Introduction to Macromolecular Chemistry

aka polymer chemistry

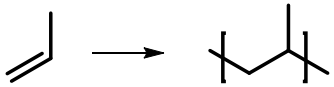
Mondays, 8.15-9.45 am, NC 02/99

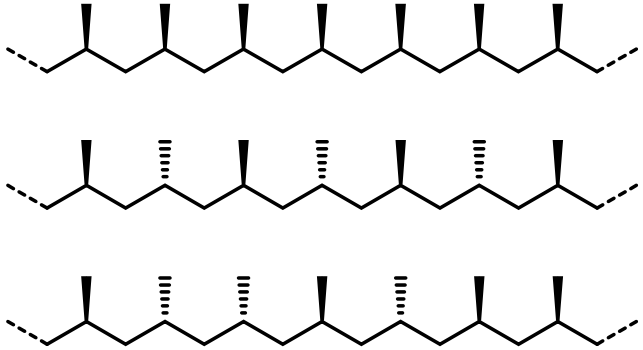
Dr. Christian Merten, Ruhr-Uni Bochum, 2019

Stereoisomerism

Similar to low-molecular weight molecules, polymers can feature stereoisomerism:

- Tacticity





Isotactic polypropylene (*it*-PP)
Highly crystalline (T_M ~ 160°C)

Syndiotactic polypropylene (*st*-PP)

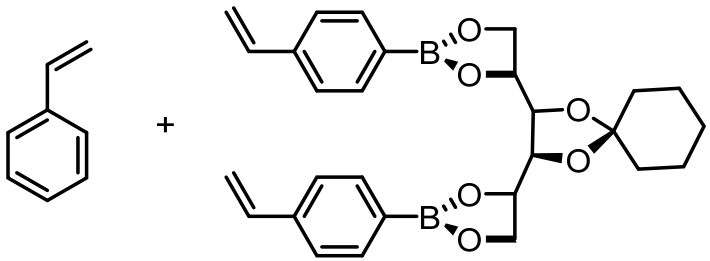
Atactic polypropylene (*at*-PP)
amorphous, sticky

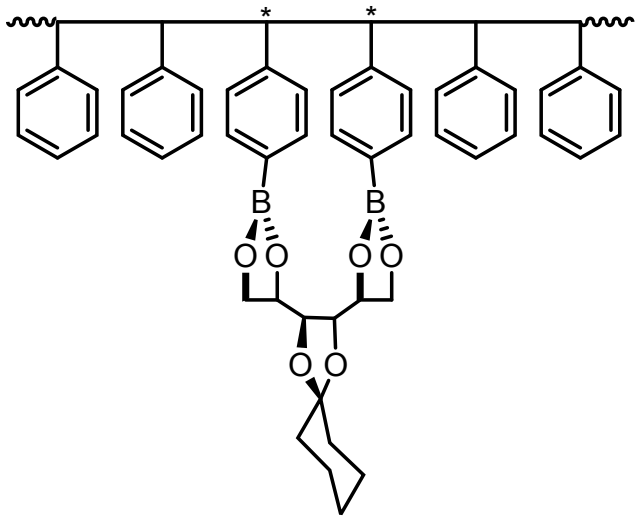
Note: Although high stereoregularity, no optical activity (mirror plane due to long chain length)!

Optically active polymers: Main chain stereochemistry

Wulff et al. *J. Am. Chem. Soc.* 1987, **109**, 7449-7457

Optically active PS from chiral precursor

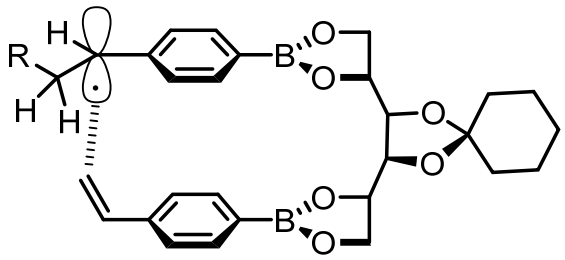


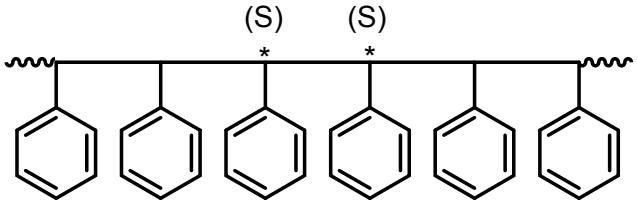


- Optical rotation of PS after removal of template:

  $[\alpha]^{30}_{365}$ of -0.5 to -3.5!

- Polymerization stereoregular: formation of (S,S)

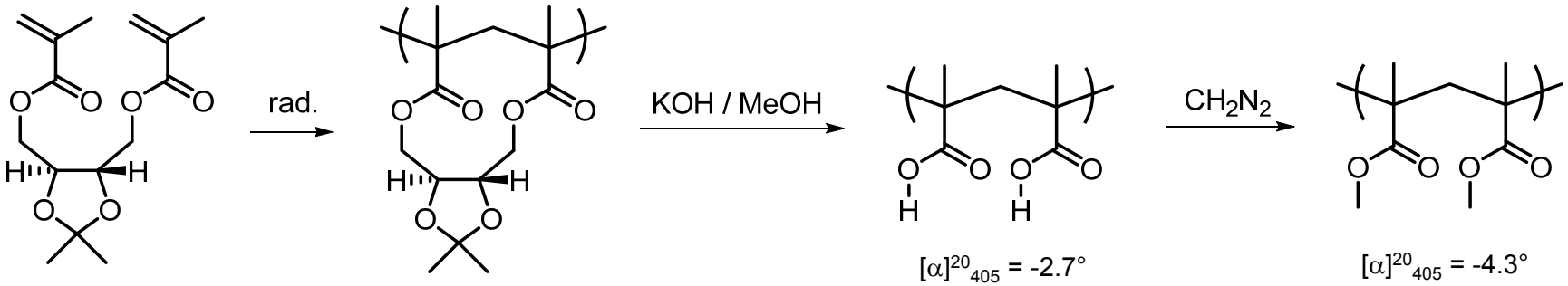




Optically active polymers: Main chain stereochemistry

Kakuchi et al., Macromolecules **25** (1992) 5545

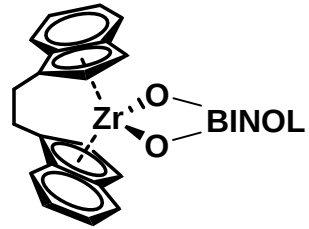
Template-assisted preparation of optically active poly(methyl methacrylate)



Optically active polymers: Main chain stereochemistry

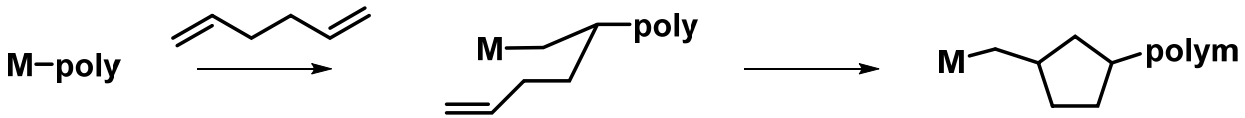
Coates and Waymouth, JACS 113 (1991) 6270-6271

Enantioselective cyclopolymerization of 1,5.hexadiene

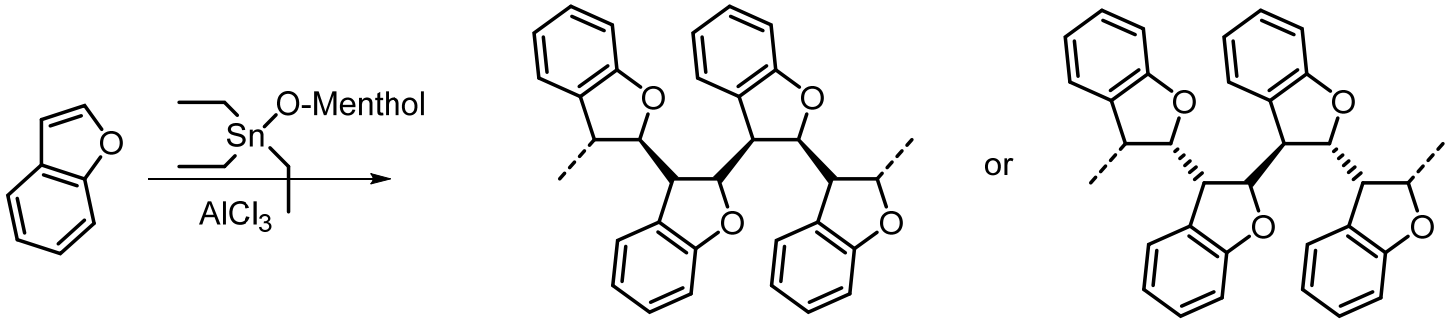


$[\alpha]_{28405}$ = - 49.3°

Mechanism:



