LINZ LECTURES

Lecture 1. The Development of Organic Conductors: Metals, Superconductors and Semiconductors

Lecture 2A. Introduction and Synthesis of Important Conjugated Polymers

Lecture 2B. Solid State Polymerization

Lecture 3. Fullerene Chemistry

Lecture 3B. Molecular Engineering

Introduction and Synthesis of Important Conjugated Polymers

Linz, June 10, 2008

General Introduction

Solution Polymerization

Oligolyacenes

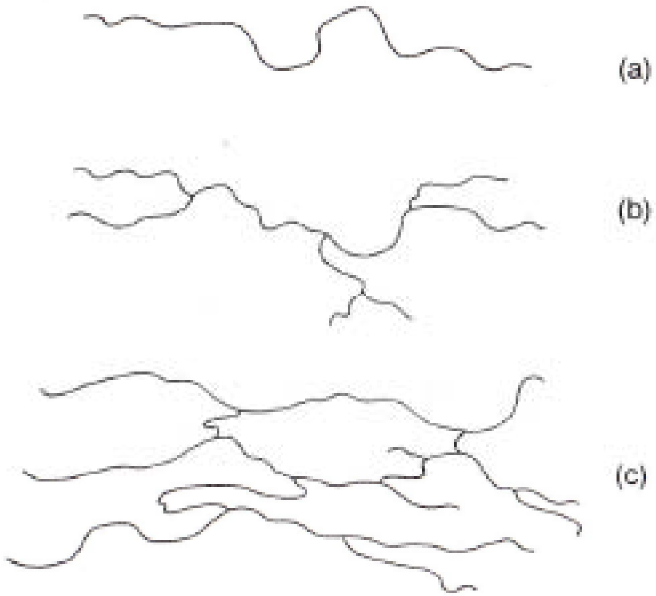
Types of Polymers

-A-A.A-A.A-A-A-A-	Homopolymer
-A-B-B-A-B-A-A-B-	Random copolymer
-A-B-A-B-A-B-A-B-	Alternating copolymer
-A-A-A-A-B-B-B-B-	Block copolymer

-A-A-A-A-A-A-A-A
        |
        B-B-B-B-B-B
	Graft copolymer

Malcolm P. Stevens “Polymer Chemistry: an Introduction” 3rd Ed. Oxford, 1999

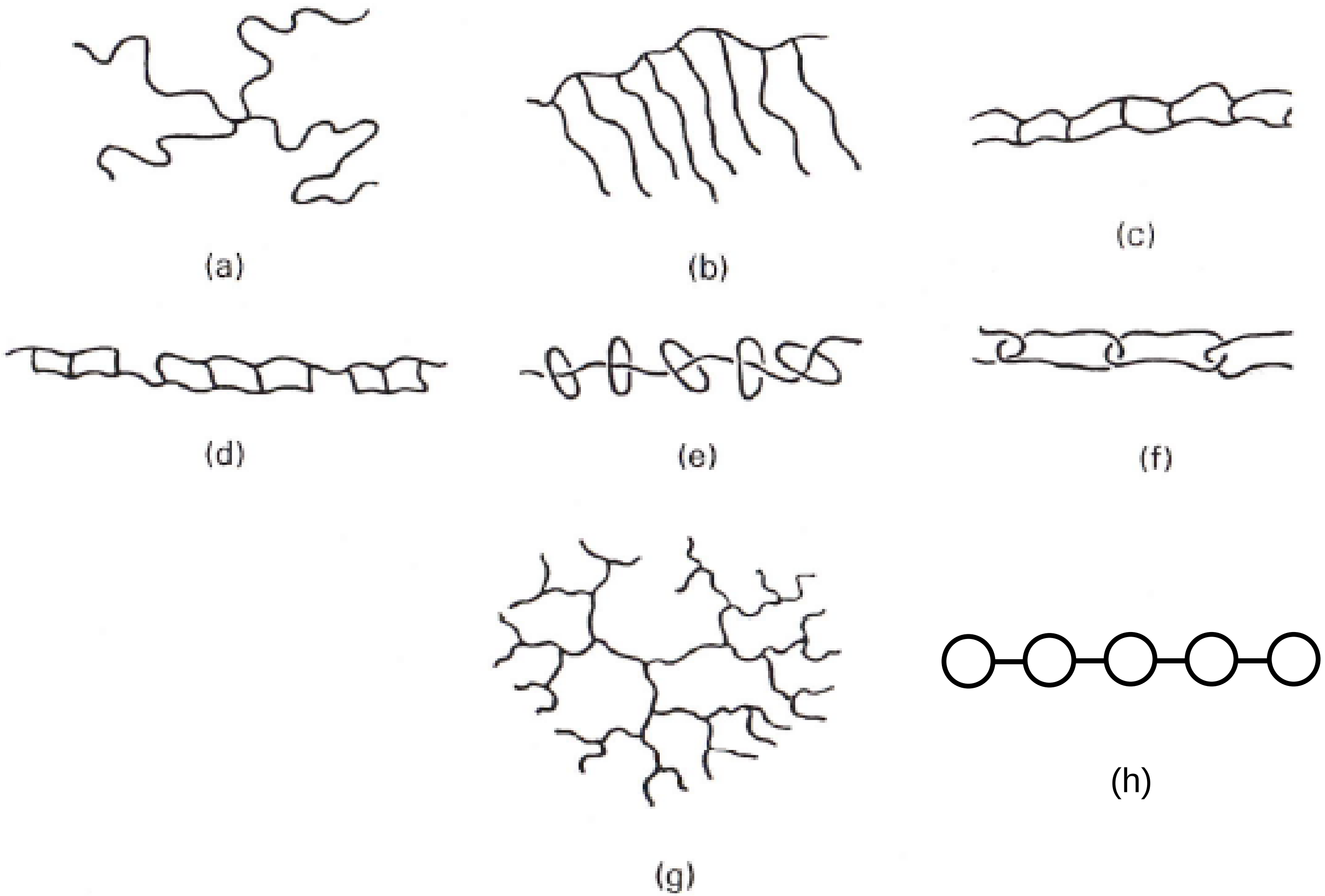
Types of Chains



(a) Linear chain, (b) branched chain, (c) network

Malcolm P. Stevens “Polymer Chemistry: an Introduction” 3rd Ed. Oxford, 1999

Types of Architectures



(a) Star, (b) comb, (c) ladder, (d) pseudo ladder, (e) rotaxane, (f) catenane, (g) dendrimer (h) rigid rod

Malcolm P. Stevens “Polymer Chemistry: an Introduction” 3rd Ed. Oxford, 1999

TABLE 4.1. Mechanical Properties of Common Homopolymers[a]

Polymer \ Property	Tensile Properties at Break: Strength[b] (MPa)	Tensile Properties at Break: Modulus[b] (MPa)	Tensile Properties at Break: Elongation (%)	Compressive Strength[b] (MPa)	Flexural Strength[b] (MPa)	Impact Strength[c] (N/cm)
Polyethylene, low density	8.3–31	172–283	100–650	—	—	No break
Polyethylene, high density	22–31	1070–1090	10–1200	20–25	—	0.23–2.3
Polypropylene	31–41	1170–1720	100–600	38–55	41–55	0.23–0.57
Poly(vinyl chloride)	41–52	2410–4140	40–80	55–90	69–110	0.23–1.3
Polystyrene	36–52	2280–3280	1.2–2.5	83–90	69–101	0.20–0.26
Poly(methyl methacrylate)	48–76	2240–3240	2–10	72–124	72–131	0.17–0.34
Polytetra-fluoroethylene	14–34	400–552	200–400	12	—	1.7
Nylon 66	76–83	—	60–300	103	42–117	0.46–1.2
Poly(ethylene terephthalate)	48–72	2760–4140	50–300	76–103	96–124	0.14–0.37
Polycarbonate	66	2380	110	86	93	9.1

[a]Values taken from Agranoff,[12a] converted to SI units, and rounded off.

[b]To convert megapascals to pounds per square inch, multiply by 145.

[c]Izod notched impact test (see Chap. 5). To convert newtons per centimeter to foot pounds per inch, multiply by 1.75.

Malcolm P. Stevens “Polymer Chemistry: an Introduction” 3rd Ed. Oxford, 1999

Table 1 Tensile properties of 'As-stretched' PPV measured parallel to the draw direction

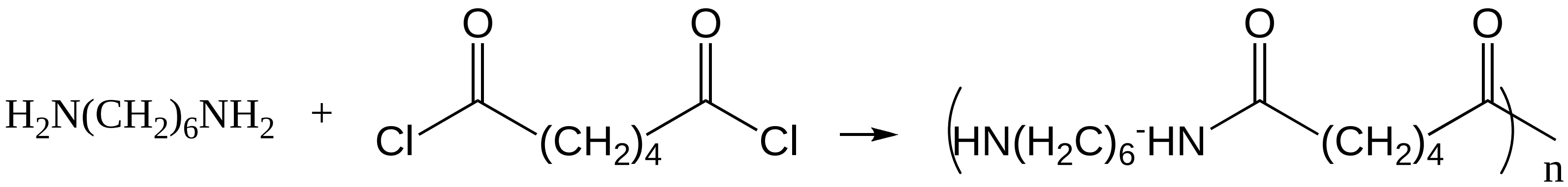
Draw ratio	Modulus (GPa)	Yield stress (MPa)	Yield strain (%)	Tensile strength (MPa)	Elongation (%)
Isotropic	2.7	45.2	3.3	48.2	38
1[a]	3.5	60	2.5	–	53
2	8.1	114	1.8	116	20
3	9.1	129	1.9	140	14
4	8.6	112	1.4	157	13
5	10.6	152	1.4	181	9.3
6	11.8	–	–	223	2.9
8	14.2	–	–	256	2.1
10	15.5	–	–	271	2.1

[a] Materials of draw ratio 1 are not isotropic because the precursor elimination/stretching process involves a substantial volume change (≈50%) and these materials are converted at constant length[11]

"For drawn samples, values for the Young's modulus as high as 37 GPa and tensile strength up to 500 MPa have been measured in the machine direction. These properties approach those of many high performance fibers."

