



Microwave-assisted McMurry polymerization utilizing low-valent titanium for the synthesis of poly 2,6-[1,5-bis(dodecyloxy)naphthylene vinylene] (PNV)

Henrik Thomas^a, Nicolai Stuhr-Hansen^{b,*}, Fredrik Westerlund^{a,c}, Bo W. Laursen^{a,c}, Magnus Magnussen^a, Henning O. Sørensen^d, Thomas Bjørnholm^{a,c}, Jørn B. Christensen^a

^a Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen East, Denmark

^b Department of Medicinal Chemistry, University of Copenhagen, Universitetsparken 2, DK-2100 Copenhagen East, Denmark

^c Nano-Science Center, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen East, Denmark

^d Center for Fundamental Research: Metal Structures in Four Dimensions, Risø National Laboratory for Sustainable Energy, Technical University of Denmark, Frederiksborgvej 399, PO Box 49, DK-4000 Roskilde, Denmark

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ABSTRACT

Poly 2,6-[1,5-bis(dodecyloxy)naphthylene vinylene] is synthesized by microwave-assisted McMurry polymerization utilizing low-valent titanium generated from titanium tetrachloride and zinc. The obtained polymer is fluorescent with an average molecular weight of approximately 65,000 g/mol and a polydispersity of $M_w/M_n \approx 3$. Absorption and fluorescence spectroscopy in solution and on spin-cast thin films reveal that the bis-alkoxy substituted PNV has a short effective conjugation length but a quite efficient exciton migration.

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1. Introduction

Since the discovery of electroluminescence (EL) in a poly(*p*-phenylenevinylene) (PPV)-based light emitting diode (LED) device,¹ derivatives of this polymer have been thoroughly studied.² A naphthalene analogue of PPV, poly 2,6-(naphthylenevinylene), has been less studied and direct transfer of PPV polymerization techniques, such as the widely applied Gilch,^{3–5} Wessling–Zimmermann,⁶ and chemical vapour deposition⁷ (CVD)⁷ polymerization methods, all seem inappropriate since these methods involve quinoid intermediates which are not favourable for the naphthalene structural unit. Polymerization methods are therefore restricted to techniques in which the aromatic system is not directly involved. The poly 2,6-(naphthylenevinylene) system has previously been synthesized using a Horner–Wadsworth–Emmons (HWE) procedure,⁸ but this method requires two different polymerization partners, a bis-phosphonate ester and the corresponding dialdehyde, which have to be present in equal stoichiometric amounts in the reaction mixture during polymerization. Synthesis of PPV derivatives by McMurry polymerization of aromatic dialdehydes utilizing low-valent titanium has been reported using conventional heating.^{9–11} Microwave-assisted McMurry reactions were first reported by us,¹² and dramatic reactivity enhancements

were found. Furthermore, this method produced only *trans* double bonds upon coupling aromatic aldehydes and even short reaction periods were found to be sufficient for complete consumption of all intermediary pinacol product.

Coupling of aromatic dialdehydes using a similar polymerization technique would most likely be a simple and valuable tool for obtaining high molecular weight vinylene-based polymers, and poly 2,6-[1,5-bis(dodecyloxy)naphthylene vinylene] (**2,6-PNV**) was utilized in this study as a model system. The present Letter describes investigations of microwave-assisted McMurry polymerizations of 1,5-bis(dodecyloxy)naphthalene-2,6-dicarbaldehyde (**3**) into poly **2,6-PNV** and the properties of the products.

2. Monomer synthesis

In order to synthesize **2,6-PNV** we initially prepared monomer **3** via a regiospecific method in order to obtain a pure polymer material with as few irregularities as possible, since even small quantities of regioisomer pollution may disrupt polymerization and result in shorter effective conjugation lengths. Direct bromination of 1,5-didodecyloxynaphthalene was not straightforward in terms of regioselectivity because variable amounts of 4,6-dibromo-1,5-bis(dodecyloxy)naphthalene formed along with the desired product 2,6-dibromo-1,5-bis(dodecyloxy)naphthalene **2**.¹³ However, 2,6-dibromo-1,5-dihydroxynaphthalene **1** could be prepared regiospecifically by bromination of 1,5-dihydroxynaph-

* Corresponding author. Tel.: +45 35336208; fax: +45 35336001.

