low solubility, monoalkylselenenyl PPV was obtained with a considerably lower average molecular weight in the proximity of 16,000 g/mol and with a polydispersity slightly larger than 3. Absorption and fluorescence spectroscopy revealed that the bis-alkylselenenyl PPV is extensively conjugated.* Heteroatom Chem 16:656–662, 2005; DOI 10.1002/hc.20167

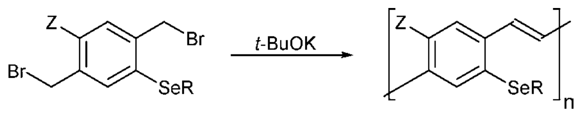
INTRODUCTION

In 1966, Gilch reported [1] the polymerization of *p*-xylylene dibromides into poly(*p*-phenylenevinylene) (PPV) using hindered alkoxides. Since the discovery [2] of electroluminescence in light-emitting diodes (LEDs) based on PPV in 1990, derivatives of PPV have aroused extreme attention [3]. Alkoxy-substituted PPVs have been the most extensively studied primarily due to easy access to these derivatives. However, apart from germyl-substituted PPV [4] and silicon-substituted derivatives [5] applied in the synthesis of trialkylsilyl PPV-derivatives [6], only a few examples of PPV substituted with heteroatoms, e.g. sulfur on the benzene ring [7], have been reported. Studies on the influence of sulfur-containing substituents [8] on the phenylene moiety indicated that alkylthio groups hardly affects the electronic properties of the PPV backbone as an electron-donating group.

In order to see how the properties of the material would be affected, we wished to extend the series of heteroatom-substituted PPVs to include selenium. Selenium-containing polymers based on selenophenes have been described [9]. The properties of these materials are directly related to the Se-atom in the heterocycle, and the lower (as compared with the corresponding thiophene derivative) PL quantum efficiency [10] was ascribed to the

---

Correspondence to: Nicolai Stuhr-Hansen; e-mail: nsh@kiku.dk.



Type A: Z = H
Type B: Z = SeR
(R =2-Ethylhexyl)

SCHEME 1

lower aromaticity of the selenophene moiety and the heavy atom effect. We thought it would be interesting to prepare PPV carrying alkylselenenyl substituents on the aromatic backbone of the polymer. Here we report, for the first time, the synthesis and characterization of such materials. Two new classes of alkylselenenyl *p*-xylylene dibromides (types A and B, Scheme 1) were synthesized by few-step procedures utilizing 1,4-bis(methoxymethyl)benzenes as masked *p*-xylylene dibromides. After conversion into the corresponding dibromides, the alkylselenenyl-substituted monomers were polymerized in a Gilch reaction using potassium *tert*-butoxide to provide π-conjugated, high molecular weight polymers (Scheme 1).

