

# Poly(triacetylene)s: A New Class of Linearly $\pi$ -Conjugated Oligomers and Polymers with an All-carbon Backbone

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**Abstract:** Linearly  $\pi$ -conjugated polymers are intensively investigated in both academia and industry for a diversity of advanced materials applications. Polyacetylenes (PAs) and poly(diacetylene)s (PDAs) were among the earliest investigated linearly  $\pi$ -conjugated polymers possessing an all-carbon backbone. They actually represent the first members in an entire progression of linear all-carbon polymers which starts with polyacetylene and ultimately extends to carbyne. Here, we describe the discovery and systematic investigation of poly(triacetylene)s (PTAs), the third class of compounds in this progression. We report both the preparation of longer-chain polydisperse PTA polymers as well as the synthesis, characterization, and physical study of monodisperse oligomers with record lengths extending up to 18 nm. We show how molecular properties evolve into the saturation range with increasing oligomeric length and report several direct determinations of the effective conjugation length (ECL), *i.e.* the oligomeric length at which saturation of molecular properties occurs. Finally, we present a new class of hybrid oligomers and polymers, with a diversity of chromophores inserted as functional spacers into the PTA backbone for further enhancement of optoelectronic properties.

**Keywords:**  $\pi$ -Electron conjugation · Molecular wires · Nanomaterials · Oxidative acetylenic coupling · Poly(triacetylene)

## 1. Introduction

Linearly  $\pi$ -conjugated organic polymers and oligomers have attracted enormous interest as advanced materials over the past two decades due to advantageous properties such as inherent synthetic flexibility, potential ease of processing, and the possibility of tailoring structural and electronic characteristics to accomplish a desired function. The range of their potential technological applications is very broad and includes electrically conducting materials [1], light-emitting diodes (LEDs) [2], laser dyes [3], scintillators [3], piezoelectric and pyroelectric materials [4], photoconductors [5], optical data storage devices [6], optical switching and signal processing [7], as well as nonlinear optical devices [8–10].

Among the first linearly  $\pi$ -conjugated polymers investigated for advanced materials properties were the polyacetylenes (PAs) [1][11] and poly(diacetylene)s (PDAs) [12]. They actually represent the first members in an entire progression of polymers featuring non-aromatic all-carbon backbones which starts with polyacetylene and extends to the elusive linear carbon allotrope carbyne (Fig. 1) [13]. Here, we describe the discovery [14–16] and investigation of the third family of compounds in this progression, the poly(triacetylene)s (PTAs). We summarize parts of our work on the synthesis and physical study of monodisperse oligomers prepared as models for the corresponding infinite polymers [17][18]. Finally we show how the advanced materials properties of PTA derivatives can be further enhanced by introduction of other chromophores into the conjugated backbone, leading to novel hybrid oligomers and polymers.

## 2. PTA Polymers

PTA polymers were synthesized for the first time after suitable monomeric

tetraethynylethene (TEE, 3,4-diethynylhex-3-ene-1,5-diyne) and (*E*)-1,2-diethynylethene ((*E*)-DEE, (*E*)-hex-3-ene-1,5-diyne) building blocks had become available [15][16][19]. Starting from such monomers, we prepared by oxidative acetylenic coupling [20] under end-capping conditions a series of longer-chain PTA polymers such as the air-stable derivatives **1–3** (Fig. 2) [15][21]. Salient general features of these polymers are high thermal and environmental stability, remarkable solubility, and large third-order nonlinear optical responses. Polymer **1** was the least soluble but could be dissolved and analyzed spectroscopically in hot chloroform or in 1,2-dichlorobenzene above 65 °C. The two other derivatives **2** and **3** are highly soluble in common organic solvents at ambient temperature. Thermal gravimetric analysis indicated that **2** is stable up to 310 °C under N<sub>2</sub> and to 250 °C under air with a maximum of 5% mass loss [21].

The optical gap of **1** was determined as  $E_g = 2.0$  eV, which is in the range of the values measured for PDAs [22]. In **2**, with laterally appended *N,N*-dialkylaniline donor groups, the optical gap is substantially reduced and appears at  $E_g =$

