Bringing (Semiconducting) Polymers to Order

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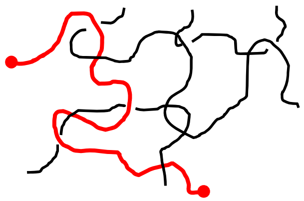
Outline

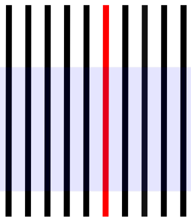
- **background**

poly(*3*-hexylthiophene), P3HT

- **routes to high**(er) **order**
- **conclusions today**
- **outlook tomorrow** & **beyond**



material **order** matters



property	unit	unordered	*perfectly* ordered
Young‘s modulus (stiffness)	GPa	**0.001**	>**100**
tensile strength (stress at break)	GPa	**0.001**	**10**
thermal conductivity	mW cm^{-1} deg^{-1}	**10**	>**100**
electrical conductivity	S cm^{-1}	**100**	**100‘000**
non-linear optical coefficient	esu	10^{-10}	10^{-9}

examples: polyethylene, polyacetylene

factors influencing „**order**“

- **molecular architecture** (chain „regularity“, stiffness)
- **molecular length** („weight“)
- **processing schemes**
- **synthesis** („physico-chemical conditions“)

PRINCIPLES OF

POLYMER CHEMISTRY

By Paul J. Flory

Professor of Chemistry, Stanford University

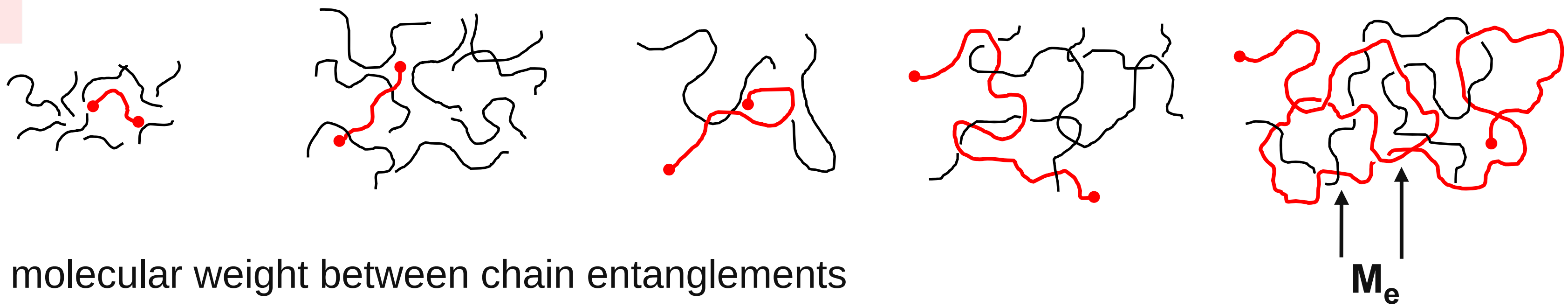
CHAPTER I

Historical Introduction

THE hypothesis that high **polymers** are composed of covalent structures **many times greater in extent** than those occurring in simple compounds, and that **this feature alone accounts for the characteristic properties which set them apart from other forms of matter**, is in large measure responsible for the rapid advances in the chemistry and physics of these substances witnessed in recent years.