Machado, J.M.; Masse, M.A.; Karasz, F.E. *Polymer*, **1989**, *30*, 1992

Step Growth or Condensation Polymerization

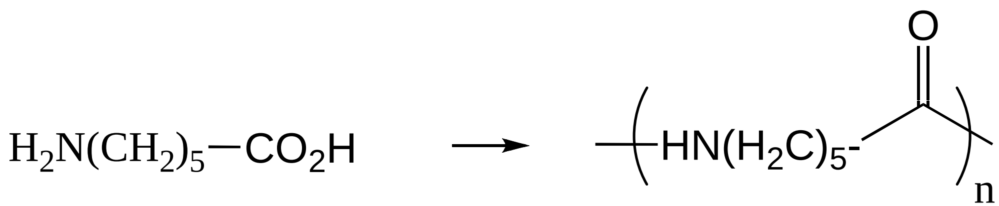


A

B

-(A-B)-$_n$

Nylon 66

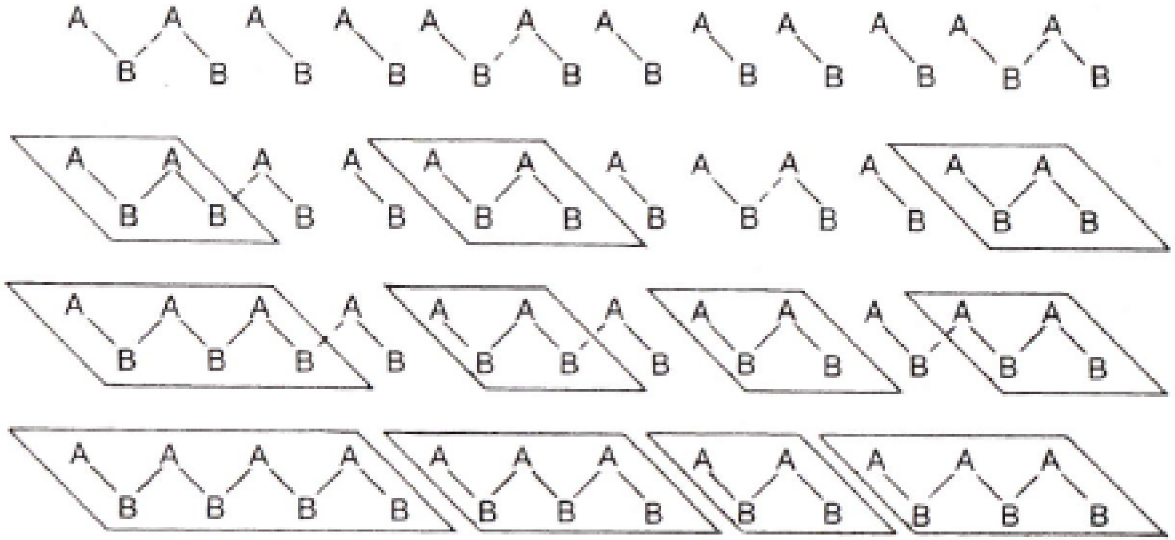


A

-(A-)$_n$

Nylon 6

Mylar, Kevlar, Kapton, PPT, PT, PPy



Step-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{\text{DP}} = 1.3$; (c) $\overline{\text{DP}} = 1.7$; (d) 100% reacted, $\overline{\text{DP}} = 3$. (Broken lines represent reacting species.)

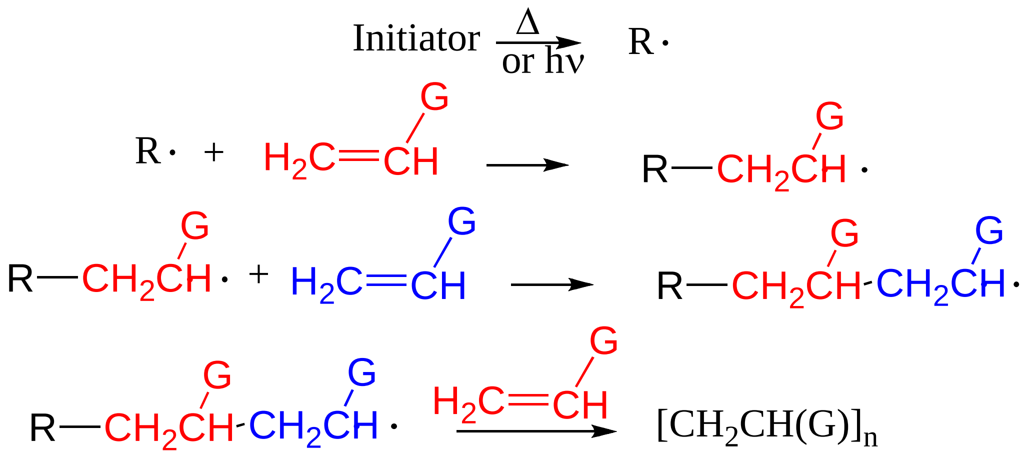
$$p = \frac{N_0 - N}{N_0} \qquad N = N_0(1 - p) \qquad \overline{\text{DP}} = \frac{1}{1 - p}$$

Carothers Equation

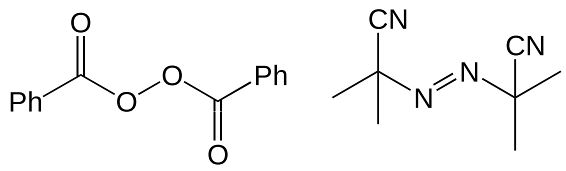
Malcolm P. Stevens "Polymer Chemistry: an Introduction" 3rd Ed. Oxford, 1999

Chain Growth or Addition Polymerization

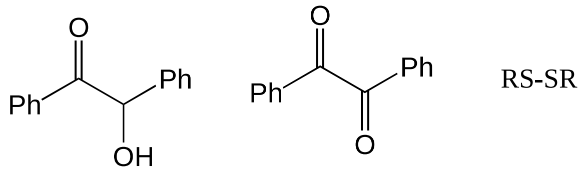
Free Radical



Initiators:



Thermal



Photochemical

$R\cdot + HC\equiv CH \longrightarrow$ Intractable products

Chain-Growth Polymerization

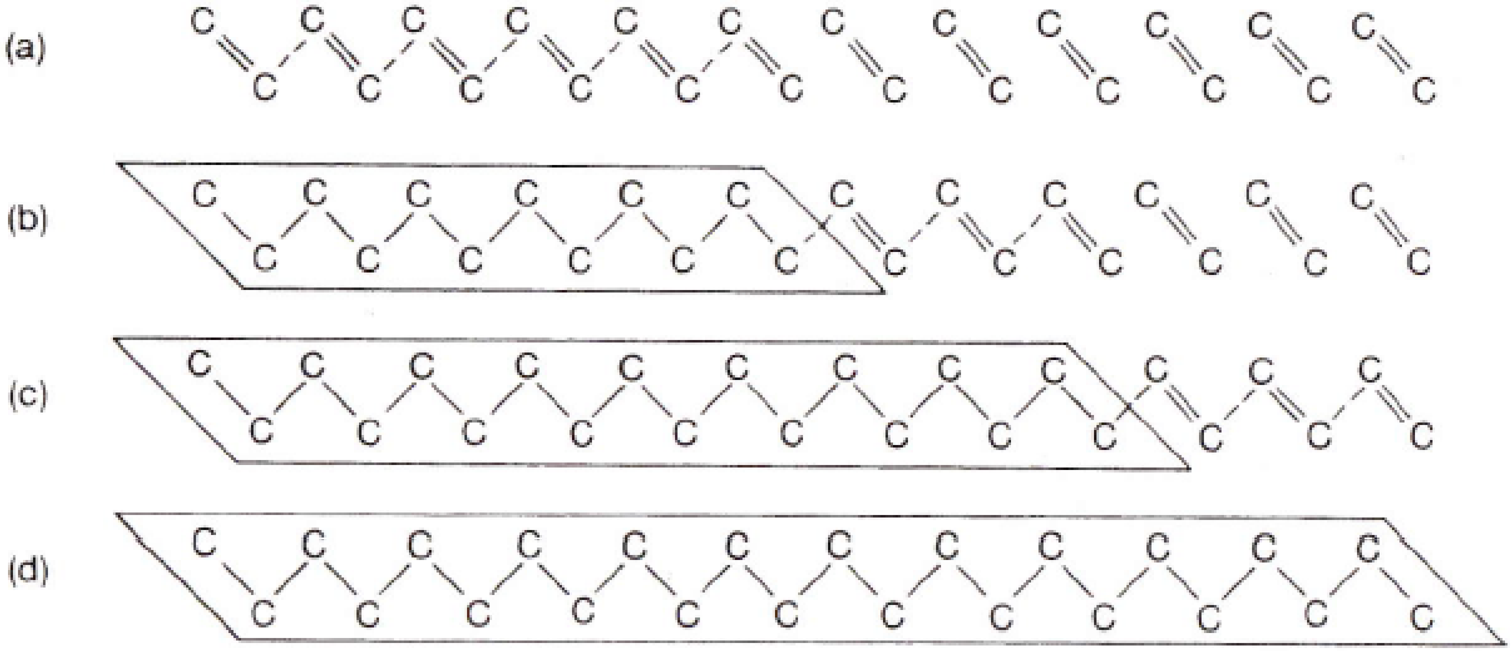
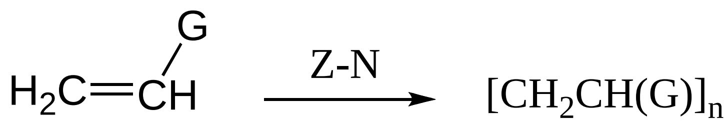


FIGURE 1.5. Chain-reaction polymerization: (a) unreacted monomer; (b) 50% reacted, $\overline{DP} = 1.7$; (c) 75% reacted, $\overline{DP} = 3$; (d) 100% reacted, $\overline{DP} = 12$. (Broken lines represent reacting species.)

Malcolm P. Stevens “Polymer Chemistry: an Introduction” 3rd Ed. Oxford, 1999

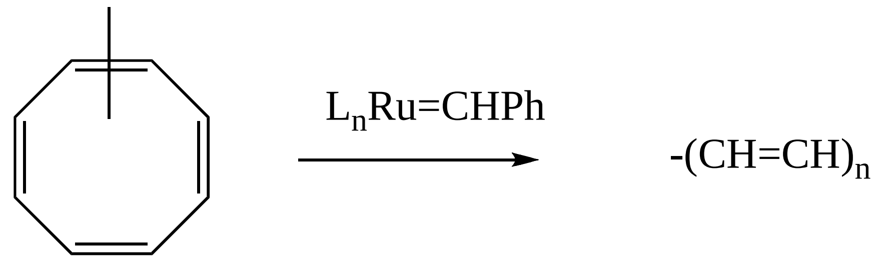
Ziegler-Natta Polymerization

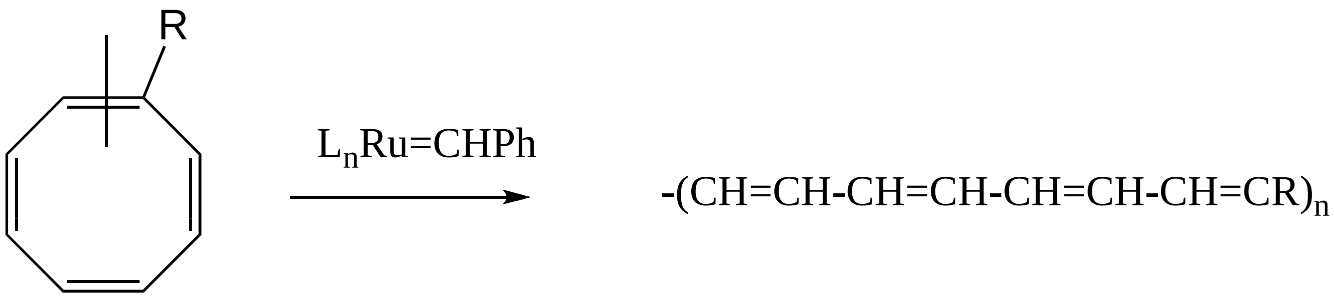


Z-N: $Ti(OR)_4$ AlR_3

Anionic, Cationic, Living

Ring Opening Metathesis Polymerization (ROMP)





$L_nRu{=}CHPh$ =

QuickTime™ and a
TIFF (Uncompressed) decompressor
are needed to see this picture.