Asymmetric Ziegler-Natta polymerization of benzofuran



Optically active polymers: polyolefins from Ziegler-Natta polymerization

Nakano and Okamoto, *Chem Rev.* **101** (2001) 4013-4038

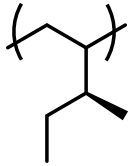


Table 1. Physical Properties of Poly[(*S*)-3-methyl-1-pentene] Fractions Having Different Steroregularities[n]

fraction	sample A,[l] catalyst Al(*i*-C_4H_9)$_3$/$TiCl_4$					sample B,[l] catalyst Al(*i*-C_4H_9)$_3$/$TiCl_3$				
	%	$[\eta]^{25}_D$[a,b] (deg)	$[\eta]$[b] (dL/g)	mp (°C)	$\Delta[\eta]_D$[a]/ΔT	%	$[\eta]^{25}_D$[c,h] (deg)	$[\eta]$[b] (dL/g)	mp (°C)	$\Delta[\eta]_D$[c]/ΔT
acetone-soluble	6.3	+29.4	d	nd	−0.08	2.4	+75.8	nd	nd	nd
acetone-insoluble, diethyl ether-soluble	2.6	+96.4	0.08	65−75[e]	−0.23	4.8	+127	0.13	93−96[f]	nd
diethyl ether-insoluble, benzene-soluble	0.9	+120	0.10	135−140[e]	−0.26	1.5	+146	0.13	187−193[f]	−0.31
isooctane-insoluble, benzene-soluble	0.4	+158	0.11	175−180[e]	−0.34	0.5	+157	nd	200−210[e]	−0.39
benzene-insoluble, decalin-soluble	2.0	+161[m]	0.50	228−232[e]	−0.36	1.7	+158[m]	0.60	200−210[e]	−0.40
residue	87.8	nd	nd	271−273[g]	nd	89.1	nd	nd	265−275[e]	nd

solubility ↑ … OR ↓ … OR

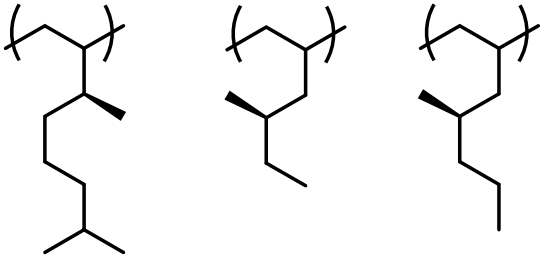
[a] In tetralin solution. [b] Determined in tetralin at 120 °C. [c] In toluene solution. [d] Molecular weight determined by cryoscopy in benzene 1200 ± 100. [e] Determined by a Kofler melting point apparatus. [f] Determined by the X-ray method. [g] Determined by the capillary method. [h] Referred to one monomeric unit. [l] Monomer optical purity 91%. [l] Monomer optical purity 89%. [m] ±10%. [n] Reprinted with permission from ref 44. Copyright 1963 Wiley-VCH.

- Due to lack of CD transitions, only OR available
- solubility ↓ … optical rotation ↑ … due to increased *it*-content
- T ↑ … OR ↓ … due to increased thermal disorder of helix chain

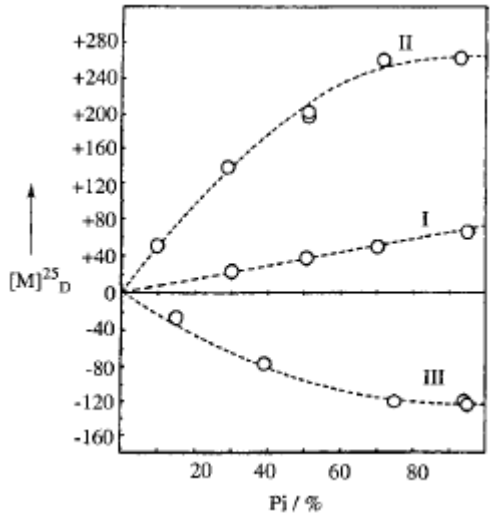
- Evidence for helix formation:

  optical purity of monomer ↑ …

  OR ↑ … non-linearly!

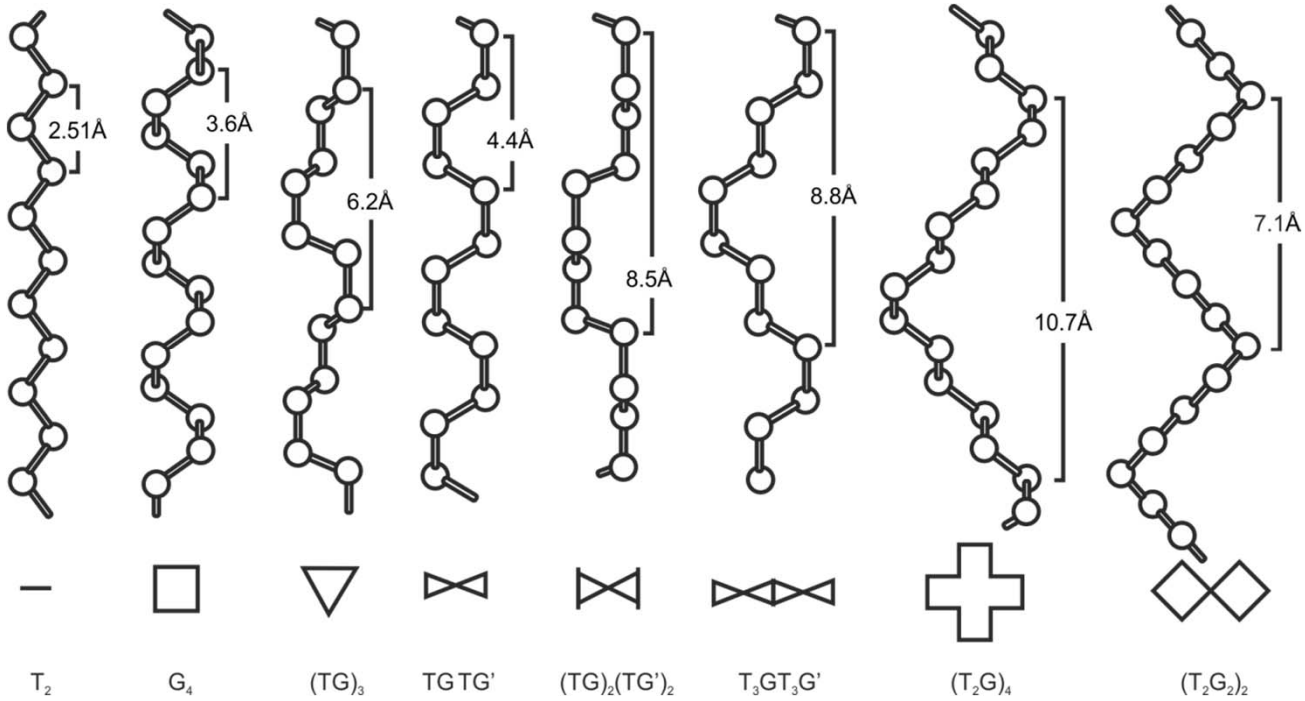


(III) (II) (I)



Helical polymer structures

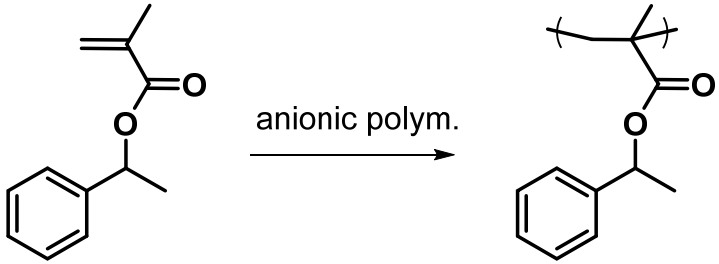
Takamoto, Structure of Crystalline Polymers, Wiley, 1979

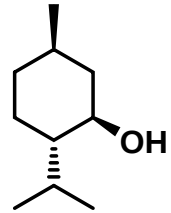


Optically active polymer: Helix-sense selective polymerizations

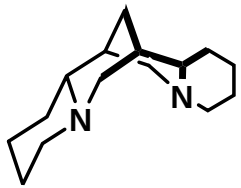
Okamoto et al., *JACS.* **101** (1979) 4763-4765

Methacrylates (Okamoto et al.)