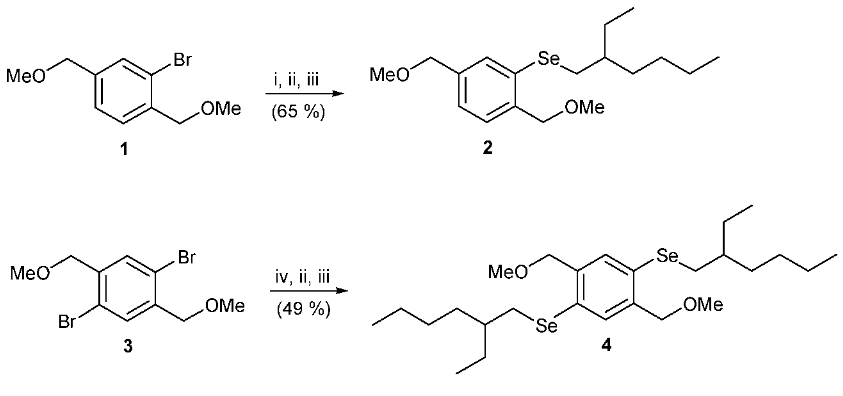
RESULTS AND DISCUSSION

An obvious route to alkylselenenyl *p*-xylylene dibromides (type A or B, Scheme 1) would involve side-chain bromination of the corresponding alkylselenenyl *p*-xylylenes. Unfortunately, the C—Se bond was attacked under radical bromination conditions and bond cleavage occurred even in the case of arylselenenyl *p*-xylylenes. In this case, arylselenenyl bromides and aryl bromides were formed. A different strategy was therefore considered. Masking the benzyl bromide functionality as a methoxymethyl moiety during the synthetic sequences, followed by conversion to the benzyl bromide in a final step, proved to be a valuable way of obtaining PPV monomers of types A and B.

A successful route to monoalkylselenenyl-substituted PPV monomers (type A) was found by metallation of 2-bromo-1,4-bis(methoxymethyl)benzene **1** with two equivalents of *tert*-butyllithium in THF at −78°C followed by addition of elemental selenium (Scheme 2). The aryllithium reagent generated in situ smoothly consumed selenium by warming the suspension to room temperature, upon which alkylation of the lithium arylselenolate with 2-ethylhexyl bromide afforded 1,4-bis(methoxymethyl)-2-(2-ethylhexylseleno)benzene **2**.

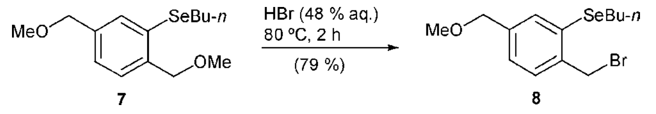
The key step in the synthesis of type B monomers was generation of benzene bis-selenolates from dilithiobenzenes prepared by using the procedures [11,12] for double transmetallation of dibromobenzenes. Two equivalents of selenium and two equivalents 2-ethylhexyl bromide were consecutively added to the slurry of the dilithio salt of 1,4-dibromo-2,5-bis(methoxymethyl)benzene **3** in THF, affording 1,4-bis(2-ethylhexylseleno)-2,5-bis(methoxymethyl)benzene **4** in analogy with the synthesis of **2** (Scheme 2).

Demasking of the benzylic ether functions into the corresponding *p*-xylylene dibromides was attempted with 48% aqueous hydrobromic acid on the model compound 1,4-bis(methoxymethyl)-2-(butylseleno)benzene **7**. Interestingly, after heating at 80°C for 2 h, exclusive monocleavage of the methyl ether function *ortho* to the alkylselenenyl group was observed. 1-(Bromomethyl)-2-(butylseleno)-5-(methoxymethyl)benzene **8** was isolated in high yield as the only cleavage product (Scheme 3). The reason for the selective formation of compound **8** could be neighboring group participation by selenium. The



Reagents and conditions: i, *t*-BuLi (2 eqiuv.), THF, -78 °C, 1h; ii, Se$_8$, r.t., 1h; iii, 2-Ethylhexyl bromide, r.t., 1h; iv, *t*-BuLi (4 eqiuv.), THF, -78 °C then r.t., 1h.

SCHEME 2



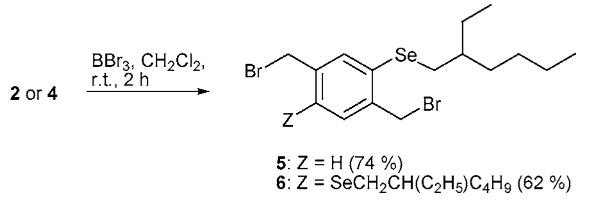
SCHEME 3

intermediate selenonium compound formed by expulsion of methanol was then attacked by bromide at the benzylic position. The corresponding *p*-xylylene dibromide formed only after several hours at reflux. The structure of **8** was established by selective INEPT experiments [13].

