Origin of the methylene bonds in poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4phenylenevinylene] prepared according to Gilch's method: novel applications

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Abstract: Impurities containing methylene bridges between 2-((2'-ethylhexyl)oxy)-5-methoxy-benzene molecules are inevitably formed during the synthesis of 1,4-bis(chloromethyl)-2-((2'-ethylhexyl)oxy)-5-methoxy-benzene, the monomer used in the preparation of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV), but they can be removed by double recrystallization of the monomer prior to polymerization. When impurities containing methylene bridges participate in a Gilch polymerization, the methylene bonds formed in the main chains are prone to break at 200 °C, that is, at least 150 °C below the major degradation temperature of defect-free MEH-PPV. Interestingly, the thermal treatment used to break the methylene bonds present reduces the chain aggregation of MEH-PPV during film formation and induces its blends with poly(2,3-diphenyl-5-octyl*p*-phenylene-vinylene) (DPO-PPV) to form a morphology similar to that of block copolymers. Both significantly enhance the luminescence properties.

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Keywords: conjugated polymers; luminescence; poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV); light-emitting diodes (LED)

INTRODUCTION

With the merits of low turn-on voltage, good solubility and high electroluminescent (EL) efficiency, poly[2methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) has attracted much attention for its potential applications in polymer light-emitting diodes (PLEDs).¹⁻⁷ The preparation of MEH-PPV is generally carried out through dehydrohalogenation of 1,4-bis(halo-methyl)-2-((2'-ethyl-hexyl)oxy)-

5-methoxy-benzene) monomer, a method that was originally proposed by Gilch and Wheelwright.⁸ Many researchers have attempted to improve its EL performance by thermal annealing above its glass transition temperature in order to reduce the imperfections of the film.^{9,10}

Recently, PPV derivatives prepared via Gilch's route were reported to have some structural defects, such as tolane-bisbenzyl (TBB) moieties,¹¹ non-eliminated groups,¹² and aldehyde.¹² The presence of TBB in MEH-PPV was shown to be detrimental to the lifetime of the prepared LEDs.^{13,14} Lately, we discovered the presence of methylene defects (or bonds) in MEH-PPV chains – defects that are prone to break at 200 °C, at least 150 °C lower than the major degradation temperature of defect-free MEH-PPV. This bond has been mistakenly assigned to the *cis* defect in our previous studies because of the similarity between their ¹H-NMR spectra.¹⁵ Through thermal annealing of MEH-PPV in order to break the methylene bonds at 200 °C, the extent of chain aggregation was significantly reduced, so that the maximum quantum yield of photoluminescence (PL) was increased to six times that of untreated MEH-PPV.¹⁶

Moreover, as MEH-PPV containing methylene bonds was blended with poly(2,3-diphenyl-5-octylp-phenylenevinylene) (DPO-PPV) and then submitted to a thermal treatment at 200°C for 2h, the broken MEH-PPV chain segments were able to chemically bond to the DPO-PPV chains by transvinylization.17,18 This chemical bonding turned the immiscible blend of polymers into a morphology similar to that of block copolymers. MEH-PPV has a solubility parameter $\delta = 20.38$ (J cm⁻³)^{1/2}, whereas DPO-PPV has $\delta = 22.93 \, (\text{J cm}^{-3})^{1/2}$, estimated by the group contribution method. These two polymers are basically immiscible and toluene ($\delta = 18.21 \text{ (J cm}^{-3})^{1/2}$) is a better solvent for MEH-PPV than for DPO-PPV. As toluene was used as a co-solvent for MEH-PPV/DPO-PPV polyblend to spin-cast a film, the DPO-PPV phase formed a domain in the upper layer, which dispersed into the more soluble MEH-PPV-rich phase in the wetting layer. Because both the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) levels of MEH-PPV in

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the wetting layer are higher than those of DPO-PPV in the upper layer, the vertically segregated morphology fits the category of so-called 'type II' heterojunction.^{19–21} As a result, the turn-on voltage of the polymer light-emitting diodes (PLEDs) prepared by the thermally treated polyblend decreased to ~ 0.6 V, and their EL emission intensities and quantum efficiencies increased to about four times those of the untreated polyblend.^{17,18}

In this contribution, we will describe how the methylene bonds form in the MEH-PPV chains and their degradation behavior. Novel applications to enhance the luminescence properties of MEH-PPV and its blends with DPO-PPV through thermal treatment were also elucidated.

