

# Poly(2-hexyl-9,10-anthrylene vinylene) – A new class of soluble poly(anthrylene vinylene)s

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## Abstract

A new class of soluble poly(9,10-anthrylene vinylene)s was synthesised using a metathesis approach. In five reaction steps the precursor polymer was derived, which was then dehydrogenated to yield the conjugated poly(2-hexyl-9,10-anthrylene vinylene) (pHAV). This polymer was chemically characterised (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FT-IR, SEC) and investigated with respect to its photo-physical (photoluminescence (PL), refractive index (n), extinction coefficient (κ)) and its film forming (atomic force microscope (AFM)) properties.

**Keywords:** transition-metal-catalysed reaction, photoluminescence, poly(phenylene vinylene) and derivatives, atomic force microscope

## 1. Introduction

Organic polymers consisting of single and double bonds have attained a strong interest in science since the discovery of their potential application in opto-electronic devices [1]. Attention has been intensively attracted by poly(arylene vinylene)s, poly(*p*-phenylene vinylene) being the prototypical representative. Little notice has been given to poly(9,10-anthrylene vinylene), the reason being its synthetic inaccessibility. So far only oligomeric model compounds [2] and the homologue poly(1,4-anthrylene vinylene) [3] have been synthesised. From investigations of such oligomers remarkable properties, such as good charge-storage and electrical conductivity in the doped state, are expected [4]. Motivated by these prospects and taking a new approach via ring opening metathesis polymerisation (ROMP) of a dibenzobarrelene derivative with subsequent dehydrogenation, we succeeded with the synthesis of poly(2-hexyl-9,10-anthrylene vinylene) (pHAV).

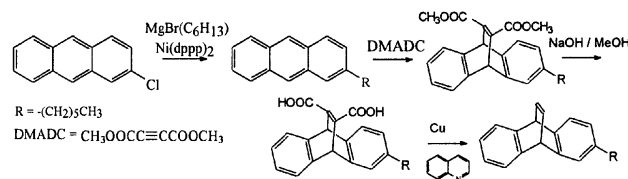
## 2. Experimental

All reactions were standard chemical reactions. Inert N<sub>2</sub>-atmosphere was used for the polymerisation with the Schrock type molybdenum carbene complex.

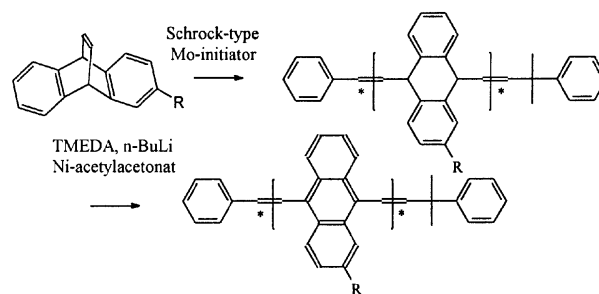
### 2.1. Syntheses

The 2-hexyldibenzobarrelene monomer was synthesised as depicted in Scheme 1. The following polymerisation and the subsequent dehydrogenation of the

precursor polymer led to pHAV as shown in Scheme 2, the end product being fully conjugated according to <sup>1</sup>H-NMR. Detailed information on the chemical syntheses will be published elsewhere [5].



Scheme 1: Four steps to gain the 2-hexyldibenzobarrelene monomer



Scheme 2: Reaction scheme showing the polymerisation and the subsequent dehydrogenation to give the fully conjugated polymer

## 3. Results and Discussion

Both polymers, the precursor polymer and the fully conjugated polymer, were examined focussing on their photo-physical properties.

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The precursor polymer and pHAV were characterised by optical absorption spectroscopy, PL excitation, emission spectroscopy and ellipsometry.

Homogeneity of the film surface was detected by atomic force microscopy, giving a surface roughness of less than 5nm – high quality thin films could be formed (Figure 1). The thickness of a typical film was measured to be approx. 85nm.