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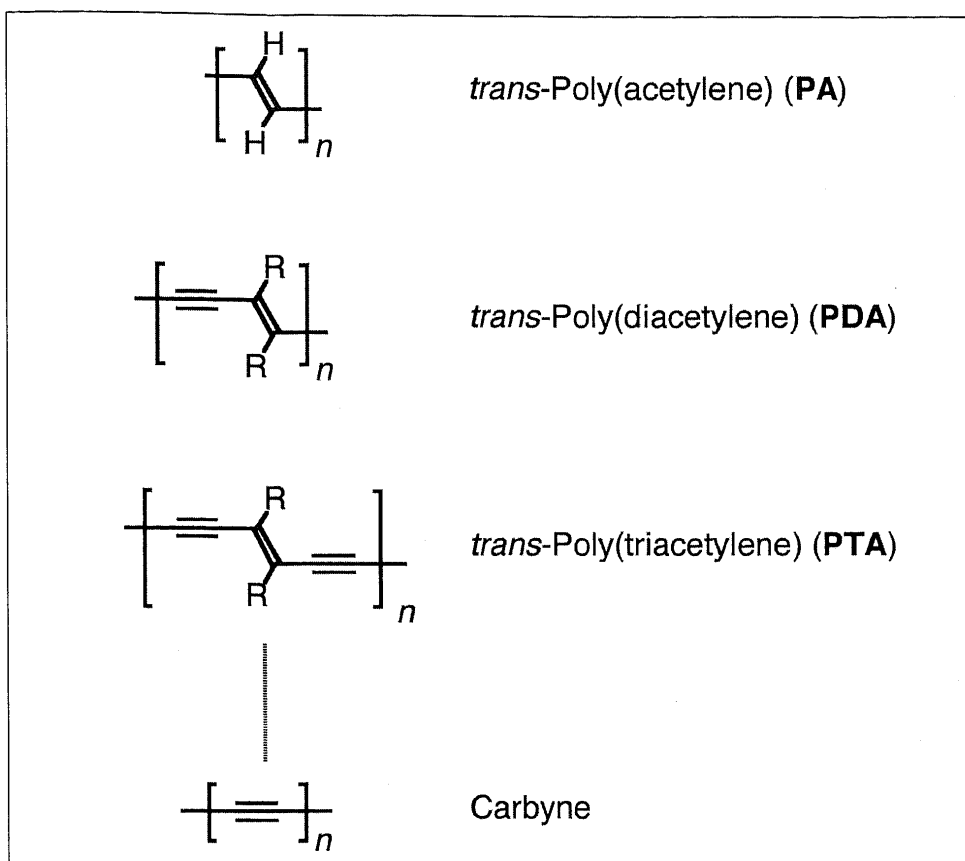


Fig. 1. Progression of linearly  $\pi$ -conjugated all-carbon backbones from *trans*-polyacetylene (PA) via *trans*-poly(diacetylene) (PDA) and *trans*-poly(triacetylene) (PTA) to carbyne.

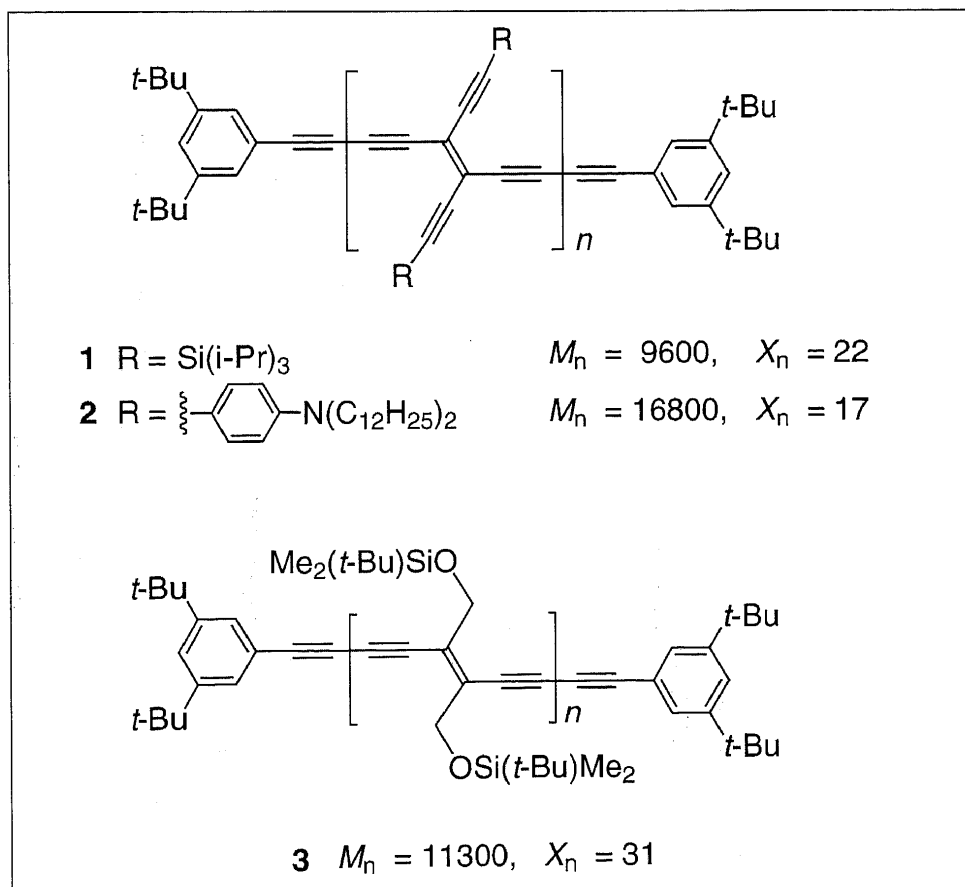


Fig. 2. Poly(triacetylene) polymers prepared by oxidative acetylenic coupling under end-capping conditions [15][21].  $M_n$  = number-averaged molecular weight,  $X_n$  = degree of polymerization (DOP).

1.6 eV. Lacking the laterally appended alkynyl groups, **3** features a much larger optical gap with  $E_g = 2.4$  eV. PTAs **1** and **3** are readily reduced electrochemically, but cannot be oxidized below 1.0 V in  $\text{CH}_2\text{Cl}_2$  or THF (vs. the ferrocene/ferricinium couple  $\text{Fc}/\text{Fc}^+$ ). Thus, **1** is reversibly reduced at the remarkably low potential of  $E = -0.65$  V (vs.  $\text{Fc}/\text{Fc}^+$ ). In contrast, **2** also undergoes additional reversible oxidations centered on the dialkylaniline chromophores.