Scherman O. A; Rutenberg I. M; Grubbs R. H *J. Am. Chem. Soc.* **2003**, *125*, 8515

Organometallic Methods:

Kumada, Yamamoto, Colon

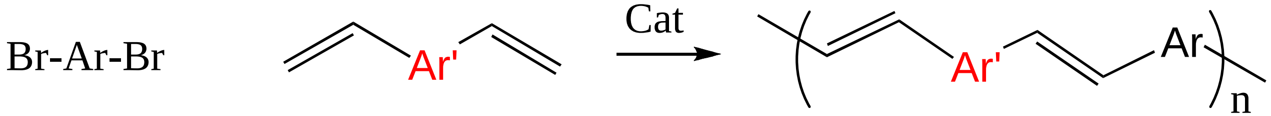
$$\text{Br-Ar-Br} \xrightarrow{\text{Cat}} (\text{Ar})_n$$

Cat: PdL_4, NiL_2

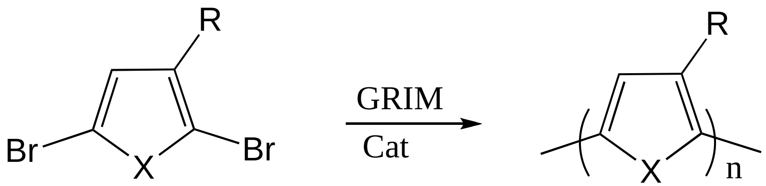
Suzuki

$$\text{Br-Ar-Br} + (\text{RO})_2\text{BAr'-B(OR)}_2 \xrightarrow{\text{Cat}} (\text{Ar-Ar'})_n$$

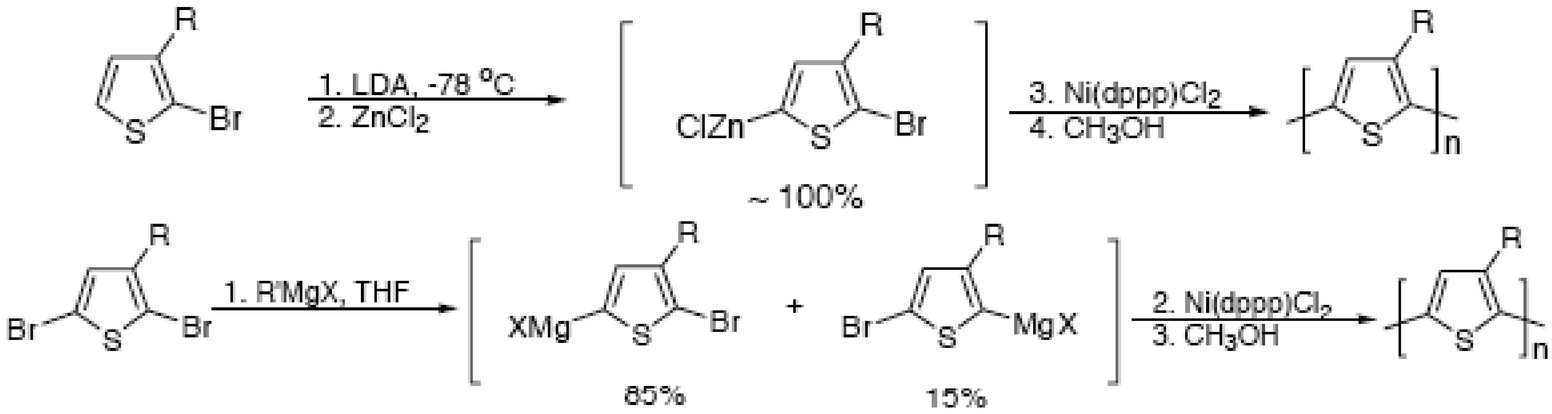
Heck



GRIM/Kumada

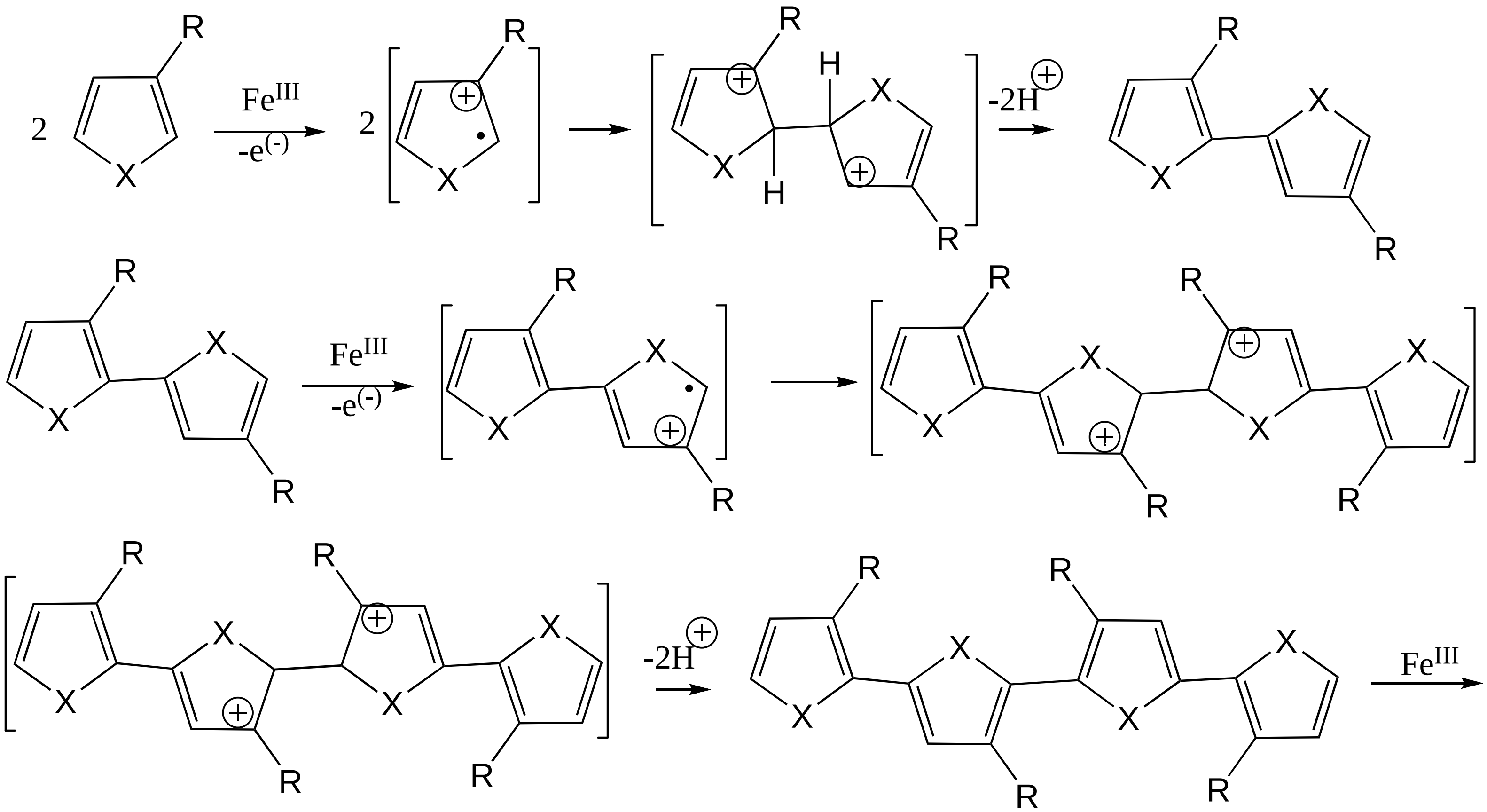


X = S



Sheina, E.E.; Iovu, M.C.; McCullough, R.D. *Polym. Prepr.* **2005**, *46(1)*, 682

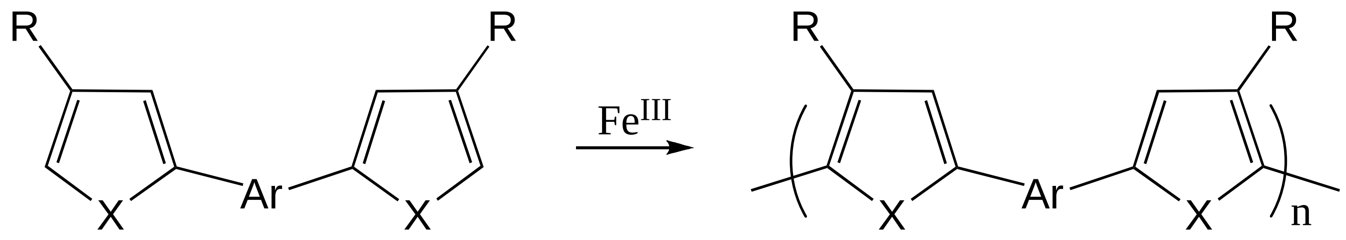
Oxidative (Cationic) Polymerization



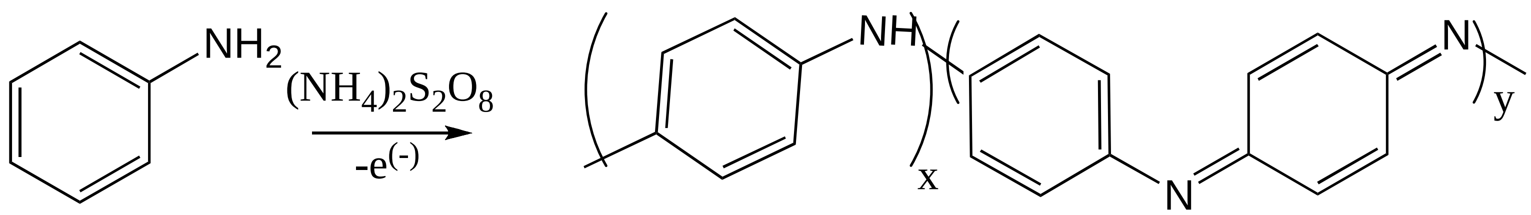
X = S, N

Oxidative Polymerization

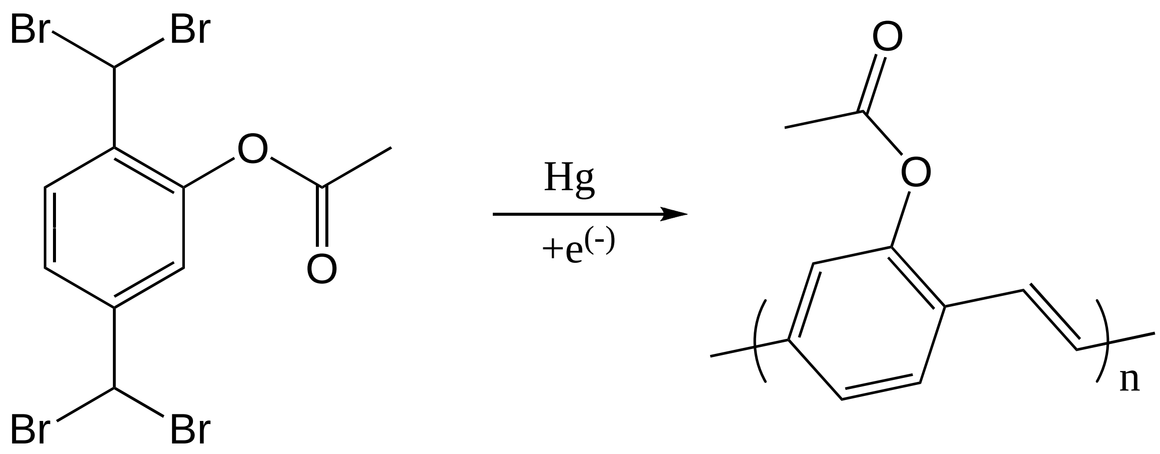
Thiophene as a “handle”