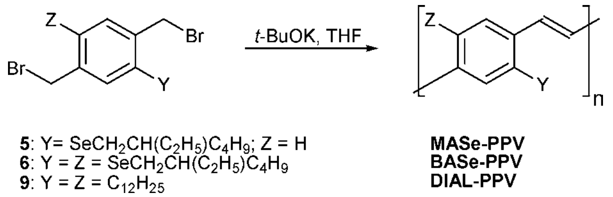
Due to poor solubility, demasking the ether functionality with hydrobromic acid proved quite inefficient when longer than butyl alkylselenenyl groups were present. Among other reagents tried for transformation of compounds **2** and **4** to the corresponding *p*-xylylene dibromides, boron tribromide turned out to be generally useful. Reaction with this reagent in dichloromethane at room temperature smoothly afforded 1,4-bis(bromomethyl)-2-(2-ethylhexylseleno)benzene **5** and 1,4-bis(bromomethyl)-2,5-bis(2-ethylhexylseleno)benzene **6** (Scheme 4).

Organoselenium containing PPV was synthesized by the Gilch polymerization of the alkylselenenylated *p*-xylylene dibromides **5** and **6**. The optimal conditions in terms of the least oligomeric contamination and lowest polydispersity were found by rapid addition of the *p*-xylylene dibromide into a solution of potassium *tert*-butoxide in THF at room temperature. Polymerization of **5** gave poly(2-{2-ethylhexylseleno}-1,4-phenylenevinylene) MASe-PPV. Molecular weight determination by SEC revealed an average molecular weight $M_w = 16{,}000$ g/mol (versus polystyrene standard) with a polydispersity M_w/M_n of approximately 3 ($\lambda_{max} = 430$ nm). The MASe-PPV was found to be only sparsely soluble in organic solvents, and precipitation during polymerization was presumably the reason for the formation of short-chained almost nonprocessable polymer.

The Gilch polymerization of the bis(alkylselenenyl) *p*-xylylene dibromide **6** gave poly(2,5-bis{2-ethylhexylseleno}-1,4-phenylenevinylene) BASe-PPV (Scheme 5), which possesses higher solubility, higher molecular weight, and lower polydispersity than MASe-PPV.



SCHEME 4



SCHEME 5

BASe-PPV was isolated in high purity. Molecular weight determination by SEC revealed an average molecular weight $M_w = 300{,}000$ g/mol and polydispersity $M_w/M_n = 2$, corresponding to an average of approximately 310 monomer units. The polymer was only slightly contaminated with oligomeric material (less than 5%). BASe-PPV was found soluble in chlorinated solvents, but the solubility dropped dramatically upon evaporation and drying. Solubility was too low to get well-defined ^{1}H-NMR data.

Only low molecular weight polymers were obtained upon the Gilch polymerization of alkoxy-substituted *p*-xylylene dibromides. For making comparative studies, we decided to synthesize a dialkyl-PPV and subjected the readily available monomer 1,4-bis(bromomethyl)-2,5-didodecylbenzene **9** [12] to the same conditions as used for the preparation of BASe-PPV. Under these Gilch conditions, **9** smoothly polymerized into poly(2,5-didodecyl-1,4-phenylenevinylene) DIAL-PPV, which in the SEC analysis displayed an average molecular weight $M_w = 200{,}000$ g/mol, and a polydispersity $M_w/M_n = 2$, which corresponds to an average of approximately 225 monomer units.

The UV/Vis absorption spectrum of a BASe-PPV solution in CHCl$_3$ was compared with the spectrum of its monomer to investigate the extent of π-conjugation after polymerization (Fig. 1). The monomer showed a featureless spectrum with an onset at 400 nm (3.1 eV), while the polymer has a clearly observable π-π^* transition with a maximum at 439 nm (2.82 eV) and an onset at 525 nm (2.36 eV). These changes indicate that the polymer is conjugated over several monomer units. The absorption spectrum in the solid state was recorded by drop casting a BASe-PPV solution in CHCl$_3$ on a quartz plate. After drying, the UV/Vis spectrum showed a π-π^* transition with a maximum at 466 nm (2.66 eV) and an onset at 600 nm (2.07 eV), similar to previously reported PPV derivatives [14]. The fluorescence spectra of BASe-PPV exhibited maxima at 518 nm (2.39 eV) and 567 nm (2.19 eV) for a solution in CHCl$_3$ and a solid-state film, respectively (Fig. 1).