(-)-menthol



(-)-sparteine

Table I
Polymerization with Et_2Mg–Chiral Alcohol Systems in Toluene at −78 °C

Chiral alcohol (R*OH)	Time, h	Yield, %	η_{sp}/C, dL/g	$[\alpha]^{20}_D$ (O.P.)[a] of polymer	Tacticity, % I	H	S
(1*S*:2*R*)-(−)-*cis*-Myrtanol	2.5	19	0.36	−2.7 (2)	7	29	64
(1*S*:2*R*)-(−)-Borneol	2.5	11	0.20	−0.9 (1)			
(1*R*:3*R*:4*S*)-(−)-Menthol	2.5	34	0.26	−1.2 (1)	3	28	69
(*S*)-(−)-2-Methylbutanol	3.0	6		~0			
(+)-1-*p*-Menthen-9-ol	4.0	5		~0			
(−)-Quinine	48	11	0.38	+14.9 (12)	23	26	51
(+)-Cinchonine	144	18	0.64	−21.3 (17)	34	32	34
(−)-Cinchonidine	22	46	1.08	+1.2 (1)	7	19	74
(−)-*cis*-Myrtanol–(−)-sparteine[b]	96	20		−42.9 (34)	39	29	32
(−)-Sparteine							

[a] Optical purity (%). [b] [Myrtanol]/[sparteine] = 1/1.2.

Table II
Polymerization with Chiral Catalyst Systems in Toluene at −78 °C

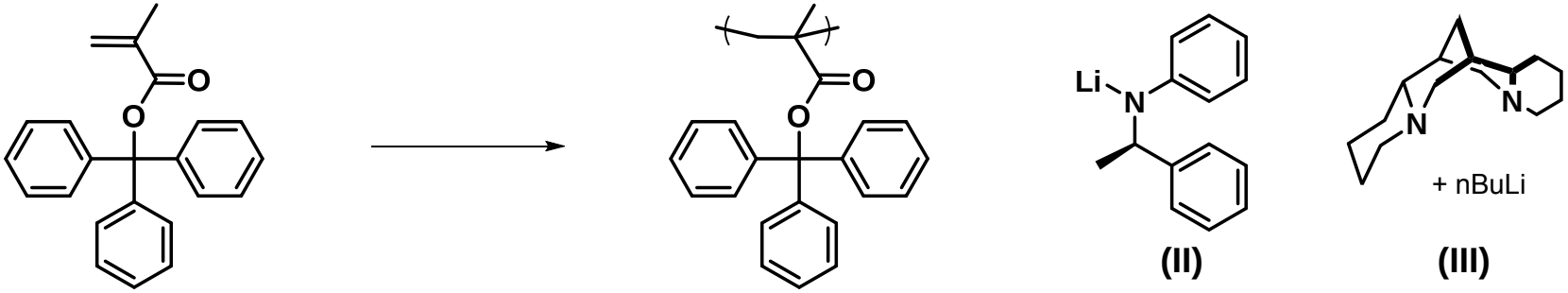
Catalyst	Time, h	Yield, %	$[\alpha]^{20}_D$ (O.P.)[a] of polymer	Tacticity, % I	H	S
MentMgCl	7	22	−4.8 (4)[b]	21	30	49
MentMgCl–strychinine(1/1.2)	24	~0				
MentMgCl–(−)-nicotine(1/1.2)	24	51	−2.4 (2)	9	37	54
MentMgCl–(−)-sparteine(1/1.5)	24	16	−108.1 (87)	89	6	5
Et_2Mg–(−)-sparteine(1/1.2)	96	~0				
n-BuLi–(−)-sparteine(1/1.2)	0.2	95	~0	8	33	59

[a] Optical purity (%). [b] $[\alpha]^{20}_{427}$ −9.7°.

Optically active polymer: Helix-sense selective polymerizations

Okamoto et al., *JACS.* **101** (1979) 4763-4765

Methacrylates (Okamoto et al.)



- High isotacticity when polymerized with nBuLi
- What happens when using a chiral initiator?

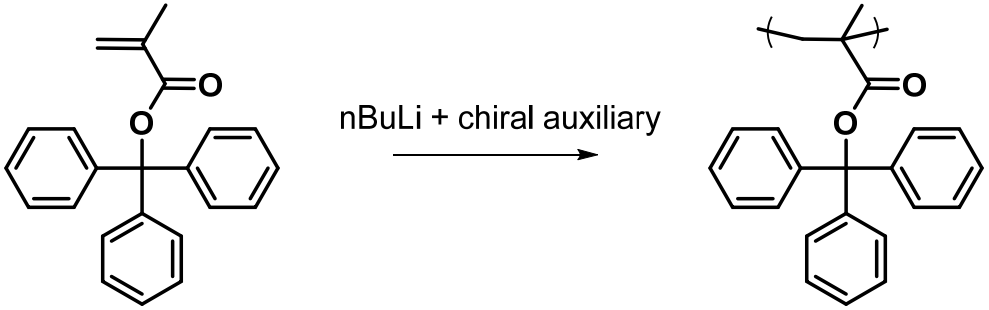
Table I. Polymerization of TrMA by II and III in Toluene[a]

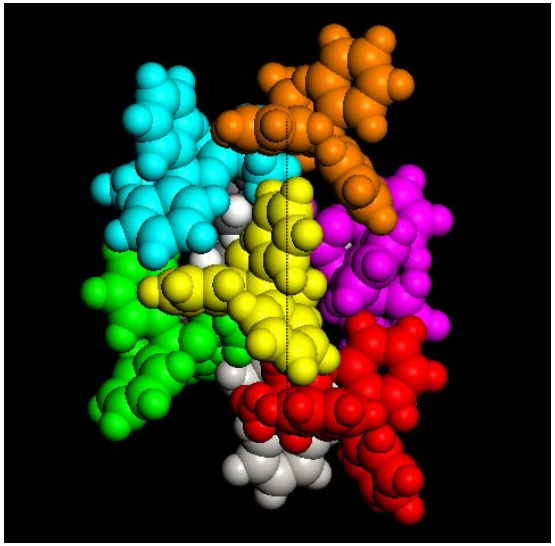
run	initiator	solvent	temp, °C	time, h	yield, %	THF-soluble polymer: yield, %	THF-soluble polymer: $\overline{DP}$[b]	THF-soluble polymer: $[\alpha]^{20}_D$, deg in THF	THF-soluble polymer: $[\alpha]^{20}_D$, deg in toluene	THF-insoluble polymer, yield, %
1	II	toluene	−78	2.9	73	72	62	−70	−85	1
2	II	THF	−78	2.3	93	93	21	−82	−104	0
3	III	toluene	−40	2.0	100	100	42	+262	+363	0
4	III	toluene	−62	0.7	66	61		+278	+380	5
5	III	toluene	−62	2.4	100	49		+334	c	51
6	III	toluene	−78	1.0	25	25	35	+137	+193	0
7	III	toluene	−78	2.0	41	41	48	+190	+258	0
8	III	toluene	−78	3.5	55	54	58	+254	c	1
9	III	toluene	−78	5.2	90	18	43	+245	c	72[d]
10	III	THF	−78	2.4	100	100	21	+7	+10	0

[a] Monomer/solvent, 1/20 (g/mL); [catalyst]/[monomer], 1/20 (mol/mol). [b] Degree of polymerization which was estimated from gel permeation chromatogram of the PMMA derived from poly(TrMA).[16] [c] A part of the polymer was insoluble in toluene. [d] The $\overline{DP}$ estimated by GPC was 74.

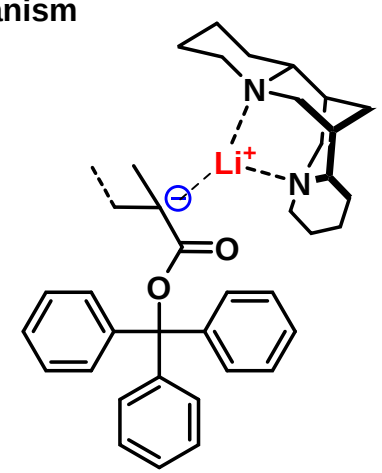
Optically active polymer: Helix-sense selective polymerizations

Methacrylates (Okamoto et al.)

