Literature Report IV

Fast Living Polymerization and Helix-Sense-Selective Polymerization

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Checker: Zhou-Hao Zhu
Date: 2020-1-13

Wu, Z.-Q. *et al. J. Am. Chem. Soc.* **2018**, *140*, 17773.
Wu, Z.-Q. *et al. Macromolecules* **2019**, *52*, 7260.

Contents

CV of Prof. Zong-Quan Wu

Zong-Quan Wu

Background:

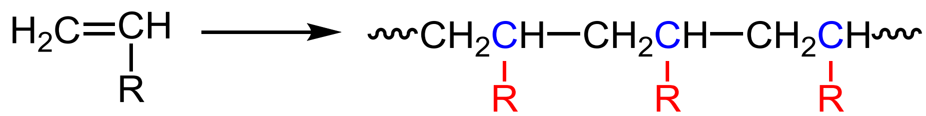
- ☐ **1997-2001** M.S., Anhui Normal University
- ☐ **2001-2006** Ph.D., Shanghai Institute of Organic Chemistry
- ☐ **2006-2008** Postdoc., Nagoya University
- ☐ **2010-2011** Postdoc., University of Texas at Austin
- ☐ **2011-now** Professor, Heifei University of Technology

Research Interests:

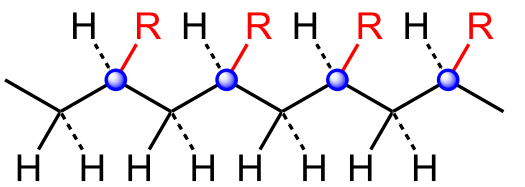
- ➢ Stereoregular polymerization
- ➢ Asymmetric polymerization

Introduction

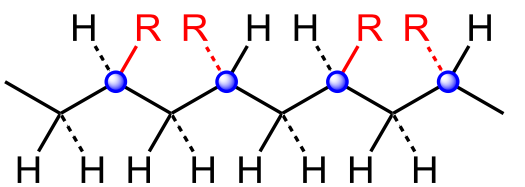
- **聚合物的立体异构现象**



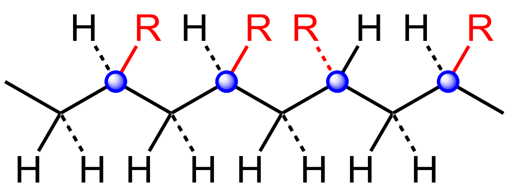
全同立构（等规）聚合物



间同立构（间规）聚合物



无规聚合物



Introduction

- 活性聚合

  不存在链转移和链终止的聚合。

- 活性聚合物

  活性聚合的增长链在单体全部耗尽后仍具有引发活性，因此将活性聚合的增长链称为活性聚合物。

Introduction

- 活性聚合特征

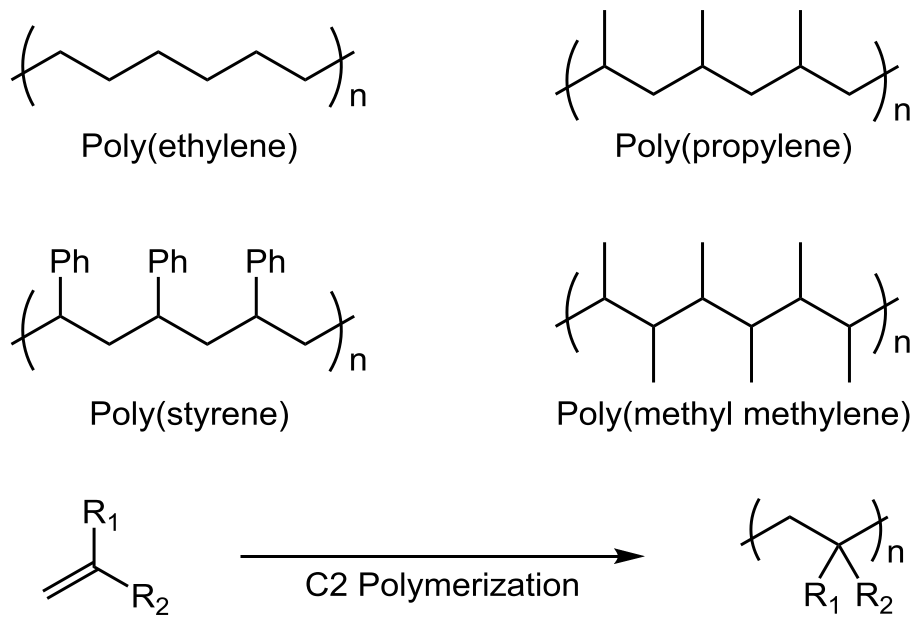
（1）聚合产物的数均分子量与单体转化率呈线性增长关系；

（2）当单体转化率达100%后，向聚合体系中加入新单体，聚合反应继续进行，数均分子量进一步增加，并仍与单体转化率成正比；

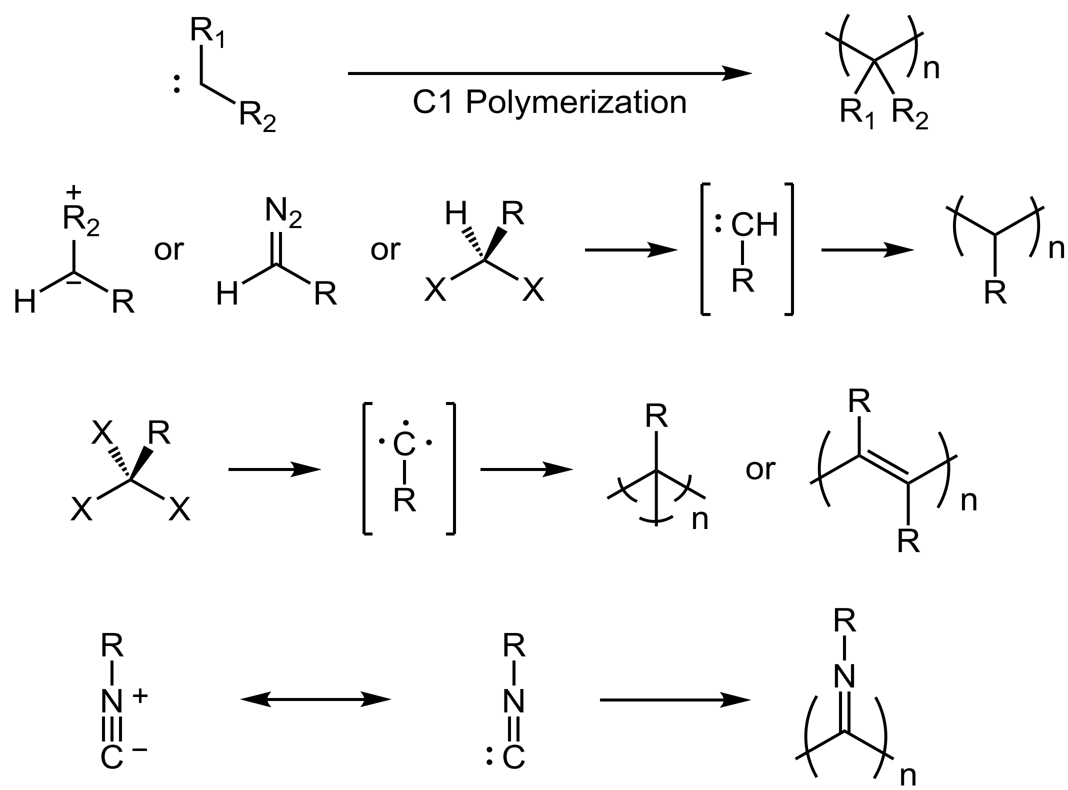
（3）聚合产物分子量具有单分散性，PDI接近1；

（4）聚合产物的实际分子量与理论分子量基本接近。聚合产物的理论分子量等于单体与催化剂的摩尔比乘以单体的相对分子量。

C2 Polymerization



C1 Polymerization



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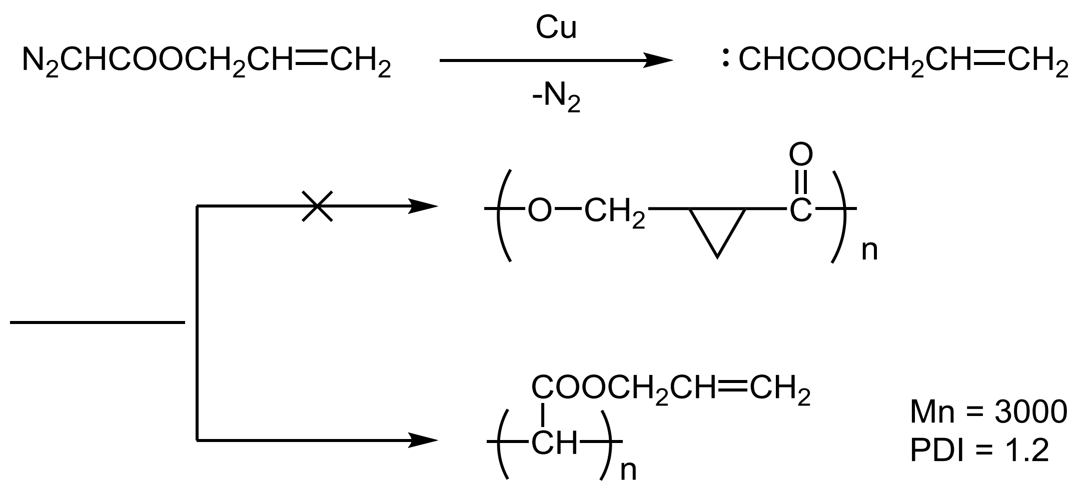
Introduction



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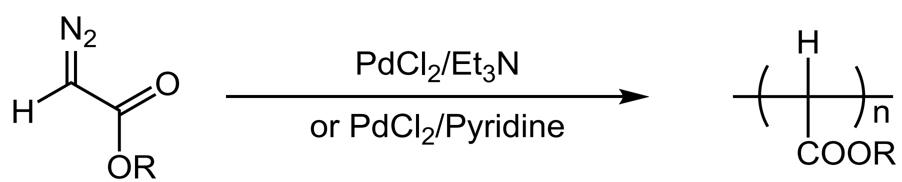

