Effective Conjugation Length (ECL) in Poly(triacetylene)s

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Introduction

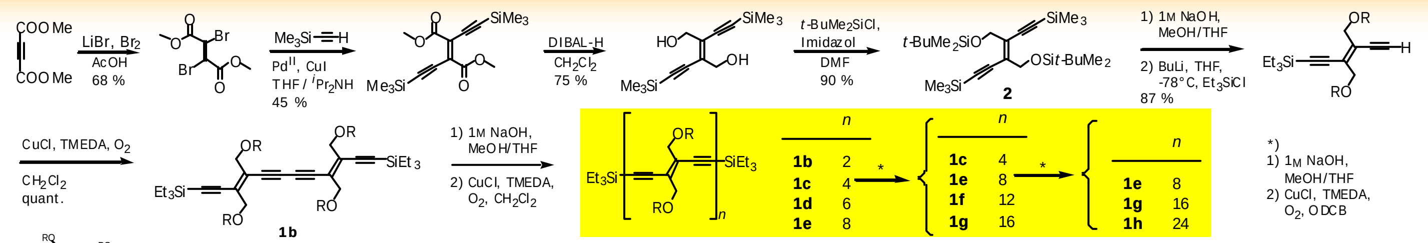
Poly(triacetylene)s (PTAs, –[C≡C–CR=CR–C≡C]$_n$–) are conjugated polymers with a non-aromatic all-carbon backbone, occupying an intermediate position between poly(acetylene) (PA, –[CR=CR]$_n$–) and carbyne (–[C≡C]$_n$–) [1]. *Trans*-PA, when doped, exhibits electrical conductivity similar to that of copper, but the material is difficult to process and is air- and moisture sensitive. Poly(diacetylene)s (PDAs, –[CR=CR–C≡C]$_n$–) are prepared by topochemical polymerization of suitable butadiynes, which limits their accessibility severly. They are not conductive but exhibit excellent second-order hyperpolarizabilities. PTAs are synthetically readily available, well soluble, and stable to normal laboratory conditions.

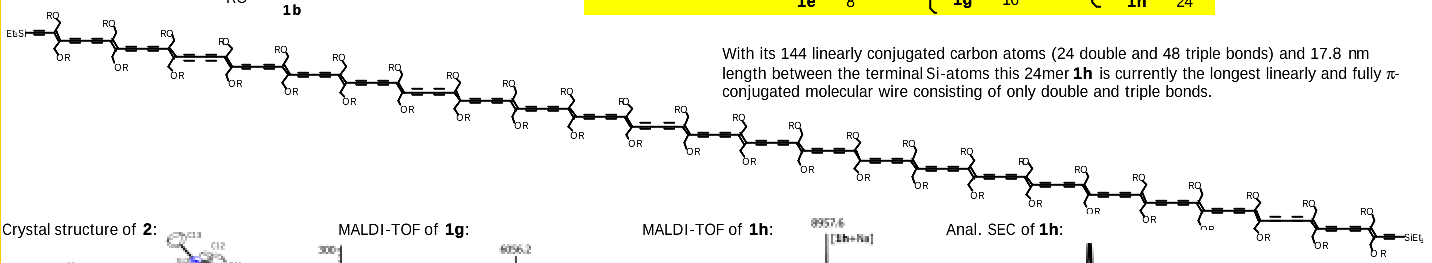
The study of soluble, monodisperse oligomers with clearly defined structure is essential for predicting the physical properties of the corresponding polydisperse conjugated polymer [2].

Objective

To investigate structure-property relationships in poly(triacetylene)s (PTAs) as a function of oligomeric length, we prepared a series of oligomers from monomer **1a** to pure tetradocontamer **1h** by oxidative coupling of a *trans*-hex-3-ene-1,5-diyne. Trends in the linear (UV/Vis), nonlinear (third harmonic generation, THG) optical properties, and Raman properties among these compounds were measured and the effective conjugation length (ECL) [3] in PTAs estimated by the various methods.

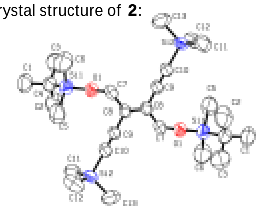
Synthesis



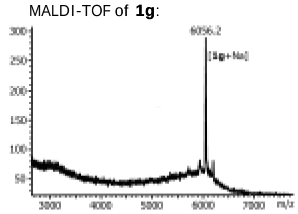


With its 144 linearly conjugated carbon atoms (24 double and 48 triple bonds) and 17.8 nm length between the terminal Si-atoms this 24mer **1h** is currently the longest linearly and fully π-conjugated molecular wire consisting of only double and triple bonds.