Polyaniline

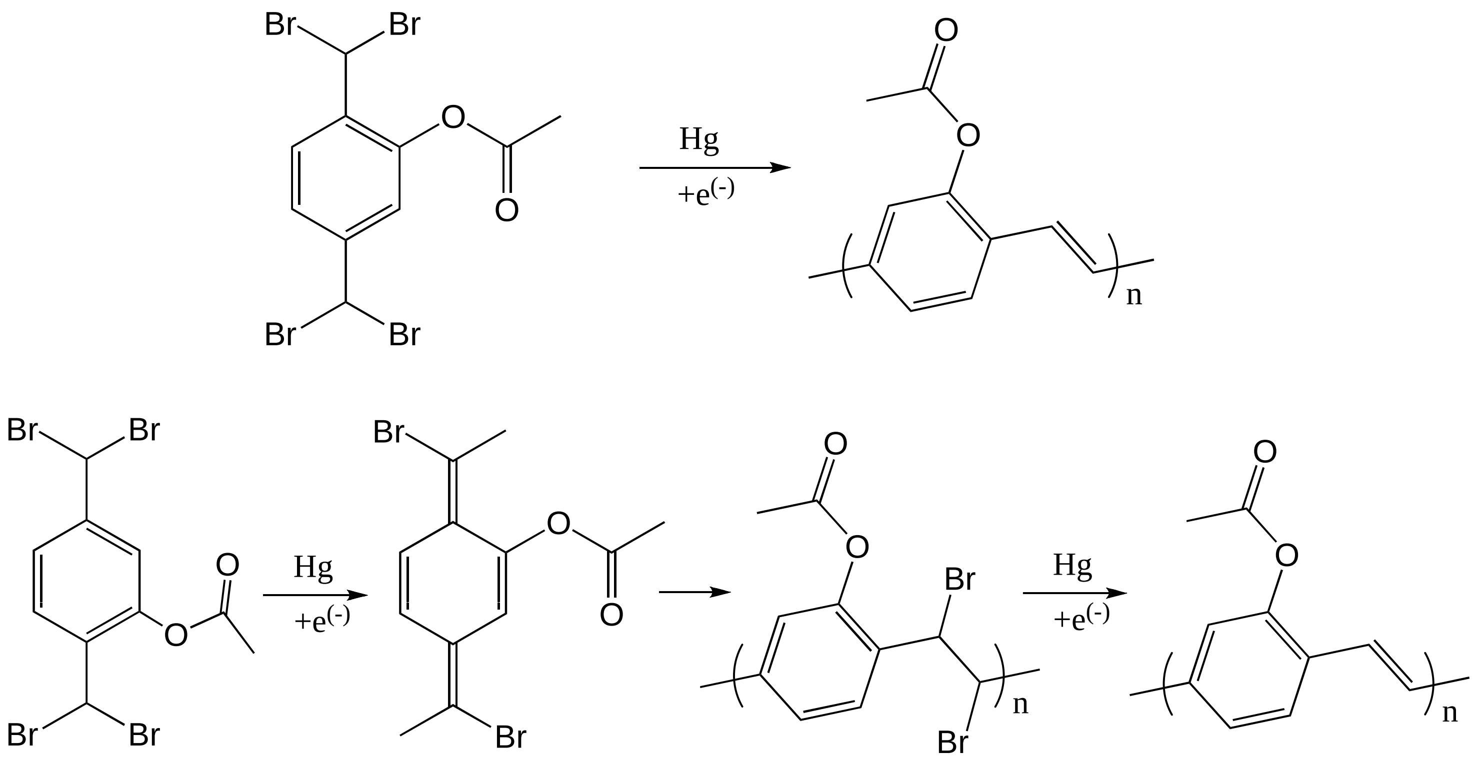


Reductive (Anionic) Polymerization



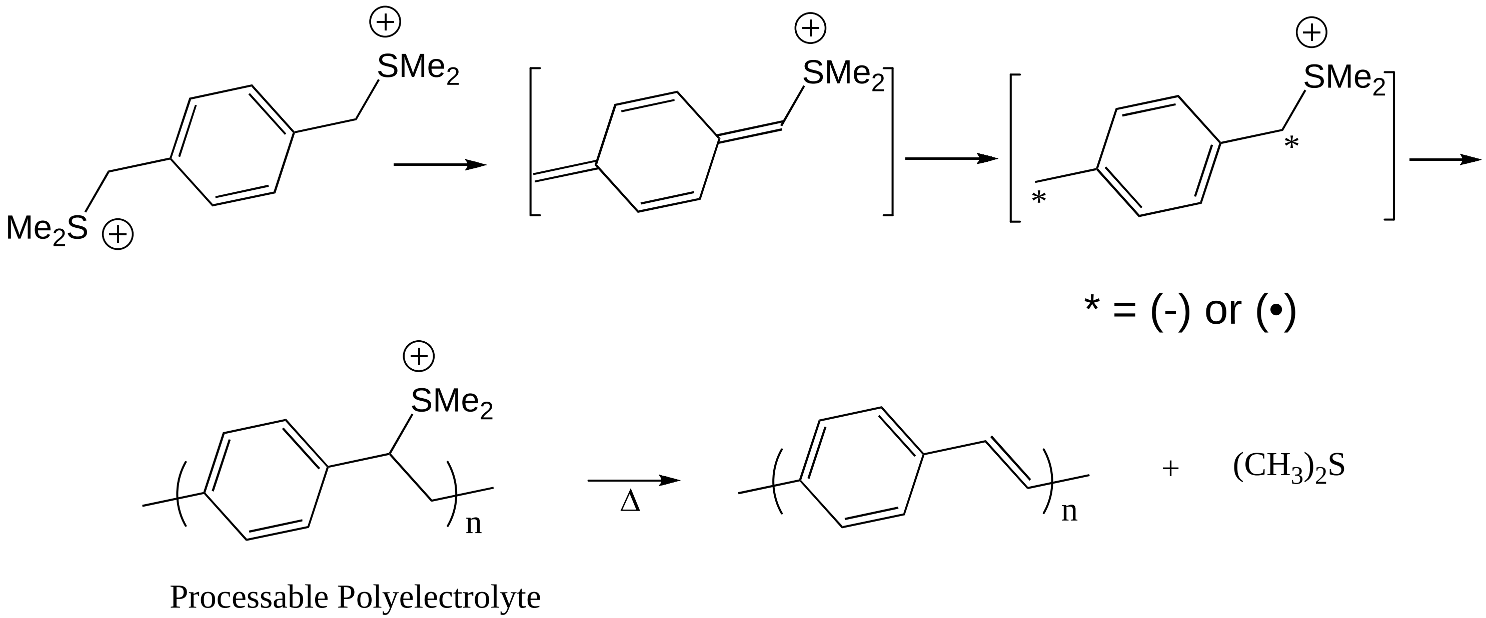
Utley, J.H.; Gao, Y.; Gruber, J.; Zhang, Y.; Munoz-Escalona, A. *Chem Mater.* **1995**, *5*, 1837

Reductive Polymerization



Utley, J.H.; Gao, Y.; Gruber, J.; Zhang, Y.; Munoz-Escalona, A. *Chem Mater.* **1995**, *5*, 1837