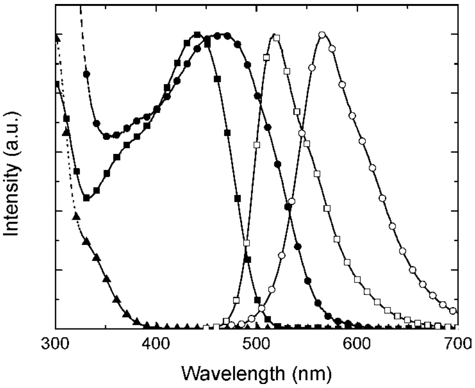


FIGURE 1 Normalized UV/Vis absorption (solid symbols) and fluorescence (open symbols) spectra of BASe-PPV in $CHCl_3$ (squares) and the solid state (circles) together with absorption spectrum of the monomer species **6** in $CHCl_3$ (triangles).

The absorption spectrum of MASe-PPV in $CHCl_3$ (Fig. 2) shows an absorption maximum at 420 nm (2.95 eV) with an onset around 530 nm (2.34 eV), whereas the maximum of the photoluminescence is observed at 497 nm (2.49 eV). The monomer **5** shows a featureless absorption spectrum with an onset at 370 nm (3.35 eV).

For a DIAL-PPV solution in $CHCl_3$, an π-π^*-absorption was observed (Fig. 1) with a maximum at 391 nm (3.17 eV) indicating that polymerization of **9** also results in a conjugated polymer, since the absorption of **9** only shows a featureless spectrum with an onset at 330 nm (3.76 eV). The fluorescence maximum in $CHCl_3$ was observed at 492 nm (2.52 eV).

These results indicate that the optical spectra for BASe-PPV and MASe-PPV are red-shifted compared to alkyl-PPV derivatives (viz. DIAL-PPV). This red-shift is similar to that observed for dialkoxy-PPV, and we infer that the most important contribution to the shift is due to electron-donating alkylselenenyl substituents [15].

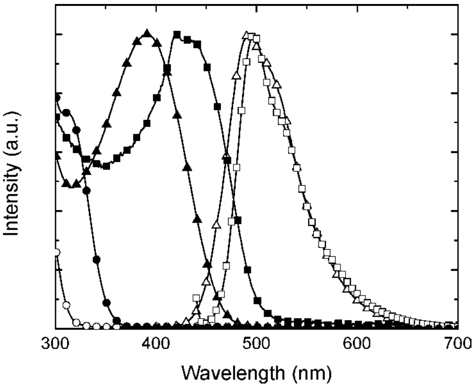


FIGURE 2 Normalized UV/Vis absorption and fluorescence spectra for MASe-PPV (solid/open squares) and DIAL-PPV (solid/open triangles) in $CHCl_3$ together with absorption spectrum of the monomeric species **5** (solid circles) and **9** (open circles) in $CHCl_3$.

EXPERIMENTAL SECTION

Characterization

UV/Vis absorption and fluorescence spectra were recorded on a Perkin Elmer Lambda 900 spectrometer and an Edinburgh Instruments FS920 double-monochromator luminescence spectrometer using a Peltier-cooled red-sensitive photomultiplier, respectively. All photoluminescence spectra were recorded by excitation of the sample at 400 nm. NMR-spectra were recorded on 250, 300, or 400 MHz NMR spectrometers. Gas chromatography mass spectrometry (GC-MS) was recorded on a HP 5972 with mass selective detector, and direct inlet spectra were recorded on a JMS-HX/HX100A (JEOL) tandem mass spectrometer by Katrine M. Petersen and Solveig K. Hansen. Size-exclusion chromatography (SEC) was performed on a Shimadzu LC10-AT versus a polystyrene standard, using a Polymer Laboratories PL Gel 5 micrometer mixed-D column and identically reproduced on a Macherey-Nagel Nucleosil 50-7 column, a Shimadzu SPD-10AV UV-Vis detector at 254 nm and chloroform as eluent. All chemicals were purchased from Aldrich Chemical Co.