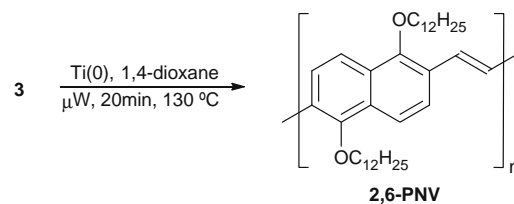
E-mail address: nsh@farma.ku.dk (N. Stuhr-Hansen).

thalene using bromine¹⁴ and successive alkylation with didodecyl bromide was expected to give isomerically pure **2**. Attempted deprotonation of **1** with aqueous base resulted in extensive decomposition presumably because this type of bromohydroxynaphthalene behaved as a reactive bromoketone. When deprotonation was performed with sodium hydride in dry NMP smooth alkylation with dodecyl bromide afforded pure **2**. Double Br/Li-exchange^{13,15,16} was accomplished by treating **2** with *n*-butyllithium followed by quenching with DMF to afford **3** (Scheme 1). Heating the reaction mixture from $-78\text{ }^{\circ}\text{C}$ to room temperature during the metalation was necessary in order to obtain complete Br/Li-exchange. Keeping the reaction mixture at $-78\text{ }^{\circ}\text{C}$ gave almost solely the mono-formylated product 6-bromo-1,5-bis(dodecyloxy)-2-naphthaldehyde after quenching with DMF according to NMR, since the mono-lithiated intermediate precipitated without reacting further with *n*-butyllithium.

3. Microwave-assisted McMurry polymerization

Initial polymerization experiments involved heating **3** in a microwave oven at $110\text{ }^{\circ}\text{C}$ for 10 min in dioxane. After this period, **3** was completely consumed and the reaction mixture was poured into water. The polymer was filtered off and Soxhlet-extracted with isopropanol in order to remove low weight material. Upon Soxhlet extraction with CHCl_3 a polymer with an average molecular weight of 16,000 g/mol was obtained. In order to obtain material with higher molecular weight, the polymerization temperature was increased and the reaction time extended. It was very important that the dioxane was absolutely dry otherwise large amounts of decomposed organic material would settle on the walls of the reaction flask. Interestingly, when the low-valent titanium reagent was prepared in dry media the reaction reached a maximum temperature of approximately $130\text{ }^{\circ}\text{C}$, even when aiming for a much higher maximum reaction temperature by subjecting the reaction to microwave pulses of up to several hundred Watts. This temperature was sufficient in all cases (Scheme 2).

It should be noted that the McMurry reagent should preferably be too diluted rather than too concentrated in order to avoid decomposition of material. Essentially, the heat-sink effect of dioxane was a key element allowing for metal reactions by keeping the temperature low, and it was necessary to have a uniform metal slurry with metal particles as small as possible suspended in the maximum amount of solvent in order to ensure optimal cooling. Visual verification of polymerization in dilution experiments facilitated selection of the optimal concentrations of reactants for polymerization. The reaction mixture must become a green-coloured finely dispersed slurry; if too concentrated, decomposition occurred due to unfavourable settling of the metal-containing particles. In the aggregated solid phase the local temperature was presumably very high and therefore caused extensive decomposition. A number of polymerization experiments with different reaction times were performed at the highest possible practical temperature of $130\text{ }^{\circ}\text{C}$. A maximum yield of 67% was obtained by heating for 20 min at this temperature. The importance of the polymerization time-span was also investigated by polymerizing at

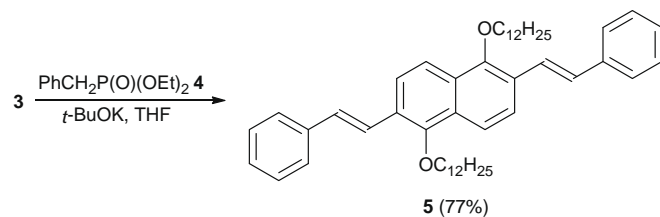


Scheme 2.

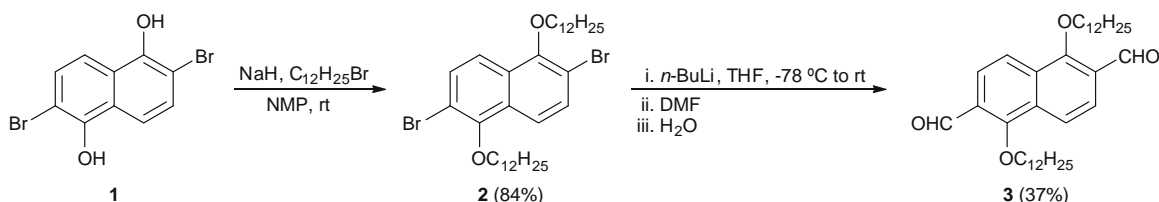
$130\text{ }^{\circ}\text{C}$ for 30 min and 1 h, respectively. Extended reaction times seemed to have no influence on the yield and polymer chain length. Isolation of **2,6-PNV** was performed by Soxhlet extraction due to its limited solubility in all the solvents examined. However, even upon prolonged extraction, non-extracted material remained in the Soxhlet filter. The results from GPC-analysis of the Soxhlet extracts versus a polystyrene standard of extracts of products obtained after extended heating were similar and showed a polymer with an average molecular weight (M_w) of approximately 65,000 g/mol and with a polydispersity of $M_w/M_n \approx 3$.