P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, 1953, p 3

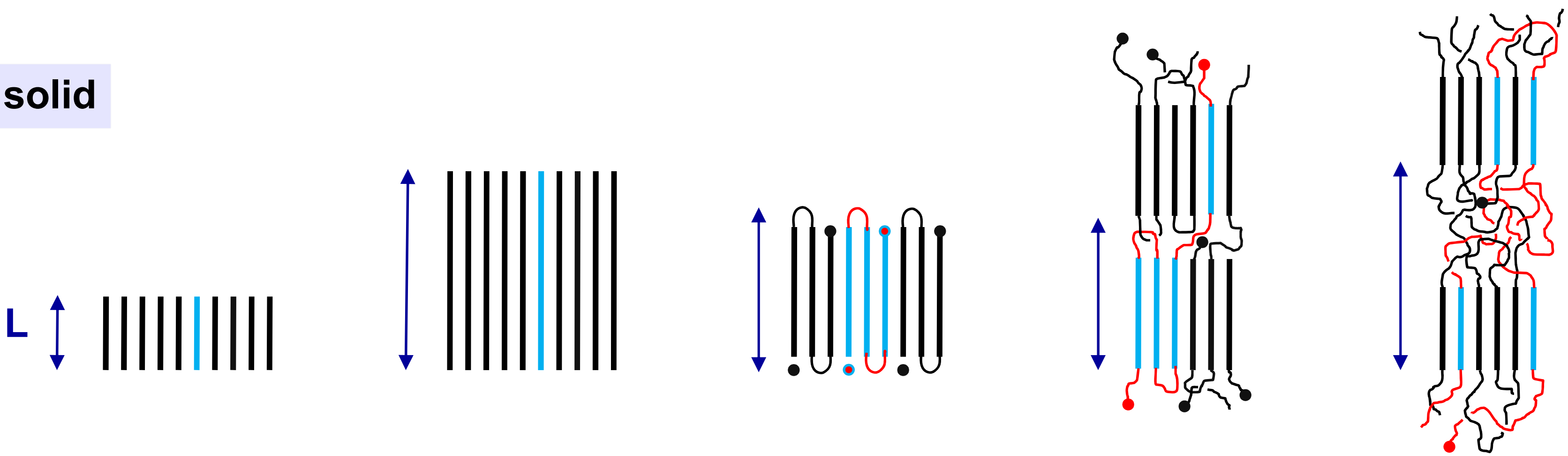
melt



M_e = molecular weight between chain entanglements

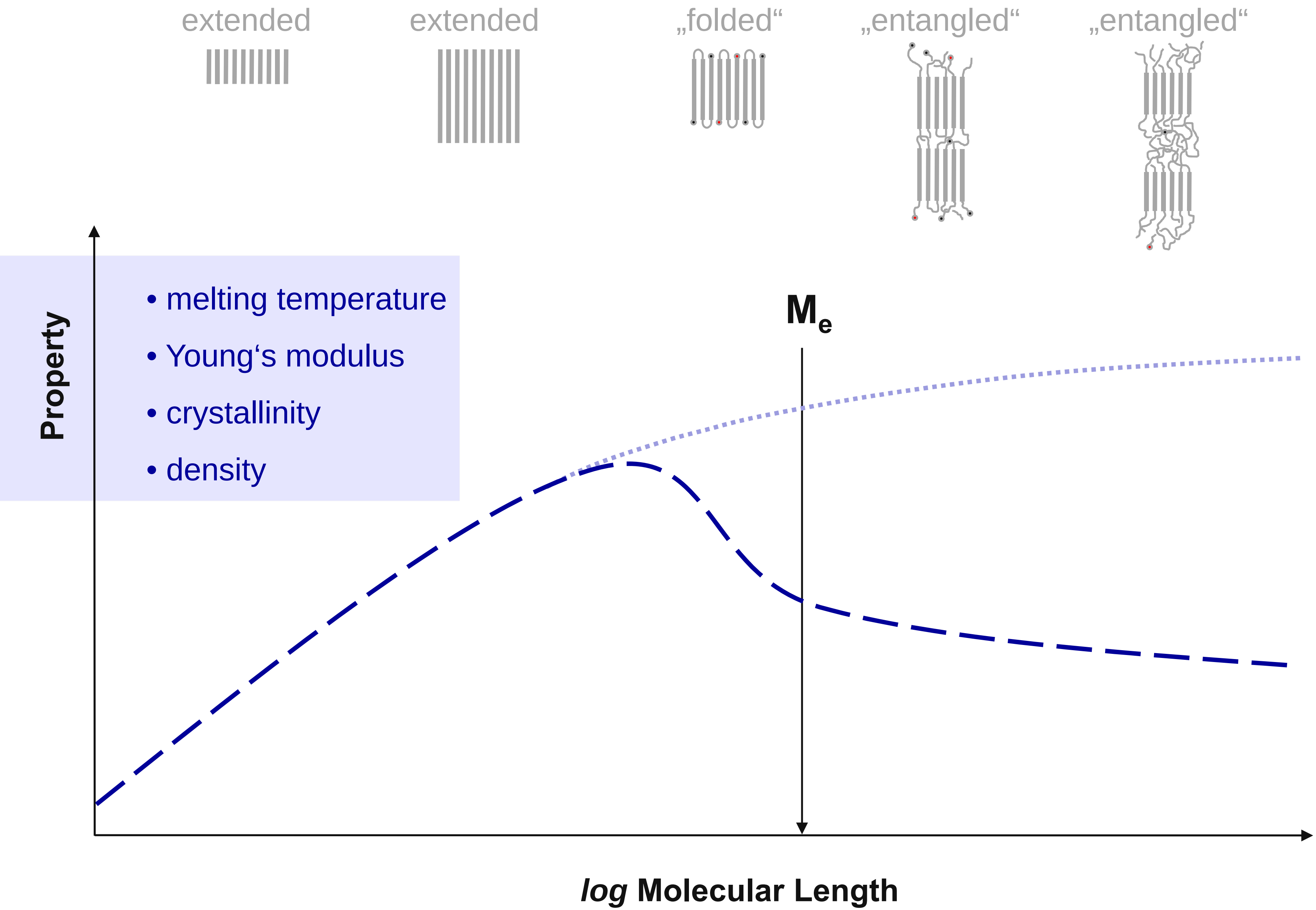
***log* Molecular Length**

solid

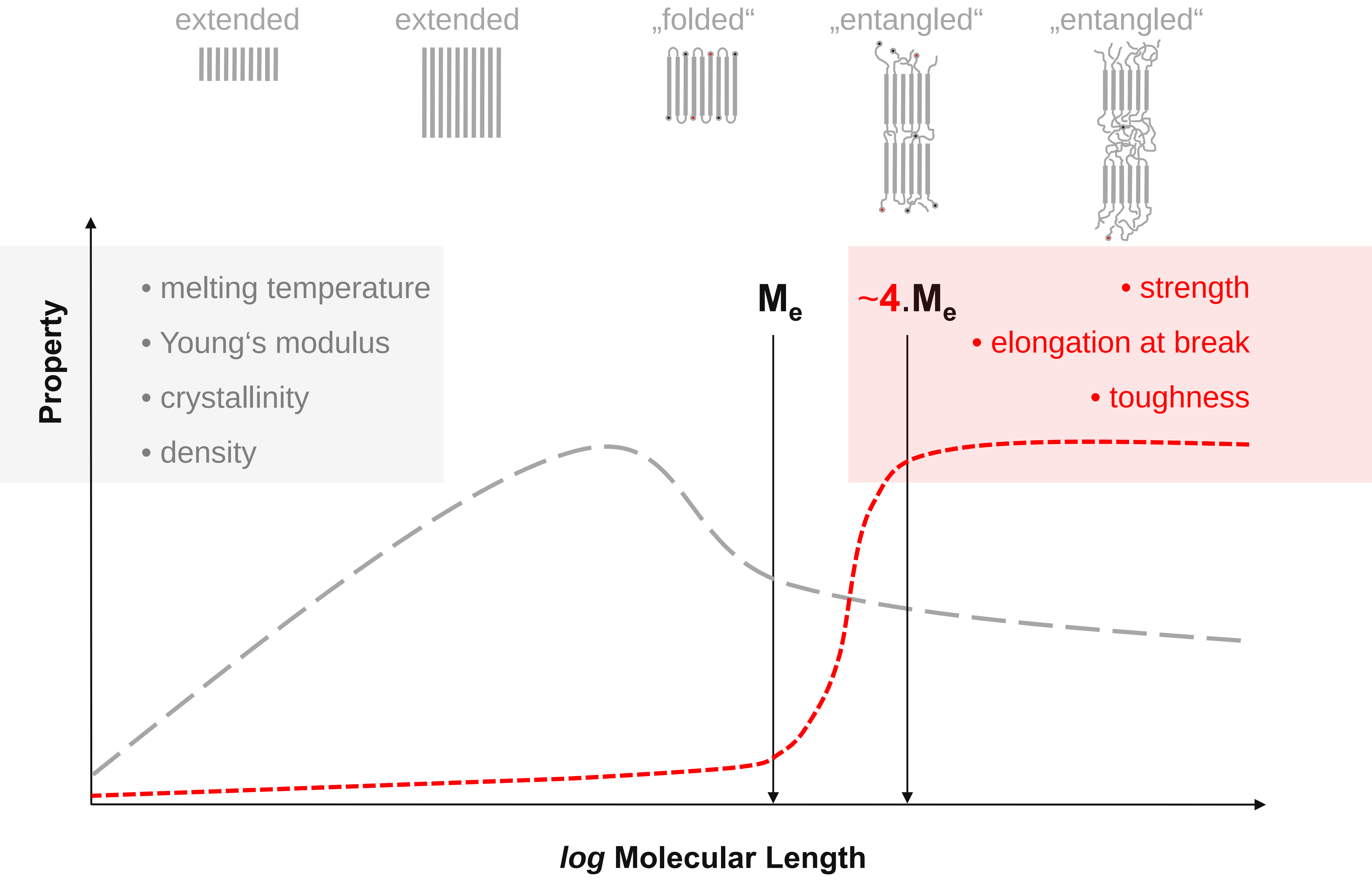


extended **extended** **„folded“** **„entangled“** **„entangled“**

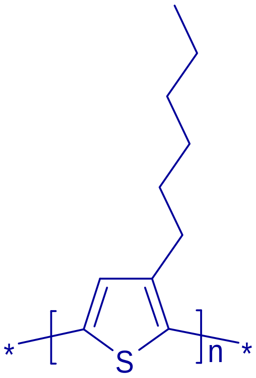
L = long period


extended
extended
„folded“
„entangled“
„entangled“
Property
• melting temperature
• Young‘s modulus
• crystallinity
• density
M_e
log Molecular Length

Order **Properties**



P3HT



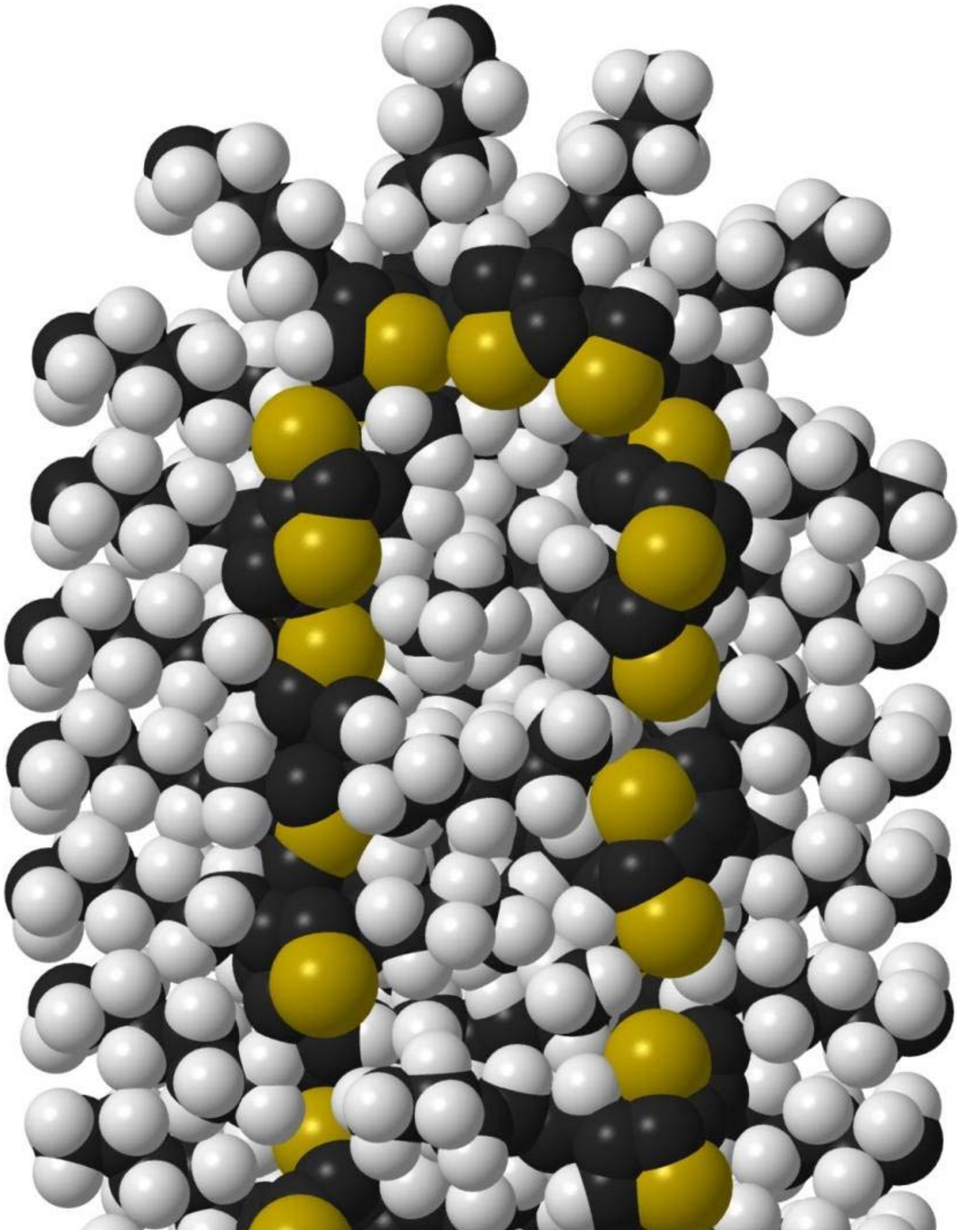
poly(*3*-hexylthiophene)