EXPERIMENTAL

Materials

All reagents were commercially available and used as received unless otherwise stated. Tetrahydrofuran (THF) was freshly distilled over sodium before it was used. All the reactions were carried out under nitrogen atmosphere. The monomer synthesis and polymerization of DPO-PPV can be found elsewhere.⁶ The monomer used to prepare MEH-PPV, 1,4-bis(chloromethyl)-2-((2'-ethylhexyl)oxy)-5methoxy-benzene, was synthesized according to Ref. 22 with some modifications, which are detailed as follows.

Synthesis of 2-((2'-ethylhexyl) oxy)-5-methoxy-benzene²² A mixture of 4-methoxyphenol (31 g, 0.25 mol) and KOH (19.8 g, 0.35 mol) in methanol was refluxed for 0.5 h. After cooling to room temperature, 2-ethylhexyl bromide (53 g, 0.275 mol) was added dropwise and further refluxed for 48 h until the brownish solution turned light yellow. After the methanol had been removed with a rotary evaporator, the remaining mixture was combined with 250 mL of ether, washed several times with water, and dried over MgSO₄. After removing the solvent, 30.5 g (51.7% yield) of clear liquid product was obtained.

Synthesis of 1,4-bis(chloromethyl)-2-((2'-ethyl hexyl)oxy)-5-methoxy-benzene

The compound (10.62 g, 0.045 mol) prepared above was dissolved in 60 mL dioxane. While the resulting solution was cooled down to 0°C, 45 mL of concentrated HCl and 35 mL of 39% aqueous formalin solution were added. The solution was further saturated with HCl by bubbling gaseous HCl for 20 min before warming up to room temperature. Afterwards, the mixture was stirred at room temperature for 3 days and then refluxed for 3.5 h. After cooling, concentrating, and storing the reaction mixture in a refrigerator overnight, a precipitate of light-yellow crude product was obtained. This crude product was dissolved in a minimum amount of warm hexane and precipitated with methanol again to afford a white crystalline product (11.5 g, \sim 76% yield). To distinguish this product (which contained a small amount of impurities having methylene bridges between 2-((2'-ethylhexyl)oxy)-5-methoxy-benzene)s from the further purified monomers, we designated it as MEH-PPV-monomer I. To remove the impurities, further purification was done by dissolving 1 g of the above product in 50 mL of isopropanol at refluxing temperature (~85 °C). After complete dissolution, the solution was maintained at 80 °C for 0.5 h and then cooled down to room temperature, and a white crystalline product precipitated. After filtration, it was redissolved in chloroform and precipitated with methanol again to obtain MEH-PPV-monomer II (0.3 g, ~30% yield).

Polymerization

Polymerization of MEH-PPV and DPO-PPV monomers were carried out by the Gilch route.^{17,18} In general, 2 g of the monomer was first dissolved in 100 mL of THF. Then, ~4.5 equiv. of potassium tertbutoxide (Lancaster) dissolved in 150 mL of THF was added slowly to the stirred monomer solution under nitrogen atmosphere. After complete addition of the base, the reaction proceeded with stirring at room temperature ($\sim 25 \,^{\circ}$ C) for a further 3 days. A large quantity of THF was used to prevent the formation of a gel in the polymerization system. At the end of the reaction, the solution was poured into rapidly stirred methanol. The precipitate was then collected by filtration. The resulting polymer was obtained after drying in vacuo. MEH-PPVs resulting from monomers I and II are designated MEH-PPV(I) and MEH-PPV(II), respectively. The molecular weights of MEH-PPVs and DPO-PPVs were determined by gel permeation chromatography (GPC) (Table 1).

Blending and thermal treatment

MEH-PPV/DPO-PPV blends in 1:1 weight ratio were prepared by dissolving the individual polymers in THF, mixing the two solutions thoroughly, and then drying *in vacuo*. For thermal treatment, ~0.1 g of the dried blend was tightly wrapped with aluminum foil to prevent contact with air. The thermal treatment was conducted at 200 °C for 2 h under vacuum. The thermally treated samples were then dissolved in 50 mL THF to remove the undissolved portion by filtration through a 0.4 μ m filter. After precipitation from the solution by addition of methanol, the

 Table 1. Molecular weight and polydispersity of MEH-PPV(I),

 MEH-PPV(II) and DPO-PPV^a

Sample	$M_{\rm W}~({\rm gmol}^{-1})$	$M_{\rm n}~({\rm gmol}^{-1})$	$M_{\rm w}/M_{\rm n}$
MEH-PPV(I)	280 000	43 000	6.51
MEH-PPV(II)	333 000	42 900	7.76
DPO-PPV	281 000	72 500	3.87

 ${}^{a}M_{w}$, weight-average molecular weight; M_{n} , number-average molecular weight.

thermally treated polyblend was obtained through filtration and drying *in vacuo*.