Inoue, K. *et al. Macromolecules* **2003**, *36*, 36.
Inoue, K. *et al. Macromolecules* **2005**, *38*, 2101.
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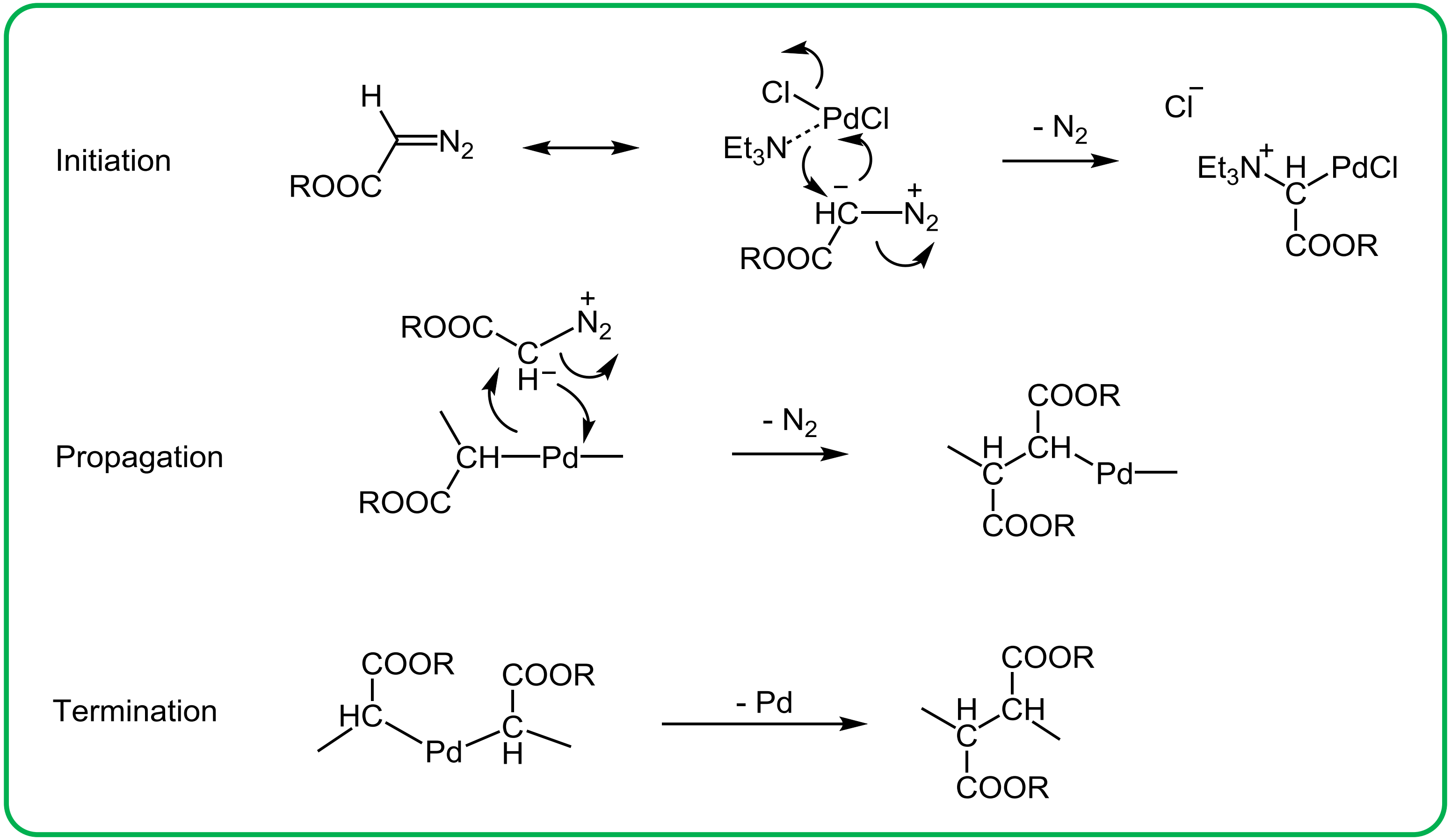
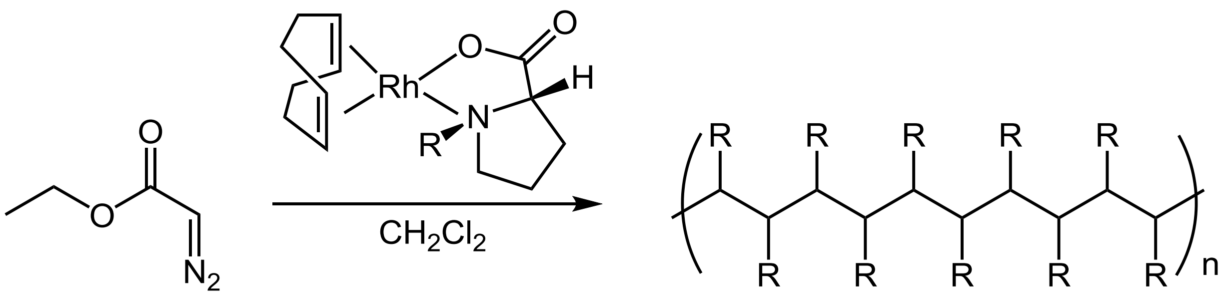
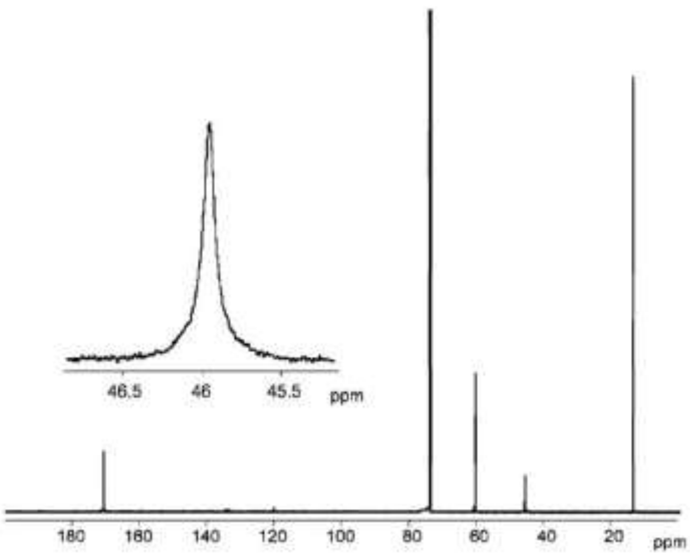
Introduction

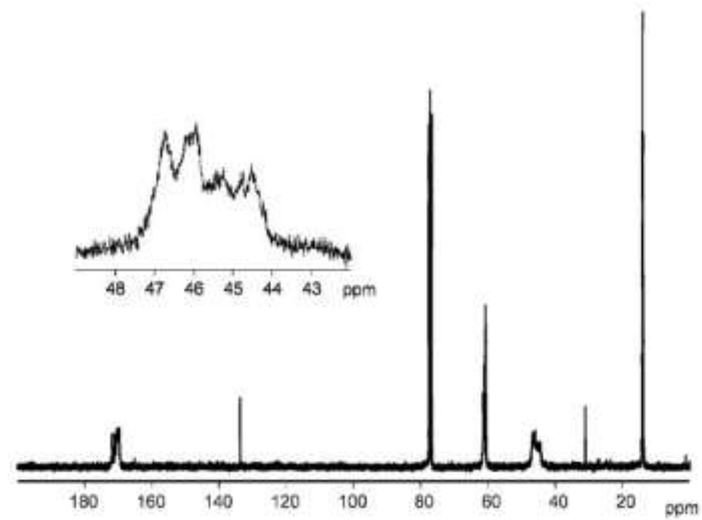


Stereoselective Polymerization



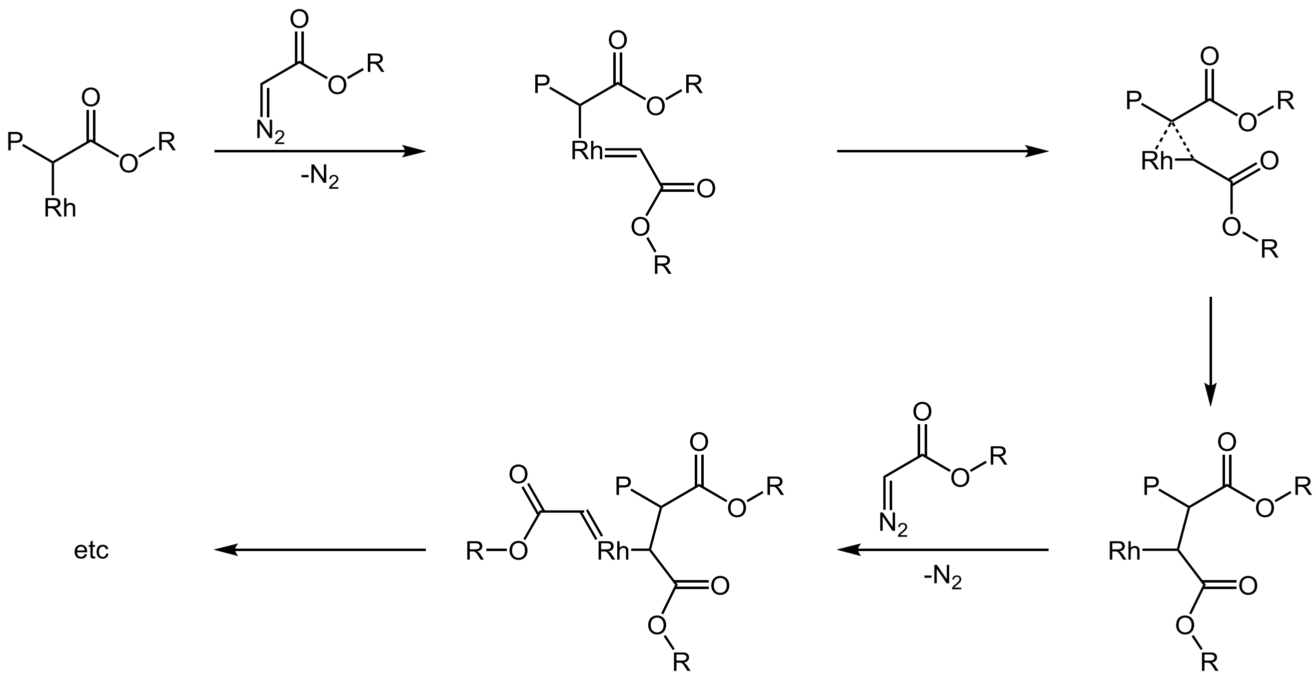
R = COOEt
Yield = 40%
Mn = 143000, PDI = 2.5

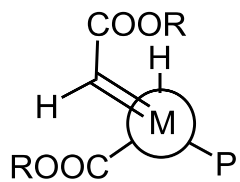




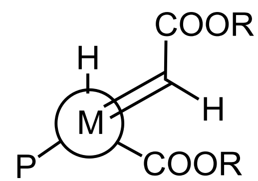
de Bruin, B. *et al*. *J. Am. Chem. Soc.* **2006**, *128*, 9746.
de Bruin, B. *et al*. *Angew. Chem. Int. Ed.* **2012**, *51*, 5157.