a semi-**flexible** polymer

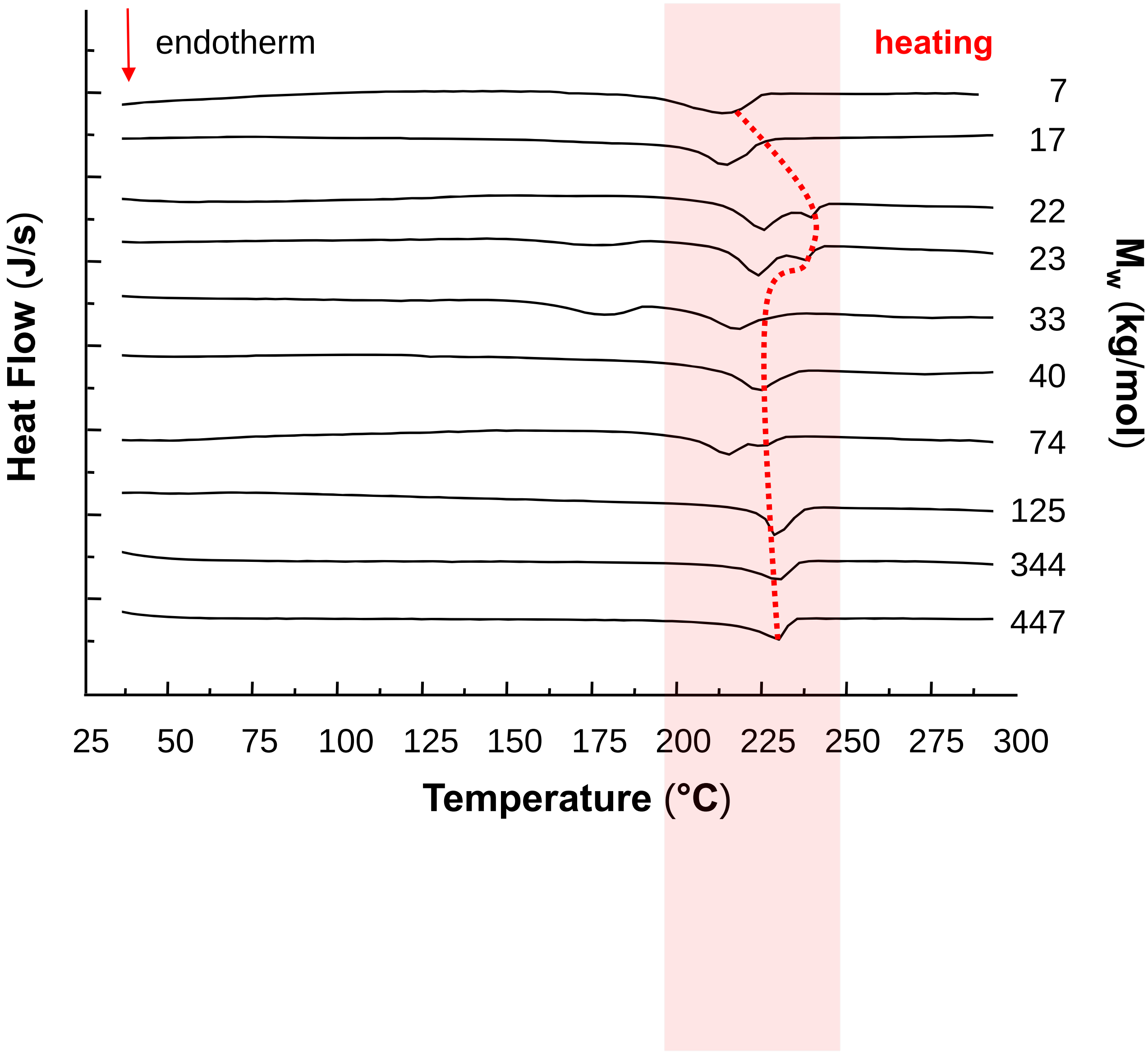
persistence length = **2.4 nm**

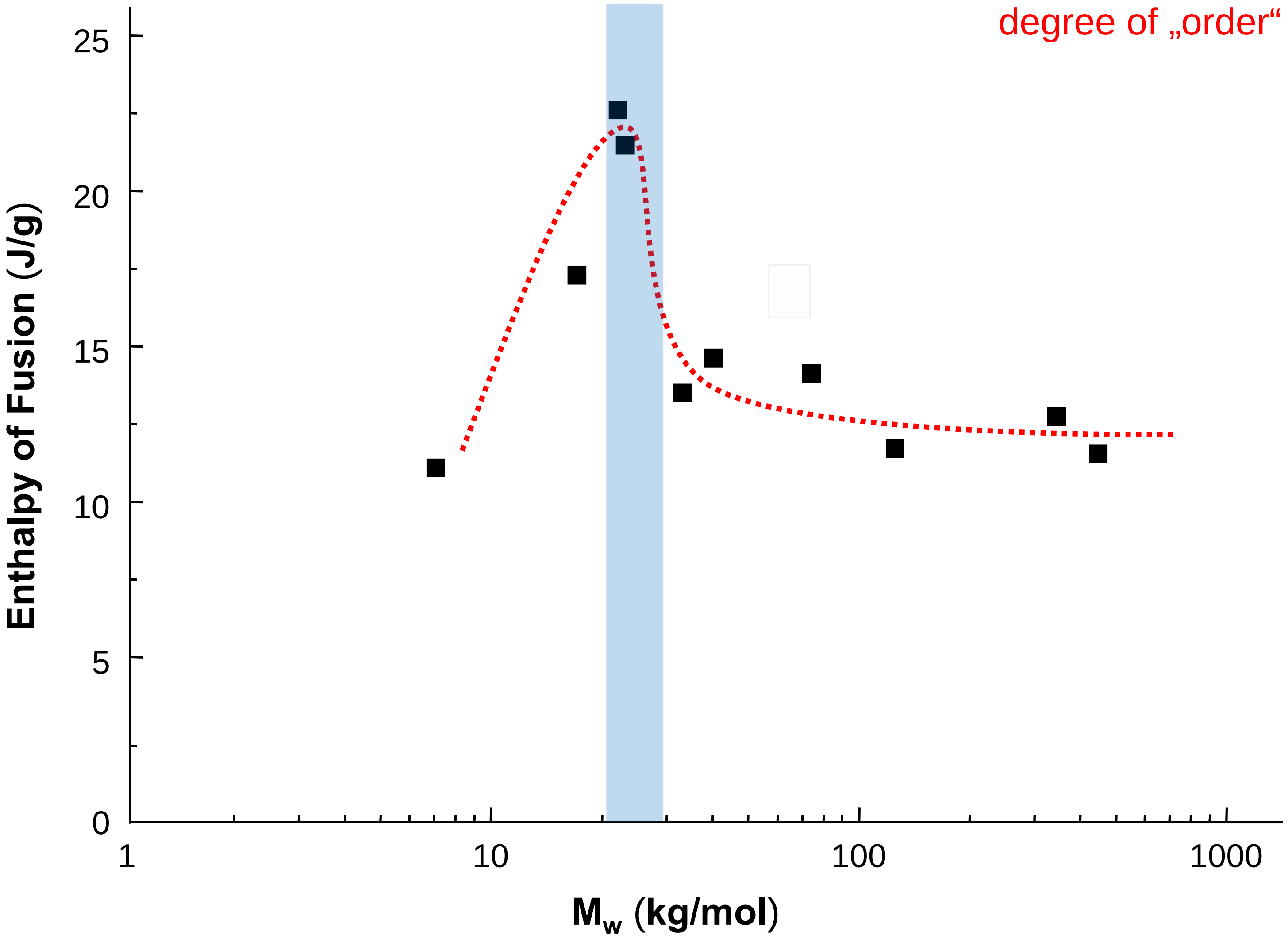
sharp fold with **6** repeat units

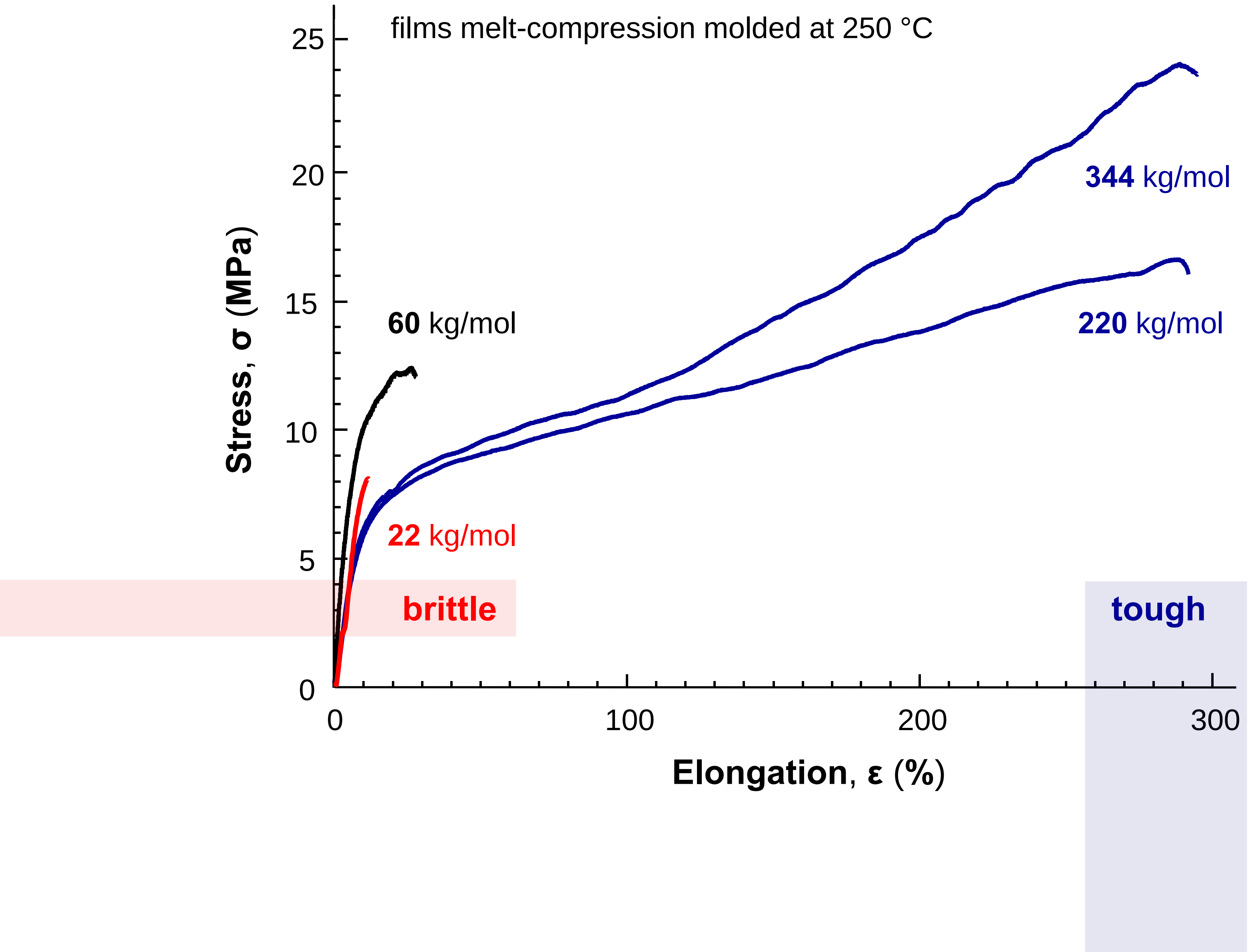
G. Heffner *et al*., *Macromolecules* **1991**, 24, 6295



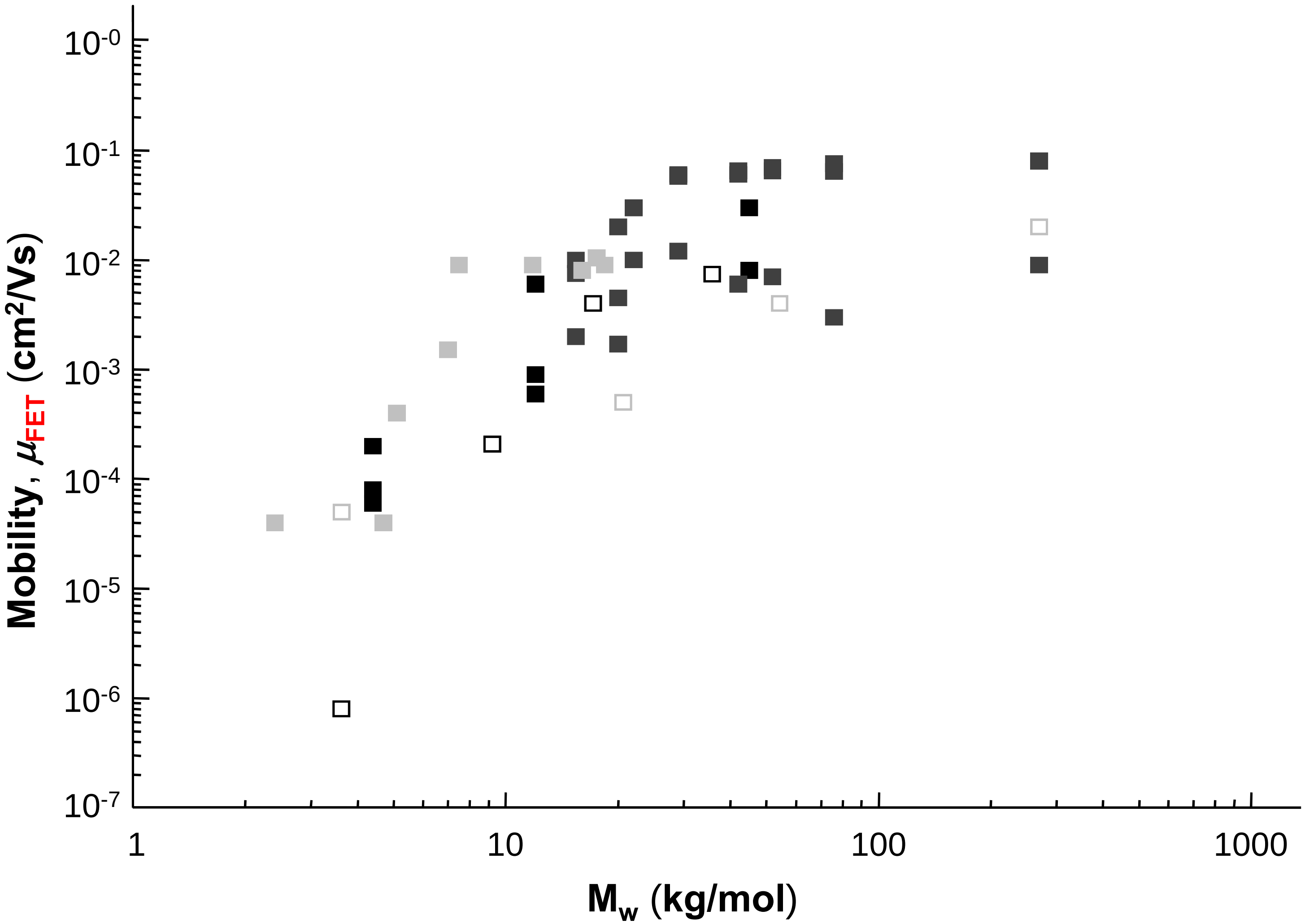
Chem3D Ultra, Version 10.0 Simulation: MM2 (Minimization)


