


# An Introduction to Polymer Physics

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## 2. Short Range Structure of Polymer Chains (近程结构)

2.1 brief introduction 4 hours


# Why & What



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### 1. Why learn polymer structure?



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### 2. What're the features?

- ① Chain-like
- ② Flexibility Where are the examples?
- ③ Diversity
- ④ Complicated Condensed State Structure




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### 3. The 4 levels of polymer structure

± 1 <sup>st</sup> level } ± 2 <sup>nd</sup> level }	→	About <b>one single</b> polymer chain <b>chain structure</b>
± 3 <sup>rd</sup> level } ± 4 <sup>th</sup> level }	→	About <b>a flock of</b> polymer chains <b>condensed state structure</b>




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### (a) 1<sup>st</sup> order structure

- **The short range structure**
  - chemical composition (组成)
  - Architecture (构造)
  - Configuration (构型)
  - sequential structure of copolymers (序列结构)
- **Microstructure of one single chain**



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## (b) 2<sup>nd</sup> order structure

- The long range structure
  - Size (尺寸)
  - Shape (形状)
  - flexibility of molecules (柔性)

- Morphology of one single chain

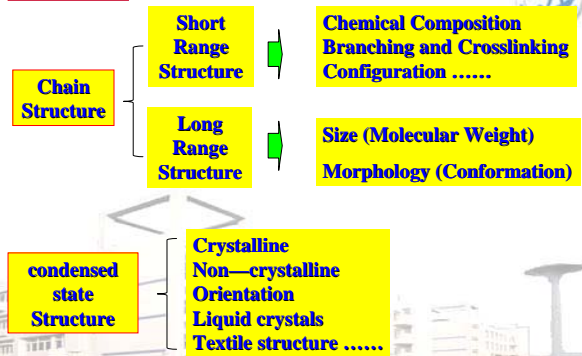
## (c) 3<sup>rd</sup> order structure

- crystalline phase structure (晶相结构)
- non-crystalline phase structure (非晶相结构)
- oriented phase structure (取向结构)
- liquid phase structure (液晶结构)
- Corresponding to a flock of chains

## (d) 4<sup>th</sup> order structure

- textile phase structure (织态结构)
- Composed of third order structures

### Key point



高分子链结构

近程结构

化学组成  
 单体单元键合单个高分子链的链接  
 (交联与支化)  
 单体单元主体构型 (空间排列)

远程结构

高分子的大小 (分子量)  
 高分子的形态 (构象)

高分子聚集态结构

晶态  
 非晶态  
 取向态  
 液晶态  
 织态

## 2.2 short range structure of polymer chains

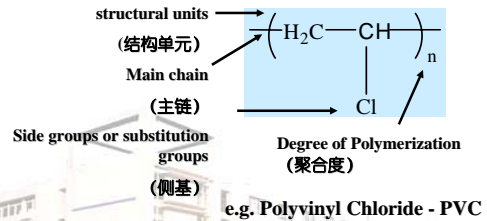
- Do you remember what is the short range structure?

- Composition
  - Branching and crosslinking
  - Sequential of structural units
  - Configuration
- Where are the examples?

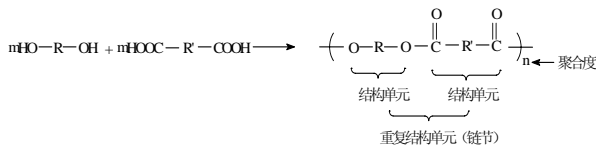
## What's the **chemical composition**?

- Polymer chain structure is **linear**, such a concept was proposed and confirmed by Staudinger et al in 1920's -1930's
- Polymer chains are always obtained by **addition reaction** or **condensation reaction**

## Addition Reactions

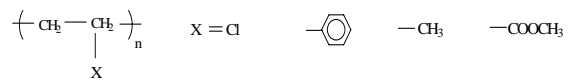


## Condensation Reactions



## Carbon Chain Polymers

polymer chain is composed of **carbons** linked by **covalent bonds** (most of them are obtained by addition reaction), for example:



These polymers are **difficult to be hydrolyzed**. In addition, they are **easy processing**, are **flammable**, are **easily aged** and **not heat-durable**.

## BESIDES CARBON CHAIN POLYMERS

Heterochain polymer  
杂链高分子

Elementary chain polymer  
元素高分子

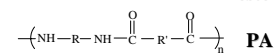
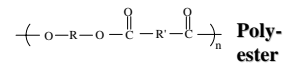
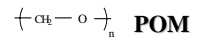
Elementary Organic polymer  
元素有机高分子

Elementary Inorganic polymer  
元素无机高分子

Due to the different structures, the properties of polymers are not the same.

## Hetero-chain polymers

- backbones are composed of carbon atoms and other atoms like O, S, N etc

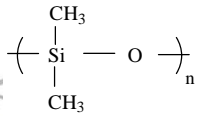


they are **easy to be decomposed** by water, alcohol or acids, but are **heat-durable** and **strong**

Most of them are used as engineering plastics.