Recently, a particularly interesting result was published by Fowler and co-workers [23], who accomplished the first PTA synthesis by topochemically controlled polymerization of hexa-1,3,5-triynes in the crystal. A sophisticated supramolecularly controlled spatial alignment of the hexa-1,3,5-triynes in the crystal lattice was required for this 1,6-polymerization to occur. Mechanistically, this 1,6-polymerization resembles the topochemical polymerization of buta-1,3-diyne to PDAs.

### 3. Monodisperse Oligomers as Models for Infinite PTA Polymers

In a first attempt to extrapolate properties of infinite PTA polymers from studies of monodisperse oligomers, we prepared in 1994 by oxidative oligomerization of a suitable TEE monomer under end-capping conditions a first oligomeric series **4a–e** [16] extending in length up to 5 nm (Fig. 3). These highly colored molecular rods are amazingly stable and can be stored on the laboratory bench for months without decomposition. Correspondingly, they are not oxidized below 1.0 V in THF (vs.  $\text{Fc}/\text{Fc}^+$ ). On the other hand, they show remarkable reduction behavior. In CV experiments, they undergo facile one-electron reductions, with the number of reversible reduction steps being equal to the number of TEE repeat

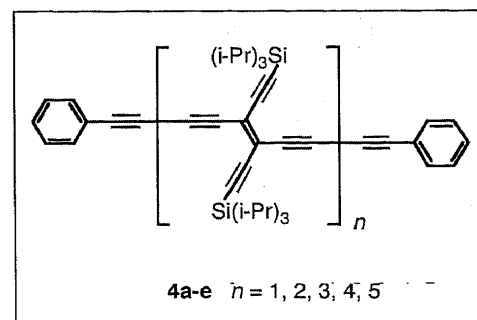


Fig. 3. Readily reducible monodisperse PTA oligomers prepared by oxidative Hay oligomerization under end-capping conditions [16].

units in each molecular rod. Thus, the first reduction of **4a** occurs at  $E = -1.57$  V (vs.  $Fc/Fc^+$  in THF) whereas the first reduction of the 49.2 Å long wire **4e** is much more facile, occurring at  $-1.07$  V.

For an authoritative investigation of structure-property relationships in PTAs, we prepared the monodisperse oligomeric series **5a–k** extending from the 0.96 nm long monomer **5a** to the 17.8 nm long tetracosamer (24-mer) **5k**. For the synthesis of this remarkable family of molecular rods, we employed a fast and efficient statistical deprotection-oxidative Hay-oligomerization protocol (Scheme 1) [24–26]. This strategy relies on a statistical deprotection of the terminal  $SiEt_3$  groups of suitable 'macromonomers' under generation of a mixture of terminally bis- and mono-deprotected oligomers next to some unreacted starting material. This is explicitly shown in Scheme 1 for the deprotection-oligomerization cycle starting from 'macromonomer' **5g**. This mixture is then directly oligomerized under Hay conditions [20b]. This efficient synthesis protocol avoids isolation and tedious purification of the rather unstable unprotected alkyne

intermediates. Tetracosamer **5k** prepared this way (Scheme 1) is the longest known monodisperse molecular rod featuring a fully  $\pi$ -conjugated, non-aromatic all-carbon backbone (for other multinanometer-long monodisperse oligomers see [17][18][27][28]). With this oligomer, we have reached the polymer size range which was previously accessible only by polydisperse material.

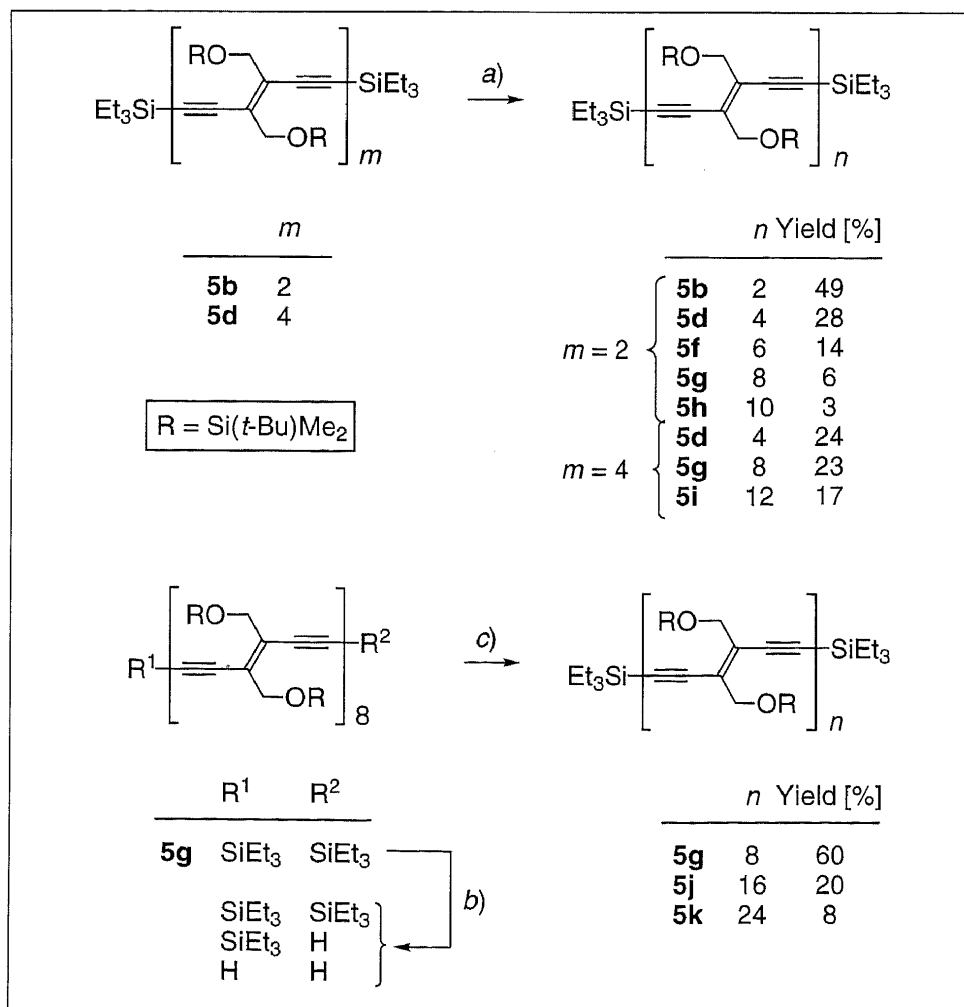
With the extended oligomeric series **5a–k** in hand, we investigated the evolution of the physicochemical properties in PTAs into the higher oligomeric regime where saturation of the properties becomes apparent. Saturation of properties such as the position of the longest-wavelength absorption maximum  $\lambda_{max}$  in the UV/VIS spectra, the second hyperpolarizability  $\gamma$ , measured by third-harmonic generation (THG) and degenerate four-wave mixing (DFWM), the frequency of the  $C\equiv C$  stretch measured by Raman scattering, and the redox potential for the first reduction step in cyclic or steady-state voltametry [24][25] was observed at about  $n = 10$  monomeric units. The UV/VIS spectra for the oligomeric series are depicted in Fig. 4 [29]. For the shorter