PPV Synthesis

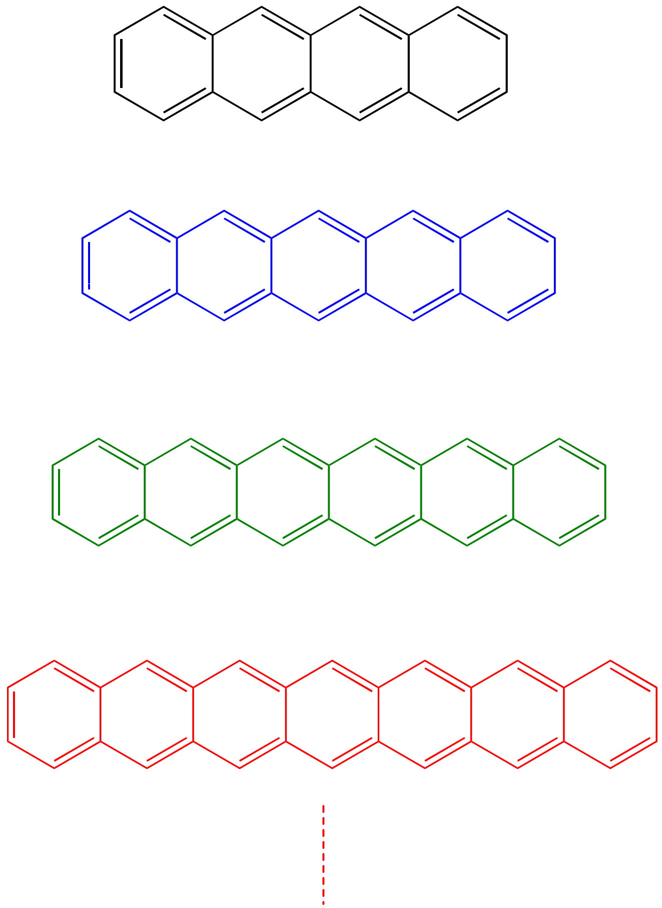


P. M. Lahti, D. A. Modarelli, F. R. Denton, III, R. W. Lenz, F. E. Karasz *J. Am. Chem. Soc*. **1988,** *110*, 7258

L. Hontis, V. Vrindts, D. Vanderzande, L. Lutsen *Macromolecules, Vol. 36, No. 9, 2003*

The Last Challenge: Linear Polyacenes

The Lower Oligoacenes

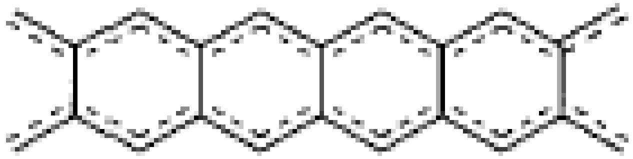


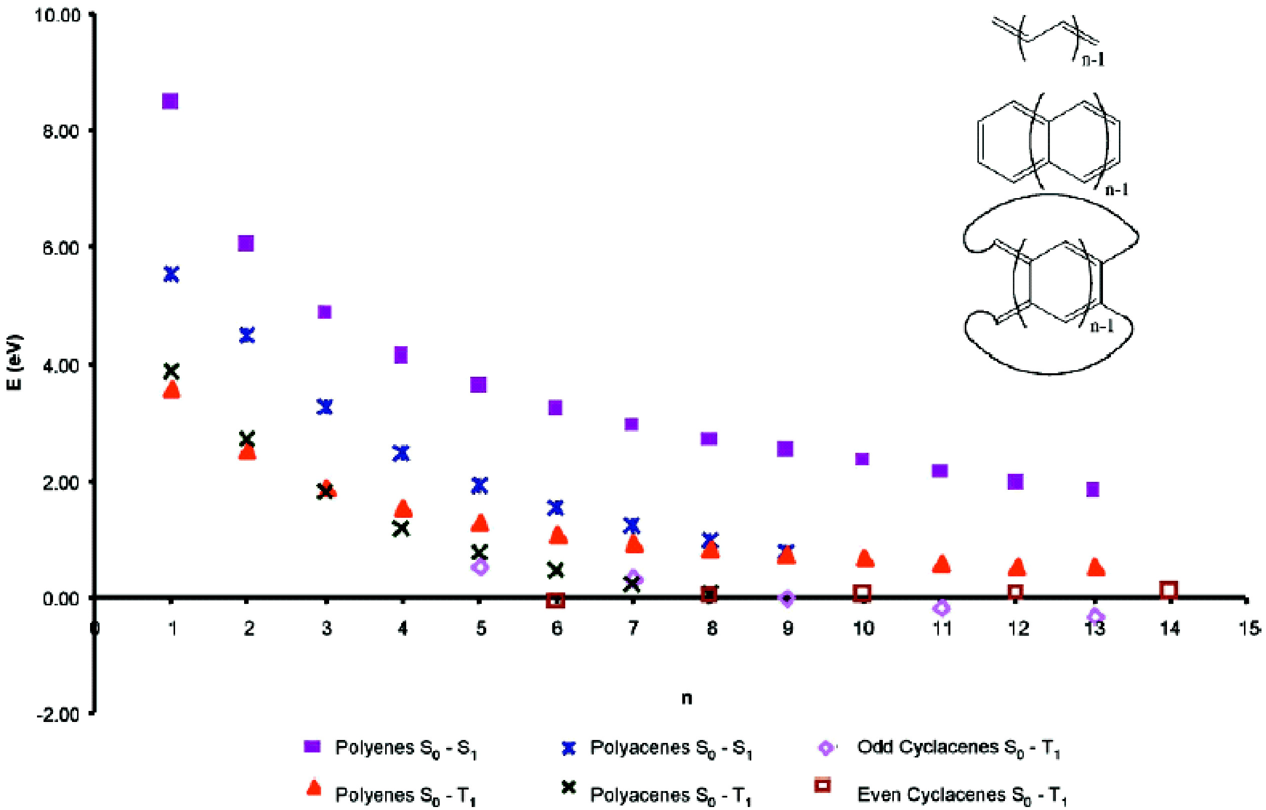
Polyacenes??

J. Org. Chem. **2001**, *66*, 5517–5521

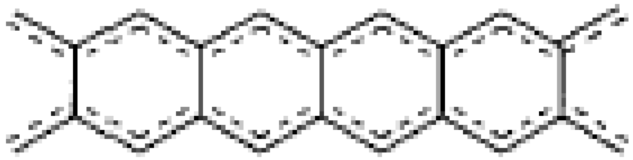
Polyacene and Cyclacene Geometries and Electronic Structures: Bond Equalization, Vanishing Band Gaps, and Triplet Ground States Contrast with Polyacetylene

K. N. Houk,* Patrick S. Lee, and Maja Nendel



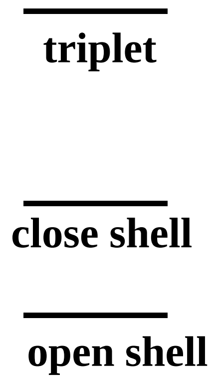


Acenes

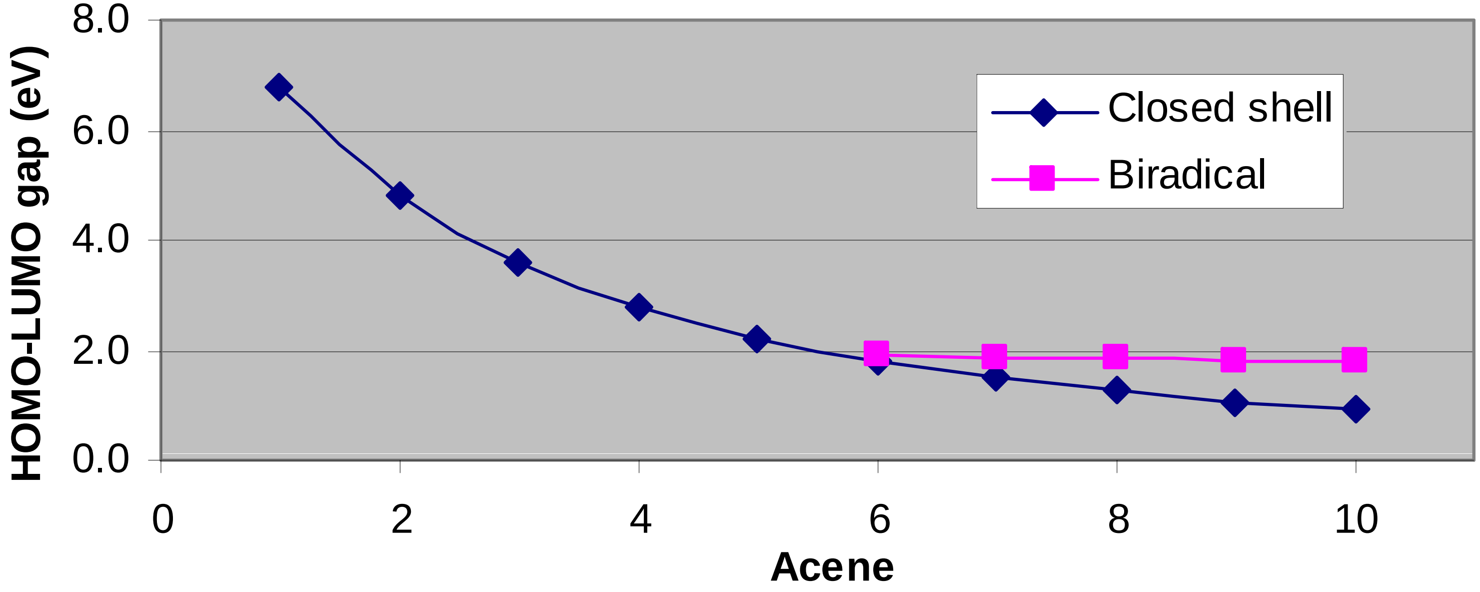


Surprisingly, we have discovered that at the RB3LYP/6-31G(d) level of theory, the wave function for as small an oligoacene as hexacene (and all longer oligoacenes) becomes unstable.

Re-optimization, using the unrestricted broken symmetry B3LYP method (UB3LYP), leads to a singlet state with large amounts of diradical character.

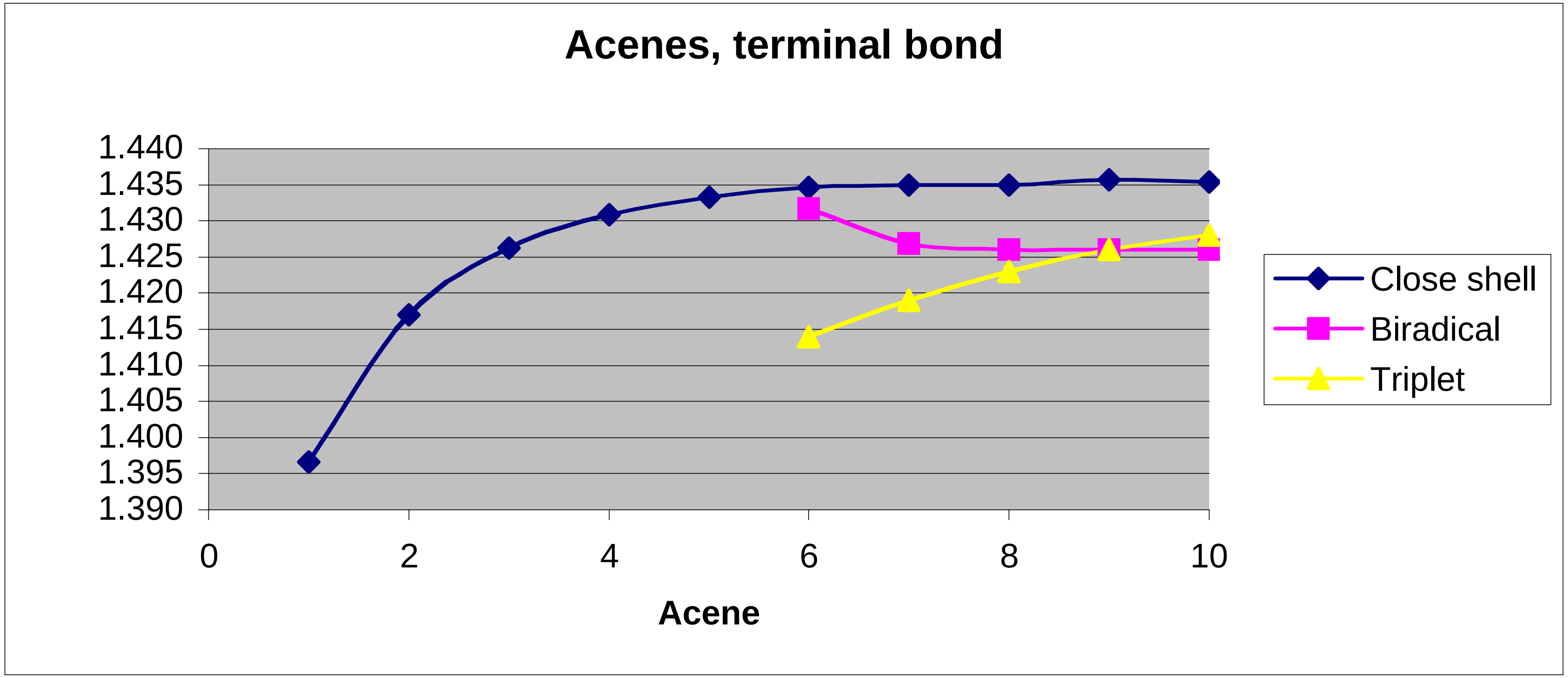


HOMO-LUMO Gap in Acenes



Plateau at *ca.* 1.8 eV

Bendikov, M.; Duong, H.M.; Starkey, K.; Houk, K.N.; Carter, E.A.; Wudl, F.; *J. Am. Chem. Soc.*, **2004**, 126(24) 7416



Acenes, terminal bond
1.440
1.435
1.430
1.425
1.420
1.415
1.410
1.405
1.400
1.395
1.390
0
2
4
6
8
10
Acene
Close shell
Biradical
Triplet

Connection Between Band Theory and Molecular Orbital Theory

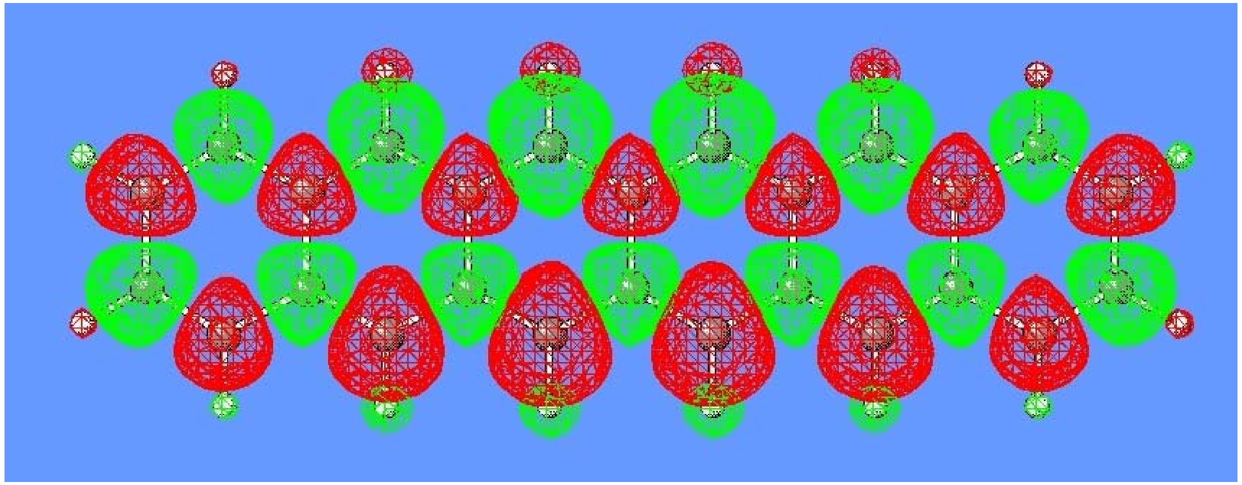
According to the Su-Schrieffer-Heeger (SSH) model, the effective length of a soliton in a σ-system is about 14 carbon atoms.