Stereoselective Polymerization





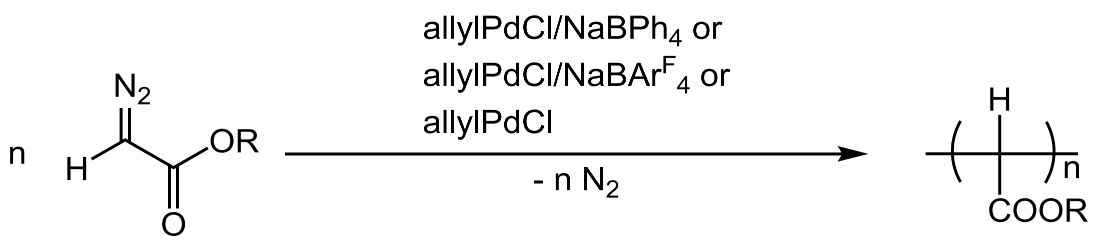
Re fece attack by chain carbon in *S* configuration



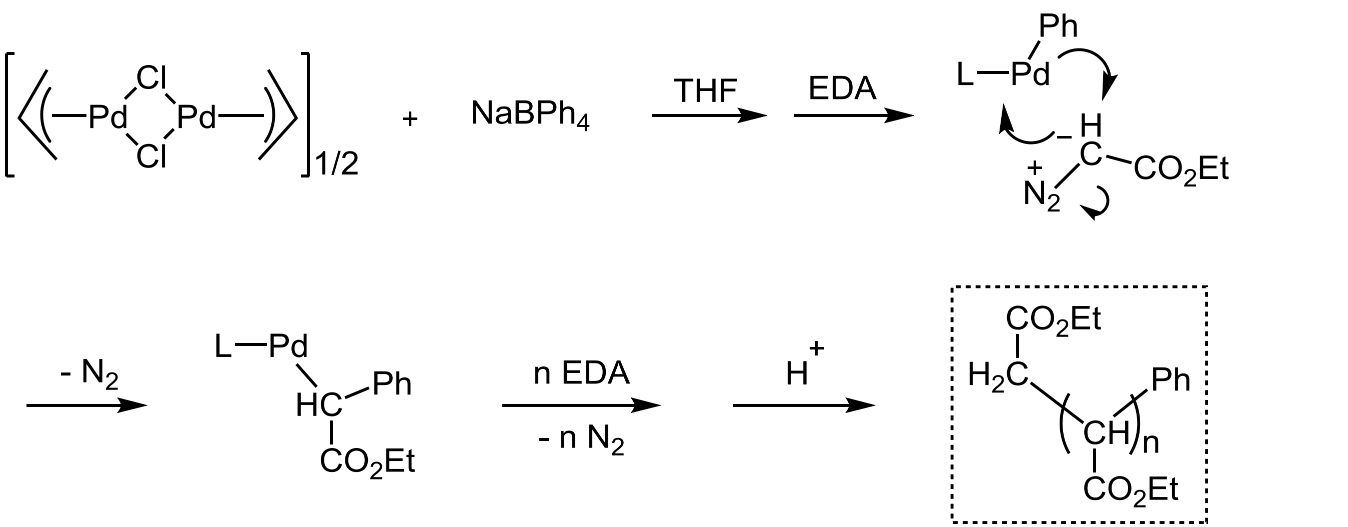
Si fece attack by chain carbon in *R* configuration

de Bruin, B. *et al*. *J. Am. Chem. Soc.* **2006**, *128*, 9746.

Introduction

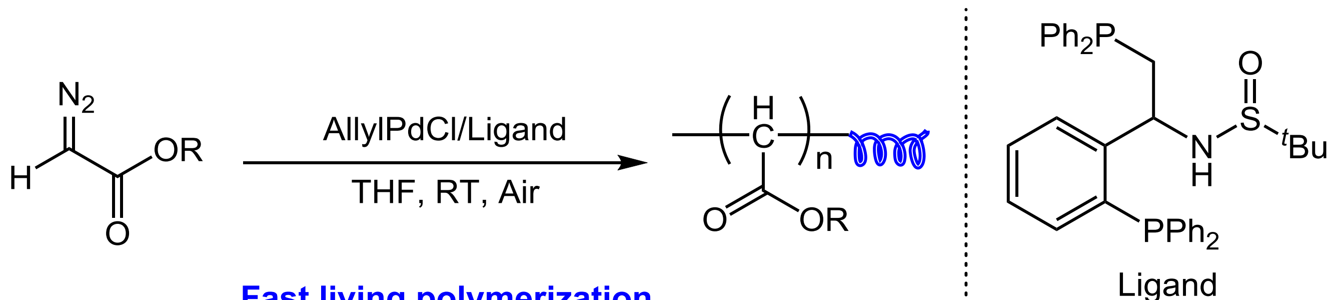


Ihara, E. *et al. Macromolecules* **2012**, *45*, 6869.



detected by MALDI-TOF-MS analysis

Fast Living and Helix-Sense-Selective Polymerization



Fast living polymerization
Controlled Mn and narrow PDI
Optically active helical polymer

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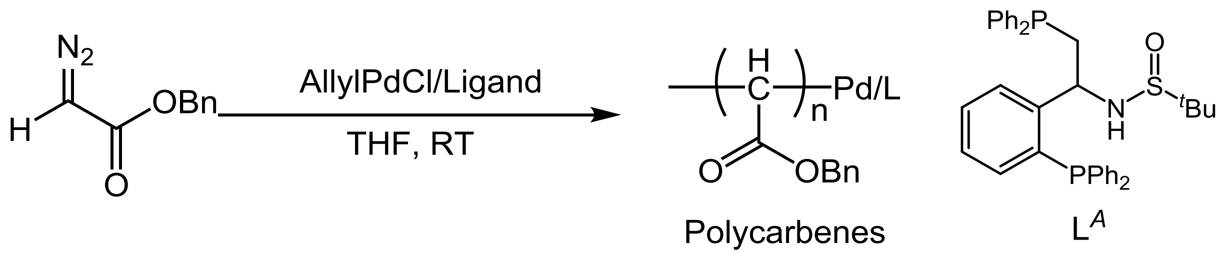
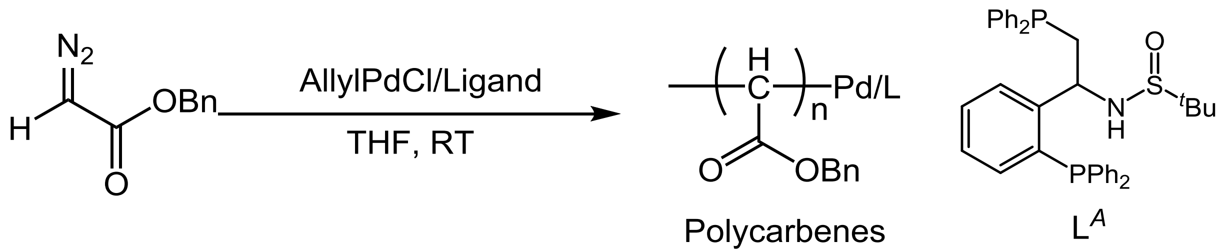
Fast Living Polymerization



Run	Ligand	[M]/[Pd]	[L]/[Pd]	Mn (KDa)	PDI	Yield(%)
1	$^{t}Bu_3P$	50	2	6.8	1.47	62
2	PPh_3	50	2	-	-	-
3	DPPP	50	1	-	-	-
4	Binap	50	1	5.8	1.57	64
5	L^{A}	50	1	7.0 (7.4)	1.16	81
6	L^{A}	50	0.5	6.8	1.34	76
7	L^{A}	50	2	6.9	1.29	78

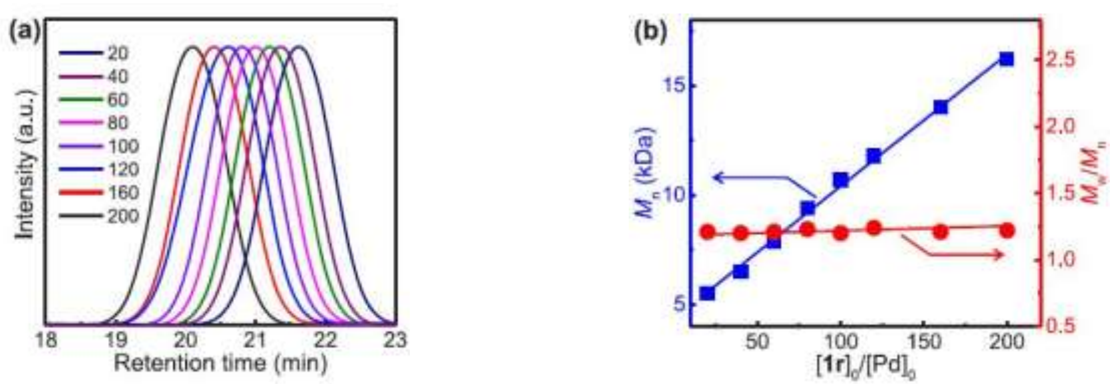
[a]The polymerizations were carried out in THF at 25 °C for 24 h.