endotherm
heating
7
17
22
23
33
40
74
125
344
447
M_w (kg/mol)
Heat Flow (J/s)
25
50
75
100
125
150
175
200
225
250
275
300
Temperature (°C)


degree of „order“
Enthalpy of Fusion (J/g)
25
20
15
10
5
0
1
10
100
1000
M_w (kg/mol)


films melt-compression molded at 250 °C
Stress, σ (MPa)
25
20
15
10
5
0
0
100
200
300
Elongation, ε (%)
60 kg/mol
22 kg/mol
344 kg/mol
220 kg/mol
brittle
tough

M_w-Dependence μ_{FET} P3HT



■ R. McCullough *et al.*, *JACS* **2006**, 128, 3480
■ R. J. Kline *et al.*, *Macromolecules* **2005**, 38, 3312
□ D. Neher *et al.*, *Macromolecules* **2006**, 39, 2162
□ A. Pron *et al.*, *Phys. Chem. B* **2006**, 110, 13305
■ H. Sirringhaus *et al.*, *Phys. Rev. B* **2006**, 74, 1098

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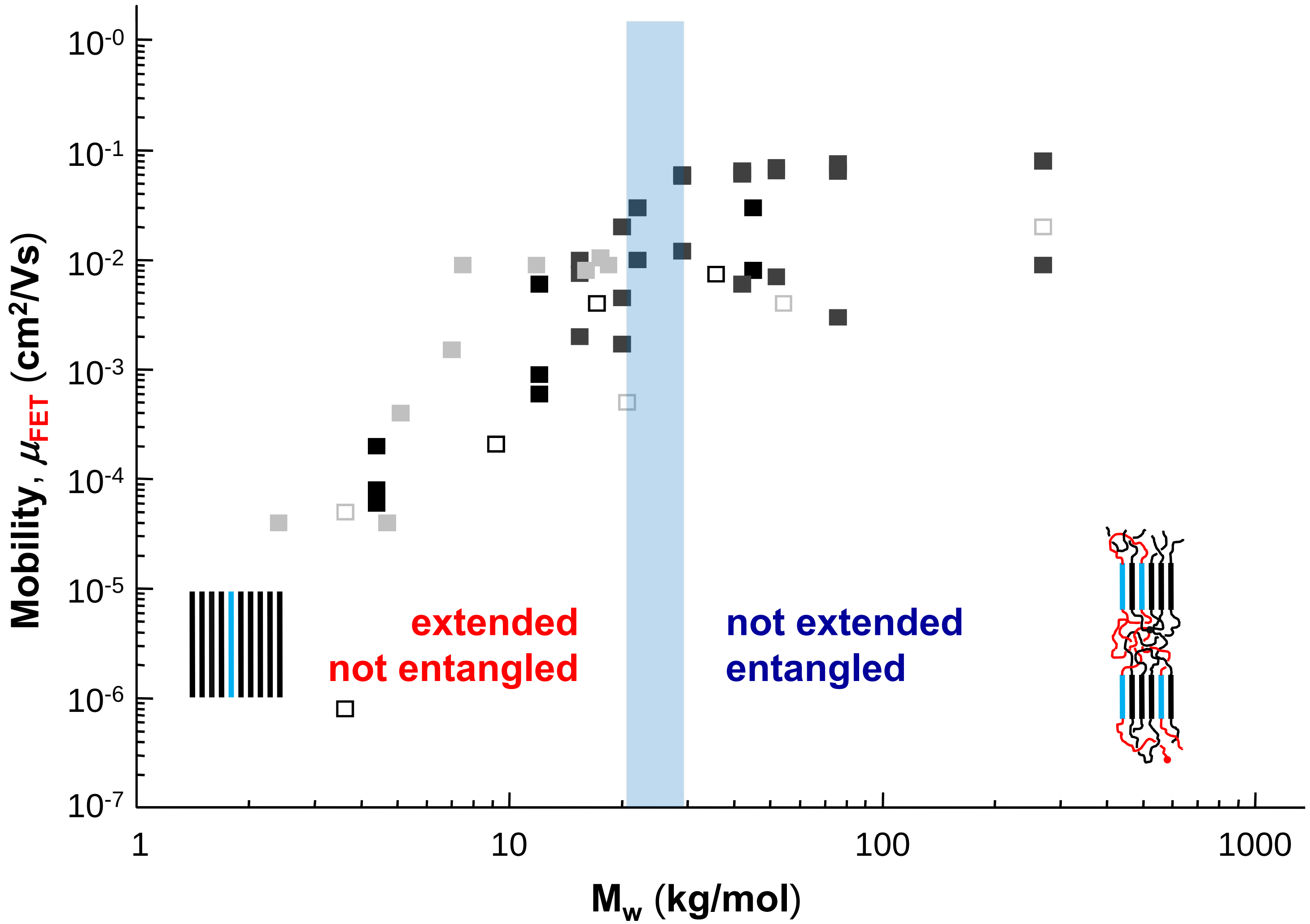

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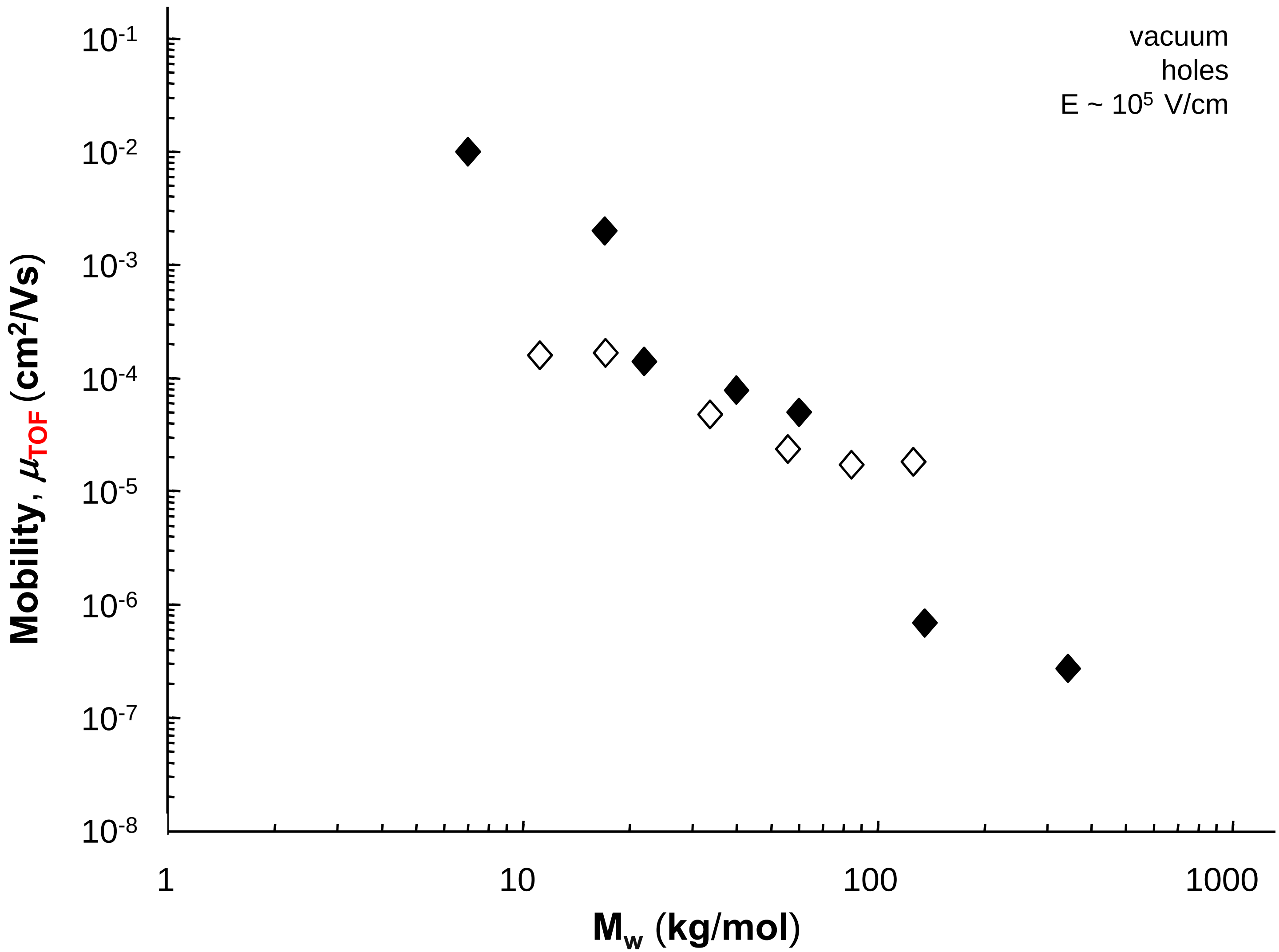
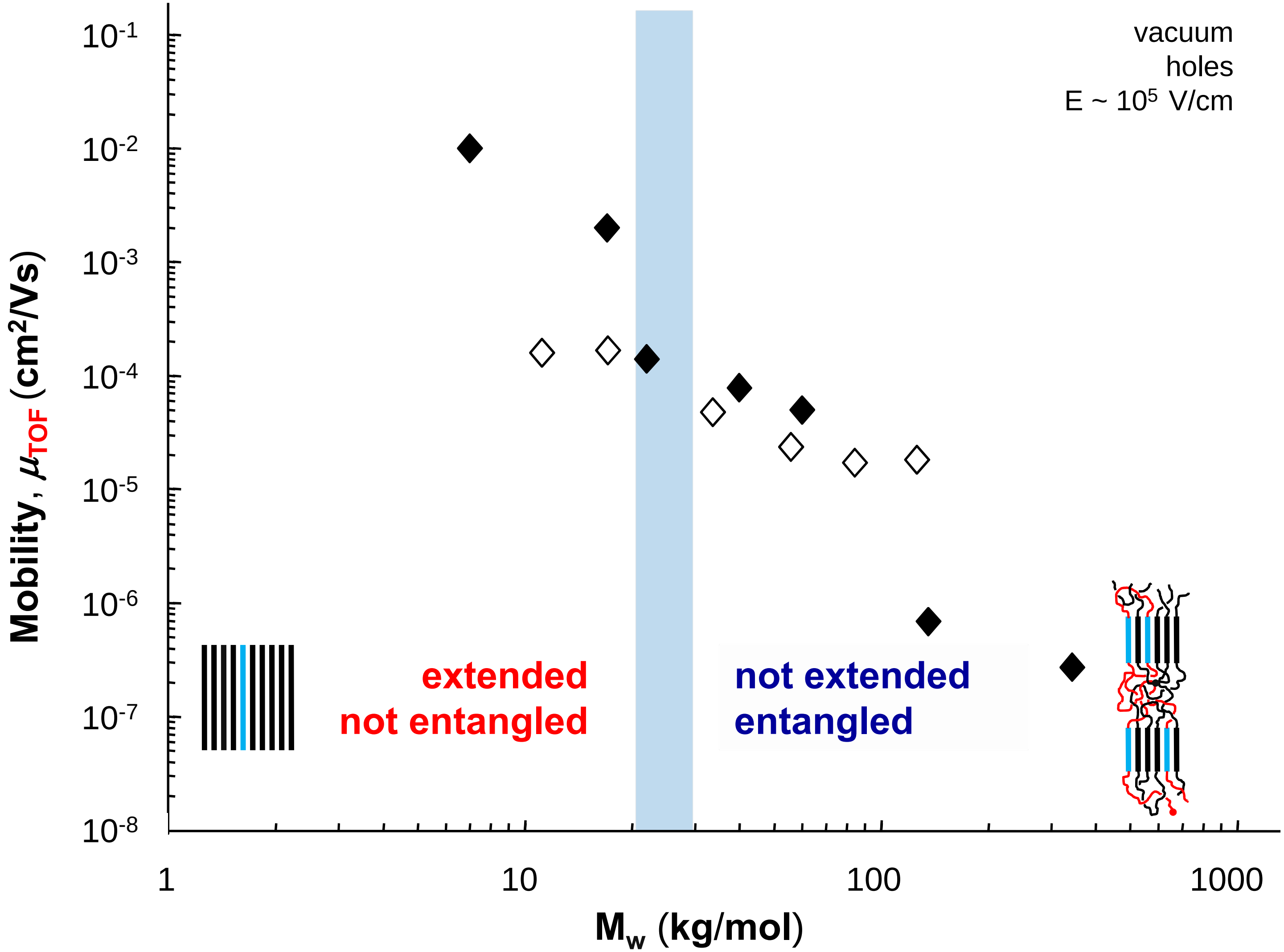
M_w-Dependence μ_{TOF} P3HT