## Elementary chain polymer

- backbones are composed of non-carbon atoms, like Si, P, Al, Ti, As, Sb, Ge

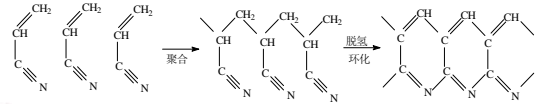


PDMS  
**Silicon rubber**

- Features: they are **thermal stable**, like inorganic compounds; but are also of **elasticity and plasticity**, like organic compounds; usually they are **weak** in mechanical properties

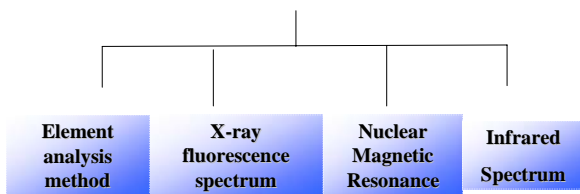
## Ladder polymer

- Molecular chain is not a single chain, but like "ladder" or "double helix"



features: **thermal stable.**

## Physical techniques for observation of the composition of polymer\*

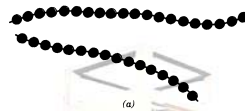


元素分析 X-射线荧光光谱 核磁共振 红外光谱

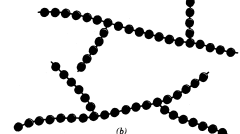
\*高聚物的结构与性能, P10

## What are branching and crosslinking?

Linear polymer chain

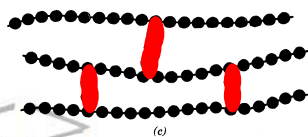


Branched polymer



Can be melted or dissolved

## Crosslinked or network polymer



Can not be melted or dissolved

Table 2.1 Comparison of different Polyethylene\*

	Low density PE	High density PE	Crosslinked PE
Density (g/cm <sup>3</sup> )	0.91-0.94	0.95-0.97	0.95-1.40
Crystallinity (%) by X-ray detection	60-70	95	-
Melting point (°C)	105	135	-
Tensile strength (MPa)	7-15	10-20	20-40
Upper using temperature	80-100	120	135
Application	Soft plastic products, thin films	Hard plastic products, pipe, sticks	Cables, electric equipments

\*高聚物的结构与性能, P25

### Physical techniques for analyzing branched and crosslinked polymers\*

- Infrared Spectrum
- Nuclear Magnetic Resonance
- Raman Spectrum

\*高聚物的结构与性能, P27

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### What's the sequential structure of copolymers

- Copolymer may contain **two or more** monomer units
- A-B-A-B-A-B-A-B- **alternating** (交替) copolymer
- A-A-A-B-B-B-B-B- **block** (嵌段) copolymer
- A-B-A-A-B-B-B-A- **random** (无规) copolymer
- A-A-A-A-A-A-A-A- **grafting** (接枝) copolymer

B B  
B B  
B B  
B B  
B B

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### Experimental methods to analyze sequential structure of copolymers\*

- Infrared Spectrum  
红外光谱
- Nuclear Magnetic Resonance  
核磁共振

\*高聚物的结构与性能, P29-37

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### What is configuration? Why it is a Key Point?

Configuration is refer to the arrangement of atoms **fixed** by the **chemical bonds** in molecules.  
构型是指分子中由**化学键**所固定的原子在空间的排列。

Same polymer, different configuration

- Optical isomerism  
旋光异构
- Geometrical isomerism  
几何异构
- Bonding manner isomerism  
键接异构

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### A. Optical isomerism 旋光异构

$$n \text{ CH}_2 = \underset{\text{R}}{\text{CH}} \longrightarrow \left[ \text{CH}_2 - \underset{\text{R}}{\text{CH}} \right]_n$$

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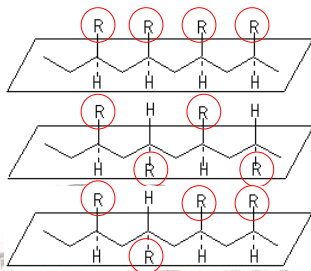
### 旋光异构分子是否必定有旋光性?

内、外消旋作用, 所以无旋光性; 但有些生物高分子和特殊结构的高分子具有旋光性

对高分子来说, 关心不是具体构型(左旋或右旋), 而是构型在分子链中的异同, 即全同(等规)、间同或无规。

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### 3 kinds of isomers



Isotactic  
全同立构

Syndiotactic  
间同立构

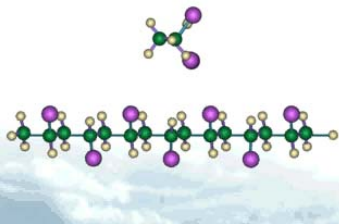
Atactic  
无规立构

全同和间同立构聚合物统称为有规立构聚合物



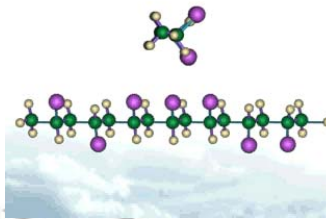
- 高分子全部由一种旋光异构单元链接而成。
- X基团处于分子平面的同一侧。
- 分子链结构规整，可结晶。
- -D-D-D-D-D- or -L-L-L-L-L-

