



Chapter 6 Ionic Polymerization (离子聚合)

2020.11.25

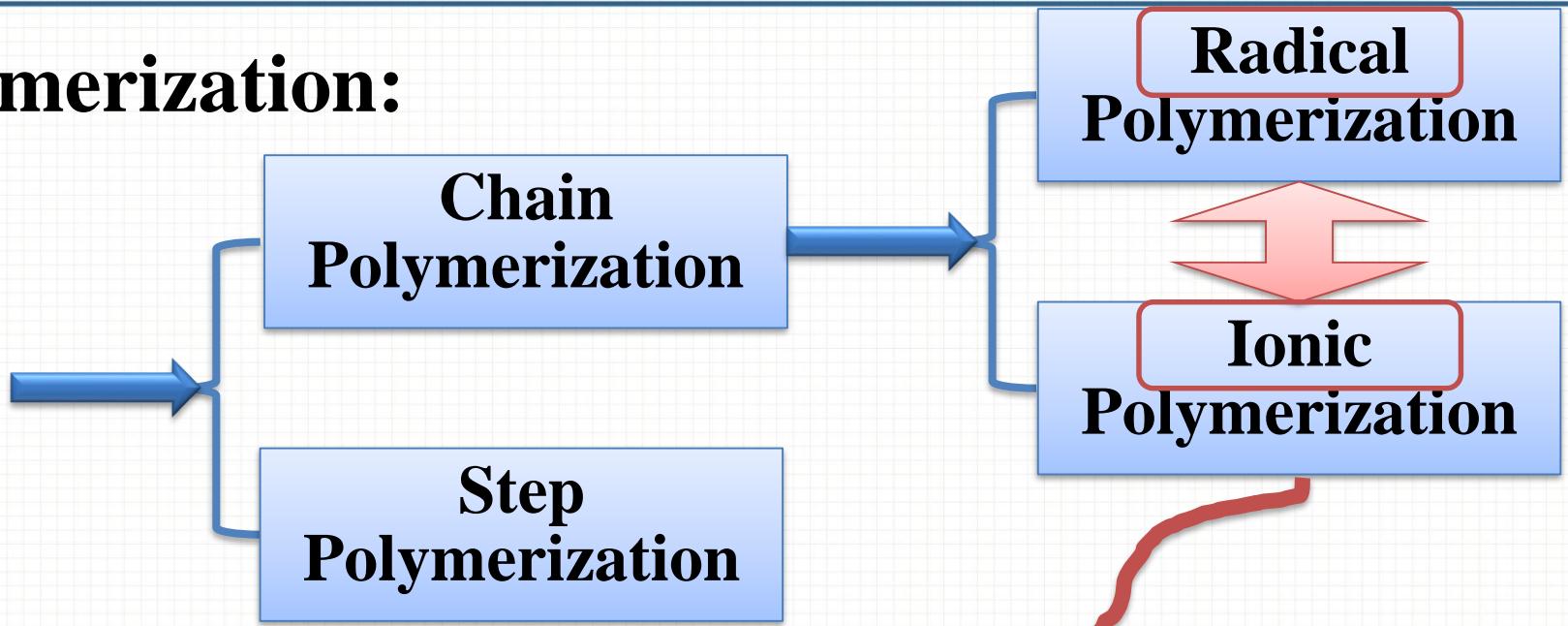


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Polymerization

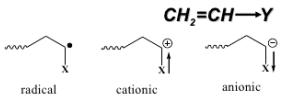
Polymerization:



Chain polymerization

Radical polym.
The C=C is prefer the Polym. by R.P. and also can be used in the steric hindrance of the substituent

Anionic polym.
Electron with drawing
substituent decreasing
the electron density on
the double bond and
facilitate the attack of
anionic species
such as cyano and
carbonyl



Cationic polym.