oligomers ( $n < 10$  monomeric repeat units), the deconvoluted longest-wavelength absorption maximum  $\lambda_{max}$  shifts bathochromically with increasing chain length whereas for the higher oligomers ( $n > 10$ ) this shift vanishes (Fig. 5).

The determination of the effective conjugation length (ECL) *i.e.* the number of monomeric repeat units  $n_{ECL}$  at which saturation of the properties occurs, can be done by using the following Eqn. 1 [30]:

$$\lambda_i(n) = \lambda_i(\infty) - \Delta\lambda_i \cdot \exp\{-b_i(n-1)\} \quad (1)$$

Herein,  $\lambda_i(n)$  belongs to the  $i$ -th absorption maximum,  $n$  corresponds to the number of monomeric repeat units,  $\lambda_i(\infty)$  is the limiting value for an infinitely long conjugated chain ( $n \rightarrow \infty$ ), and  $\Delta\lambda_i$  is the total difference of the  $i$ -th absorption maximum from the monomer ( $n = 1$ ) to the infinitely long conjugated chain ( $n = \infty$ ). To calculate the ECL ( $n_{ECL}$ ), the saturation criterion is  $\lambda_{max}(\infty) - \lambda_{max}(n_{ECL}) = 1$  nm. Fitting the data to Eqn. (1) and solving for  $n$  with the saturation criterion gives  $n_{ECL}$ , which in this oligomeric series is  $n = 10$  (Fig. 5) [24][25]. An oligomer longer than the decamer (10-



Scheme 1. Synthesis of the oligomeric PTA series **5b, d, f–k** by statistical deprotection-oligomerization cycles [24–26]. a) 1M NaOH, THF/MeOH 1:1, 20 °C, 15 min (generation of a mixture of terminally bis- and mono-deprotected **5b** or **5d** as well as unreacted starting material); then CuCl, *N,N,N',N'*-tetramethylethylenediamine (TMEDA), air,  $CH_2Cl_2$ , 20 °C, 4 h. b) 1M NaOH, THF/MeOH 6:1, 10 min. c) CuCl, TMEDA, air, 1,2-dichlorobenzene, 80 °C, 2 h.