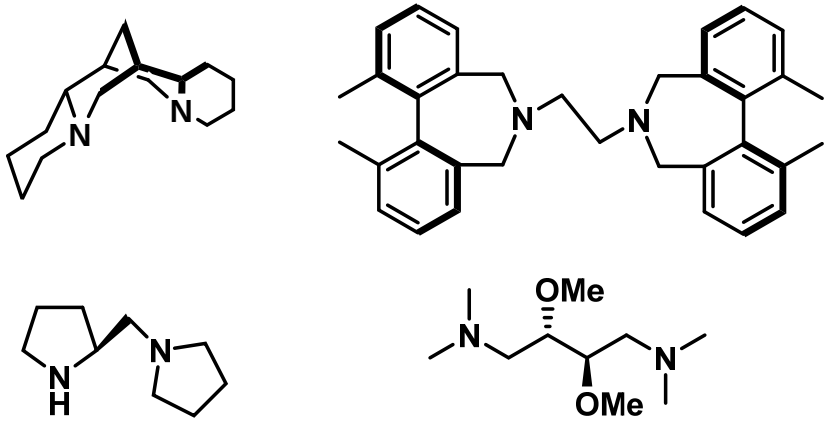




Mechanism



Common auxiliaries

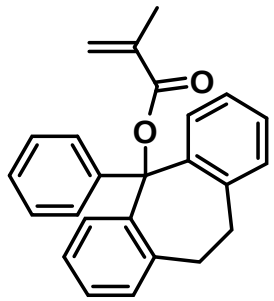


Optically active polymer: Helix-sense selective polymerizations

Nakano and Okamoto, *Chem Rev.* **101** (2001) 4013-4038

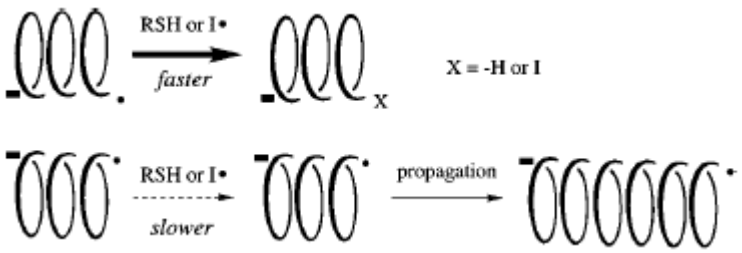
Methacrylates (Okamoto et al.)

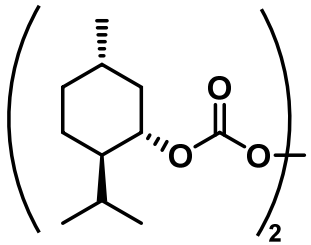
- Radical polymerization generally works, but does not necessarily give high isotacticity
- PDBSMA was found to give nearly completely it-polymer



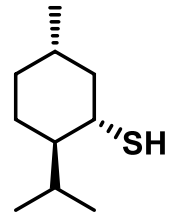
PDBSMA

- Polymerization with chiral initiators / chain transfer agents / solvents induces optical activity even through radical polymerizations!





(-)-DMP



(+)-NMT

Table 4. Radical Polymerization of PDBSMA[a]

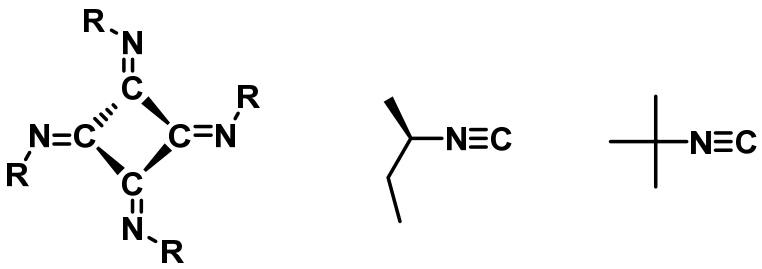
initiator	chain-transfer agent or solvent	$[M]_o$ (M)	$[I]_o$ (M)	yield[c] (%)	THF-soluble part[b] yield (%)	THF-soluble part[b] $[\alpha]_{365}$[d] (deg)	THF-soluble part[b] DP
(−)-DMP	none	0.16	0.16	75	3	+40	44
(*i*-PrOCOO)$_2$	(+)-NMT (0.032 M)	0.16	0.003	71	5	−140	42
(*i*-PrOCOO)$_2$	(−)-menthol (4.6 M)/toluene	0.05	0.0017	45	1	+180	50

[a] Data cited from ref 72. Polymerization in toluene at 40 or 50 °C. [b] Washed with a benzene/hexane (1/1) mixture. [c] Hexane-insoluble products. [d] In THF.

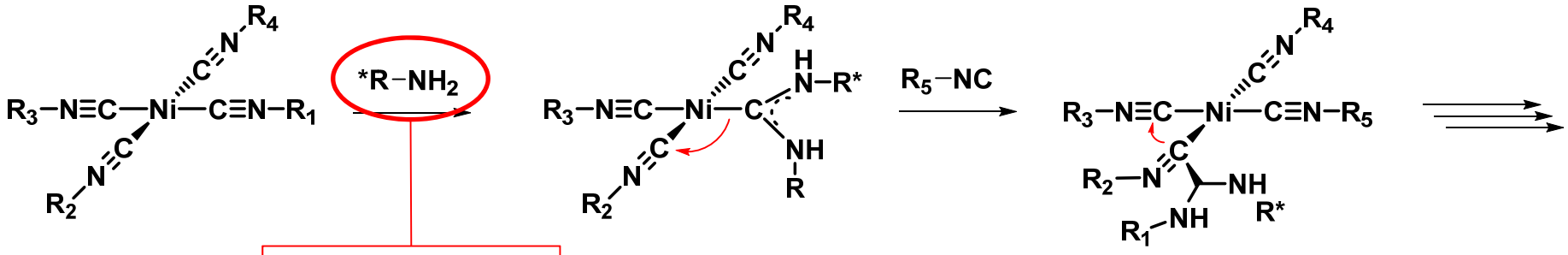
Optically active polymer: Helix-sense selective polymerizations

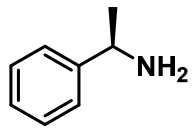
Isocyanides (Novak, Nolte et al.)

- Stiff 4/1 helix
- Polymerizable with Ni^{II}-salts (e.g. NiCN)
- First with only helical chiral backbone:
  Resolution of poly(tert-butyl isocyanide) on stationary phase of poly((S)-sec-butyl isocyanide)



Mechanism:





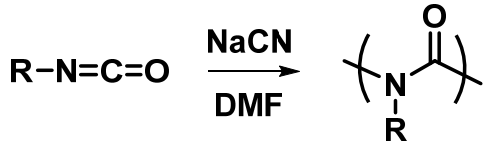
Chiral amines induce single-handed helix!

Optically active polymer: Helix-sense selective polymerizations

Okamoto and Nakano, *Chem Rev.* **94** (1994) 349-372

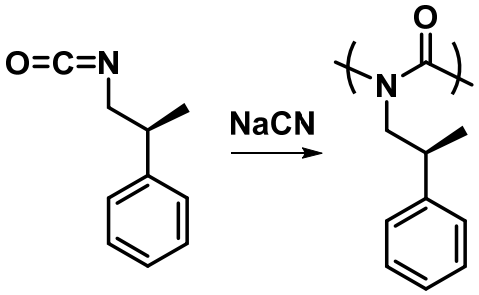
Isocyantes (Shashua, Chen, Green, …)

- Isocyanates are polymerizable with NaCN
- Helical rigid conformation of backbone (8/3 helix)

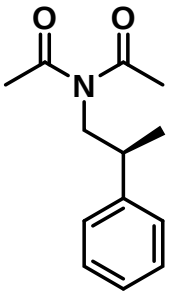


- Optically active poly(isocyanates) are obtainable with chiral side groups

$[\alpha]_D^{25} = +35°$

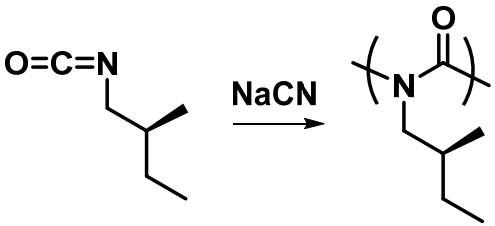


$[\alpha]_D^{25} = -469°$

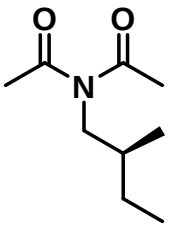


$[\alpha]_D^{25} = +114°$

$[\alpha]_D^{25} = +3°$



$[\alpha]_D^{25} = 160°$



$[\alpha]_D^{25} = -6°$

Optically active polymer: Helix-sense selective polymerizations

Okamoto and Nakano, *Chem Rev.* **94** (1994) 349-372
Green et al., *JACS* **110** (1988) 4063-4065
Green et al., *Chirality* **3** (1991) 285-291

Isocyantes (Shashua, Chen, Green, …)

- CD of deuterated poly(isocyanate) similar to that of polymer with sterically more demanding stereocenter ➢➢ excess of single-handed helix

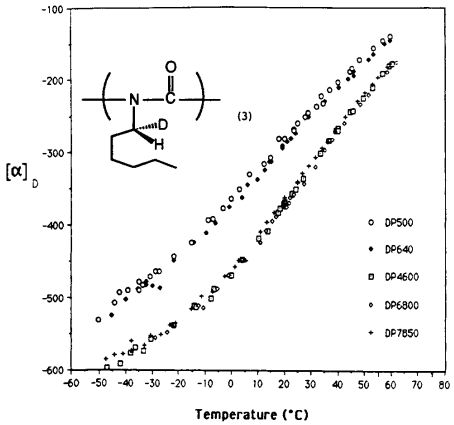


Fig. 1. Optical rotation as a function of degree of polymerization (*DP*) for poly((R)-1-deuterio-1-hexyl isocyanate) (*3*).