Synthesis of 1,4-Bis(2-ethylhexylseleno)-2,5-bis(methoxymethyl)benzene **4**

tert-Butyllithium was titrated with *N*-pivaloyl-*o*-toluidine [16] prior to use. 1,4-Dibromo-2,5-bis(methoxymethyl)benzene **3** [17] (4.86 g, 15 mmol) was added in one portion to a solution of *t*-BuLi (1.5 M in hexane, 40 mL, 60 mmol) and TMEDA (10 mL) in THF (100 mL) efficiently cooled in a dry ice/acetone bath under Ar. The reaction mixture was then allowed to warm to room temperature. Already after a few minutes at room temperature, the dilithio salt began to form as a white precipitate [18]. The reaction mixture was stirred at room temperature for 1 h and then cooled again in a dry ice/acetone bath, after which selenium (2.37 g, 30 mmol) was added in one portion. Subsequently, the reaction mixture was stirred at room temperature for 1 h under argon. Then 2-ethylhexyl bromide (6.37 g, 33 mmol) was added in one portion, and stirring under nitrogen was continued at room temperature for another 1 h. The reaction mixture was poured into water (200 mL) and after separation of the phases the water phase was further extracted with diethyl ether (3 × 25 mL). The combined etheral phases were evaporated on silica gel 60 (2 g), and a foul-smelling fraction was washed through silica gel 60 (10 g) by means of pentane. Subsequent elution with dichloromethane gave the masked *p*-xylylene dibromide **4** (4.01 g, 49%) as a colorless oil. Anal. calcd for $C_{26}H_{46}O_2Se_2$: C 56.93, H 8.45; found: C 57.07, H 8.44. Mass spectrum (EI; *m/z*, relative intensity): 550 (M^+, 100), 406 (22), 294 (9), 262 (23). ^1H NMR (250 MHz, DMSO-d_6): $\delta = 0.79$–0.87 (m, 12H), 1.19–1.21 (m, 8H), 1.30–1.48 (m, 10H), 2.90 (d, 4H, $J = 5.8$ Hz), 3.29 (s, 6H), 4.44 (s, 4H), 7.49 (s, 2H). ^{77}Se NMR [19] (57.3 MHz, DMSO-d_6): $\delta = 200$ ppm.

Synthesis of 1,4-Bis(methoxymethyl)-2-(2-ethylhexylseleno)benzene **2**

2-Bromo-1,4-bis(methoxymethyl)benzene **1** [20] (2.45 g, 10 mmol) in THF (50 mL) was cooled in a dry ice/acetone bath while *tert*-butyllithium (1.5 M in hexane, 13.3 mL, 20 mmol) was added dropwise under nitrogen during a 10-min period. The reaction mixture was stirred under nitrogen for 1 h at –78°C. Selenium (0.79 g, 10 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 45 min. 2-Ethylhexyl bromide (1.93 g, 10 mmol) was added in one portion, and the reaction mixture was further stirred at room temperature for 30 min. The clear reaction mixture was diluted with water (200 mL), and the phases were separated. The aqueous phase was further extracted with diethyl ether (2 × 25 mL). The combined etheral phases were washed with water (15 mL). After evaporation of the solvent and removal of a bad-smelling nonpolar material on a silica gel 60 (10 g) column by means of pentane, the product was eluted with dichloromethane. Evaporation of the solvent gave selenide **2** (2.33 g, 65%) as a light yellow oil (purity >99% (GC-MS)). Anal. calcd for $C_{18}H_{30}O_2Se$: C 60.49, H 8.46; found: C 60.54, H 8.34. Mass spectrum (EI; *m/z*, relative intensity): 358 (M^+, 42), 245 (87), 214 (100), 183 (47). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.85$–0.90 (m, 6H), 1.21–1.31 (m, 6H), 1.36–1.52 (m, 2H), 1.54–1.62 (m, 1H), 2.91–2.93 (m, 2H), 3.36 (s, 3H), 3.40 (s, 3H), 4.42 (s, 2H), 4.55 (s, 2H), 7.17 (d, 1H, $J = 8.9$ Hz), 7.34 (d, 1H, $J = 8.9$ Hz), 7.48 (s, 1H). ^{77}Se NMR (57.3 MHz, $CDCl_3$): $\delta = 251$ ppm.