This is in agreement with our calculations, predicting diradical character in oligoacenes, and thus, hexacene-heptacene have already enough σ-length (two 13-15 carbon atom chains, respectively) to produce two oligoacetylene solitons.

The instabilities found for heptacene-octacene appear to indicate that they are the "connector" between band theory and molecular orbital theory.

Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W.-P. *Rev. Mod. Phys.* **1988**, *60*, 781.

Spin Density



Bendikov, M.; Duong, H.M.; Starkey, K.; Houk, K.N.; Carter, E.A.; Wudl, F.; *J. Am. Chem. Soc.*, **2004**, 126(24) 7416

Summary

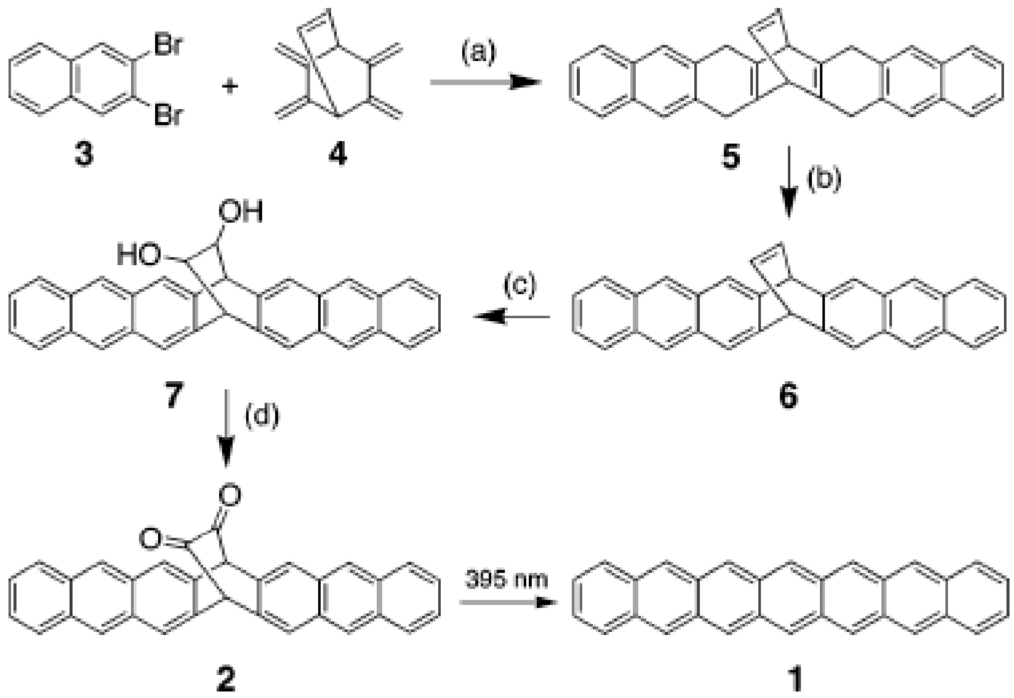
In contrast to the common view that acenes are closed shell systems or have triplet ground states, we predict that larger oligoacenes possess an open-shell singlet ground state, where the triplet lies above singlet.

We have shown computationally that oligoacenes and probably a variety of polyacene derivatives and analogues should exhibit a nonzero band gap.

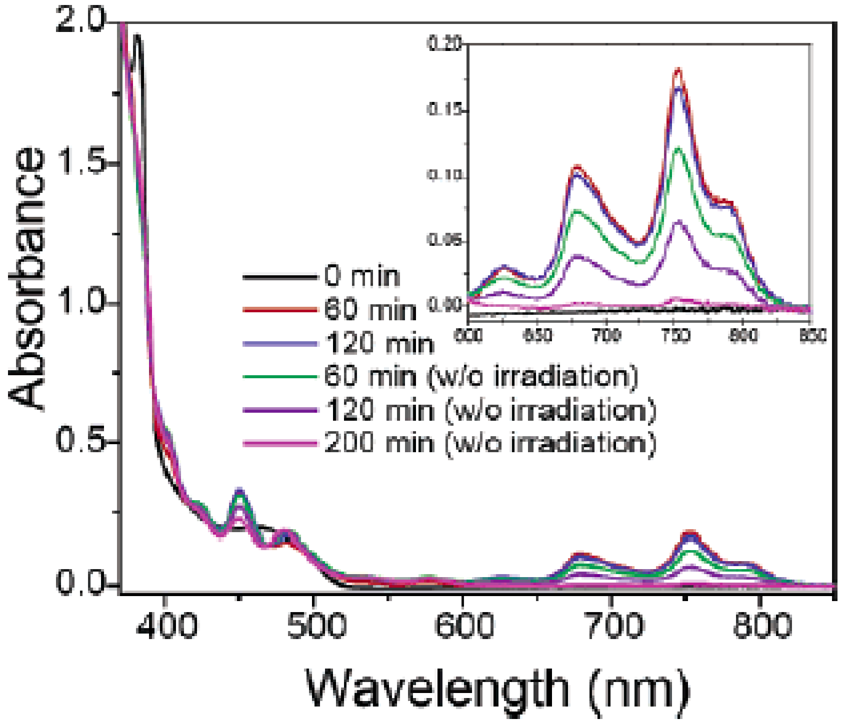
It should be possible to prepare a linear polyacene, provided it is formed as a solid, with minimum lifetime in solution. In analogy with oligoenes vs polyacetylene.