- Temperature-dependence lead to model of polymer having both right- and left-handed helices with helix-reversal point

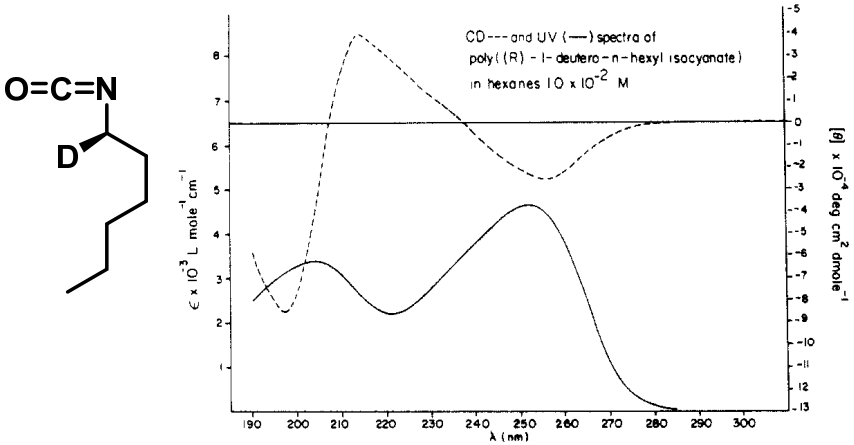


Figure 1.

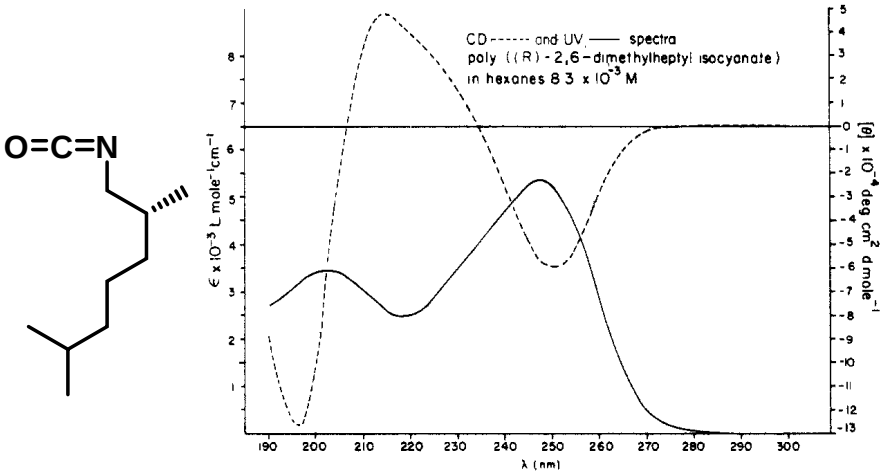


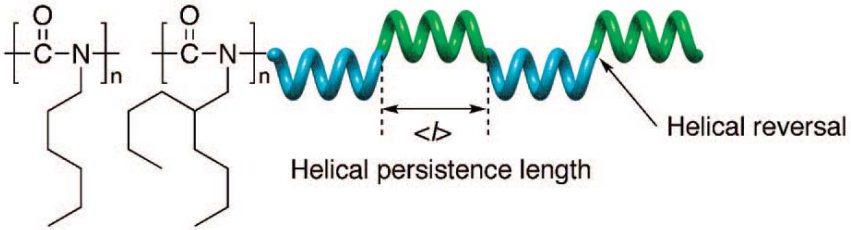
Figure 2.

Optically active polymer: Helix-sense selective polymerizations

Yashima et al., *Acc Chem Res.* **41** (2008) 1166-1180
Maeda, K.; Okamoto, Y. *Polym. J.* **1998**, *30*, 100.

Isocyantes (Shashua, Chen, Green, …)

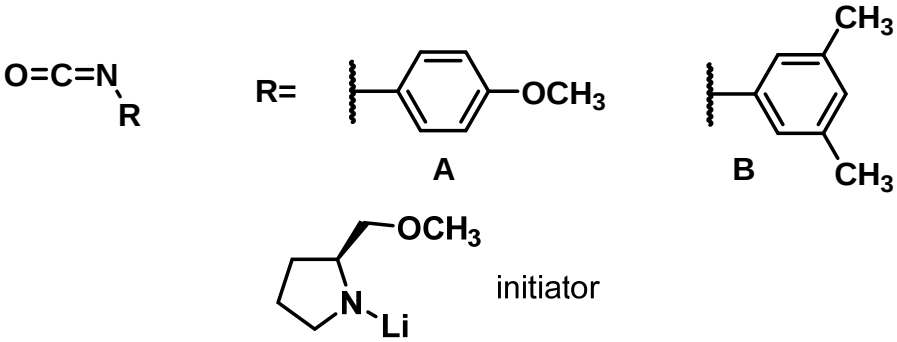
- Helix-reversal point: Dynamic helical structure

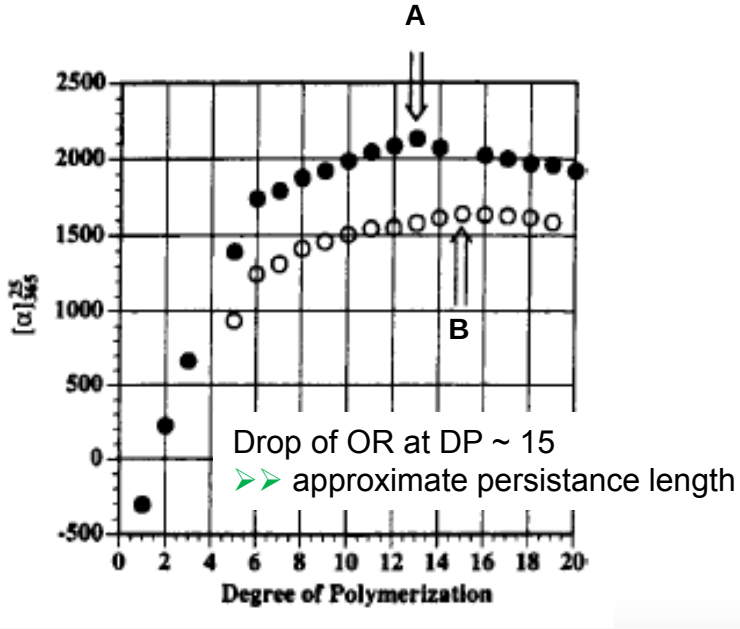


- Further experimental proof:

  Polymerization of achiral monomers with chiral initiator

  ➢➢ chiral information localized on chain end

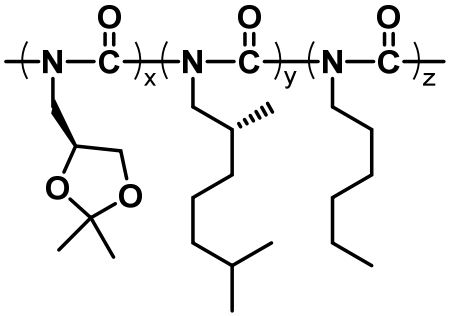




Optically active polymer: Helix-sense selective polymerizations

Green and Reidy, *JACS* **111** (1989) 6452-6454
Yashima et al., *Acc Chem Res.* **41** (2008) 1166-1180