Synthesis of 1,4-Bis(methoxymethyl)-2-(butylseleno) benzene **7**

Procedure is identical to the synthesis of **2**. Kugelrohr distillation (air-bath 230°C, 10 mmHg) gave **7** (2.42 g, 80%) as a colorless oil (purity >99% (GC-MS)). Anal. calcd for $C_{14}H_{22}O_2Se$: C 55.81, H 7.36; found C 56.10, H 7.44. Mass spectrum (EI; *m/z*, relative intensity): 302 (M^+, 35), 270 (3), 245 (100). ^1H-NMR (250 MHz, $CDCl_3$) δ: 0.91 (3H, t, $J = 7.3$ Hz), 1.35–1.50 (2H, m), 1.61–1.73 (2H, m), 2.90 (2H, t, $J = 7.4$ Hz), 3.36 (3H, s), 3.39 (3H, s), 4.42 (2H, s), 4.54 (2H, s), 7.17 (1H, dd, $J = 7.8$, 1.4 Hz), 7.35 (1H, d, $J = 7.8$ Hz), 7.46 (1H, d, $J = 1.4$ Hz) ppm. ^{77}Se-NMR (57.3 MHz, $CDCl_3$): $\delta = 249$ ppm.

Synthesis of p-Xylylene Dibromides **5** *and* **6**

General Procedure. To a mixture of bis(methoxymethyl)benzene **2** or **4** (10 mmol) in dichloromethane (40 mL) was added boron tribromide (1 M in dichloromethane, 22 mL, 22 mmol) in one portion and stirring was maintained at room temperature for 2 h. The clear dark reaction mixture was poured into water, and the phases were separated. The aqueous phase was further extracted with pentane (2 × 30 mL). The combined organic phases were pooled, washed with water (15 mL), and filtered through silica gel 60 (10 g) by means of pentane. Evaporation of the solvent and drying (vacuum oven, 50°C) afforded the products.

Synthesis of 1,4-Bis(bromomethyl)-2-(2-ethylhexylseleno)benzene **5**. Following the general procedure, a colorless oil (3.36 g, 74%) was obtained. Anal. calcd for $C_{16}H_{24}Br_2Se$: C 42.22, H 5.31; found: C 42.56, H 5.34. Mass spectrum (EI; *m/z*, relative intensity): 456 (M^+, 7), 375 (9), 345 (5), 252 (22), 183 (60), 91 (62), 57 (100). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.85$–0.90 (m, 6H), 1.23–1.28 (m, 4H), 1.31–1.49 (m, 4H), 1.55–1.61 (m, 1H), 2.98 (d, 2H, $J = 6.0$ Hz), 4.40 (s, 2H), 4.68 (s, 2H), 7.19 (dd, 1H, $J = 7.8$, 1.6 Hz), 7.33 (d, 1H, $J = 7.8$ Hz), 7.53 (d, 1H, $J = 1.6$ Hz). ^{77}Se NMR (57.3 MHz; DMSO-d_6): $\delta = 210$ ppm.