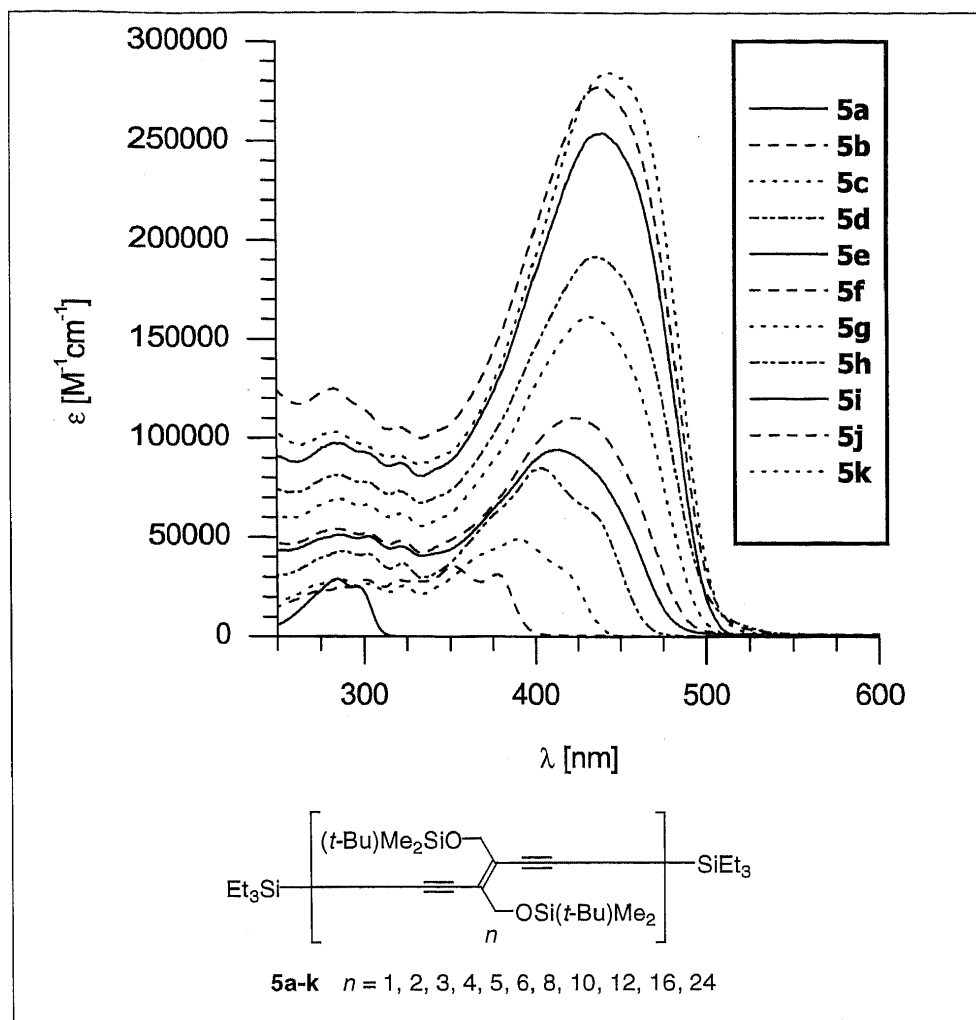


Fig. 4. UV/VIS spectra of PTA oligomers **5a–k** recorded in  $\text{CHCl}_3$  at room temperature, showing the occurrence of saturation of the position of the longest-wavelength absorption maximum. The spectral sequence shown starts with monomer **5a** which displays the highest-energy end absorption and extends to the 24-mer **5k** with the lowest optical gap.

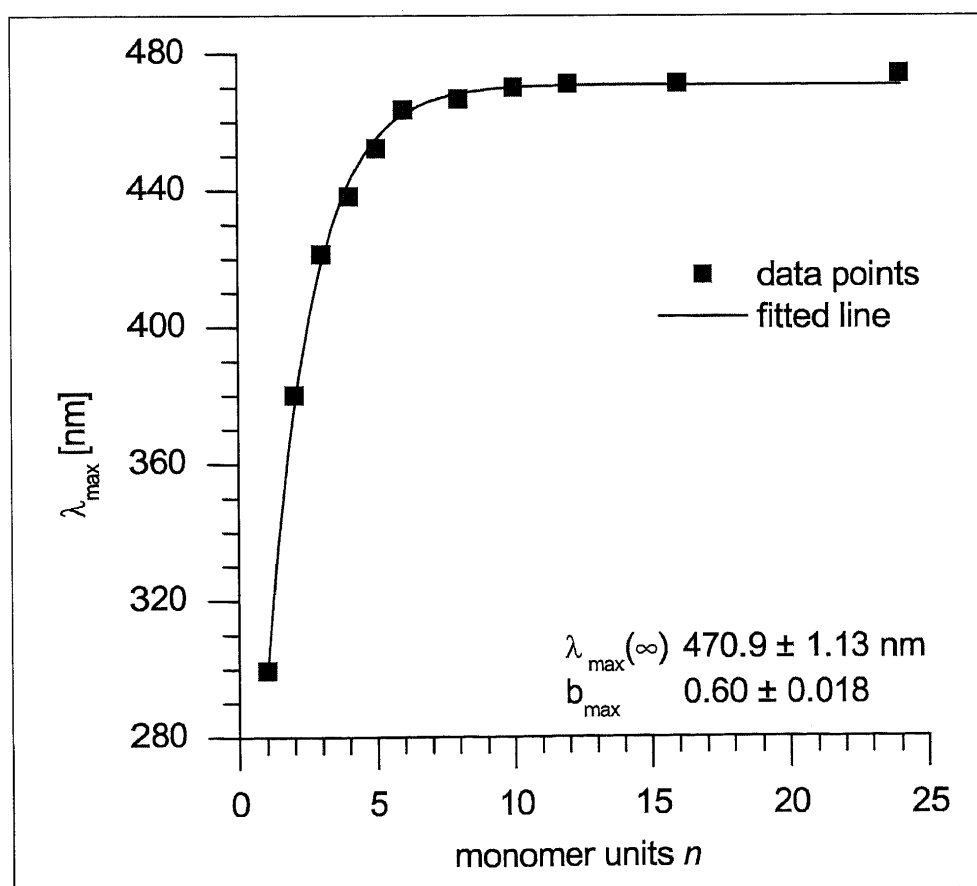


Fig. 5. Convergence of the position of the deconvoluted longest-wavelength absorption maximum  $\lambda_{\text{max}}$  of oligomers **5a–k** in  $\text{CHCl}_3$  at room temperature.

mer) should show the same physical properties than the corresponding infinite polymer, *e.g.* the position of the longest-wavelength absorption maximum  $\lambda_{\max}$  at 471 nm ( $E_{\max} = 2.65$  eV).

Interestingly, end-capping of PTA oligomers similar to **5a–k** with two-electron donor (4-(dimethylamino)phenyl) instead of  $\text{SiEt}_3$  groups was found to substantially lower  $n_{\text{ECL}}$  [31]. The preference of the planar PTA oligomeric backbone for conformations in which all C=C double bonds adopt an *s-trans* orientation with respect to the bridging buta-1,3-diyne diyl fragments was recently confirmed by an X-ray crystal structure analysis of tetrameric **5d** [26].