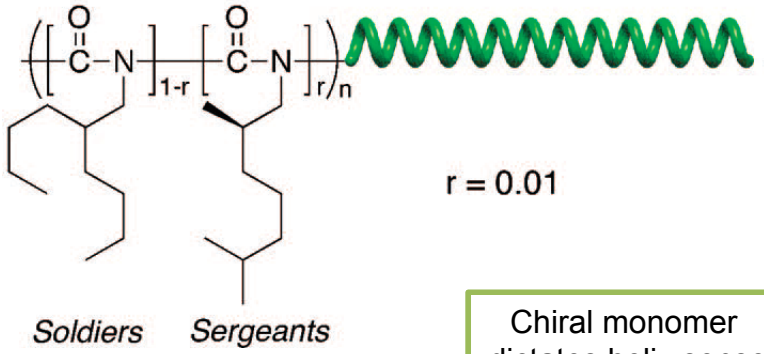
The sergeants-and-soldiers experiment



	x	y	z	−20 °C	+20 °C	Mv[c]
A[d]		100		−514	−500	490 000
B[d]	100			−336	−310	640 000
C		37.3	62.7	−549	−519	630 000
D		15.0	85.0	−532	−480	660 000
E		4.0	96.0	−436	−308	400 000
F	1.0		99.0	−251	−138	670 000
G		1.0	99.0	−165	−75	690 000
H		0.5	99.5	−140	−66	1 100 000
I	0.12		99.88	−64	−26	1 300 000
J			100.0	0.0	0.0	

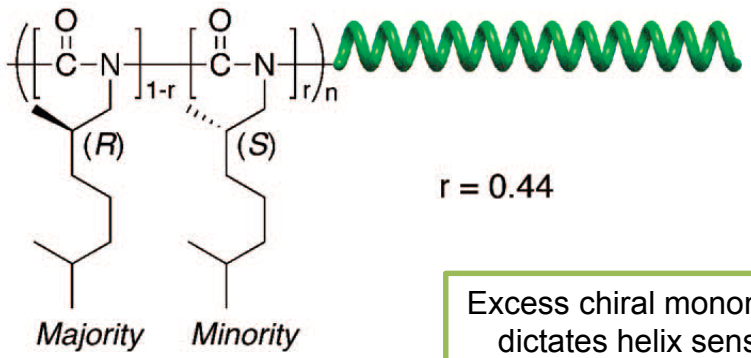
[a] Measured at the sodium -D line in $CHCl_3$ (c = 0.5 mg/mL). [b] x = mole percent of (S)-(−)-2,2-dimethyl-1,3-dioxolane-4-methylene isocyanate (monomer (1)); y = mole percent of 2,6-dimethylheptyl isocyanate (monomer (2)); z = mole percent of n-hexyl isocyanate. [c] Viscosity average molecular weights. See Berger and Tidswell in ref 4. [d] For the characteristics of the optically active homopolymers A and B see ref 13 and 14, respectively.

Sergeants and Soldiers effect



Chiral monomer dictates helix sense

Majority rule



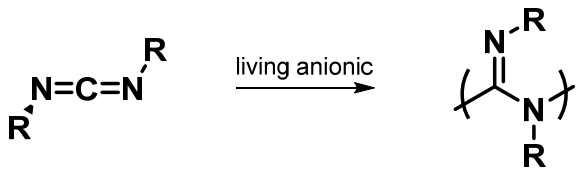
Excess chiral monomer dictates helix sense

Optically active polymer: Helix-sense selective polymerizations

Kennemur and Novak, *Polymer* **52** (2011) 1693-1710

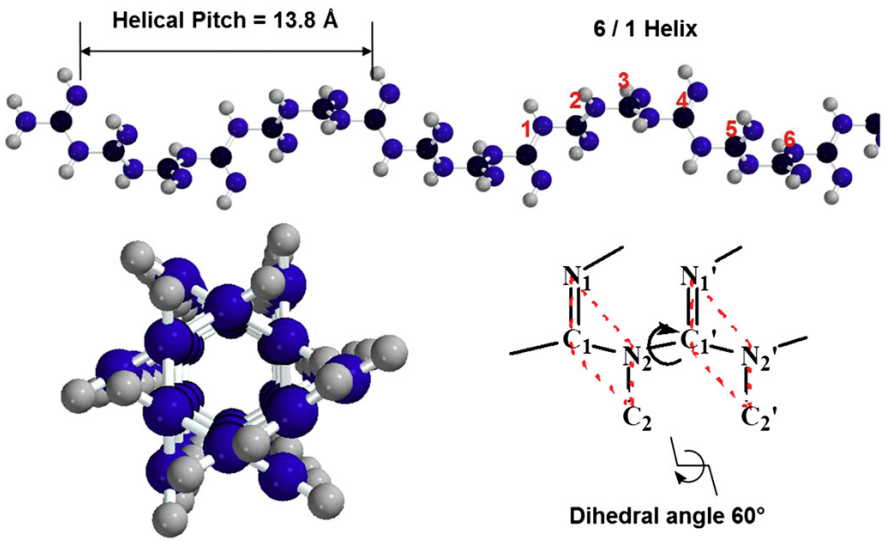
Carbodiimides (Goodwin, Novak)

- Polycarbodiimide: Hybrid between dynamic poly(NCO) and static poly(NC)



- Structure of dimethyl polycarbodiimide ($R=CH_3$):

  6/1 helix

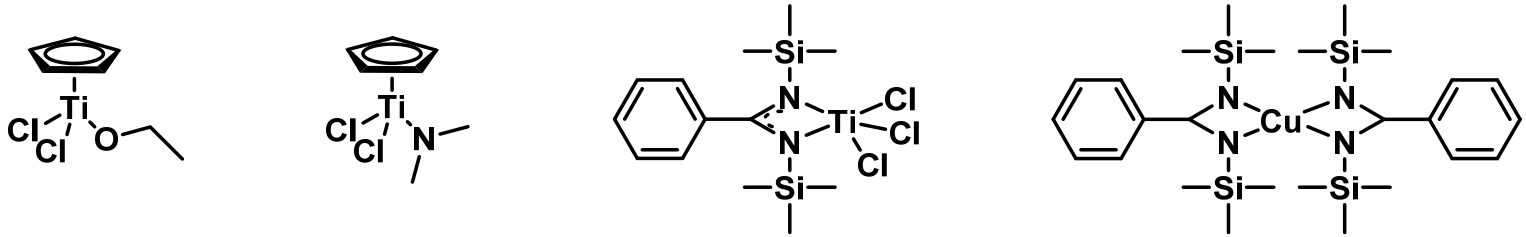


Optically active polymer: Helix-sense selective polymerizations

Kennemur and Novak, *Polymer* **52** (2011) 1693-1710

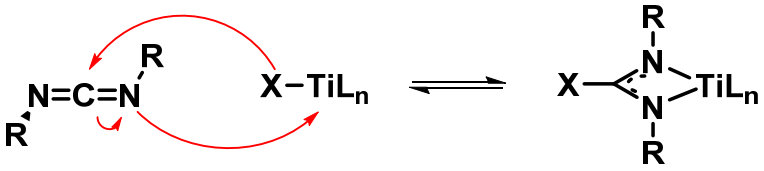
Carbodiimides (Goodwin, Novak)

- Catalyst/Initiators: Ti-/Cu-catalysts



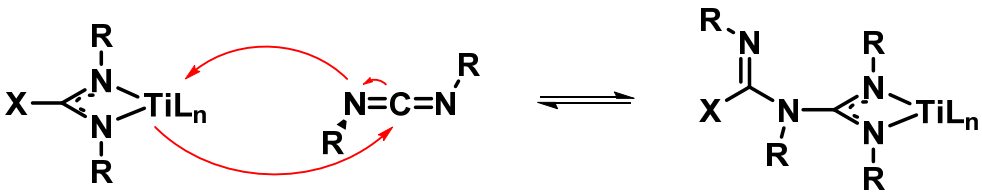
- Mechanism

Initiation:



X = -NMe$_2$, -OR, -R

Propagation:

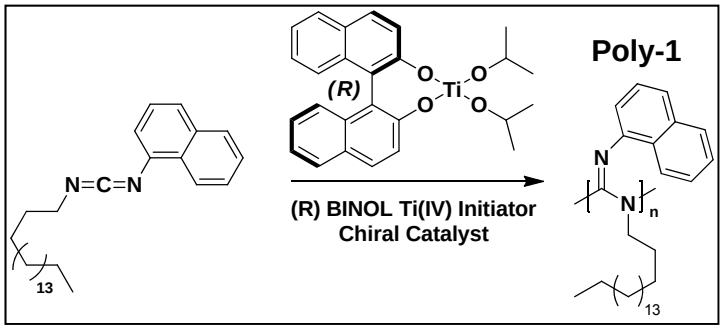


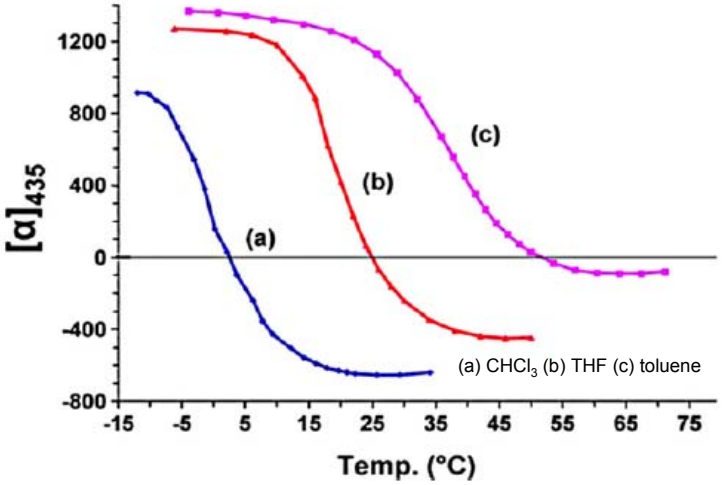
Optically active polymer: Helix-sense selective polymerizations