Fast Living Polymerization

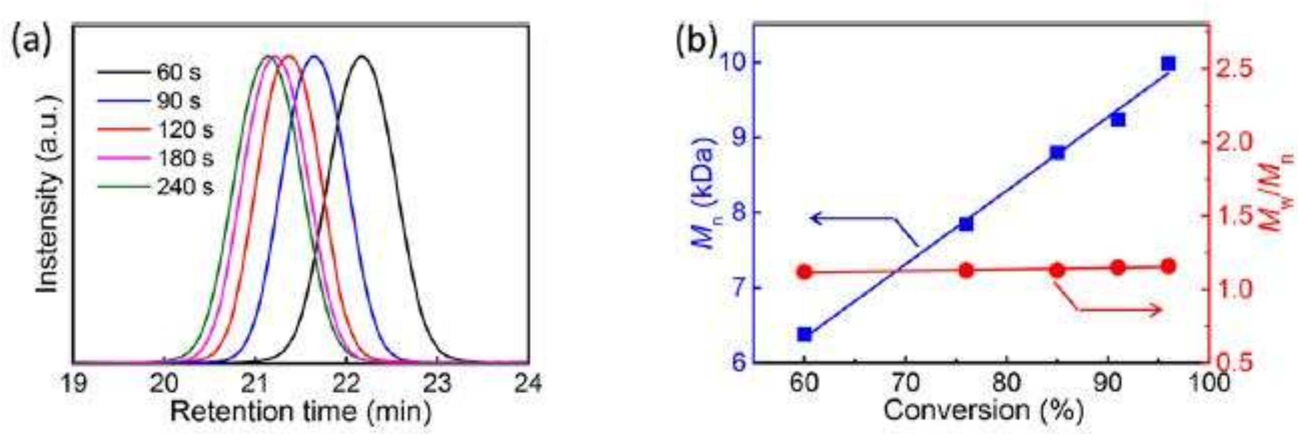


Run	Ligand	[M]/[Pd]	[L]/[Pd]	Mn (KDa)	PDI	Yield(%)
8	L^A	100	1	10.1	1.17	83
9	L^A	150	1	13.7	1.18	81
10	L^A	200	1	16.9	1.19	82

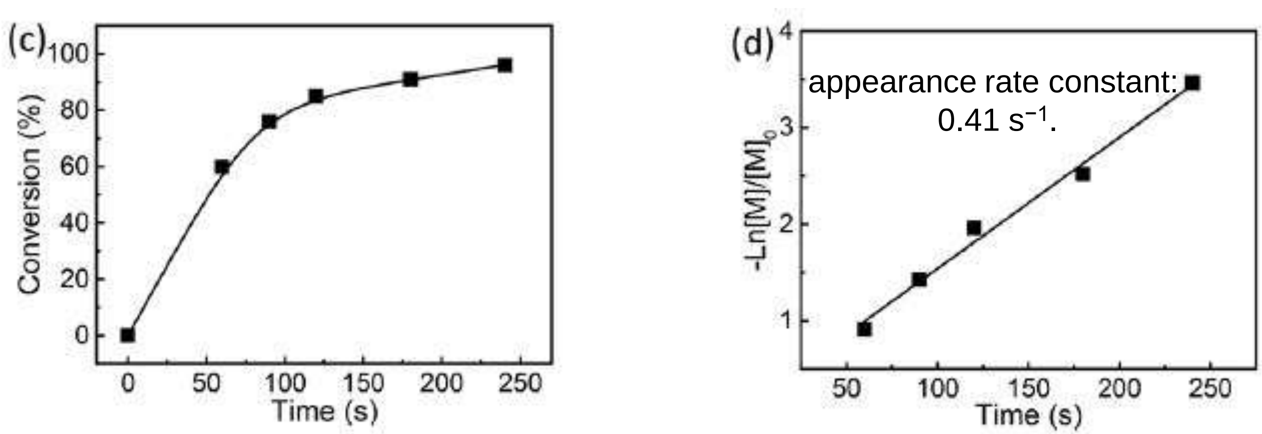
[a]The polymerizations were carried out in THF at 25 °C for 24 h.



Fast Living Polymerization

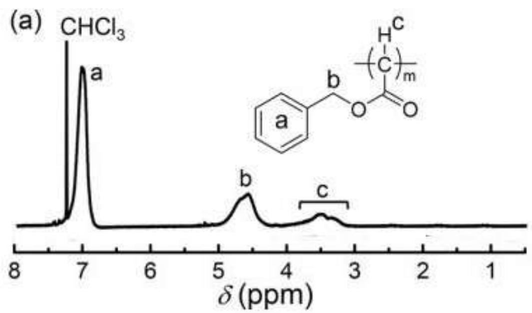


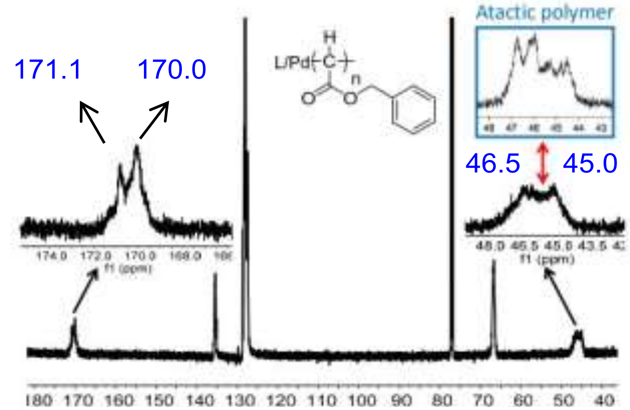
The polymerization proceeded in a living/controlled manner.

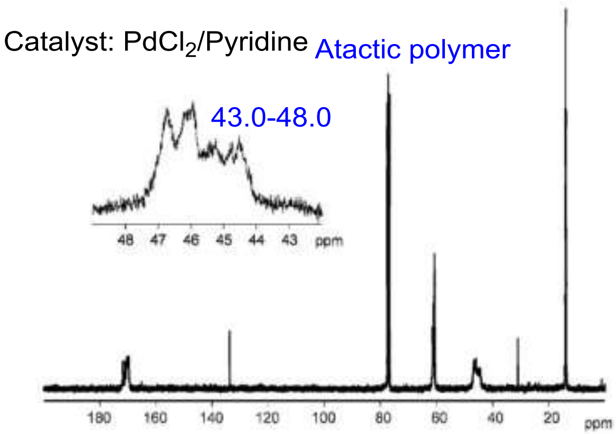


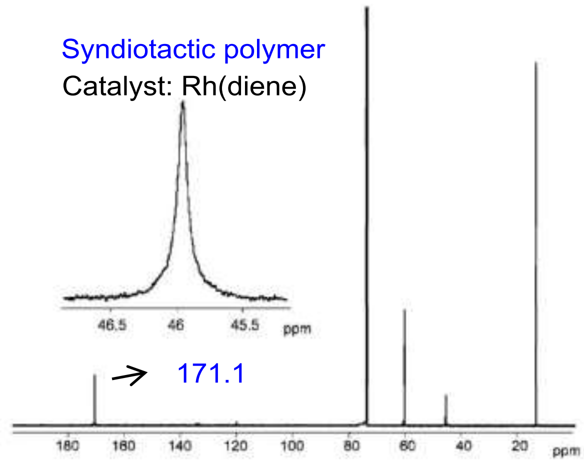
The polymerization was relatively fast.
The polymerization obeys a first-order reaction rate law.

NMR Spectrum



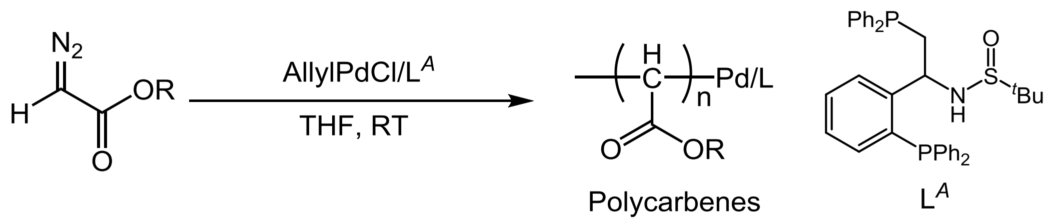




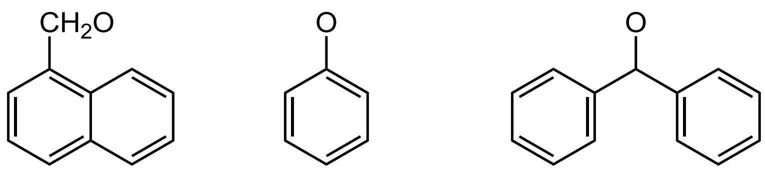


The polymer possess some content of stereoregularity.
The polymer contains a rather enhanced isotactic sequence.

Substrate Scope



OR = OBn **1** OC_6H_{13} **2** $O(CH_2CH_2O)_3CH_3$ **3**

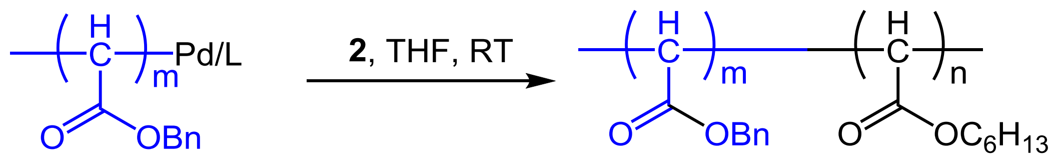


4 **5** **6**

Run	Monomer	[M]/[Pd]	Mn	PDI	Yield(%)
1	**2**	100	11.3	1.20	84
2	**3**	50	6.2	1.20	55
3	**4**	50	6.1	1.18	78
4	**5**	150	8.7	1.18	81
5	**6**	50	3.1	1.13	43

[a]The polymerizations were carried out in THF at 25 °C for 24 h.