◇ A. M. Ballantyne *et al.*, *Adv. Funct. Mater.* **2008**, 18, 2373

M_w-Dependence μ_{TOF} P3HT



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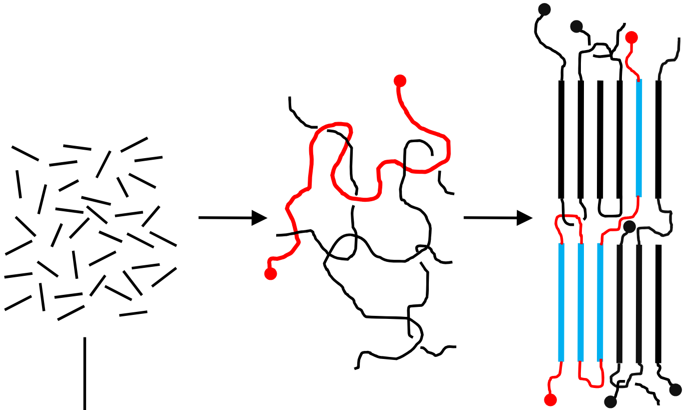
Routes to High(er) Order



high-**temperature** crystallization

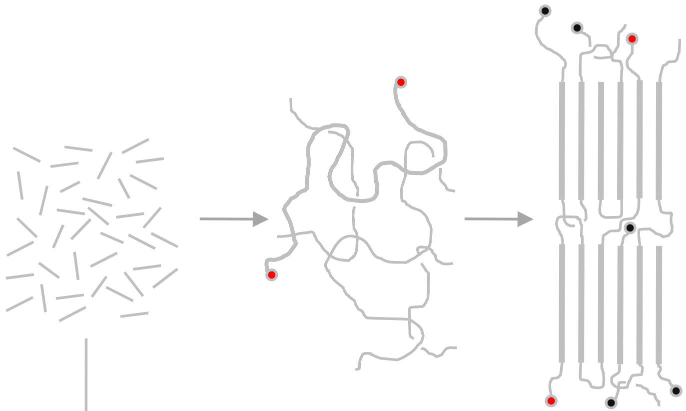
solution crystallization

tensile **deformation**

high-**pressure** crystallization

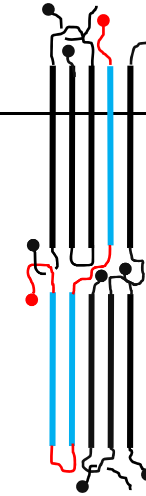
solid-state processing of „***virgin***“ polymers

Routes to High(er) Order



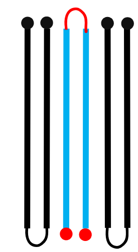
high-**temperature** crystallization

crystal thickness ↑



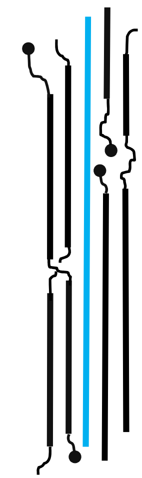
solution crystallization

fold length ↑



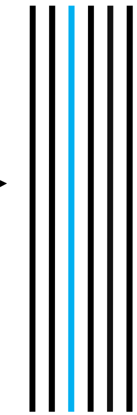
tensile **deformation**

continuous „defect“ crystal



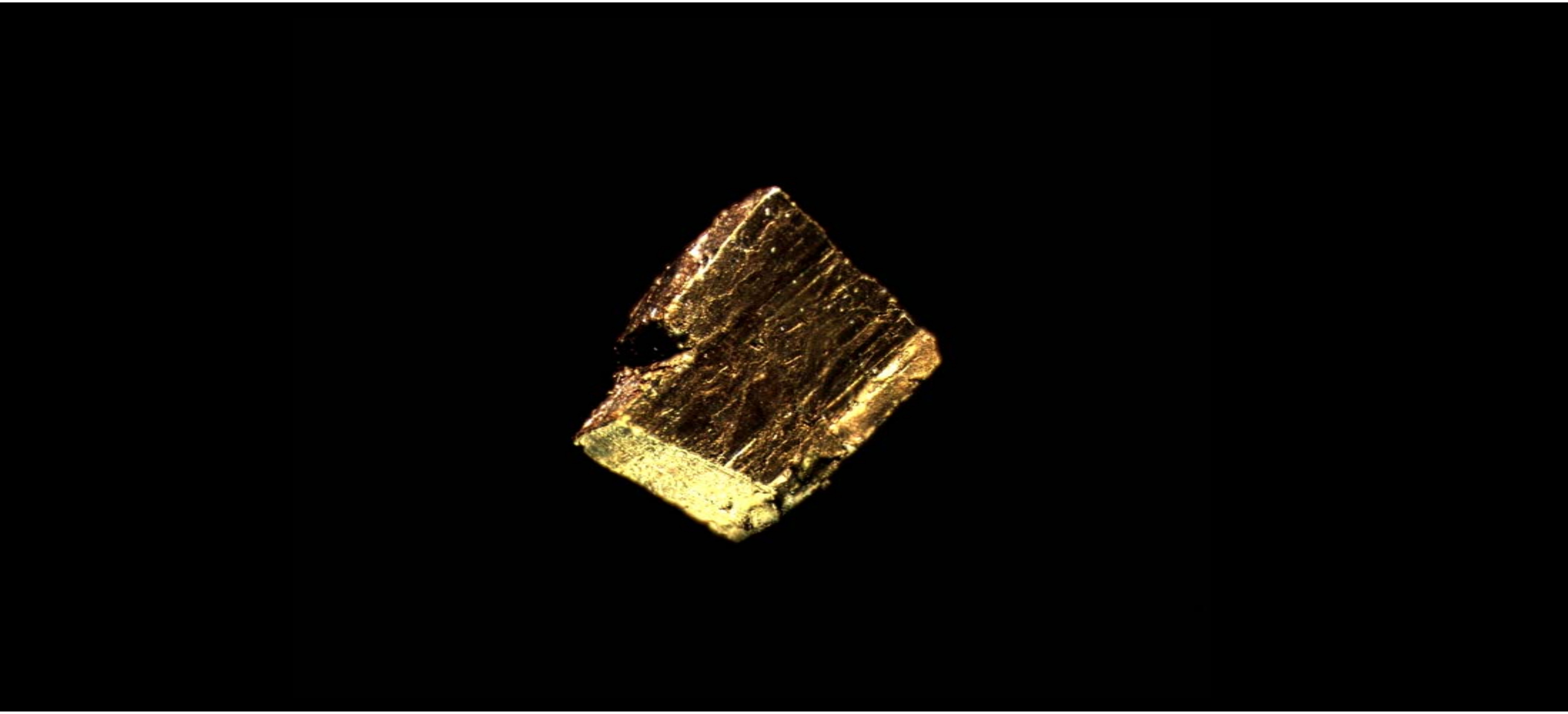
high-**pressure** crystallization

extended chains



solid-state processing of „***virgin***“ polymers .....