PTA oligomers were also dendritically encapsulated [32] into shells of Fréchet-type [33] dendrons [34]. UV/VIS studies of the first- to third-generation compounds **6–9** (Fig. 6) demonstrated that the insulating dendritic layers did not alter the electronic characteristics of the PTA backbone, even at the higher generation levels. These results support that  $\pi$ -electron delocalization and effective conjugation length of the encapsulated PTA backbone are not affected by distortions out of planarity due to steric compression of the bulky dendritic wedges. Apparently,  $\pi$ -electron conjugation involving the acetylenic fragments in the PTA backbone is best described as cylindrical and is maintained upon rotation about C(sp)–C(sp<sup>2</sup>) and C(sp)–C(sp) single bonds.

#### 4. Enhanced Molecular Properties in PTA-Hybrid Oligomers and Polymers

TEE and DEE monomeric building blocks for the preparation of PTAs are readily combined with other chromophores resulting in novel oligomers and polymers with further enhanced advanced materials properties. The modulation of the electronic properties of PTA oligomers by other chromophores was first tested by inserting the latter as spacers into the center of a PTA dimer [35].  $\pi$ -Electron-deficient and -rich aromatic and heteroaromatic rings, or organometallic *trans*-Pt(PET<sub>3</sub>)<sub>2</sub> fragments [36] were used as spacers, and the properties of the resulting hybrid trimers ('hetero-trimers') **9a–k** (Fig. 7) were compared to those of the PTA 'homo-dimer' **10a** and 'homo-trimer' **10b**.

Insertion of the spacers had a profound influence on molecular properties such as fluorescence behavior. Whereas the fluorescence quantum yields of PTA

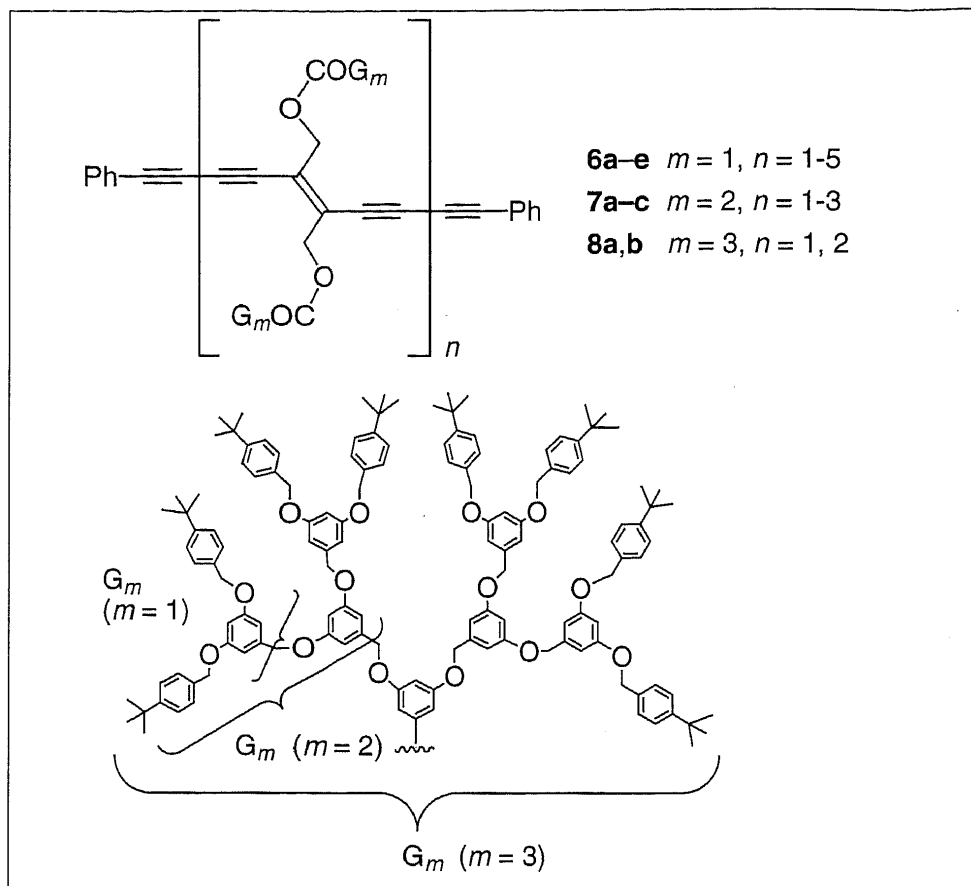


Fig. 6. Dendritic PTA oligomers with the linearly  $\pi$ -conjugated all-carbon backbone encapsulated by Fréchet-type dendrons of first to third generation [34].