Chain Extension Reaction

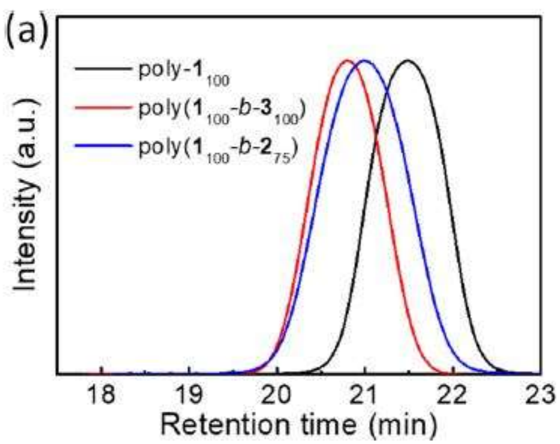


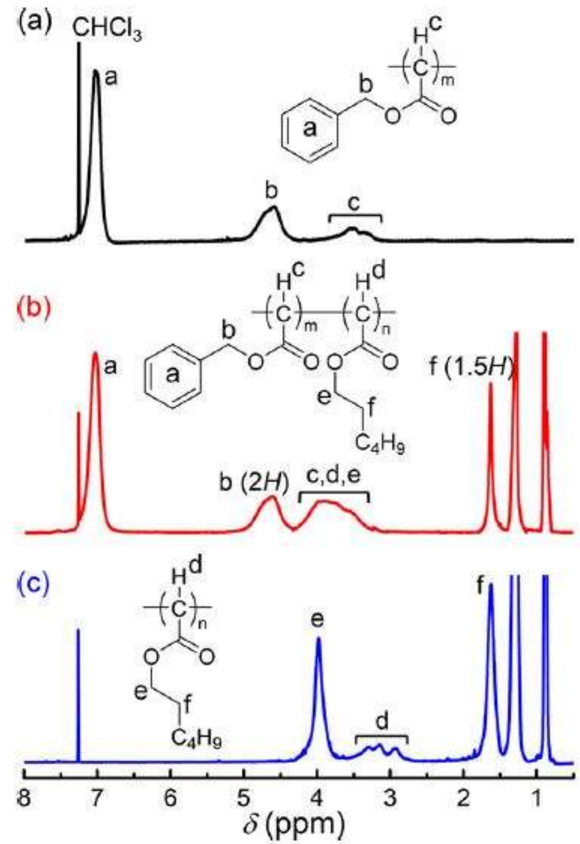
poly-1_m

Mn = 10.1 KDa
PDI = 1.18

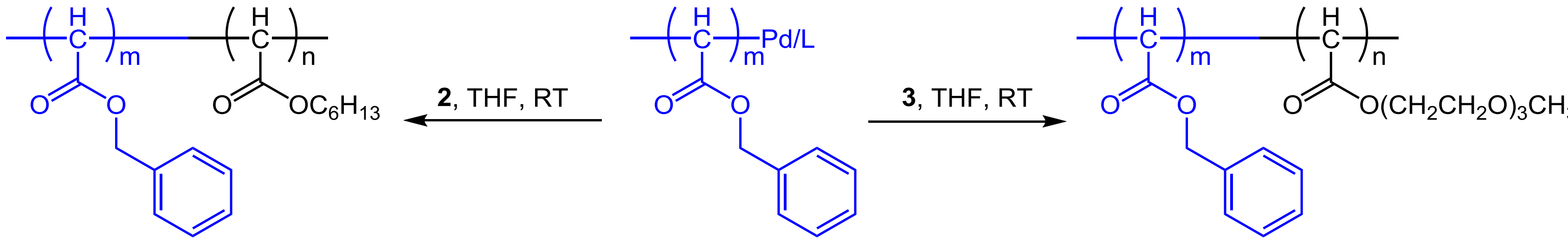
poly(1_{100}-*b*-2_{75})

Mn = 18.6 KDa
PDI = 1.20





Block Copolymerization



poly(1_m-*b*-2_n)

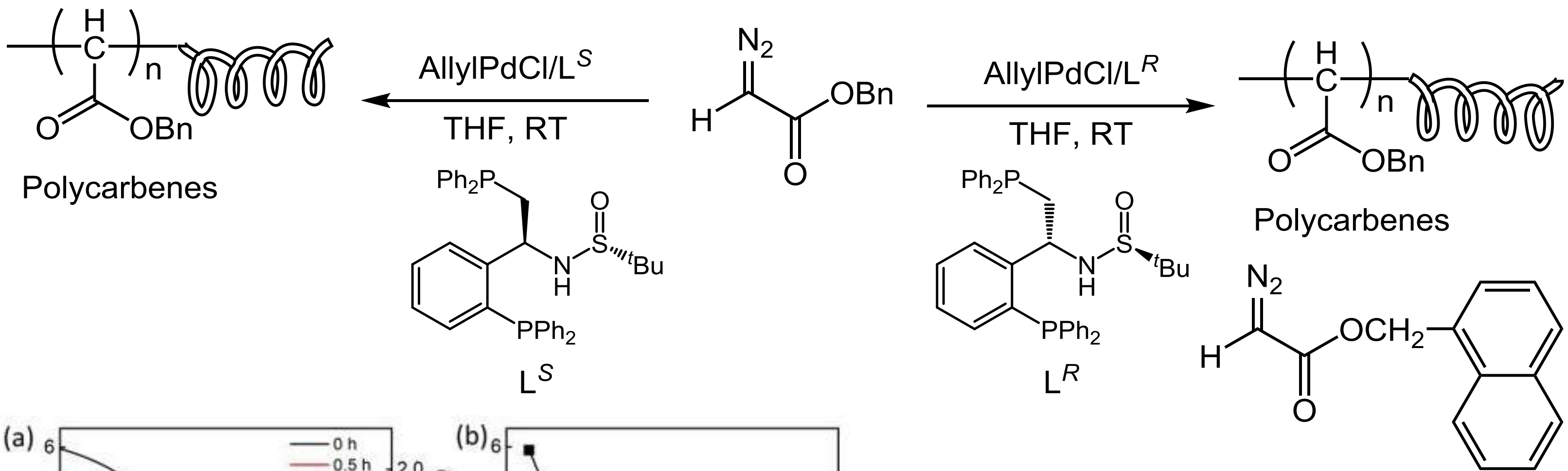
poly-1_m
Mn = 10.1 KDa
PDI = 1.18

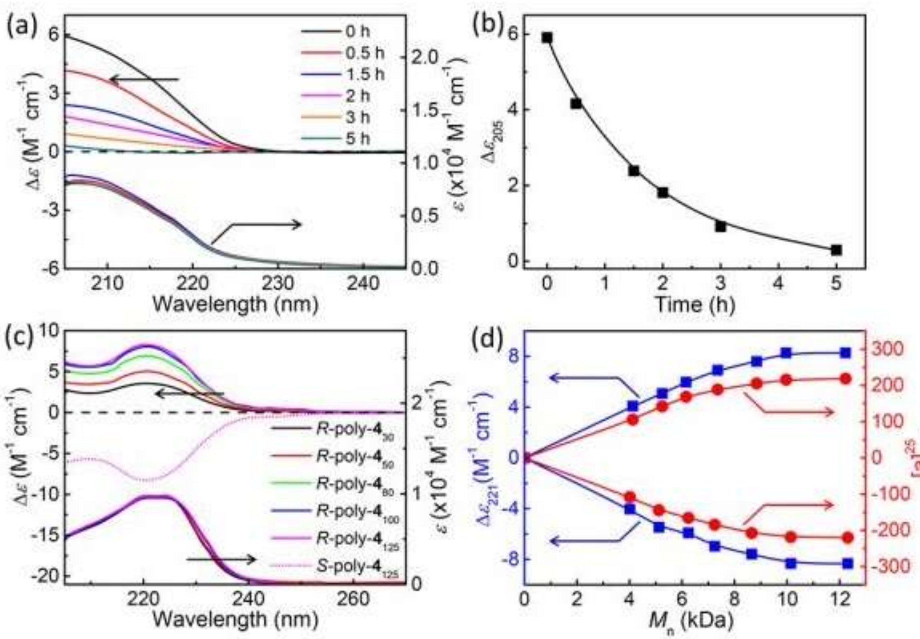
poly(1_m-*b*-3_n)

		Homopolymer		Block Copolymer		
Run	Polymer	Mn (KDa)	PDI	Mn (KDa)	PDI	Yield
1	**Poly-(1_{50}-*b*-2_{50})**	7.0	1.15	14.2	1.19	80
2	**Poly-(1_{100}-*b*-2_{75})**	10.1	1.18	18.6	1.20	84
3	**Poly-(1_{50}-*b*-3_{50})**	7.1	1.16	14.0	1.20	68
4	**Poly-(1_{100}-*b*-3_{100})**	10.3	1.18	21.5	1.21	67

[a]The block copolymerizations were performed in THF at 25 ^oC for 8 h.