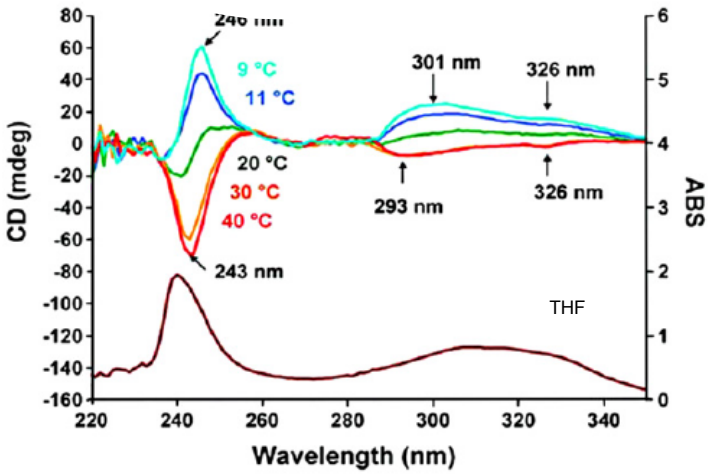
Kennemur and Novak, *Polymer* **52** (2011) 1693-1710

Carbodiimides (Goodwin, Novak)

- Solvent- and temperature dependent chiroptical switching

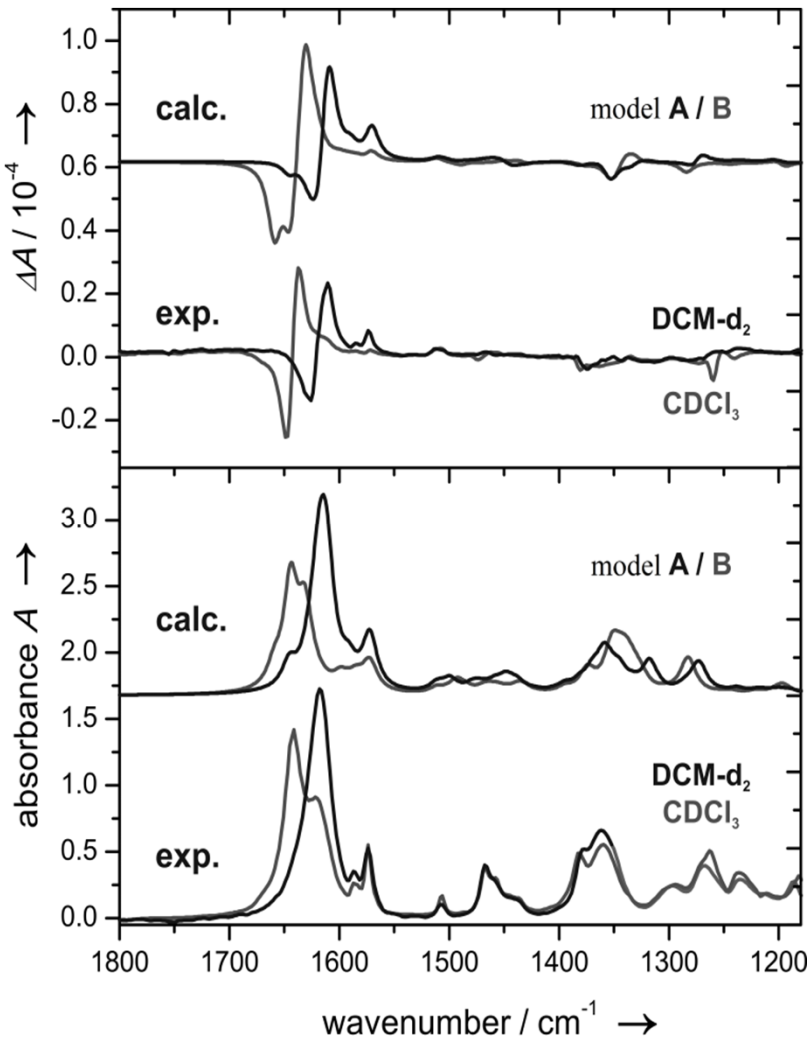


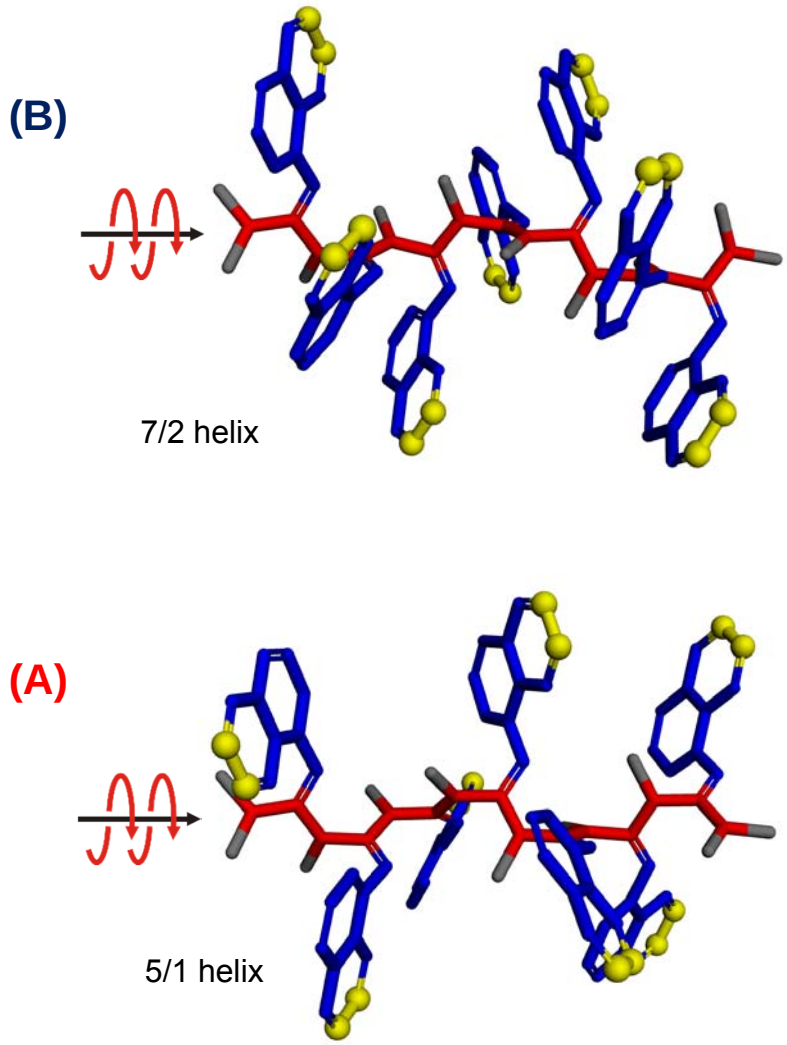




Optically active polymer: Helix-sense selective polymerizations

Reuther, Novak, *JACS 135* (2013) 19292−19303
Merten, Reuther, de Sousa, Novak, *Phys Chem Chem Phys*, **16** (2014) 11456-11460

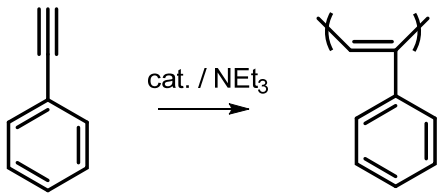


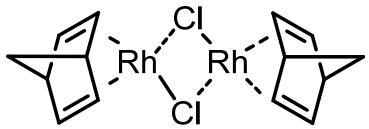


Optically active polymer: Helix-sense selective polymerizations

Phenylacetylenes (Yashima)