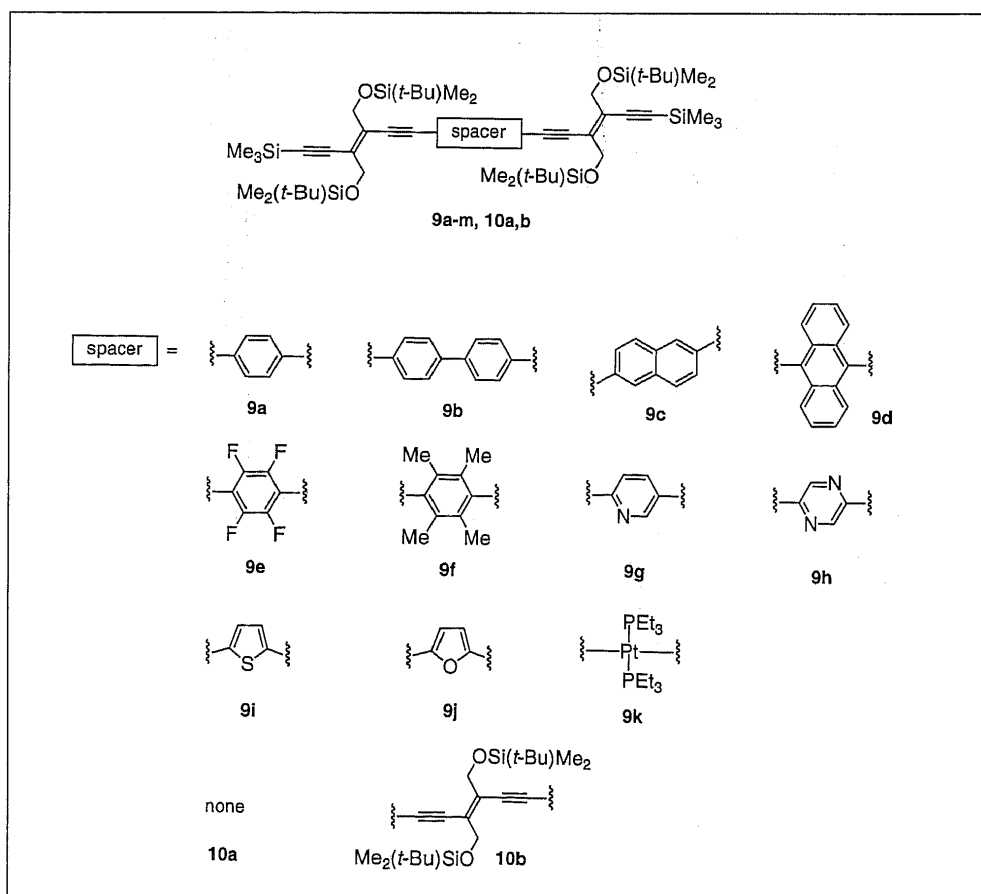


Fig. 7. Incorporation of spacer moieties into PTA dimer **10a** generates homo-trimer **10b** and hetero-trimers **9a–k** [35].

derivatives **10a,b** and hetero-trimers **9j** and **9k** were below 5%, hybrid derivatives **9a**, **9e**, **9g**, and **9i** already gave fluorescence quantum yields between 20 and 50%. An even stronger emission behavior was displayed by hybrid trimers **9b–d**, **9f**, and **9h** for which fluorescence quantum yields above 50% were measured.

We subsequently conducted first polymerization attempts in order to explore whether the results of the model studies with hybrid trimers would provide successful guidance for the design and synthesis of functional longer-chain polymers [37]. Therefore, we undertook Hay-oligomerizations of terminally bis-deprotected hybrid trimer **9b** under end-capping conditions (Scheme 2) and obtained two polymers **12a** and **12b** with a degree of polymerization  $X_n = 23$  (20 600 Dalton, by size exclusion chromatography (SEC)), and  $X_n = 19$  (16 900 Dalton, SEC), respectively. Both polymers are highly fluorescent in  $\text{CHCl}_3$  solution, in films, and in the solid state. The fluorescence quantum yields in  $\text{CHCl}_3$  solutions were determined as 51% (**12a**) and 44% (**12b**), respectively, confirming that small hybrid oligomers such as **9a–k** are valid models for extrapolating the properties of the corresponding longer-chain polymers. The potential use of the novel fluorescent polymers in light-emitting diodes is currently under investigation.