Helix-Sense-Selective Polymerization

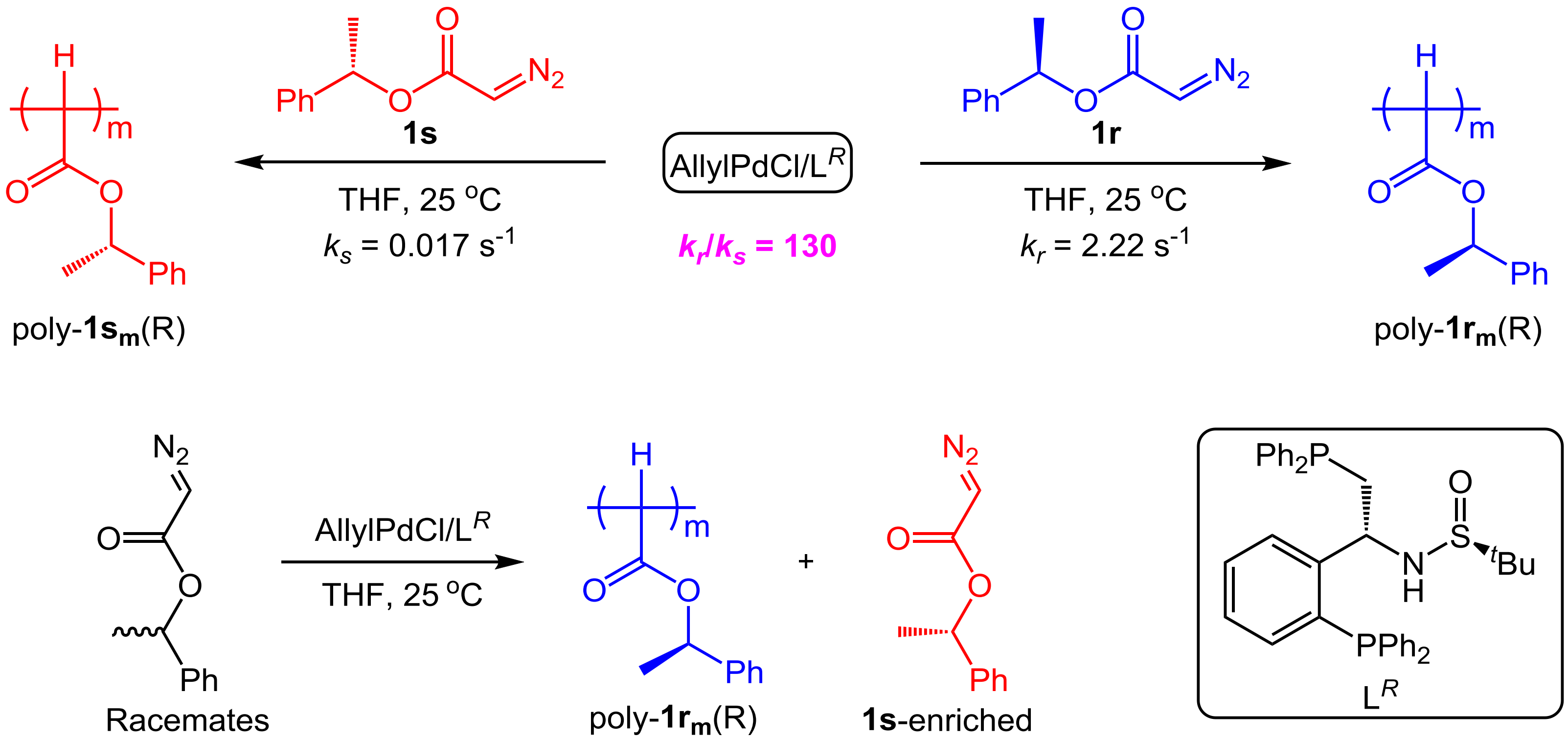




1. **The optical activity was reasonably ascribed to the predominantly one-handed helical conformation of the polymer backbone induced by the chiral catalyst during the process of the helix-sense-selective polymerization.**

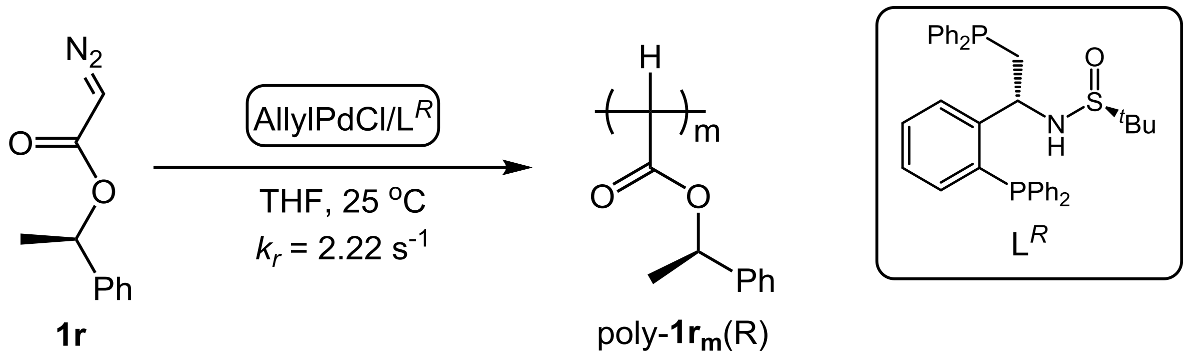
2. **Introducing bulky substituents onto a polymer pendant can stabilize the helical conformation.**

Highly Enantioselective Polymerization

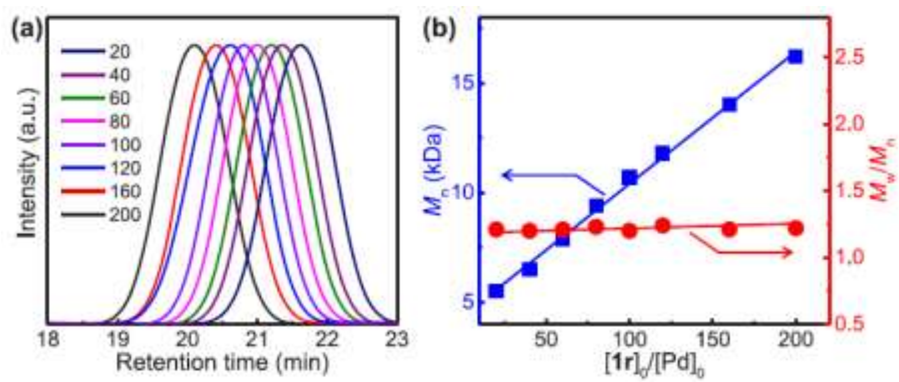


Wu, Z.-Q. *et al*. *Macromolecules* **2019**, *52*, 7260.

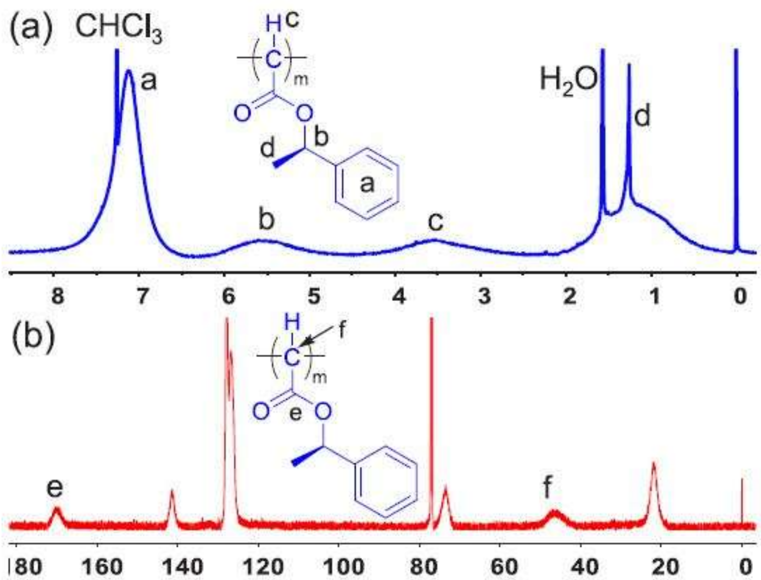
Fast Living Polymerization



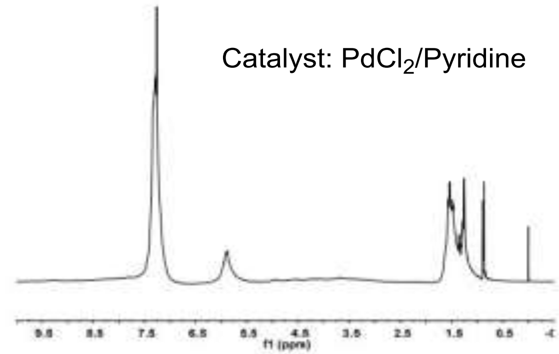
Run	Polymer	Mn	PDI	Yield
1	Poly-$\mathbf{1r}_{60}$(R)	7.90	1.21	73
2	Poly-$\mathbf{1r}_{100}$(R)	10.7	1.20	68
3	Poly-$\mathbf{1r}_{160}$(R)	13.9	1.21	66
4	Poly-$\mathbf{1r}_{200}$(R)	16.2	1.22	59