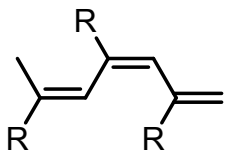
- Polymerization with Rh-catalysts



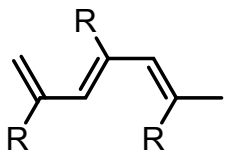


Catalyst for cis-transoidal backbone

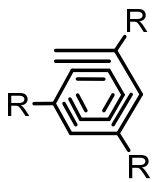
- Several main chain conformations possible (determined by catalyst)



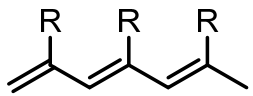
cis-transoidal



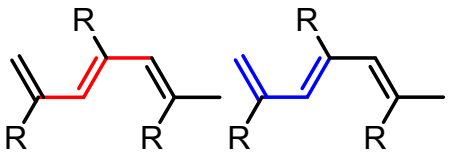
trans-cisoidal



cis-cisoidal



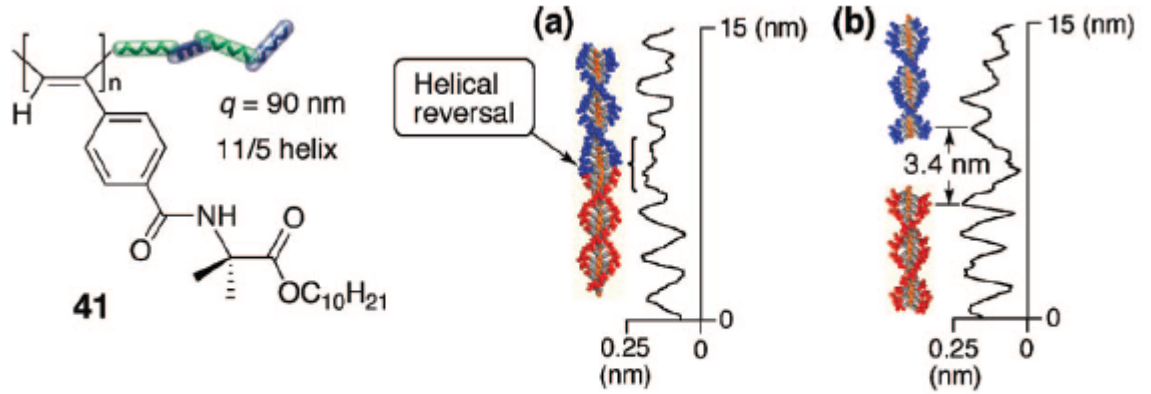
trans-transoidal

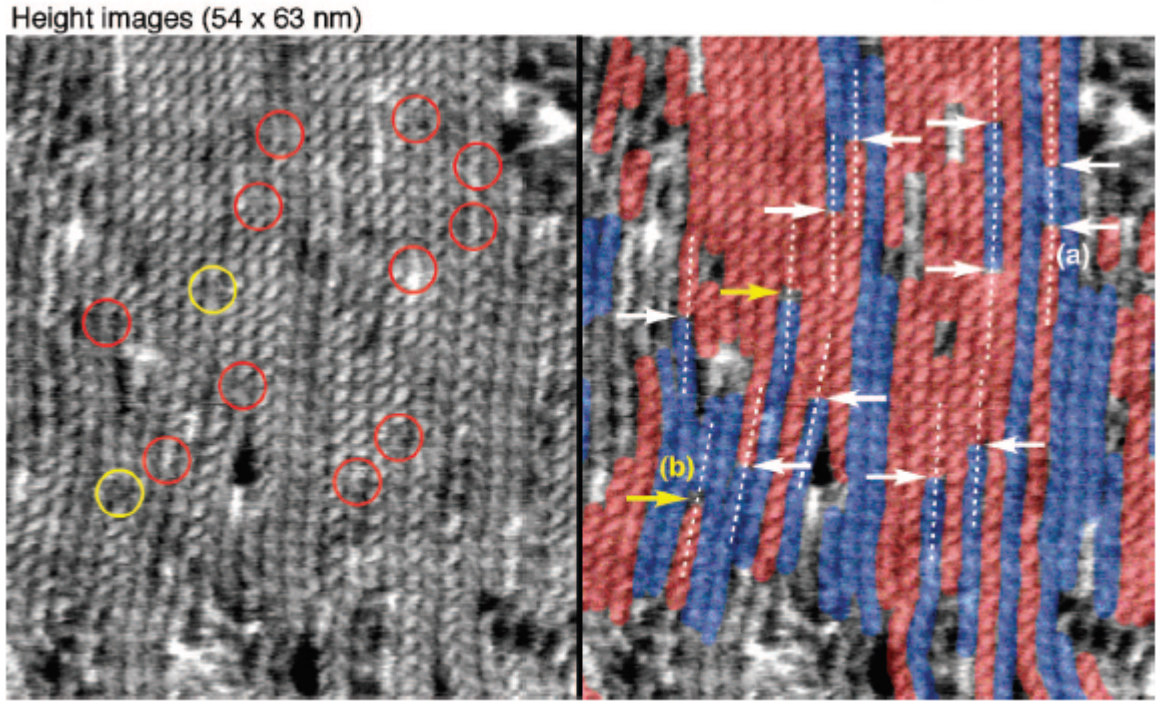


Optically active polymer: Helix-sense selective polymerizations

Yashima and Maeda, *Macromolecules* **41** (2008) 3

Phenylacetylenes (Yashima)



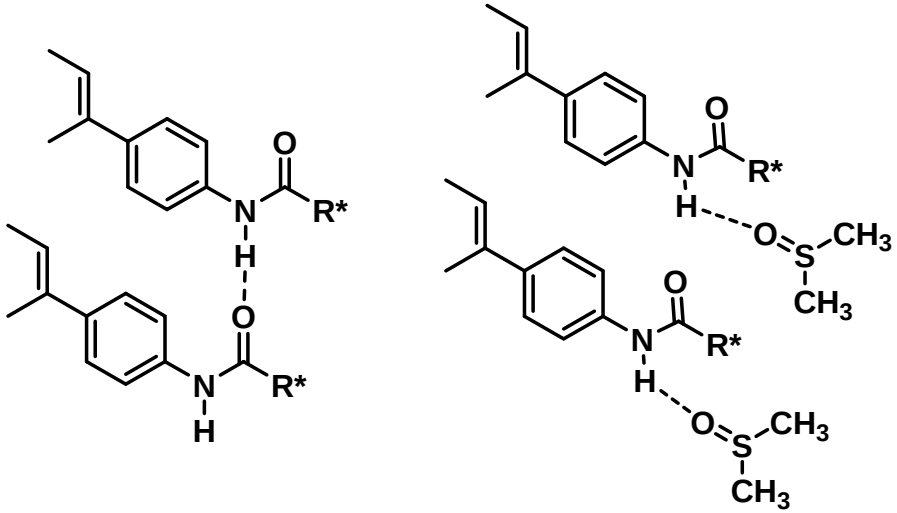


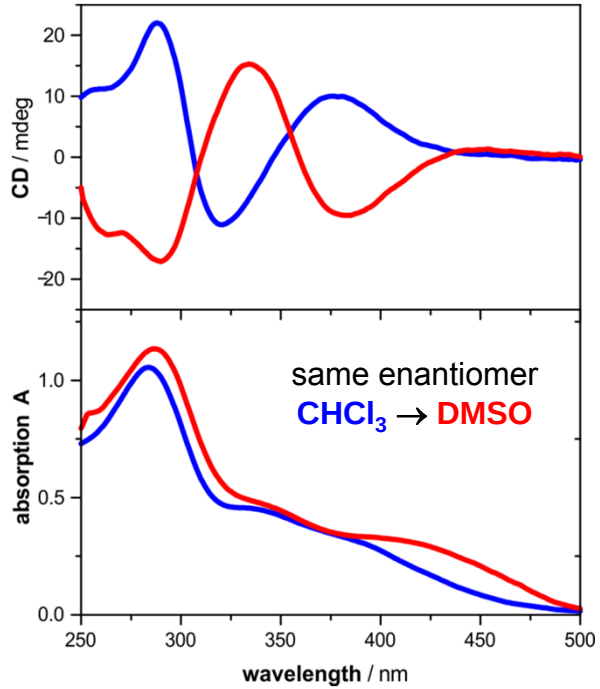
- Dynamic helical structure, both left- and right handed can easily interconvert in solution
- AFM shows presence of both helix senses in the same polymer
- Can be shown by MD as well

Optically active polymer: Helix-sense selective polymerizations

Phenylacetylenes (Yashima)

- Helix-inversion can be triggered by solvent!





Optically active polymer: Helix-sense selective polymerizations

Yashima and Maeda, *Macromolecules* **41** (2008) 3

Phenylacetylenes (Yashima)

- Induction of preferential helical screw sense into achiral polymer via interaction with small chiral molecule