Characterization

Gel permeation chromatography measurements on MEH-PPV and DPO-PPV were carried out at 40 °C with a Testhigh series III pump and a Testhigh UV detector. One PhenolGEL 550A column and two PhenolGEL MXL columns in series were used with THF as the mobile phase (1 mLmin^{-1}) . The molecular weights were estimated by reference to polystyrene standards with a narrow molecular weight distribution. ¹H- and ¹³C-NMR spectra of all the samples were recorded on a Bruker Avance 500 spectrometer at frequencies of 500 MHz for ¹H and 125 MHz for ¹³C. All spectra were obtained in CDCl₃ at room temperature. Chemical shifts refer to tetramethylsilane for ¹H and to chloroform-d₁ for ¹³C. Thermogravimetric analysis (TGA) of the polymer samples was conducted in a TA model TGA-51 thermogravimetric analyzer at a heating rate of $10 \,^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$ under nitrogen.

The photoluminescence spectrum was recorded on a SPEX 1403 fluorescence spectrophotometer using a xenon lamp as an excitation source. Two-photon excitation microscopy of thermally treated polyblends in film form was carried out with a Leica TCS SP2 confocal spectral microscope imaging system. The wavelength of excitation source was 488 nm, whereas that of the emitting light was collected in the range $500 \sim 700$ nm. Film samples were prepared by dissolving the thermally treated polyblend in toluene at room temperature, and then spin-casting onto a glass plate. The preparation procedure of PLED device has been given elsewhere.¹⁶ The EL spectrum of thermally treated polyblend was recorded on a SPEX1403 fluorescence spectrophotometer at a forward bias of 15 V.

RESULTS AND DISCUSSION Origin of the methylene bonds

Figure 1 shows the ¹H-NMR spectrum of MEH-PPV-monomer I. Interestingly, a tiny split peak appeared at $\delta = 6.6 \sim 6.7$ ppm, which can only be observed by magnification of the spectrum as shown in the top of the figure. Using column chromatography (silica gel, hexane:ethylacetate = 90:10 by volume) to separate this species from monomer I, and then measuring its heteronuclear multiple quantum correlation (HMQC) spectrum, yielded the result shown in Fig. 2(a). By referring



Figure 1. ¹H-NMR spectrum of MEH-PPV-monomer I. Top: Magnified spectrum of the selected area.

to the reported chemical shift values of bis(4-methyl-2,5-dimethoxyphenyl) methane (Fig. 2(b)) which has a methylene bridge between its 2,5-dimethoxybenzenes,²³ we confirmed that the impurities in MEH-PPV-monomer I contained a similar methylene bridge in between 2-((2'-ethylhexyl)oxy)-5-methoxybenzenes. The original tiny split peak coupled to the carbons at $\delta = 113.4$ and 114 ppm in the HMQC spectrum (Fig. 2(a)) was attributed to the phenylene protons of these 2-((2'-ethylhexyl)oxy)-5-methoxybenzenes. The resonance peak of methylene protons at $\delta = 3.9 \text{ ppm}$ was also coupled to the carbon at $\delta = 29.6$ ppm. Because the reaction scheme to prepare MEH-PPV monomer is similar to that of phenolformaldehyde (except for its higher content in HCl) it ought to have a chance to form the methylene bridge during the early stage of monomer synthesis. The species also carried methylene chloride groups on the other side of 2-((2'-ethylhexyl)oxy)-5-methoxybenzenes as indicated by the presence of the peak at $\delta = 4.7$ ppm (Fig. 2(a)) so that it performed like a monomer. The impurities reached ~10 mol% of the MEH-PPV monomer I as estimated from the ratio of peak area at $\delta = 6.6-6.7$ ppm to its area plus that at $\delta = 6.95$ ppm (Fig. 1). However, it could be completely removed through double recrystallization of monomer I. We designated the fully purified monomers as MEH-PPV monomer II.