The model compound, 1,5-bis(dodecyloxy)-2,6-distyrylnaphthalene (**5**) prepared for optical studies of an isolated 2,6-naphthylene vinylene segment, was obtained by a Horner–Wadsworth–Emmons (HWE)^{16,17} reaction between **3** and diethyl benzylphosphonate (**4**) (Scheme 3).

The crystal structures of **3** and **5** were determined by single crystal X-ray diffraction.¹⁸ The molecular inversion symmetry of both molecules was utilized in their crystal packing. The packing motifs of both compounds are comparable as they consist of layers of mainly the aromatic moieties in between layers of alkoxy chains (see Fig. 1). Despite this similarity, there are minor differences in the crystal packing. The interactions between the aromatic system in compound **3** consist purely of $\pi \cdots \pi$ interactions (overlapping ring systems), whereas the interactions between the aromatic systems in **5** are comprised of $\pi \cdots \pi$ as well as perpendicular edge-to-plane interactions ($\text{C-H} \cdots \pi$). This introduces a small difference in the direction of the alkoxy groups with respect to the plane of the aromatic ring system. In compound **5** the alkoxy groups extend parallel to the plane, and in **3** they extend about 25° out of the plane, see Figure 2. Overall the packing of both compounds is very efficient, as reflected by the similar crystal densities of 1.14 and 1.12 g cm^{-3} for **3** and **5**, respectively. The conjugated aromatic system of **5** is slightly distorted, with an angle between the least-



Scheme 3.



Scheme 1.

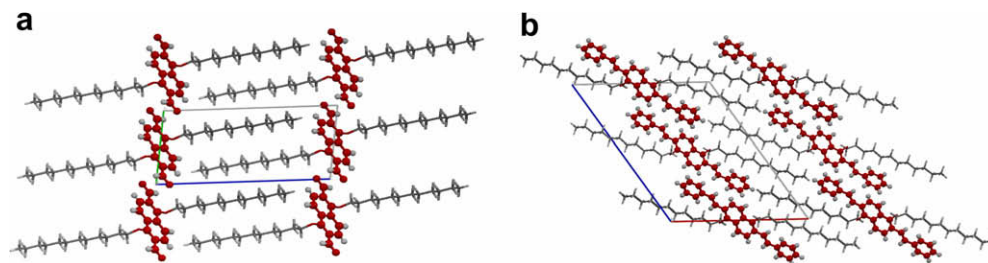


Figure 1. Illustration of the layered structure in the crystal packing of **3** (a) and **5** (b).

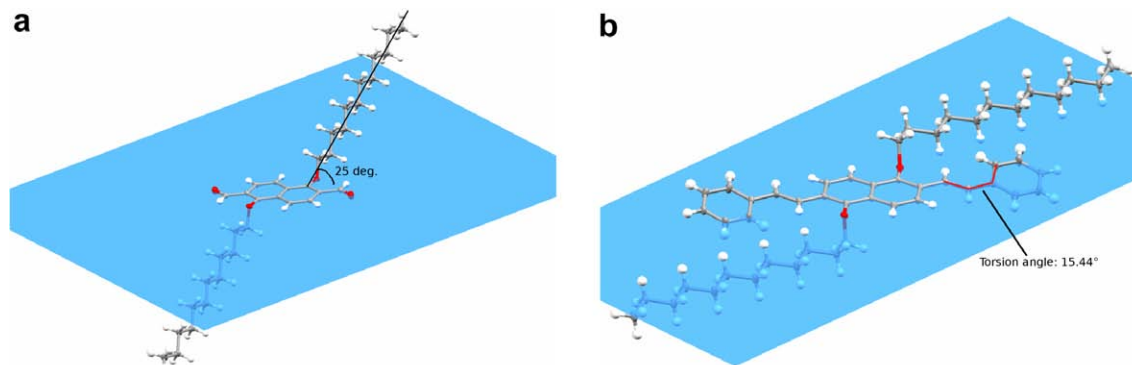


Figure 2. The molecular structures of **3** (a) and **5** (b) obtained by X-ray diffraction. The least-squares plane of the C atoms in the naphthalene group is shown in blue.

squares plane of the naphthalene unit and the phenyl group of only 15.44(5)°.