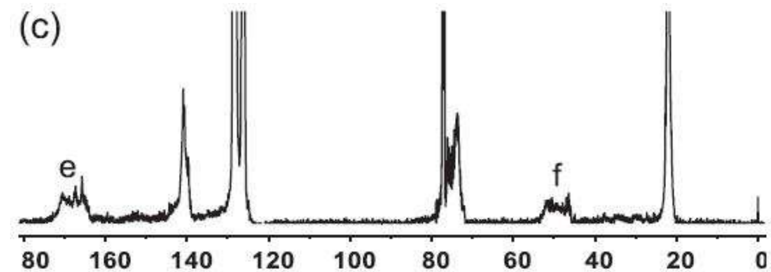


Stereoregular Polycarbenes

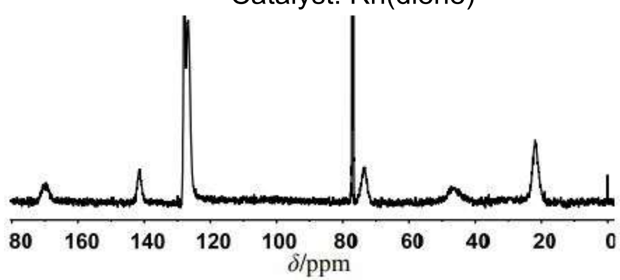


Catalyst: $PdCl_2$/Pyridine



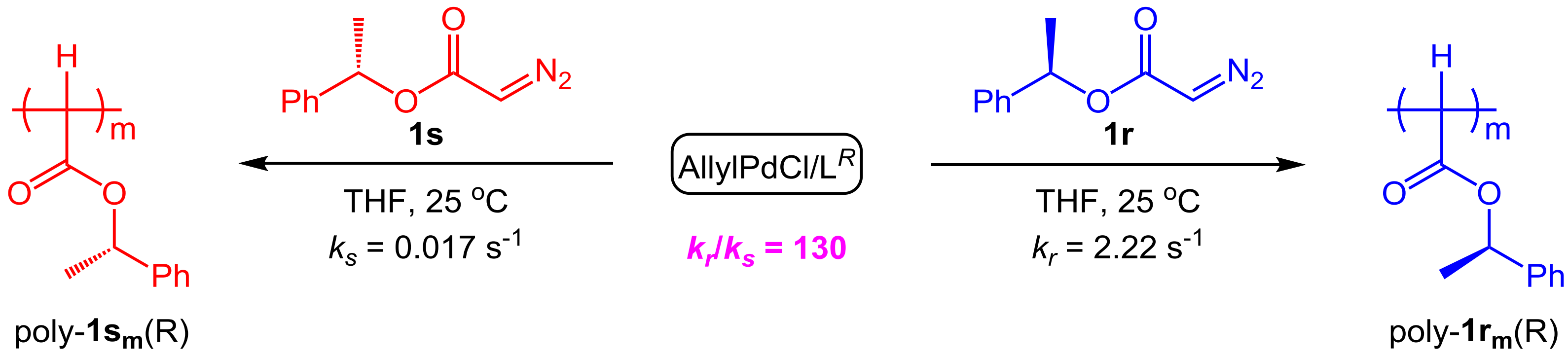


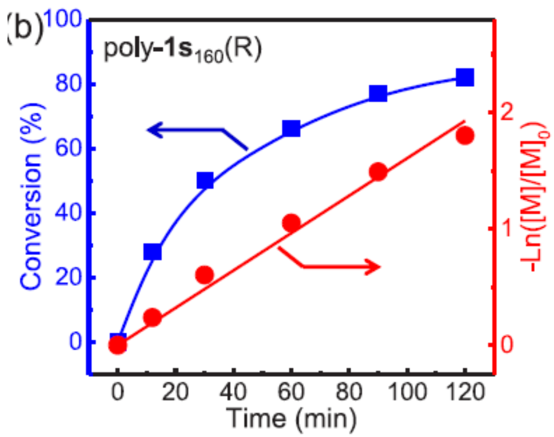
Catalyst: Rh(diene)



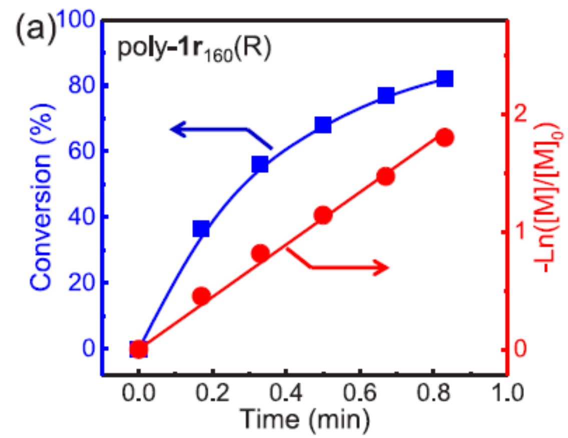
The polymer possess a high stereoregularity.

Highly Enantioselective Polymerization





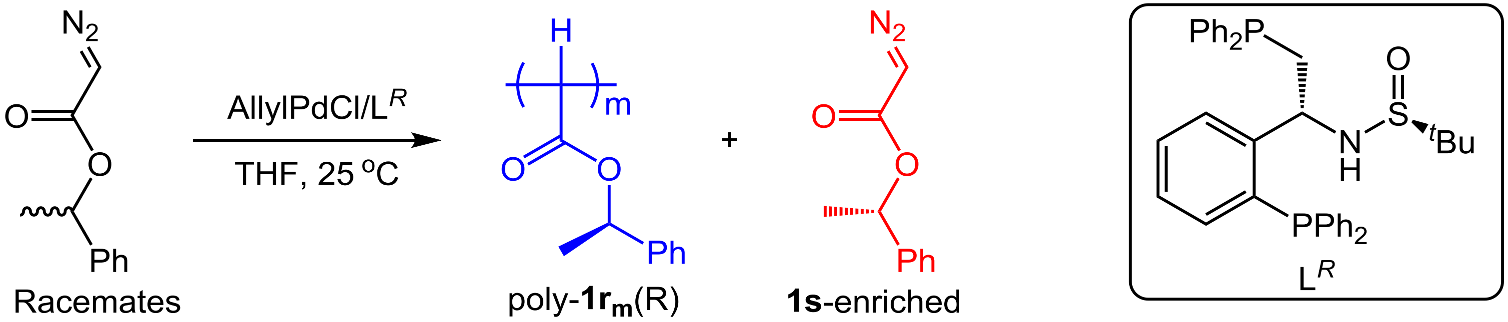
1s: 2 h, > 80% *Conv.*

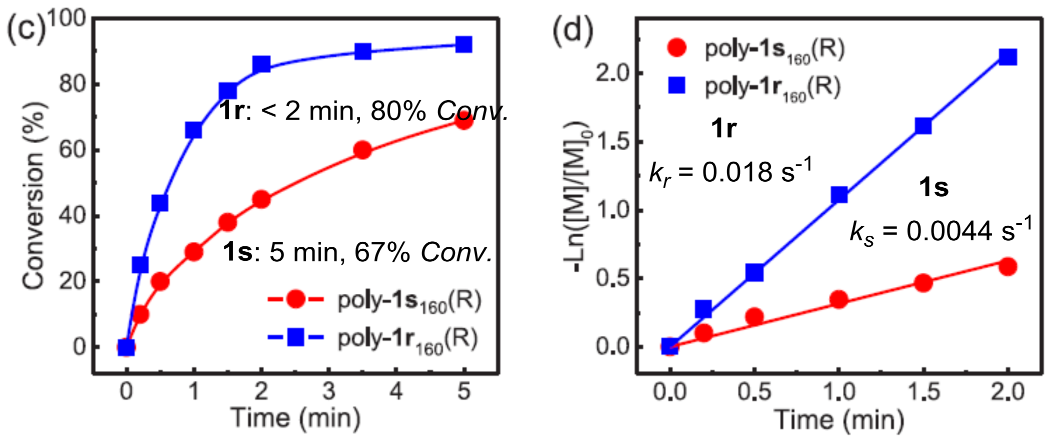


1r: < 1 min, 80% *Conv.*

This result indicated the polymerization of the diazoacete enantiomers was proceeded in a good enantioselective fashion.

Highly Enantioselective Polymerization

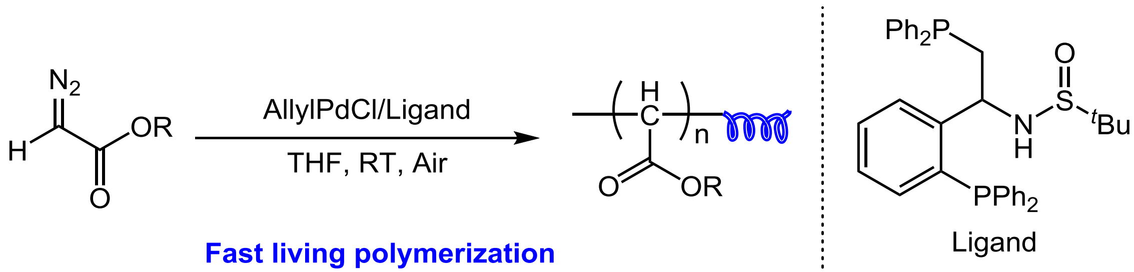




The reason for decreased enantioselectivity of the polymerization:

1. **The intermolecular interaction of the two enantiomers**
2. **The incorporation of an unfavorable enantiomer onto the living chain-end may slow down the polymerization rate**

Summary



Fast living polymerization
Controlled Mn and narrow PDI
Optically active helical polymer

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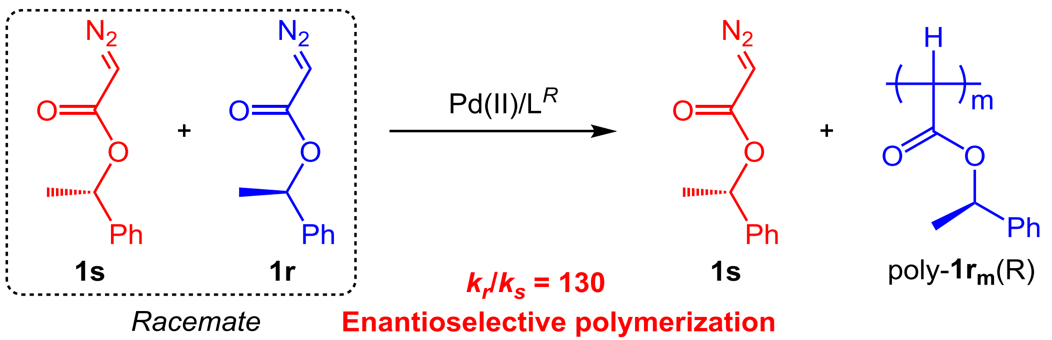