## 5. Summary and Perspectives

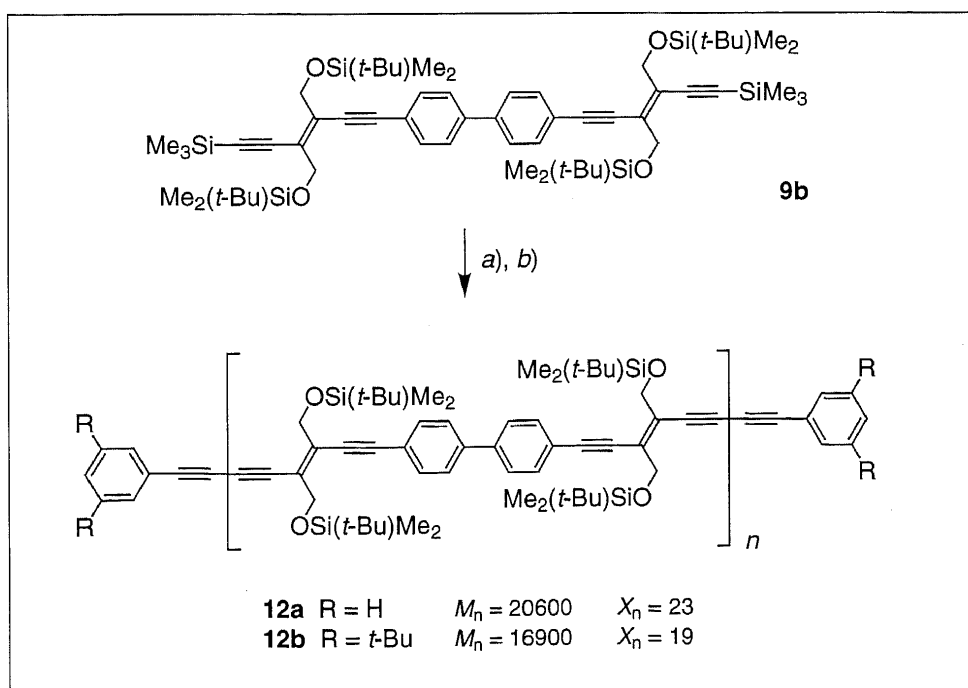
Poly(triacetylene)s (PTAs) are a novel class of linearly  $\pi$ -conjugated polymers with high environmental stability and interesting advanced materials properties that can be further tuned by lateral attachment of functional side chains. Their synthesis by oxidative acetylenic coupling tolerates a wide range of functionality, thereby providing ample opportunity for tailoring and tuning of the optoelectronic and/or mechanical properties of the targeted polymers. Monodisperse PTA oligomers extending up to 17.8 nm in length were prepared, thereby penetrating dimensions on the multianometer scale that were previously accessible only with polydisperse polymers. The effective conjugation length in PTA polymers was determined as  $n_{\text{ECL}} = 10$  monomeric sub-units, corresponding to 60 carbon-carbon bonds. It is noticeable that most linearly  $\pi$ -conjugated polymers show an ECL in this length range [18]. In future work, PTA oligomers with a length beyond 10 nm will be end-capped with thioether groups for bridging gaps between gold electrodes, thereby contributing to the ongoing efforts targeting molecular circuitry development [27]. A wide range of designer polymers with made-to-order properties is becoming accessible by conjugating DEEs, TEEs, and PTAs with other chromophores. First ex-

periments with such hybrid systems described in this article show that the properties of these mixed polymers can be extrapolated from model investigations on short monodisperse oligomeric analogs. Finally, the progression of oligomers and polymers with  $\pi$ -conjugated non-aromatic all-carbon backbones, leading from polyacetylene to carbyne, will be expanded with the preparation of higher representatives such as poly(pentaacetylene)s (PPAs), poly(heptaacetylene)s (PHAs), and poly(nonaacetylene)s (PNAs). A first series of PPA oligomers is already in hand [34b], and we hope that the expansion of this progression will eventually allow extrapolation of the physical properties and stability of the still elusive linear carbon allotrope carbyne.

## 6. Experimental

*General:* See Experimental in [26].

*Synthesis of Polymer 12b.*  $\text{K}_2\text{CO}_3$  (0.03 g, 0.129 mmol) was added at 20 °C to monomer **9b** (0.83 g, 0.81 mmol) in THF/MeOH 1:1 (8 ml). After TLC ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ) indicated full deprotection (approx. 70 min), the reaction was quenched by addition of sat. aq.  $\text{NH}_4\text{Cl}$  soln. (100 ml). After extraction with  $\text{CH}_2\text{Cl}_2$  (2 x 50 ml), the combined org. layers were dried ( $\text{MgSO}_4$ ) and the solvent evaporated at water aspirator pressure (*in vacuo*). 1,2-Dichlorobenzene (34 ml) containing 4-Å molecular sieve was added, followed by TMEDA (0.160 ml, 1.07 mmol) and  $\text{CuCl}$  (30.3 mg, 0.31 mmol). The mixture was stirred under air at 70 °C. 3,5-Bis(*tert*-butyl)phenylacetylene (6.9 mg, 0.032 mmol) was added after 23 min and the mixture stirred under air at 85 °C for 4 h. A soln. of ethylenediaminetetraacetic acid (EDTA, pH = 8, 0.2 M, 100 ml) was added, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (5 x 100 ml), and the combined org. layers were dried ( $\text{MgSO}_4$ ). Evaporation *in vacuo*, preparative gravity SEC (8 x 90 cm glass column filled with *Bio-Beads S-XI*; THF) followed by precipitation with MeOH from concentrated THF soln. gave **12b** (0.20 g, 24%). M.p. > 200 °C (dec.). UV/VIS ( $\text{CHCl}_3$ , relative optical densities in parenthesis): 292 (0.42), 309 (0.61), 331 (0.69), 391 (1.12). Fluorescence ( $\text{CHCl}_3$ ,  $\lambda_{\text{exc}} = 380$ ): 457, 484 (*sh*).  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ): 0.15 (2 s); 0.95 (2 s); 1.33 (s, 36 H); 4.56 (2 s); 7.30–7.70 (*m*).  $X_n = 18$ –26,  $M_n = 16$  200–23 200 ( $^1\text{H}$  NMR, evaluation of the integral of the terminal *t*-Bu resonance relative to the integral of the *t*-Bu or Me signals of the



Scheme 2. Synthesis of the fluorescent polymers **12a** and **12b**. a)  $\text{K}_2\text{CO}_3$ , MeOH/THF 1:1, room temperature, 70 min. b)  $\text{CuCl}$ , TMEDA,  $\text{Ph-C}\equiv\text{CH}$  or 3,5-di(*t*-Bu) $\text{C}_6\text{H}_3\text{-C}\equiv\text{CH}$ , 1,2-dichlorobenzene, 80 °C, 4 h, 75% (**12a**), 24% (**12b**).

laterally appended  $\text{CH}_2\text{OSi}(t\text{-Bu})\text{Me}_2$  groups).  $X_n = 19$ ,  $M_n = 16\,900$  (anal. SEC trace for the most abundant polymer).

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