4. Optical properties of PNV

The optical properties of the PNV-polymer **2,6-PNV** and model compound **5**, in CHCl_3 and as thin films spin-cast on glass were investigated by UV-vis and fluorescence spectroscopy (Fig. 3). Model compound **5** displays an absorption spectrum with clear vibrational fine structure, with a peak separation of approximately 1300–1400 cm^{-1} (Fig. 3a, left). The transition at 392 nm is assigned to the (0,0') vibrational transition. This corresponds to a red-shift of more than 60 nm compared to unsubstituted 1,5-dialkoxy-naphthalene for which Guldi et al. reported the (0,0') transition at ca. 330 nm.¹⁹ However, it is also blue-shifted by approximately 20 nm relative to the PNV trimer for which the (0,0') transition was reported at 413 nm.¹⁹ The thin film spectrum of **5** is red-shifted by 20 nm compared to the solution spectrum and shows a somewhat different intensity pattern for the vibrational peaks, but with a similar splitting between the peaks. The model compound **5** displays a small Stokes shift (less than 1000 cm^{-1}), both in solution and in thin film, which is in agreement with that reported for the PNV trimer.¹⁹ We observed a similar vibrational pattern for the emission as for the absorption and again, the thin film spectrum was red-shifted by approximately 20 nm relative to the spectrum in solution.

The absorption spectra for the PNV-polymer **2,6-PNV** in CHCl_3 and as a thin film were identical, with a maximum absorption at 385 nm and a dominating low energy vibrational transition at 420 nm (Fig. 3b, left). The vibrational spacing of 1300–1400 cm^{-1} was similar to the model compound **5**. As mentioned above, the trimer had a maximum absorption at 413 nm. The small difference between the trimer and the polymer suggests that the average absorbing chromophore-unit in the polymer consists of only 3–5 effectively conjugated monomer units. Geometry optimization of **5** by semi-empirical methods²⁰ suggests that a

large torsion angle between the plane of the central naphthalene group and the flanking phenylene group may exist. This distortion of the conjugated system could be the reason for the decoupling of the units from each other in the polymer and the low number of monomer units in the average chromophore, even in the polymer with an average chain length of approximately 125 units. In contrast to the large angle between the ring systems obtained in the theoretical calculations, only a small angle was observed in the crystal structure of **5** (see Fig. 2a). This difference can be explained by the solid-state packing effect and low-energy barrier for rotation of the phenylene. When looking at the shape of the absorption spectra of **5**, the trimer and the polymer, it is evident that there is a much larger tail at the red edge of the absorption spectrum for the polymer (up to 470 nm). This is most likely due to absorption from much longer coplanar segments. That there is no difference between the absorption spectra in solution and as a thin film indicates that there is no significant improvement of coplanarity or strong inter-chain interactions in the thin film and hence the polymer is quite disordered both in solution and in the spin-cast films.

The most interesting observation in the emission spectra of the polymer is the much larger apparent Stokes shift compared to both **5** and the trimer. While the trimer emits at 427 nm, the polymer emits at 500 nm in solution and at even longer wavelengths in the thin film. This observation is best explained by efficient exciton transport in the disordered polymer which funnels the excitation energy to the segments with the most effectively conjugated monomer units and thus the lowest energy, resulting in a significant red-shift of the fluorescence. A careful investigation of the emission spectrum of **2,6-PNV** in solution reveals that there are small shoulders at the blue-edge of the spectrum, corresponding to emission from shorter segments, in agreement with this prediction. The shoulders on the blue side of the spectrum are lost in the thin film, where the probability of inter-chain exciton transfer is higher and hence a larger fraction of excitons will reach the long conjugated segments.