High-Pressure Solidification

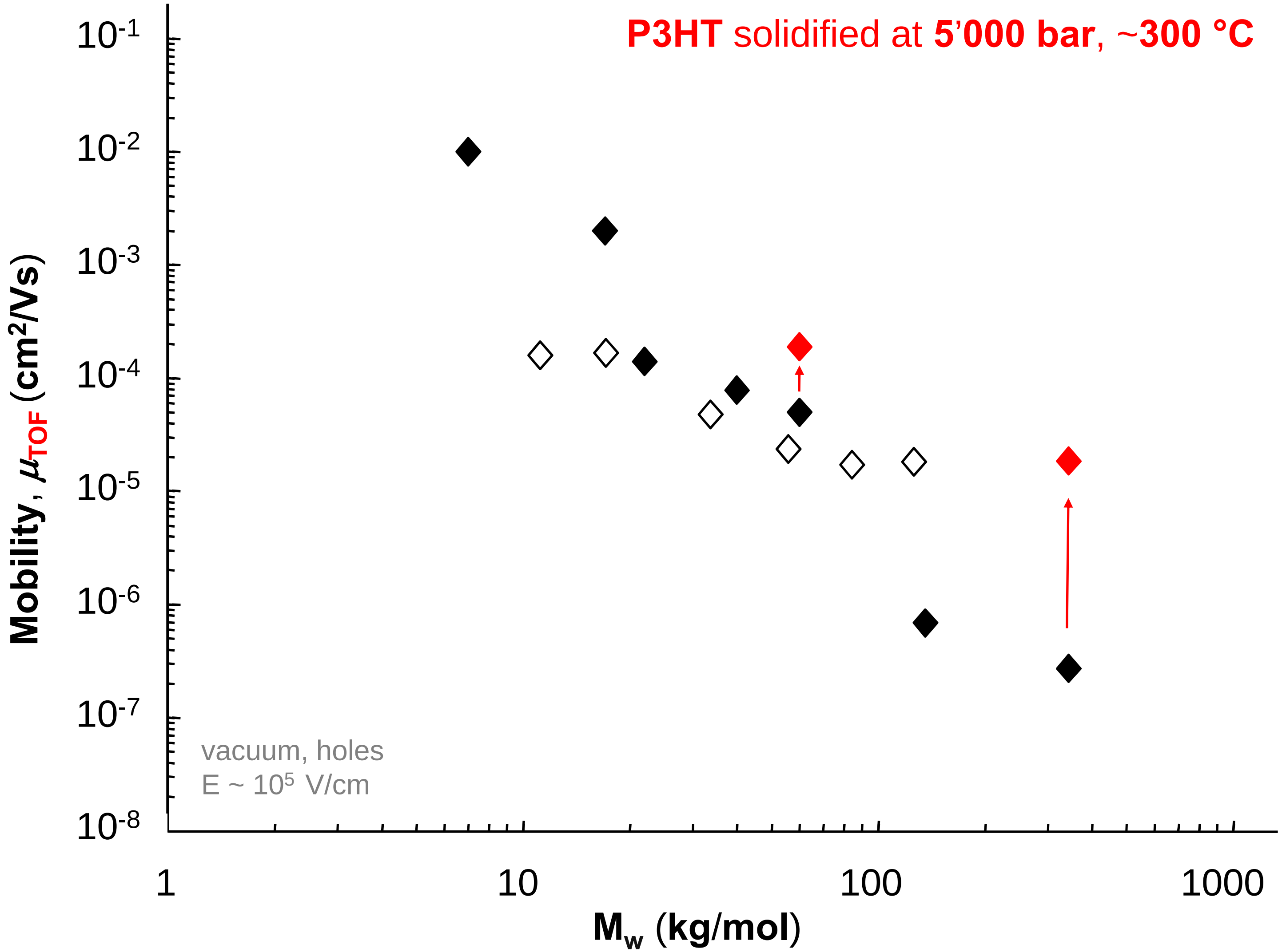


2 mm

P3HT M_w = 344 kg/mol

T_c ~300 °C at 5‘000 bar

M_w-Dependence μ_{TOF} P3HT



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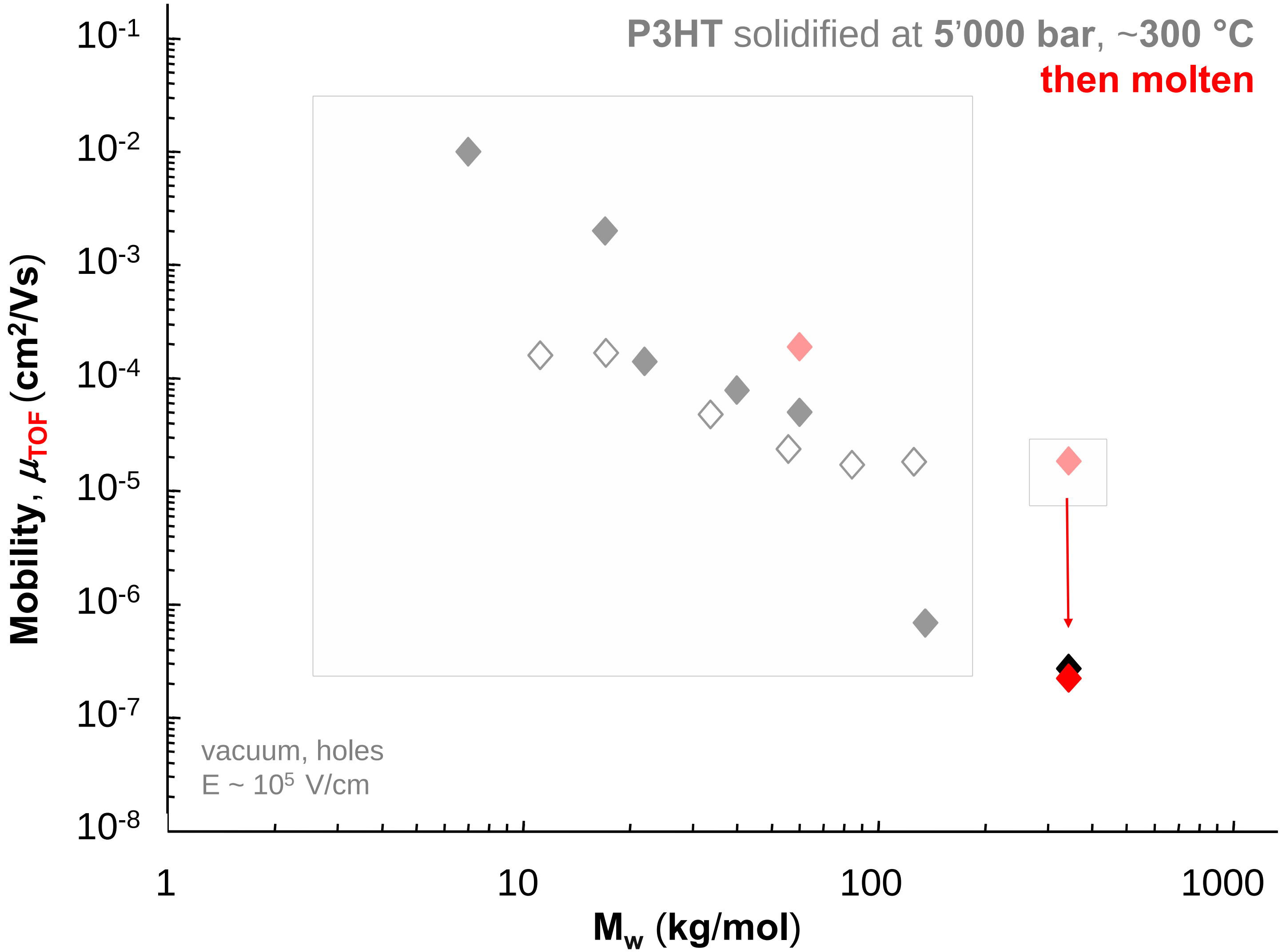
M_w-Dependence μ_{TOF} P3HT



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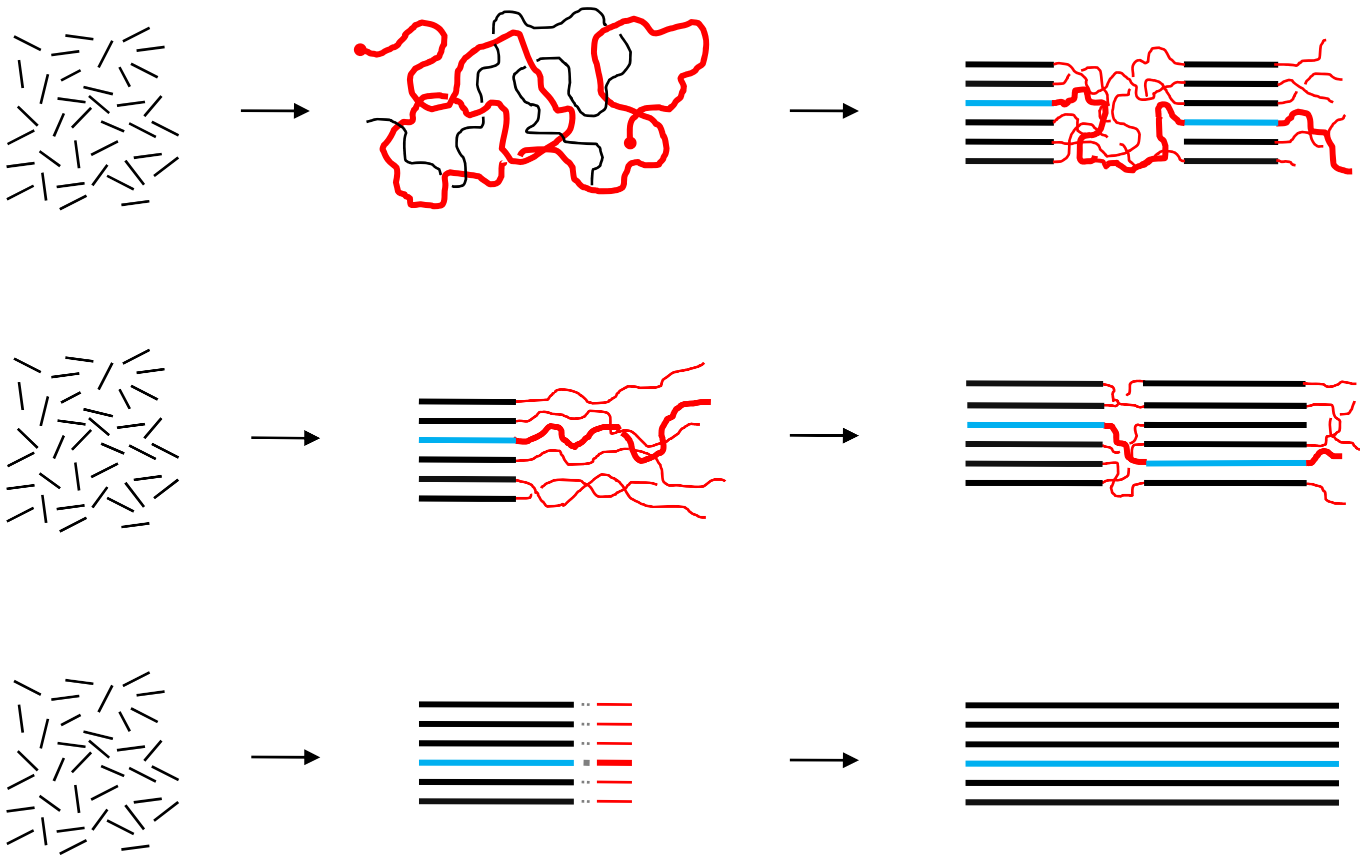
physico-chemical polymerization conditions | **physical state** | **solid-state structure**