Isotactic



- 两种旋光异构单元交替链接而成。
- X基团交替分布于分子平面两侧。
- 分子链结构规整，可结晶。
- -D-L-D-L-D-L-D-L-D-L-D-L-

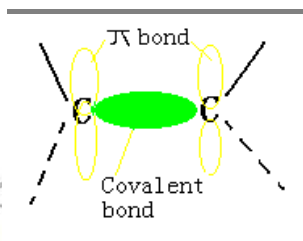
Syndiotactic



- 两种旋光异构单元无规链接而成。
- X基团无规分布于分子平面两侧。
- 分子链结构不规整，不能结晶。
- -D-L-D-L-L-L-L-L-D-D-

atactic

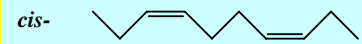
### B. Geometrical isomerism



Double bonds on the main chain

### Poly(1,4-butadiene)

cis-顺式

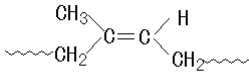


trans-反式

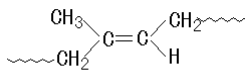


In Latin, *trans* means “on the other side”;  
and *cis* in Latin means “on the same side”

$$\left[ \text{CH}_2 - \overset{\text{CH}_3}{\text{C}} = \text{CH} - \text{CH}_2 \right]_n$$
 聚异戊二烯  
 Polyisoprene



顺式构型  
Cis



反式构型  
Trans

What kind of isomerism can be obtained for polyisoprene in 1, 2 addition?

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### C. Bonding manner isomerism

$\text{CH}_2 = \overset{\text{R}}{\text{C}} - \text{CH}$

**1,2 addition**

$-\text{CH}_2 - \underset{\text{R}}{\text{CH}} - \text{CH}_2 - \underset{\text{R}}{\text{CH}} - \text{CH}_2 - \underset{\text{R}}{\text{CH}} - \text{CH}_2 -$ 

head-to-tail

**1,1 addition**

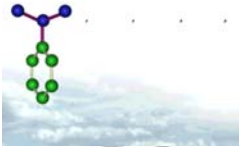
$-\text{CH}_2 - \underset{\text{R}}{\text{CH}} - \underset{\text{R}}{\text{CH}} - \text{CH}_2 - \text{CH}_2 - \underset{\text{R}}{\text{CH}} -$ 

head-to-head or tail-to-tail


**Random head to tail**

In general, polymers are like to be linked in head-to-tail manner. (why?)

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Head to tail



Head to head or tail to tail

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### Possible configuration of divinyl polymer

$\text{H}_2\text{C} = \underset{\text{Cl}}{\text{C}} - \text{CH} = \text{CH}_2$

$\left[ \text{CH}_2 - \underset{\text{Cl}}{\text{C}} = \text{CH} - \text{CH}_2 \right]_n$

$\left[ \text{CH}_2 - \underset{\text{Cl}}{\text{C}} \right]_n$   
 $\text{HC} = \text{CH}_2$

$\left[ \text{CH}_2 - \underset{\text{Cl}}{\text{C}} \right]_n$   
 $\text{C} = \text{CH}_2$

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**Q1. Which kind of isomer they are for the following polymers?**

- (1) -D-D-D-D-D-D-D-
- (2) -L-L-L-L-L-L-L-
- (3) -D-L-D-L-D-L-D-L-
- (4) -D-D-L-D-L-L-L-

Answer: (1) isotactic; (2) isotactic; (3) syndiotactic; (4) atactic

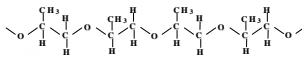
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**Q2. Propylene oxide (环氧丙烷) can form different isomers through ring-open reaction, try to illustrate their structures**

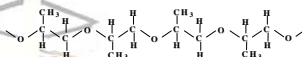
Poly (propylene oxide)/PPO  $\left[ \text{CH}(\text{CH}_3) - \text{CH}_2 - \text{O} \right]_n$

Due to the chiral C atoms, the structure of PPO will be

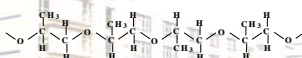
isotactic



syndiotactic



atactic

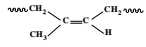


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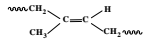
### Q3. Isomers of polyisoprene



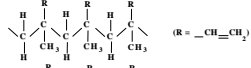
1) Cis 1,4



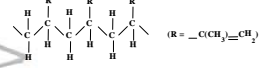
2) Trans 1,4



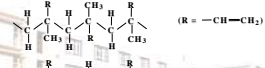
3) 1,2-isotactic



4) 3,4-isotactic



5) 1,2-syndiotactic



6) 3,4-syndiotactic