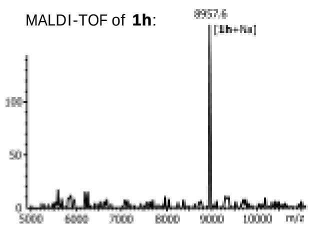
Crystal structure of **2**:



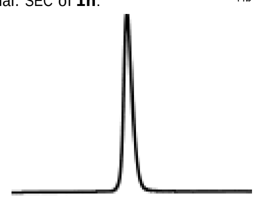
MALDI-TOF of **1g**:



MALDI-TOF of **1h**:

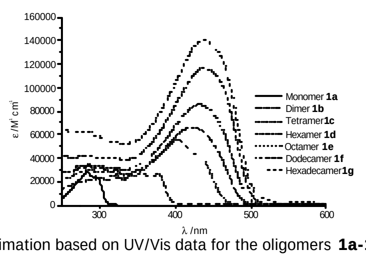


Anal. SEC of **1h**:



Results and Discussion

UV/Vis of the oligomers **1a-1g**:



Raman scattering data of the oligomers **1a-1g**:

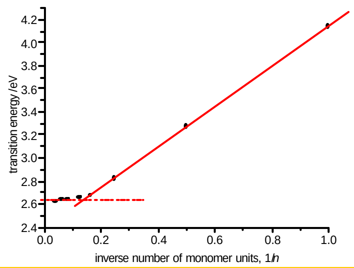
	n	ν1(C≡C) /cm^{-1}	ν2(C=C) /cm^{-1}
1a	1	2217	1574
1b	2	2187	1568
1c	4	2169	1558
1d	6	2164	1556
1e	8	2160	1553
1f	12	2158	1556
1g	16	2158	1555

Second-order hyperpolarizabilities γ of the oligomers **1a-1g**:

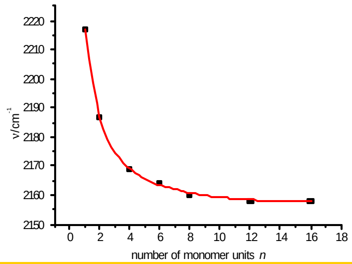
	n	γ /10^{-36}esu	γ /10^{-48}m^{5}V^{-2}
1a	1	12	0.16
1b	2	54	0.75
1c	4	360	5.0
1d	6	890	12
1e	8	1810	25
1f	12	2570	36
1g	16	4200	59

Rotational average of the g tensor. Measured relative to fused silica with a nonlinearity of $c^{(3)}$ = 1.6·10^{-22} m^{2}V^2.

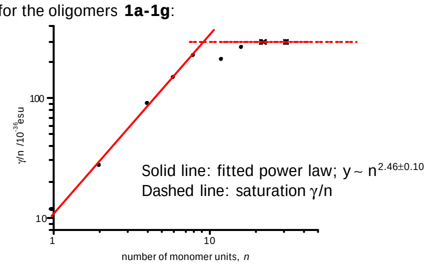
ECL estimation based on UV/Vis data for the oligomers **1a-1h**:



ECL estimation based on Raman data for the oligomers **1a-1g**:



ECL estimation based on second-order hyperpolarizability data for the oligomers **1a-1g**:



Conclusions

- PTAs show high solubility in a wide range of solvents and high stability.
- Linear (UV/Vis), nonlinear (THG), and Raman experiments revealed nearly the same effective conjugation length of $n \approx 10$ monomer units (60 carbon centers) for PTA polymers.
- The increase of nonlinear optical properties follows a power law with an exponent a ≈ 2.5.

Literature

[1] M. Schreiber, J. Anthony, F. Diederich, M. E. Spahr, R. Nesper, M. Hubrich, F. Bommeli, L. Degiorgi, P. Wachter, P. Kaatz, C. Bosshard, P. Günter, M. Colussi, U. W. Suter, C. Boudon, J.-P. Gisselbrecht, M. Gross, *Adv. Mater.* **1994**, *6*, 786-790.

[2] S. A. Jenekhe, *Macromolecules* **1990**, *23*, 2848-2854.6

[3] U. Gubler, Ch. Bosshard, P. Günter, M. Y. Balakina, J. Cornil, J. L. Brédas, R. E. Martin, F. Diederich, *Opt. Lett.* **1999**, *24*, 1599-1601.