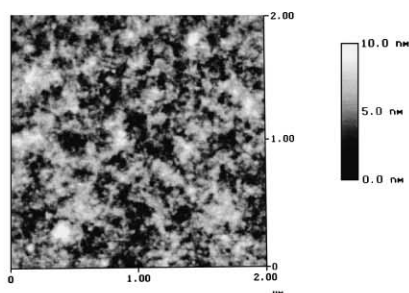


Figure 1: AFM graph of a spin cast thin film of pHAV showing the smoothness of the film

The spectral dependence of the optical constants (refractive index ( $n$ ), extinction coefficient ( $\kappa$ )) was obtained by variable angle scanning ellipsometry (VASE).

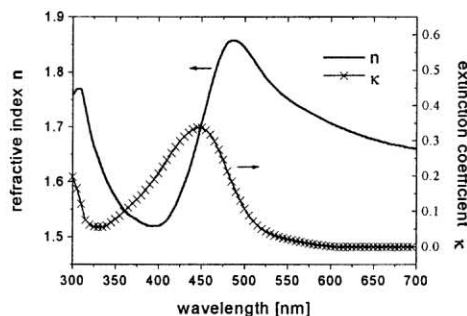


Figure 2: Determination of the optical constants  $n$  and  $\kappa$  for a film of pHAV

In the optical absorption spectra of solution (in  $\text{CHCl}_3$ ) and thin film (spin cast from solution) of pHAV, the width of the absorption spectrum is caused by the conjugation length distribution present in this polymer in solid film as well as in solution. The shape of the optical absorption for film and solution led to the conclusion that the conjugation length distribution and therefore the conformation of the polymer chain are about the same in solution and in solid state. For the precursor no absorption was detected.

In Figure 3 the PL emission spectra for the precursor and the conjugated polymer in solid state (spin cast thin film) are depicted. Comparison with the 9,10-dihydroanthracene shows that the structure of the spectrum gets lost due to the broad distribution of conjugation lengths in the precursor polymer. Upon excitation at the absorption peak (450nm) of the conjugated polymer we observe a structure less photoluminescence emission (peak

at 580nm) from the singlet excited state in the conjugated backbone, similar to what was observed for thin films of poly(naphthylene vinylene) [6].

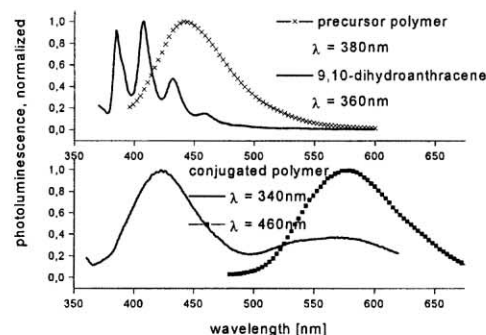


Figure 3: Photoluminescence spectra of the precursor, the conjugated polymer and of 9,10-dihydroanthracene in film

From preliminary cyclic voltammetric (CV) studies we observe an onset for the p-doping around 800mV corresponding to a HOMO level value of  $E_{\text{HOMO}} = 5.5\text{eV}$ , a  $E_{\text{HOMO-LUMO}} = 2.4\text{eV}$  (see Figure 2) and  $E_{\text{LUMO}} = 3.1\text{eV}$ . The peaks on the reverse scan refer to the “de-doping” of the polymer, presumably going in two distinct steps.

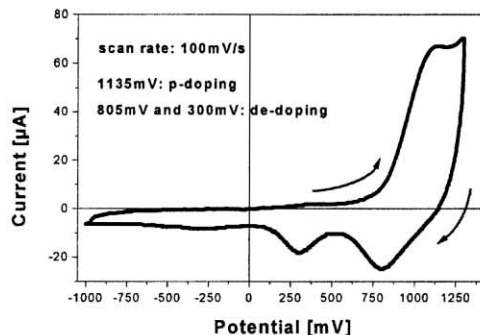


Figure 4: CV of a film of pHAV; 0.1 M  $\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_3\text{CN}$ ; working electrode: Pt foil; reference electrode: Ag/AgCl wire; scan rate: 100 mV/s

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