EXPERIMENTAL RESULTS

Matrix Isolated Heptacene

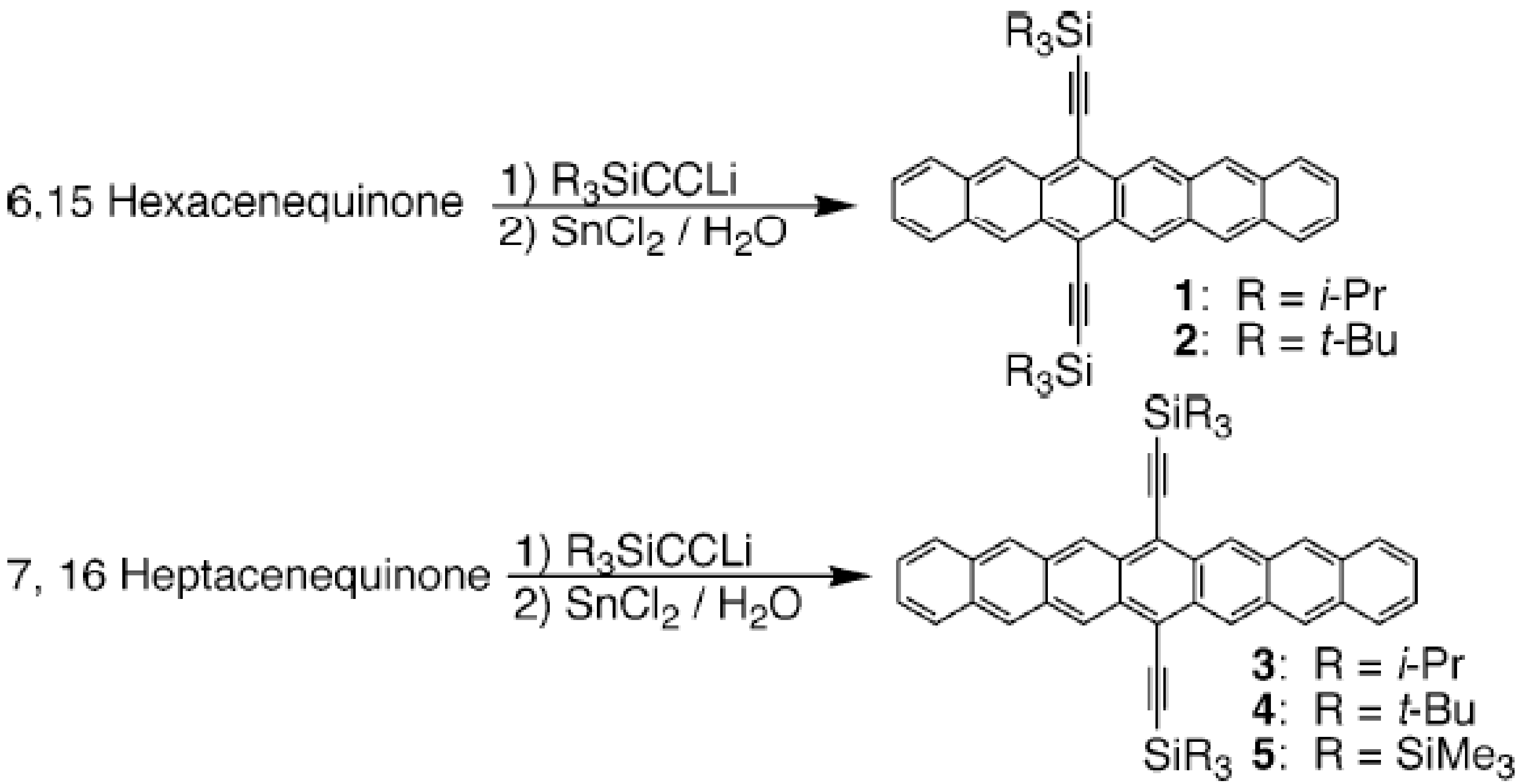


R. Mondal, B. K. Shah, D. C. Neckers *J. Am. Chem. Soc.* **2006**, *128*, 9612

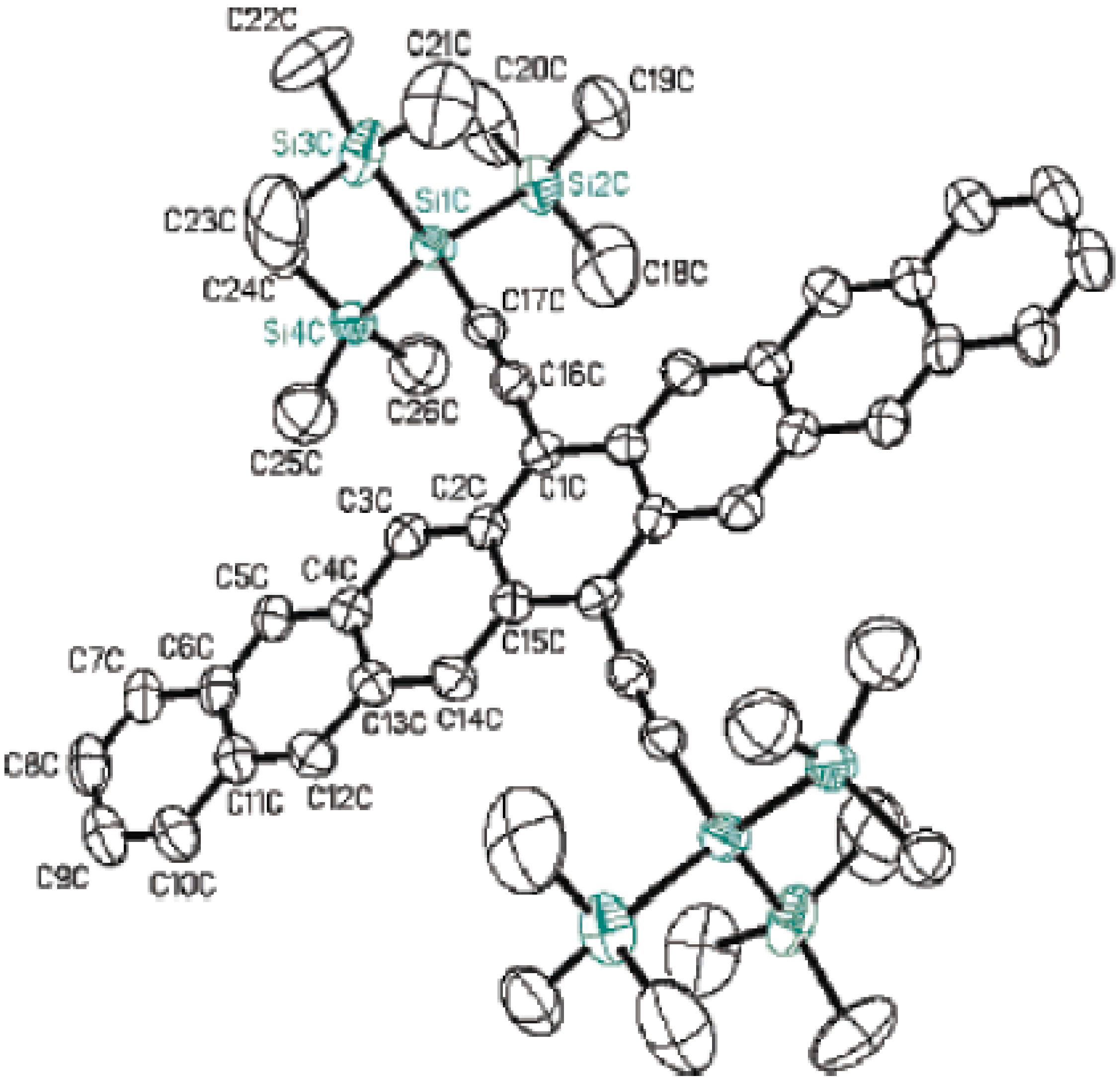


R. Mondal, B. K. Shah, D. C. Neckers *J. Am. Chem. Soc.* **2006**, *128*, 9612

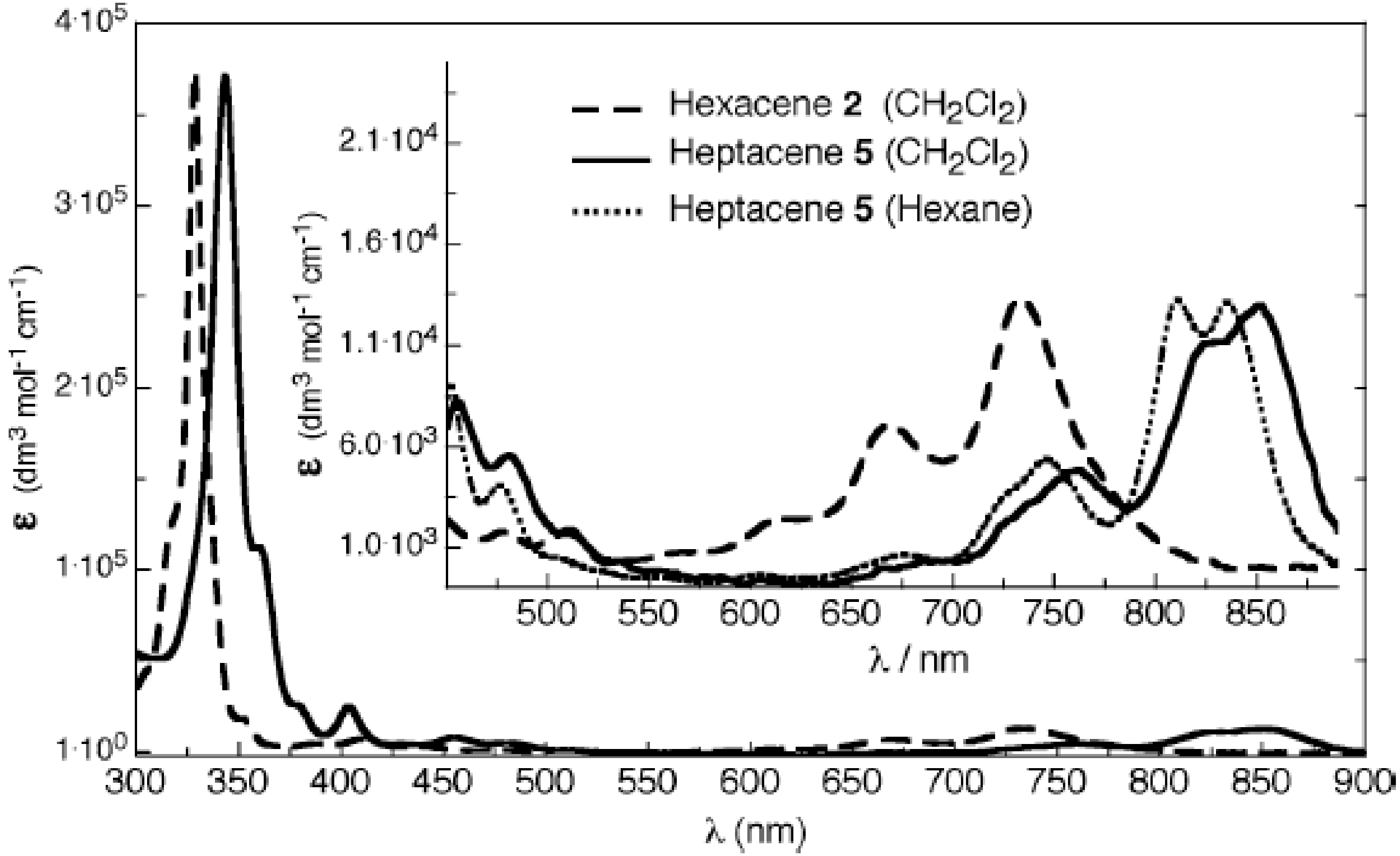
Isolable But Very Short-Lived Substituted Heptacene



Marcia M. Payne, Sean R. Parkin, and John E. Anthony **2005**, *127*, 8028

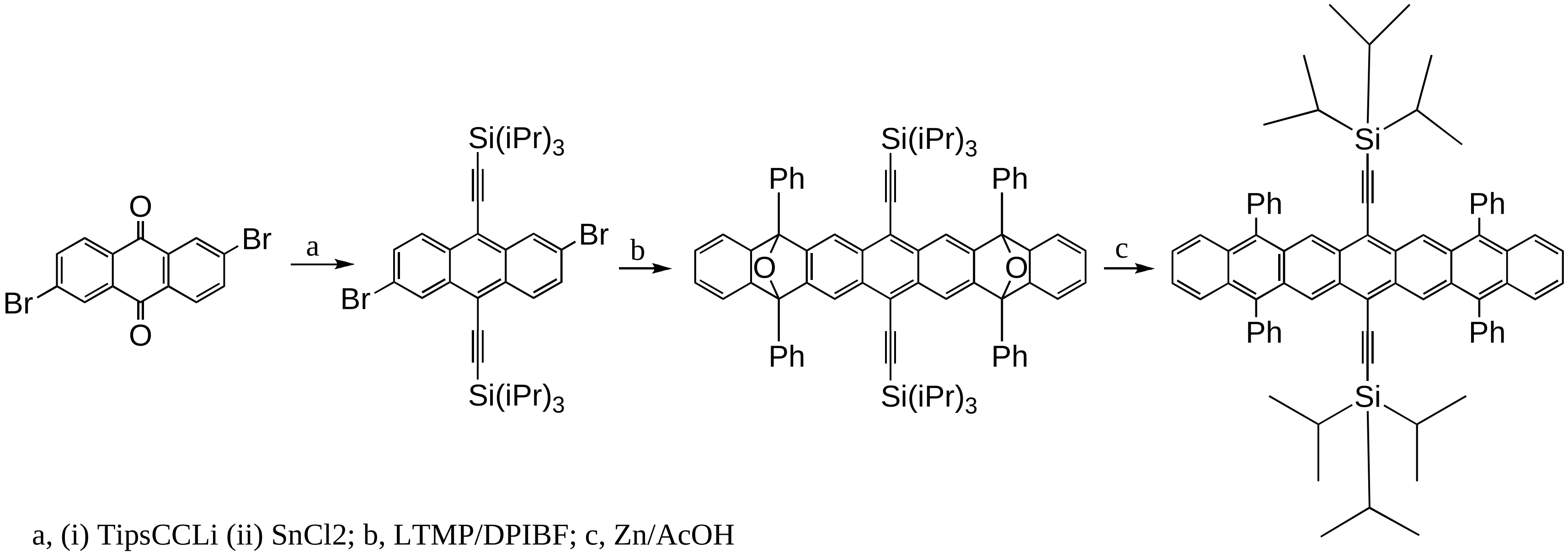


Marcia M. Payne, Sean R. Parkin, and John E. Anthony **2005**, *127*, 8028



Marcia M. Payne, Sean R. Parkin, and John E. Anthony **2005**, *127*, 8028

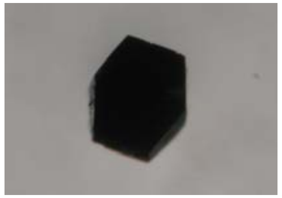
TIPS ACETYLENE TETRAARYLHEPTACENE ISOLABLE AND RELATIVELY STABLE



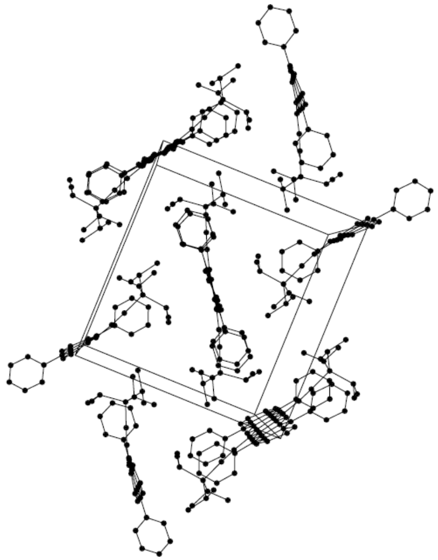
a, (i) TipsCCLi (ii) SnCl2; b, LTMP/DPIBF; c, Zn/AcOH