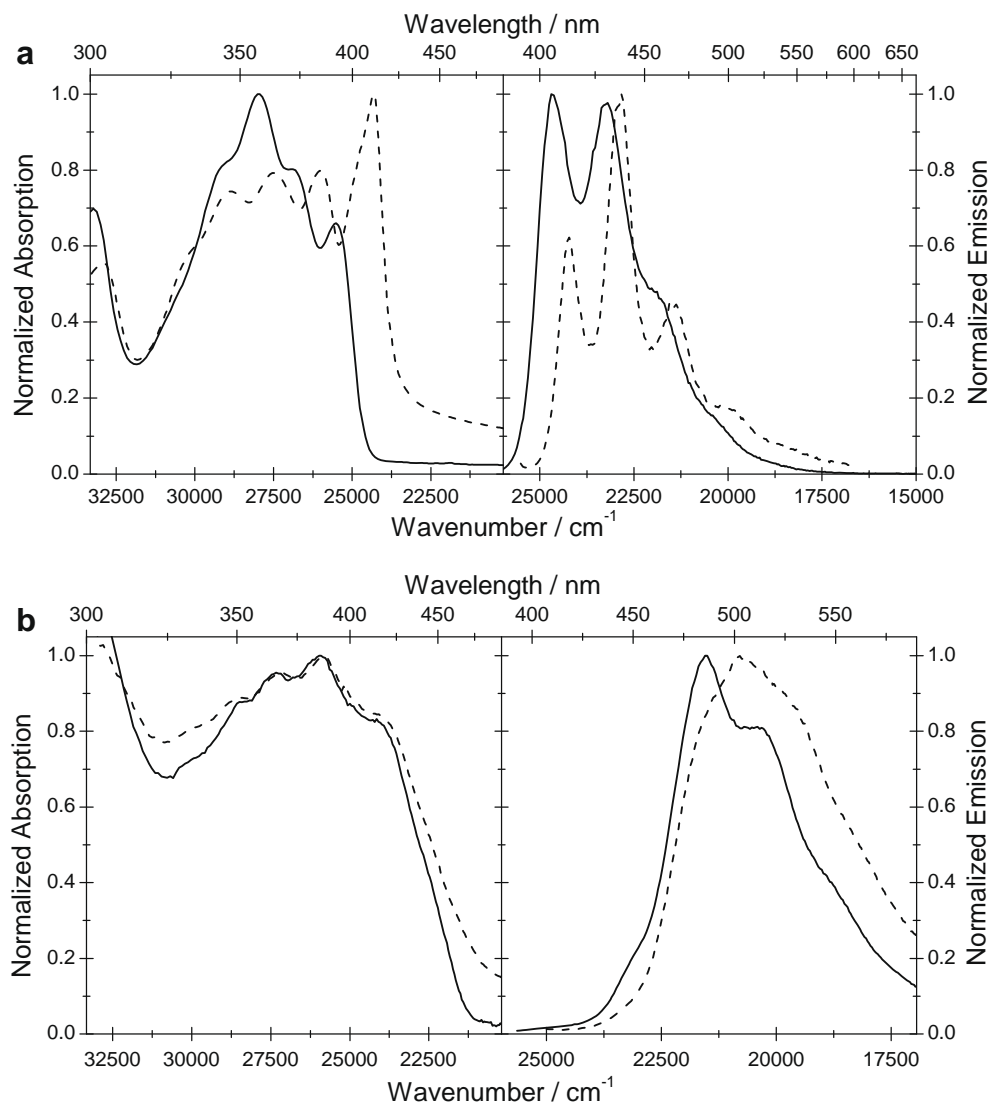


Figure 3. (a) Absorption (left) and emission (right) spectra of model compound **5** in CHCl₃ (solid lines) and as spin-cast thin films (dashed lines). For the emission measurements the sample was excited at 373 nm (solution) and 384 nm (on glass), respectively. The shape of the absorption spectrum in solution is invariant between concentrations of at least 1×10^{-6} and $2 \times 10^{-5} \text{ M}^{-1}$; emission spectra were recorded at an absorption below 0.10 to avoid inner filter effects. (b) Absorption (left) and emission (right) spectra of the PNV-polymer (**2,6-PNV**) (solid lines) and as spin-cast thin film (dashed lines), excitation at 385 nm for both solution and thin film. The shape of the absorption spectrum in solution is invariant between concentrations of at least 1×10^{-6} and $2 \times 10^{-5} \text{ M}^{-1}$ (monomer units in the polymer); emission spectra were recorded at an absorption below 0.10 to avoid inner filter effects.

We have demonstrated that the microwave-assisted McMurry reaction using low-valent titanium is a useful method for symmetrical coupling of dialdehydes into polymeric materials, viz. **2,6-PNV**. This polymer was obtained with a relatively high molecular weight, but due to only limited solubility in organic solvents, the maximum molecular weight of 65,000 g/mol might represent the chain length of the largest extractable polymer. The described method, and microwave-assisted McMurry reactions in general, are highly facile and should be extendable to rapid effective polymerization of any aromatic dialdehyde. The polymer has a relatively high optical band gap (approximately 425 nm), probably due to geometrical distortions in the backbone.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.10.083.

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