Enantioselective polymerization

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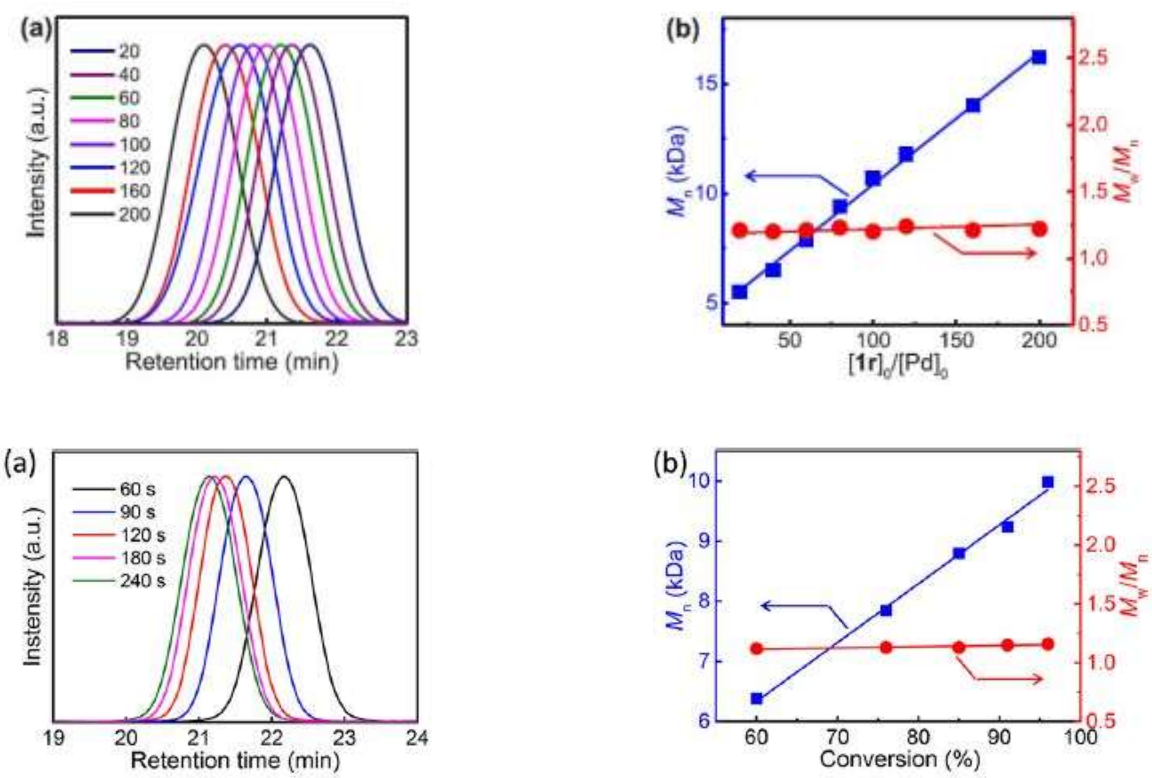
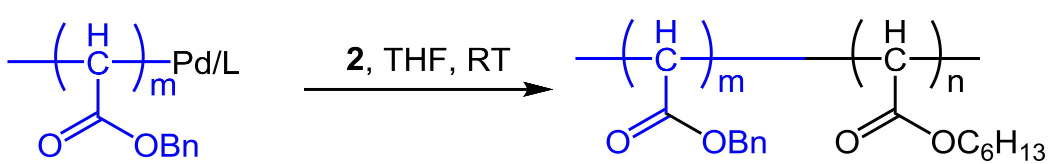
Summary - Living Polymerization

Mn is close to the theoretical value, PDI is close to 1.





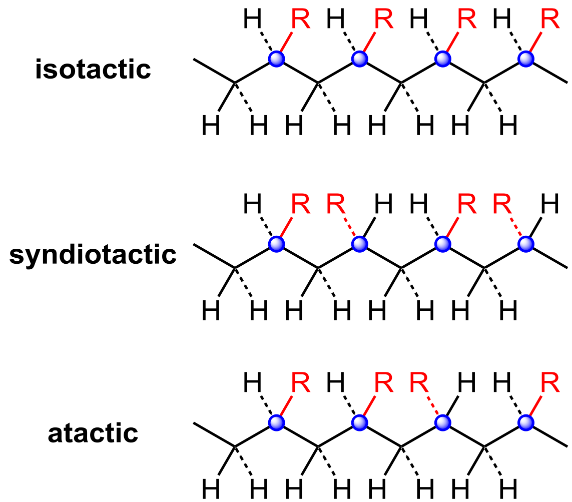
poly-1_m

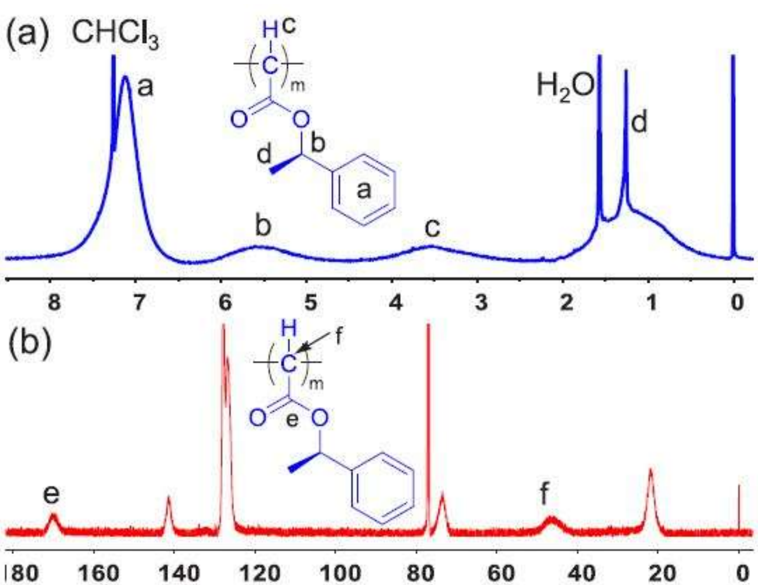
poly(1_{100}-*b*-2_{75})

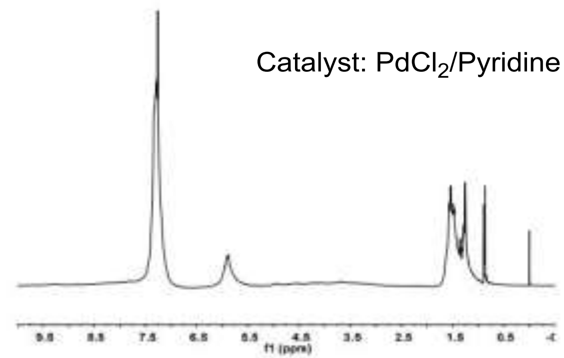
Mn = 18.6 KDa

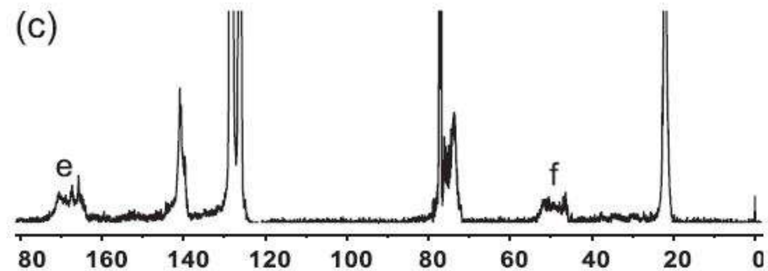
PDI = 1.20

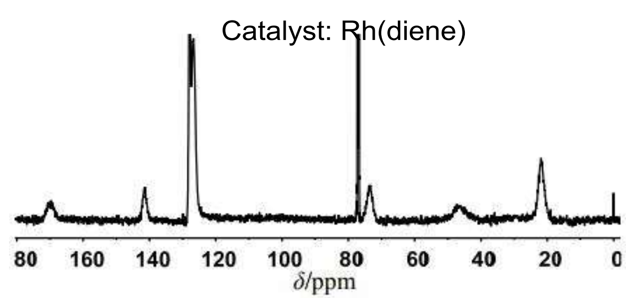
Summary - Stereoselective Polymerization











The First Paragraph

It is well-known that C−C main-chain polymers are one of the most important classes of synthetic polymers and have been widely used in our modern life. These polymers are generally prepared via the polymerization of vinyl monomers. An alternating method is the polymerization of one-carbon (C1) units such as isocyanide and diazocarbonyl compounds. The last compound is of particular interest because it can afford well-defined C−C main-chain polymers bearing polar substituents at every main-chain carbon, which cannot be accessed by Ziegler−Natta catalysts. Thus, the diazoacetate polymerization seems to be an attractive route to prepare C−C main-chain functional polymers. It can be argued that the radical polymerization of dialkyl fumarates or maleates can also produce polymers with similar structures. However, the living/controlled polymerizations of these monomers have never been attained so far.

The Last Paragraph

In summary, we have developed a family of novel Pd(II)-based catalysts, which could promote a fast living polymerization of various diazoacetates under mild conditions in air. The polymerization was very fast and can be accomplished within several minutes, affording polycarbenes in high yields with controlled Mn and narrow Mw/Mn. With use of this method, a variety of block copolymers were facilely prepared through chain extension reactions. Moreover, fast living polymerization of diazoacetates bearing bulky substituents by chiral Pd(II) catalysts afforded well-defined polycarbenes with high optical activity due to the formation of a predominantly one-handed helix. The present study not only provided a novel method for fast living polymerization of various diazoacetates under mild conditions but also for the first time revealed the helical conformation of polycarbene, which may have great potential in many fields, including chiral recognition, enantiomer separation, asymmetric catalysis, and so on.

Representative Examples

Although tremendous research has been focused on controlled synthesis of polymers with a helical conformation, the types of synthetic helical polymers are very finite. **尽管大量的研究集中在控制螺旋构象的聚合物的合成，但是合成的螺旋聚合物种类非常有限。**

Introducing appropriate substituents on the polycarbenes pendants may endow the polymer with a stable helical conformation due to the steric hindrance between the adjacent pendants. **引入合适的取代基在聚卡宾侧链赋予聚合物一个稳定的螺旋构象，这是因为相邻侧链的空间位阻导致的。**

The ^{1}H NMR spectrum further supports the formation of expected polymers because characteristic resonances coming from the phenyl pendants and the backbone were clearly discerned. **氢谱进一步确定了聚卡宾的结构，因为主链骨架和芳基区的氢都可以被辨识。**

Thanks
for your attention