Synthesis of 1,4-Bis(bromomethyl)-2,5-bis(2-ethylhexylseleno)benzene **6**. Following the general procedure, light-yellow crystals (3.99 g, 62%, after precipitation from ethanol) were obtained; mp 51–52°C. Anal. calcd for $C_{24}H_{40}Br_2Se_2$: C 44.60, H 6.24; found: C 44.88, H 6.14. Mass spectrum (EI; *m/z*, relative intensity): 646 (M^+, 100), 534 (8), 455 (32). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 0.81$–0.85 (m, 12H), 1.20–1.21 (m, 8H), 1.33–1.40 (m, 8H), 1.48–1.50 (m, 2H), 3.01 (d, 4H, $J = 5.5$ Hz), 4.77 (s, 4H), 7.71 (s, 2H). ^{77}Se NMR (57.3 MHz; DMSO-d_6): $\delta = 189$ ppm.

Synthesis of 1-(Bromomethyl)-2-(butylseleno)-5-(methoxymethyl)benzene **8**

1,4-Bis(methoxymethyl)-2-(butylseleno)benzene **7** (0.90 g, 3 mmol) was vigorously stirred in hydrobromic acid (48 aq., 25 mL) at 80°C for 2 h. The cooled reaction mixture was then diluted with water (100 mL) and extracted with pentane (3 × 25 mL). The combined organic phases were filtered through silica gel 60 (6 g) by means of pentane-dichloromethane (1:1). Evaporation of the solvent and drying (vacuum oven, 50°C) gave selenide **8** (0.83 g, 79%) as a colorless oil. Anal. calcd for $C_{13}H_{19}BrOSe$: C 44.59, H 5.47; found: C 44.68, H 5.32. Mass spectrum (EI; *m/z*, relative intensity): 350 (M^+, 18), 293 (8), 271 (9), 239 (13), 183 (35), 135 (28), 91 (60), 45 (100). ^1H NMR (250 MHz, $CDCl_3$): $\delta = 0.89$–0.94 (m, 3H), 1.38–1.48 (m, 2H), 1.60–1.75 (m, 2H), 2.95–3.00 (m, 2H), 3.39 (s, 3H), 4.44 (s, 2H), 4.72 (s, 2H), 7.19 (d, 1H, $J = 8.0$ Hz), 7.39 (1H, d, $J = 8.0$ Hz), 7.51 (s, 1H). ^{77}Se NMR (57.3 MHz, $CDCl_3$): $\delta = 250$ ppm.

Synthesis of Poly(2,5-bis{2-ethylhexylseleno}-1,4-phenylenevinylene) (BASe-PPV)

1,4-Bis(bromomethyl)-2,5-bis(2-ethylhexylseleno)-benzene **6** (0.19 g, 0.3 mmol) was added in one portion to a vigorously stirred solution of potassium *tert*-butoxide in THF (1 M, 3 mL, 3 mmol) at room temperature. After the addition, the reaction mixture became yellow. The reaction mixture was stirred at room temperature under Ar for 3 h, during which it became dark orange, and then poured into water (50 mL). The polymer was filtered off and washed by Soxhlet extraction with methanol for 12 h. The filter was dried in a vacuum oven (110°C, 10 mmHg) overnight. The polymer was then Soxhlet extracted with chloroform for 12 h and analyzed with GPC and UV/Vis at this stage. Evaporation and drying in a vacuum oven (110°C, 10 mmHg) gave the bis-alkylselenenyl PPV, BASe-PPV (0.10 g, 69%) as a yellow gum. Anal. calcd for $C_{24}H_{38}Se_2$: C 59.50, H 7.91; found: C 58.97, H 7.65.

Synthesis of Poly(2-{2-ethylhexylseleno}-1,4-phenylenevinylene) (MASe-PPV)

MASe-PPV was prepared following the procedure used for synthesizing BASe-PPV using **5** instead of **6** in 74% yield (yellow gum; contains approximately 15% unreacted monomer according to SEC).