As the MEH-PPV monomer I was subjected to Gilch polymerization, the tiny peak still appeared at $\delta = 6.6-6.7$ ppm in the ¹H-NMR spectrum of the resulting MEH-PPV(I) (Fig. 3(a)). However, most of the PPV derivatives prepared via the Gilch route also contain tolane-bisbenzyl (TBB) due to head-to-head or tail-to-tail reactions.¹¹ The phenylene protons of bisphenzyl groups happen to resonate at $\delta = 6.6-6.7$ ppm, which can be seen in the ¹H-NMR spectrum of MEH-PPV(II) (Fig. 3(b)). Dividing the peak intensity at $\delta = 6.6 \sim 6.7$ ppm by that at $\delta = 7.5$ ppm contributed by the *trans*-vinylene bonds for



Figure 2. (a) HMQC spectrum of the species containing methylene bridge separated from monomer I through column chromatography and (b) reported chemical shift values of protons and carbons (bold) for the methylene bridge and phenylene groups of bis(4-methyl-2,5-dimethoxyphenyl)methane.²³



Figure 3. ¹H-NMR spectra of (a) MEH-PPV(I) and (b) MEH-PPV(II).

both polymers, the obtained ratio for the MEH-PPV (I) after subtracting the ratio for the MEH-PPV(II) is also $\sim 10\%$, which is almost equal to the content of the impurities having a methylene bridge in monomer I. The result indicates that most of the impurities containing methylene bridges participated in the Gilch polymerization.

Degradation of methylene bonds and its novel applications

It is generally agreed that *cis*-vinylene protons also resonate at $\delta = 6.5 - 6.8$ ppm for the PPV derivatives prepared by the Wittig reactions.^{24–26} In our previous study, we have mistakenly attributed the peak at $\delta = 6.6-6.7$ ppm for the MEH-PPV prepared from monomer I to the formation of *cis*-vinylene bonds during Gilch polymerization.¹⁵ As the resulting polymer was subjected to thermal treatment at 200 °C for 1-2h, half of the methylene bonds were broken as indicated by the decrease of the peak at $\delta = 6.6-6.7$ ppm.¹⁶ In this study, we have also found that the MEH-PPV(I) began to degrade at $\sim 200 \,^{\circ}$ C, but that the major degradation took place at 367 °C (Fig. 4). In contrast to MEH-PPV(I), MEH-PPV(II) started degrading at ~350 °C but with its major degradation at 395 °C. For MEH-PPV(I), the broken polymer segments during thermal treatment at 200 °C were highly reactive and tended to chemically bond to the adjacent polymer chains, provoking a reduction of chain aggregation. As a result, the PL quantum efficiency in film form was increased to ~ 6 times that of untreated MEH-PPV.¹⁶

The copolymerization of MEH-PPV and DPO-PPV monomers through the Gilch route tended to form an alternate copolymer with reactivity ratios of MEH-PPV and DPO-PPV monomers equal to 0.16 and 0.19, respectively.⁶ As MEH-PPV(I)/DPO-PPV blend in



Structure 1.

1:1 weight ratio was subjected to thermal treatment at 200 °C for 2 h, the broken MEH-PPV chain segments had a tendency to bond to the DPO-PPV chains by trans-vinylization; this is at the origin of the small peak at $\delta = 7.35$ ppm in ¹H-NMR, which stems from the vinylene protons of the moiety (Structure 1), which is the sole vinylene peak for the alternative copolymer prepared from 1:1 molar ratio of MEH-PPV and DPO-PPV monomers.^{17,18} MEH-PPV and DPO-PPV are immiscible. It was also interesting to observe that each DPO-PPV domain (green) of the thermally treated MEH-PPV(I)/DPO-PPV blend was surrounded by a thin layer of red MEH-PPV domains (Fig. 5). As the thermally treated blend was employed as a light-emitting layer for PLED, the turn-on voltage was 0.6 eV - much lower than for that prepared from the untreated polyblend. Its maximum EL intensity was $\sim 2700 \text{ cd m}^{-2}$, about four times that of the untreated blend. The EL quantum yield was $2 \text{ cd } \text{A}^{-1}$, which barely changed with the applied current density, whereas that of the untreated blend decreased from 0.7 to $0.4 \text{ cd } \text{A}^{-1}$ by increasing the current density.^{17,18}

The heterojunction formed between MEH-PPV and DPO-PPV is shown schematically in Fig. 6. MEH-PPV acts like a hole-transport polymer and DPO-PPV like an electron-transport polymer. The energy gap of the heterojunction is only 1.98 eV – lower than the band gap of pristine MEH-PPV (2.14 eV). For the thermally treated blend, the maximum emission wavelength of EL spectrum was at 577 nm (2.15 eV), while that of the PL was at 544 nm (2.28 eV) as indicated in Fig. 7. The difference is 0.13 eV, close to the energy barrier of 0.16 eV between their LUMOs for the excitons to jump from DPO-PPV to MEH-PPV in order to cross the LUMO of the heterojunction (Fig. 6). On the contrary, for the untreated MEH-PPV/DPO-PPV blend, the



Figure 4. TGA plots of (a) MEH-PPV(I) and (b) MEH-PPV(II).