$T_p > T_{m,\,d}$

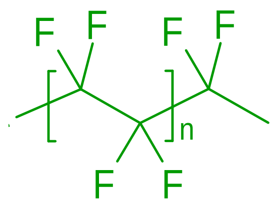
$T_p < T_{m,\,d}$

$T_p << T_{m,\,d}$

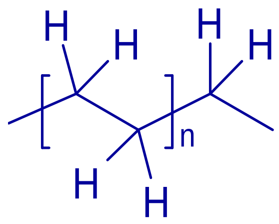


examples

- poly(tetrafluoroethylene) **PTFE**



- ultra-high molecular weight polyethylene **UHMW PE**

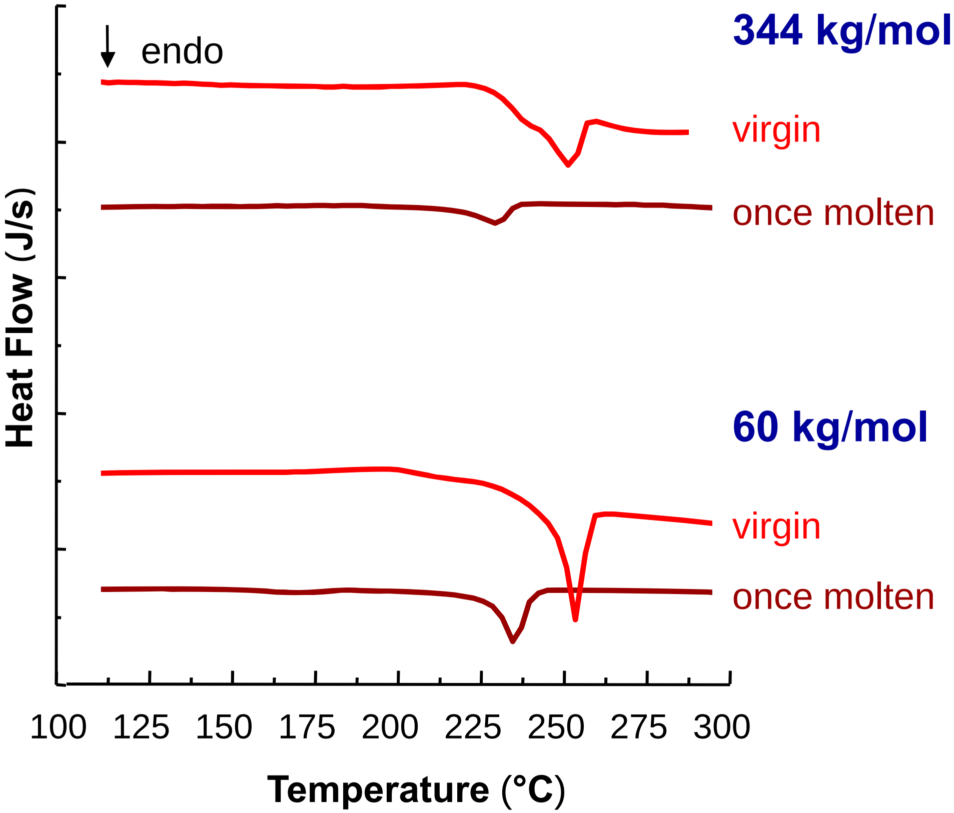


characteristics

- high melting temperature
- high degree of crystallinity

low entanglement density, *if any*

- irriversible first melting



	virgin	once molten
T_m (°C)	251	230
X (%)	39	13

T_m (°C)	253	233
X (%)	42	21

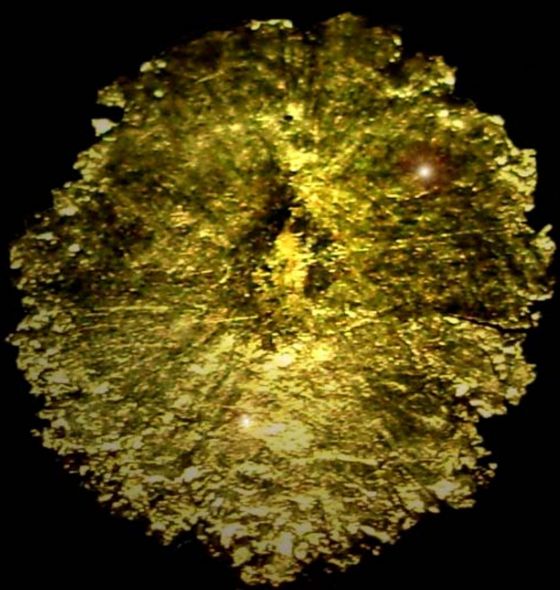
low entanglement density in „virgin“ polymers permits flow in the **solid state** allowing manufaturing of ***mechanically coherent*** objects below T_m

P3HT (344 kg/mol)