Synthesis of Poly(2,5- didodecyl-1,4-phenylenevinylene) (DIAL-PPV)

DIAL-PPV was prepared following the procedure used for preparing BASe-PPV using **9** [12] instead of **6** in 87% yield (yellow flakes). Anal. calcd for $C_{32}H_{54}$: C 87.60, H 12.40; found: C 87.01, H 11.98.

CONCLUSIONS

In summary, we have presented a route to novel PPVs incorporating alkylselenenyl substituents. The alkylselenenyl-*p*-xylylene dibromide precursors used for preparing PPV via the Gilch route were prepared by implementing organometallic procedures [11,12] during which benzylic bromide moieties were masked as ether functions. The bis-alkylselenenyl PPV was obtained with a high molecular weight. The optical properties are similar to those of dialkoxy PPVs and characterized by strong absorption and fluorescence bands of a π-π^* transition. Going from solution to a thin solid-state film, there is a distinct red shift of the optical transitions that is ascribed to interchain interactions occurring in the film.

ACKNOWLEDGMENTS

We thank Dr. Magnus Besev for carrying out the selective INEPT experiments. We are grateful to Dr. Tommi Remonen, Dr. Jonas S. E. Hellberg, Dr. Jonas Malmström, and Dr. Lars Henriksen for supporting fundamental ideas.

REFERENCES

[1] Gilch, H. C.; Wheelwright, W. L. J Polym Sci Part A, Polym Chem 1966, 4, 1337.

[2] Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Nature 1990, 347, 539.

[3] Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. Handbook of Conducting Polymers, 2nd ed.; Marcel Dekker: New York, 1997.

[4] Hwang, D.-H.; Lee, J.-I.; Cho, N.-S.; Shim, H.-K. J Mater Chem 2004, 14, 1026.

[5] Hwang, D.-H.; Kim, S. T.; Shim, H. K.; Holmes, A. B.; Moratti, S. C.; Friend, R. H. J Chem Soc, Chem Commun 1996, 2241.

[6] Ahn, T.; Ko, S.-W.; Lee, J.; Shim, H.-K. Macromolecules 2002, 35, 3495.

[7] Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. Nature 1993, 365, 628.

[8] Yoon, C.-B.; Moon, K.-J.; Hwang, D.-H.; Shim, H.-K. Mol Cryst Liq Cryst 1996, 280, 181.

[9] Yang, R.; Tian, R.; Yan, J.; Zhang, Y.; Yang, J.; Hou, Q.; Yang, W.; Zhang, C.; Cao, Y. Macromolecules 2005, 38, 244.

[10] Yang, R.; Tian, R.; Hou, Q.; Zhang, Y.; Li, Y.; Yang, W.; Zhang, C.; Cao, Y. J Polym Sci Part A; Polym Chem 2005, 43, 823.

[11] Engman, L.; Hellberg, J. S. E. J Org Chem 1985, 296, 357.

[12] Stuhr-Hansen, N.; Christensen, J. B.; Harrit, N.; Bjørnholm, T. J Org Chem 2003, 68, 1275.

[13] Bax, A. J Magn Reson 1984, 57, 314.

[14] Hide, F.; Diaz-Garcia, M. A.; Schwartz, B. J.; Heeger, A. J. Acc Chem Res 1997, 30, 430.

[15] Andersson, M. R.; Yu, G.; Heeger, Synth Met 1997, 85, 1275.

[16] Suffert, J.; J Org Chem 1989, 54, 509.

[17] Bedard, T. C.; Moore, J. S. J Am Chem Soc 1995, 117, 10662.

[18] 1,3-Dilithiobenzene and 1,4-dilithiobenzene also form as white precipitates under these conditions by heating 3- or 4-bromolithiobenzene solutions from −78°C to room temperature in presence of two equivalents of tert-butyllithium.

[19] Eggert, H.; Nielsen, O.; Henriksen, L. J Am Chem Soc 1986, 108, 1725.

[20] Khanapure, S. B.; Biehl, E. R. J Org Chem 1987, 52, 1333.