D. Chun, F. Wudl, unpublished

CRYSTAL STRUCTURE OF BIS(TIPSTHYNYL) TETRAPHENYL HEPTACENE

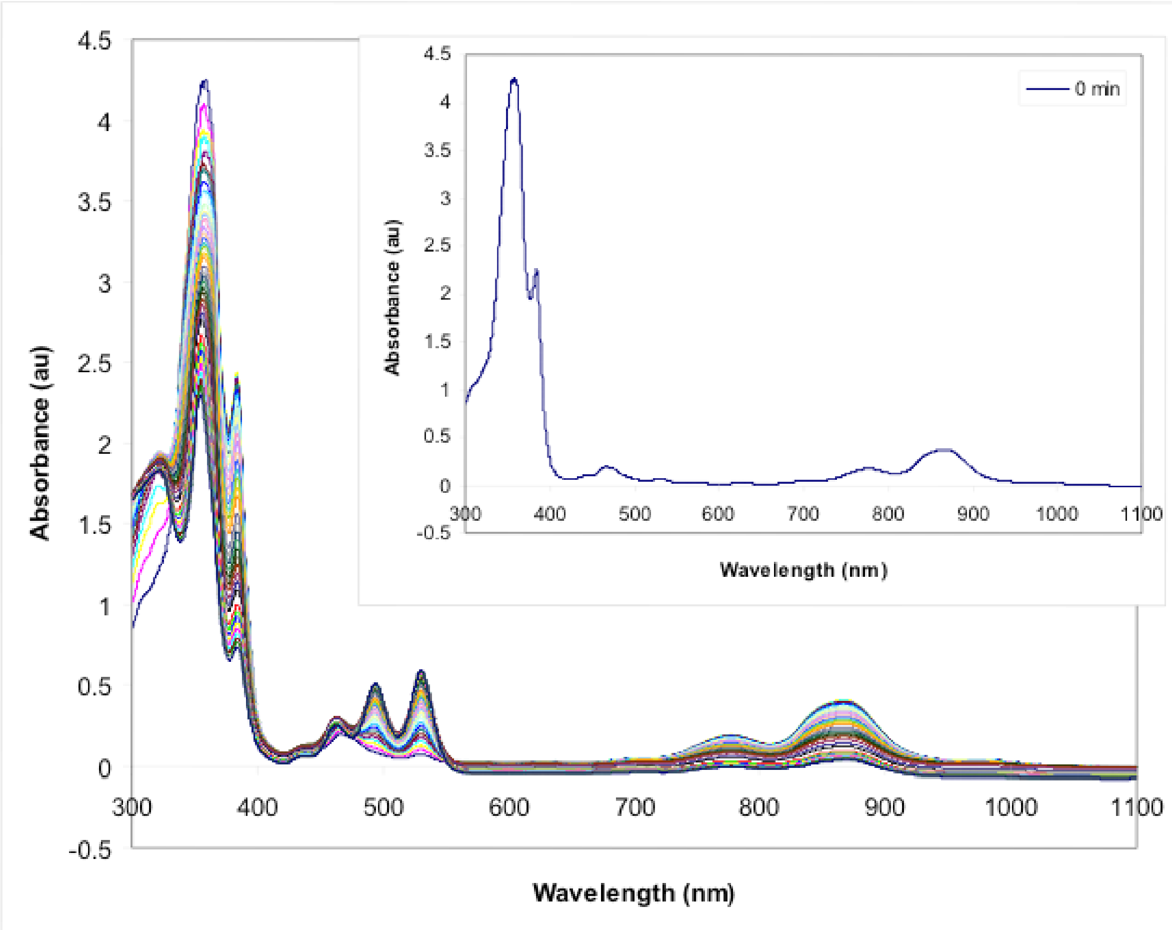


QuickTime™ and a
TIFF (LZW) decompressor
are needed to see this picture.

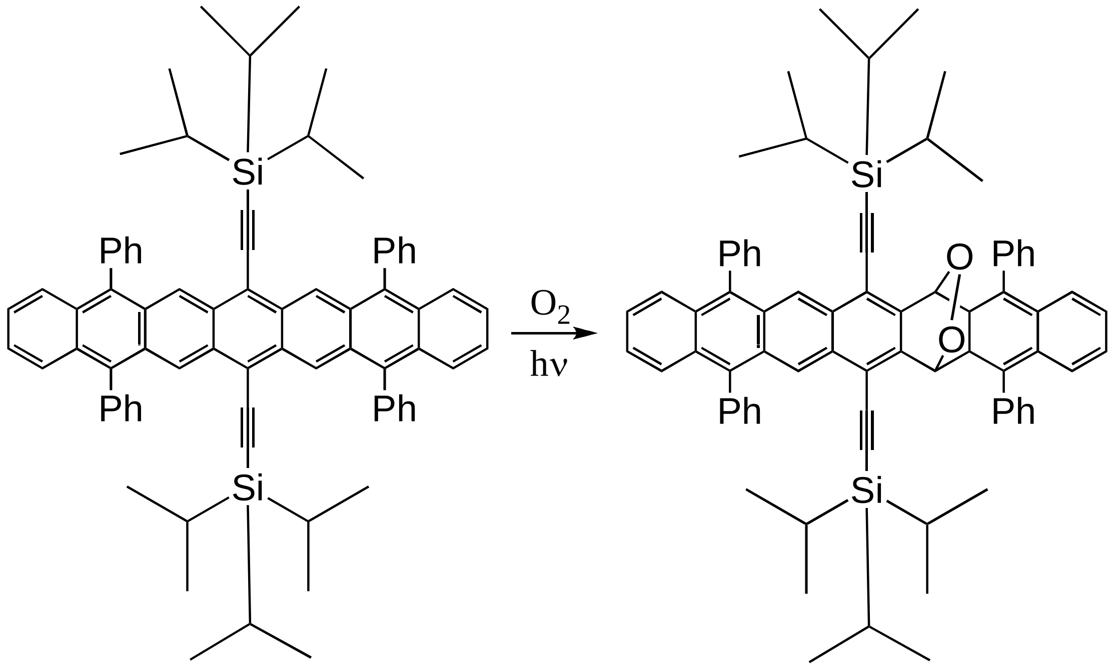


D. Chun, F. Wudl, unpublished

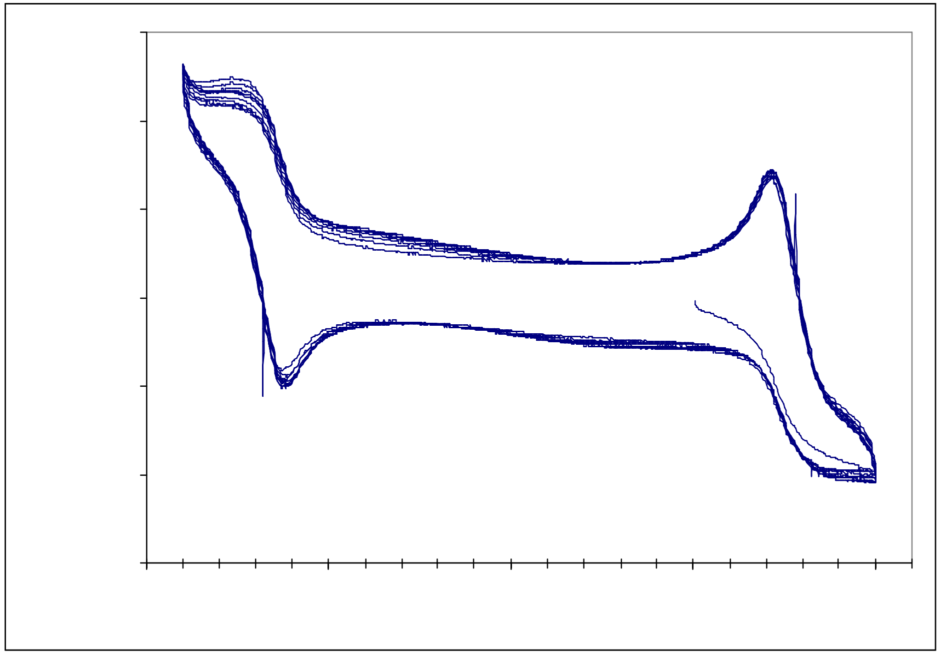
Electronic Spectroscopy



PHOTOINDUCED OXYGEN DEGRADATION



LIMITED CYCLIC VOLTAMMETRY



Photoinduced Charge Generation

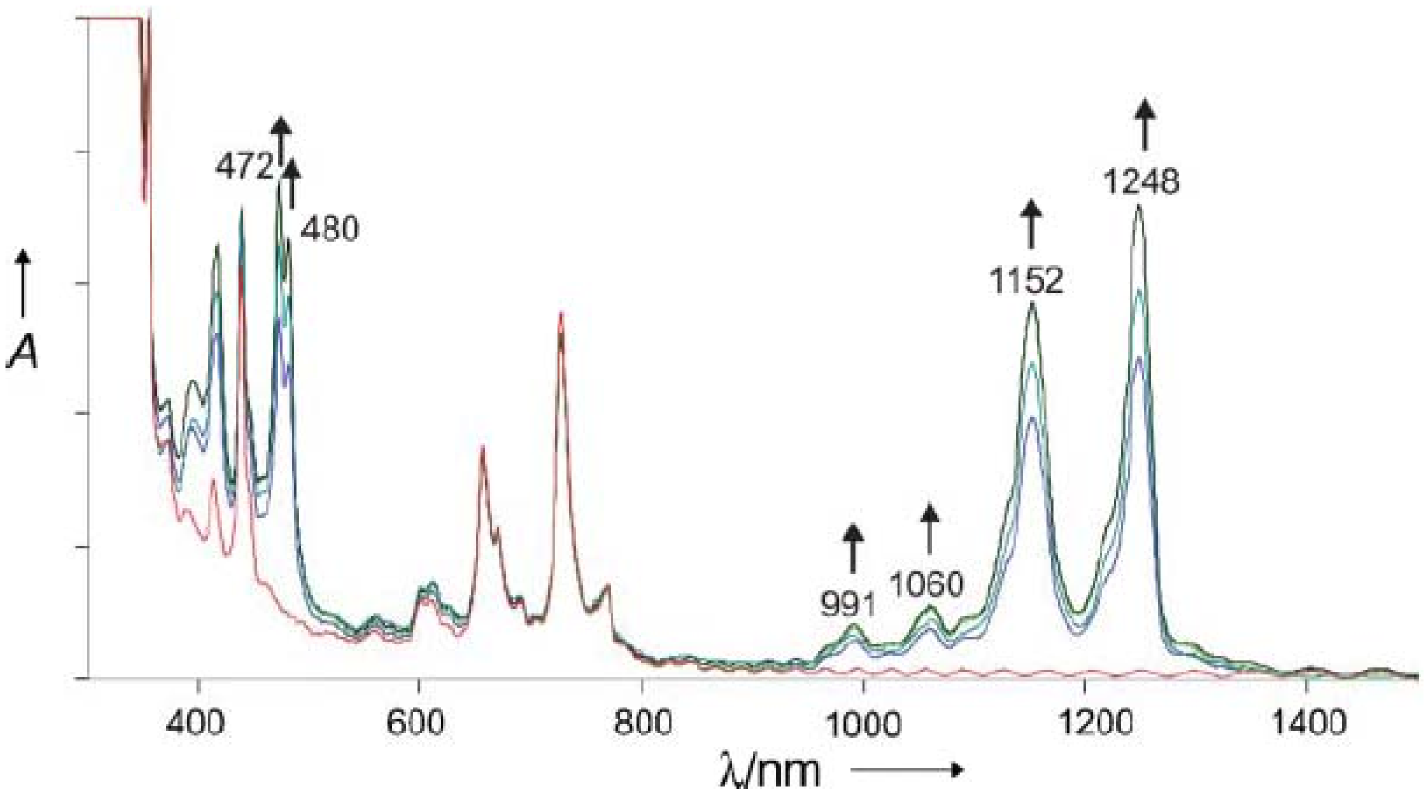


Fig. 3 Electronic absorption spectra obtained after irradiation ($\lambda < 225$ nm) of heptacene in Ar. Red trace: before irradiation.

H. F. Bettinger, R. Mondalb and D. C. Neckers *Chem. Commun*., **2007**, 5209