T_p = room temperature; *i.e.* T_m - 225 °C

high order in „virgin“ polymers is retained

when processed ***below*** the melting temperature



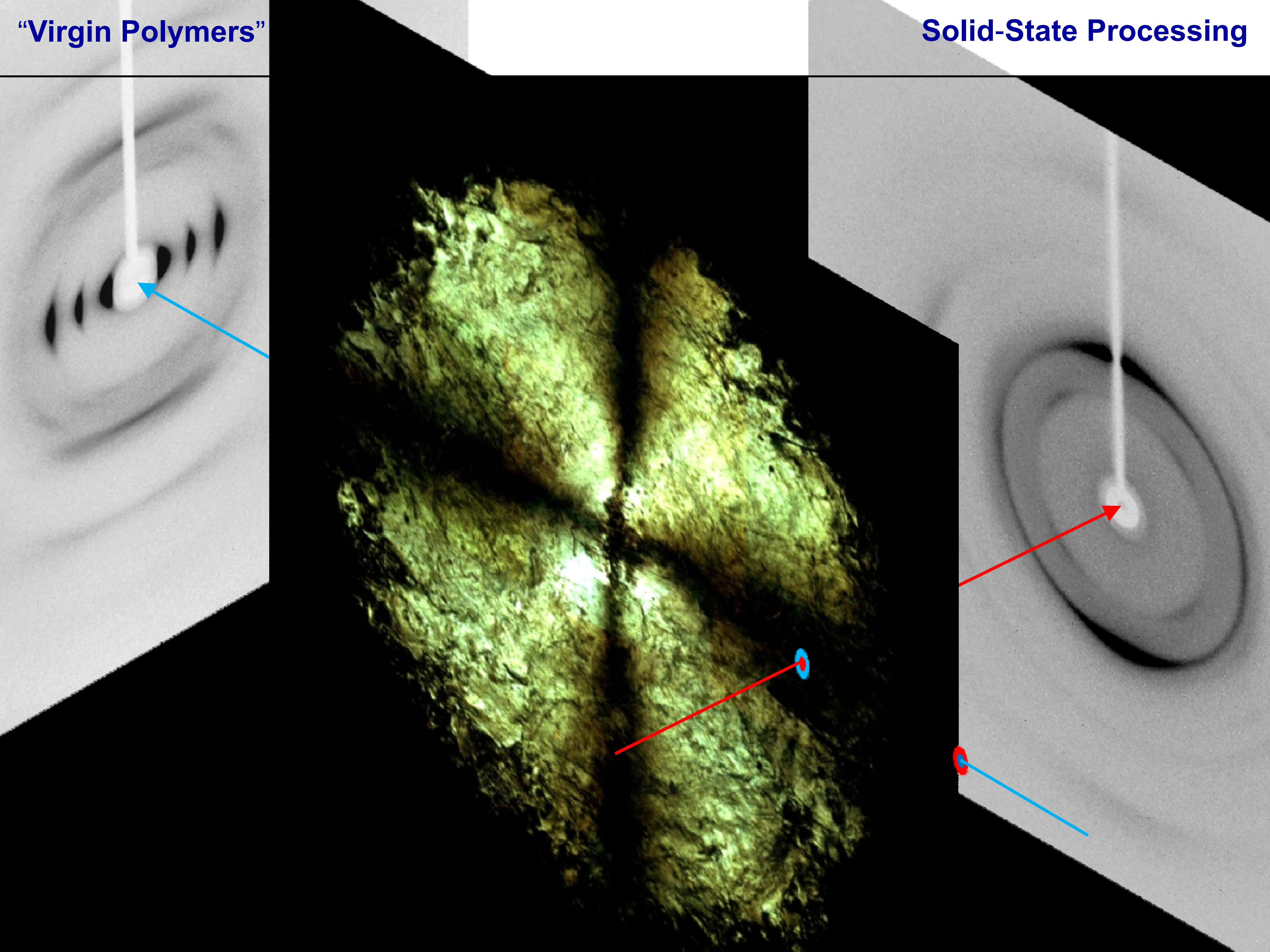
reflected light

crossed polarizers

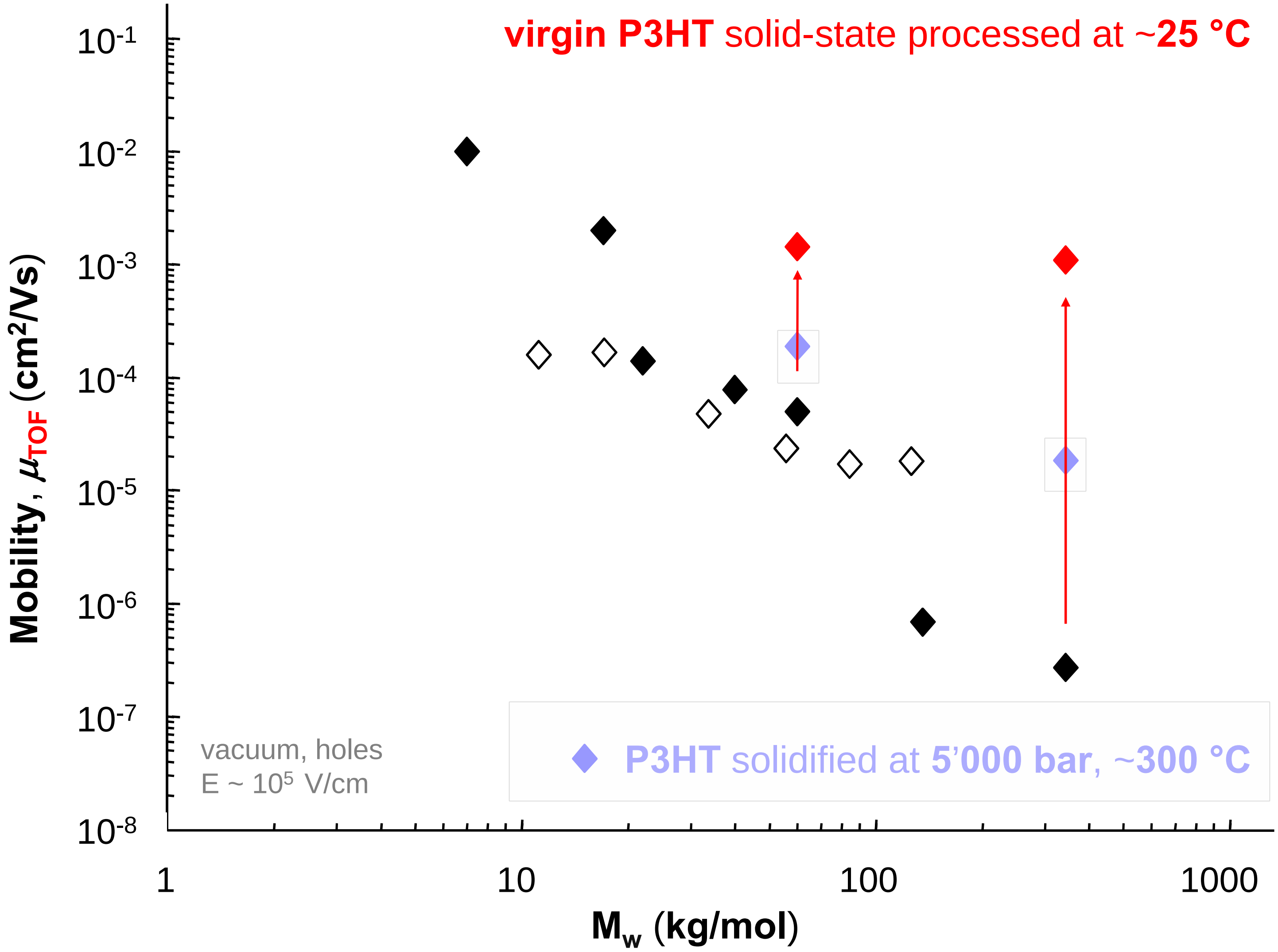
dubbeltje

“Virgin Polymers”

Solid-State Processing



M_w-Dependence μ_{TOF} P3HT



◇ A. M. Ballantyne *et al.*, *Adv. Funct. Mater.* **2008**, 18, 2373

Conclusions *Today*

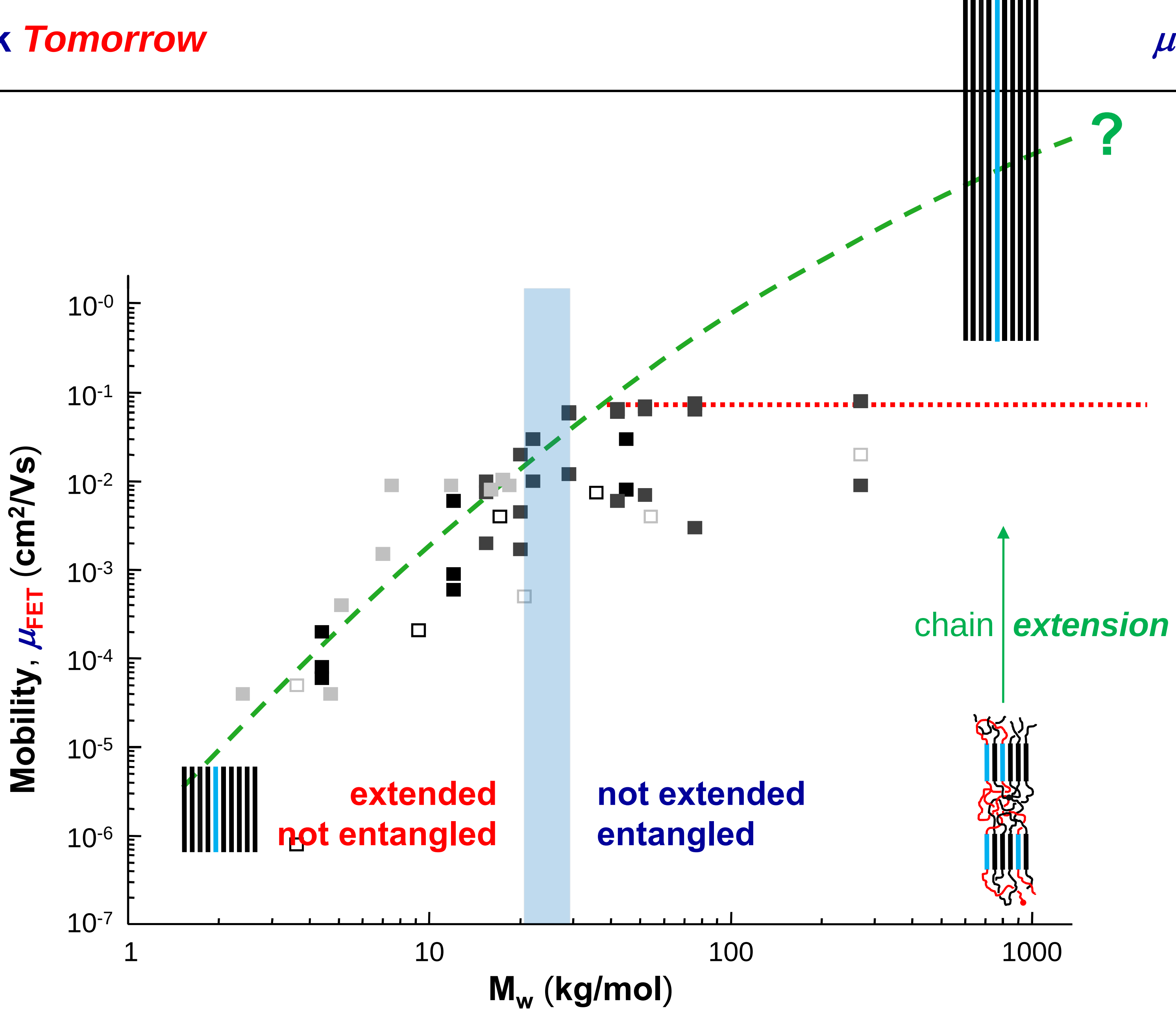
P3HT exhibits **classical MW** / **solid-state structure** correlations of flexible chain polymers

order can be improved by classical methods

improved **physico-chemical conditions during synthesis** yields material of higher order

solid-state processing of **„virgin“** polymers may not require solubilizing (diluting) side-chains

Outlook *Tomorrow*



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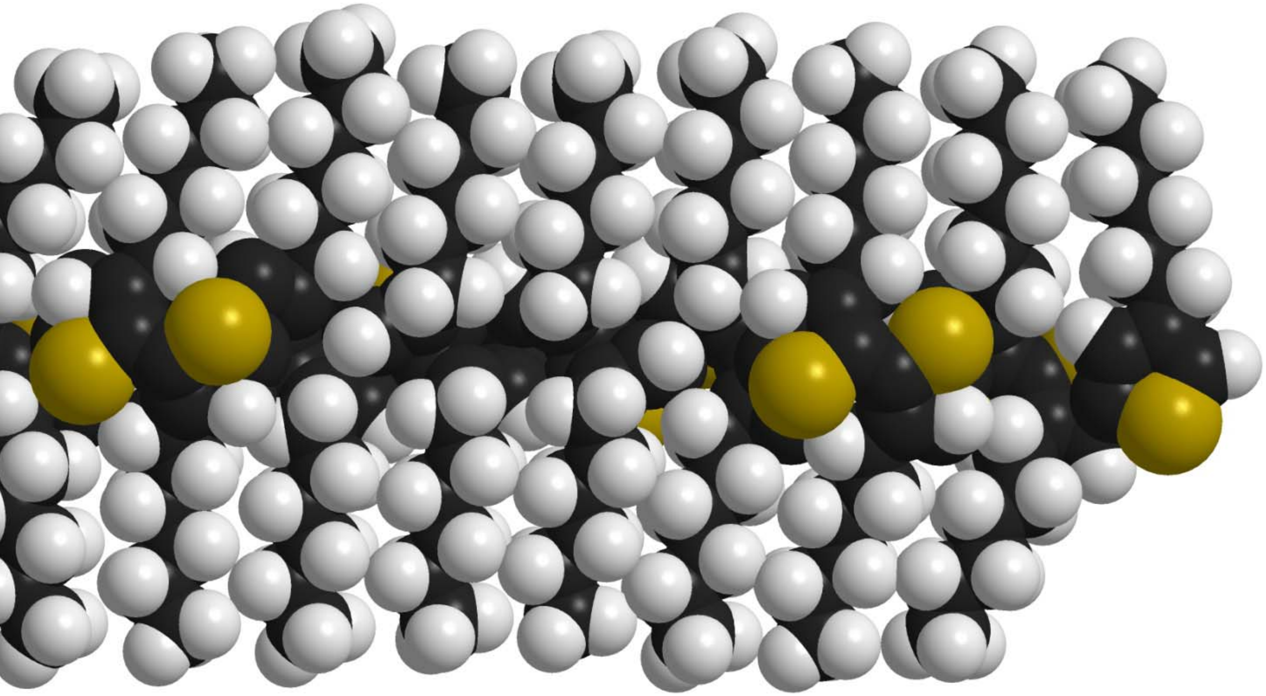
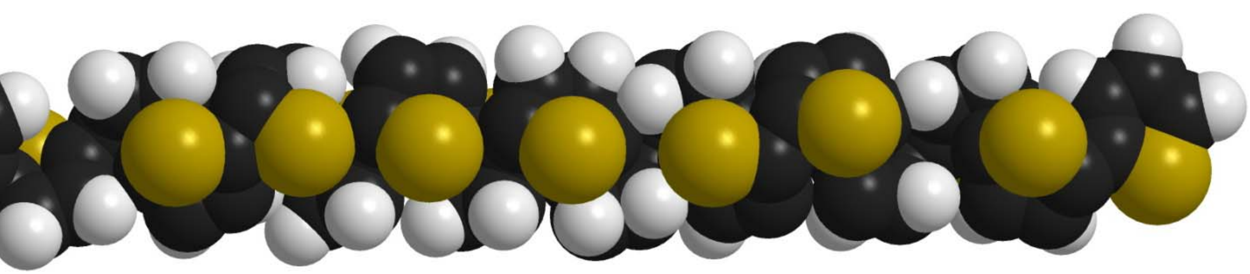
Outlook *Beyond* — Solid-State Processing



P3HT ✓



PT ?