Figure 5. Photo-excitation micrographs of (a) thermally treated and (b) untreated MEH-PPV(I)/DPO-PPV blend.^{17,18}

maximum emission wavelength of PL spectrum is similar to that of the EL spectrum.^{17,18} Therefore, it can be concluded that the thermally treated MEH-PPV(I)/DPO-PPV blend has more heterojunction regions to generate exciplexes than the untreated blend, so that the EL emission is dominated by exciplexes. The EL quantum efficiency was thus significantly increased.

CONCLUSIONS

We discovered methylene defects in MEH-PPV chains, which could only be eliminated by double



Figure 6. Scheme for heterojunction formed between MEH-PPV and DPO-PPV. Electrons from DPO-PPV and holes from MEH-PPV are trapped and form the exciplexes at the heterojunction during EL emission.



Figure 7. EL and PL spectra of thermally treated MEH-PPV(I)/DPO-PPV blend.

recrystallization of the monomers. Because the methylene bonds are prone to break at 200 °C, a thermal treatment could reduce chain aggregation of MEH-PPV in film form, and also turn MEH-PPV(I)/DPO-PPV blends into block copolymer type structures. Both substantially enhanced the luminescence properties.

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REFERENCES

- 1 Braun D and Heeger AJ, Appl Phys Lett 58:1982 (1991).
- 2 Parker ID, J Appl Phys 75:1656 (1994).
- 3 Padmanaban G and Ramakrishnan S, J Am Chem Soc 122:2244 (2000).

- 4 Collison CJ, Rothberg LJ, Treemaneekarn V and Li Y, *Macro*molecules **34**:2346 (2001).
- 5 Chen SH, Su AC, Huang YF, Su CH, Peng GY and Chen SA, *Macromolecules* **35**:4229 (2002).
- 6 Chiu C-C, Lin K-F and Chou H-L, J Polym Sci Part A: Polym Chem 41:2180 (2003).
- 7 Parekh BP, Tangonan AA, Newaz SS, Sanduja SK, Ashraf AQ, Krishnamoorti R, et al, Macromolecules **37**:8883 (2004).
- 8 Gilch HG and Wheelwright WL, J Polym Sci Part A: Polym Chem 4:1337 (1966).
- 9 Lee TW and Park OO, Adv Mater 12:801 (2000).
- 10 Lee TW, Park OO, Do LM and Zyung T, *Synth Met* **117**:249 (2001).
- Becker H, Spreitzer H, Ibrom K and Kreuder W, Macromolecules 32:4925 (1999).
- 12 Roex H, Adriaensens P, Vanderzande D and Gelan J, Macromolecules 36:5613 (2003).
- 13 Becker H, Gelsen O, Kluge E, Kreuder W, Schenk H and Spreitzer H, Synth Met 111:145 (2000).
- 14 Becker H, Spreitzer H, Kreuder W, Kluge E, Vestweber H, Schenk H, et al, Synth Met 122:105 (2001).

- 15 Fan Y-L and Lin K-F, *J Polym Sci Part A: Polym Chem* **43**:2520 (2005).
- 16 Chou H-L, Lin K-F, Fan Y-L and Wang D-C, *J Polym Sci Part B: Polym Phys* 23:1705 (2005).
- 17 Chou H-L, Lin K-F and Wang D-C, *J Polym Sci Part B: Polym Phys* 44:62 (2006).
- 18 Chou H-L, Lin K-F and Wang D-C, *J Polym Res* 13:79 (2006).
- 19 Corcoran N, Arias AC, Kim JS, MacKenzie JD and Friend RH, Appl Phys Lett 82:299 (2003).
- 20 Kim J-S, Ho PH, Murphy CE and Friend RH, *Macromolecules* 37:2861 (2004).
- 21 Morteani AC, Fiend RH and Silva C, Chem Phys Lett **391**:81 (2004).
- 22 Wudl F and Srdanov G, US Patent 5 189 136 (1993).
- 23 Rathore R and Kochi JK, J Org Chem 60:7479 (1995).
- 24 Pang Y, Li J, Hu B and Karasz FE, *Macromolecules* **32**:3946 (1999).
- 25 Fan Q-L, Lu S, Lai Y-H, How X-Y and Huang W, *Macro-molecules* **36**:6976 (2003).
- 26 Drury A, Maier S, Rüther M and Blau WJJ, *Mater Chem* **13**:485–490 (2003).