Electron donating substituent increasing the electron density on the double bond and facilitate the attack of cationic species such as alkoxy, alkyl, alkenyl, and phenyl

➤ Anionic Polymerization

➤ Cationic Polymerization 阳离子聚合



6.1 Anionic Polymerization

- High selectivity for monomers;
- Harsh polymerization conditions;
- Extremely fast polymerization rate;
- Heterogeneous system;
- The solvents show great effect on the polymerization.



6.1 Anionic Polymerization

6.1.1 Monomer and Initiator

6.1.2 Mechanism

6.1.3 Living Polymer

6.1.4 Kinetics

**6.1.5 Comparison between Radical & Ionic
Polymerization**



6.1 Anionic Polymerization

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Overview

- 1877 ---- Waitz ring-opening polymerization of ethylene
- 1949 --- Styrene : liquid anion initiator, anionic polymerization.
- 1952---- Quantitative
- 1956 ---- Szwarc initiation.

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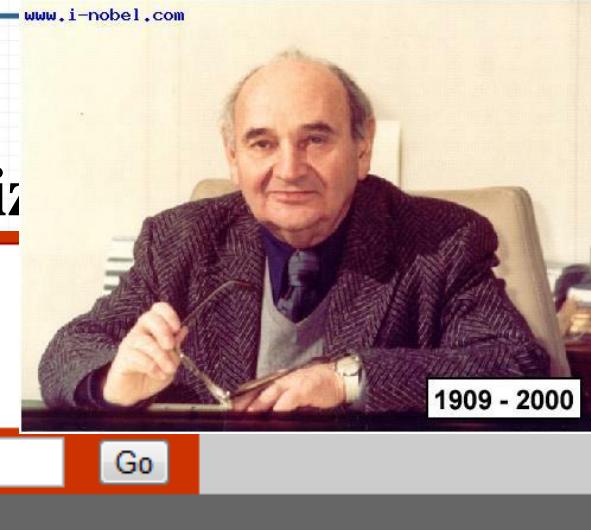
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Nature 178, 1168 - 1169 (24 November 1956); doi:10.1038/1781168a0

‘Living’ Polymers

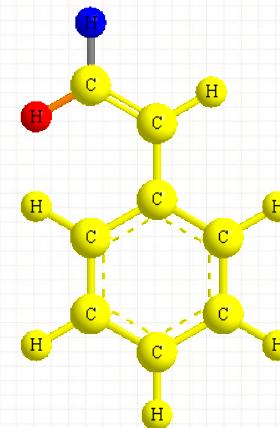
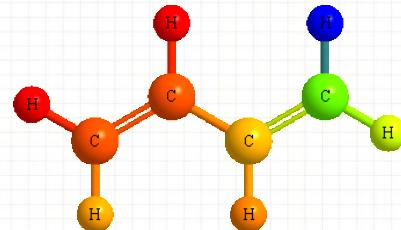
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6.1 Anionic Polymerization

Polymers of specific structure, like ABA **block** copolymer, **star shaped** polymer and **comb-like** polymer, could be synthesized, meeting the aim of **polymer molecular design**. Industrial practice is realized, for example, the produce of liquid **butadiene styrene rubber** and butadiene styrene block copolymer **SBS resin** has been industrialized.





6.1.1 The Initiator and Monomer

The occurrence of bottle green solution indicates the produce of radical anionic initiator.

Water or wet air must be strictly removed, or the activity of initiator will be destroyed.





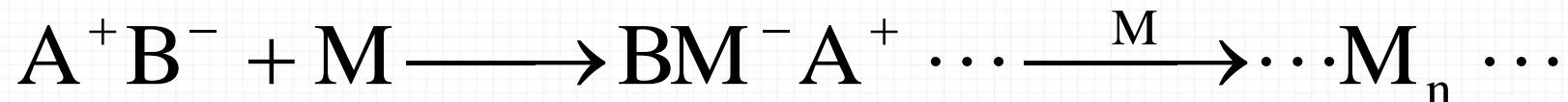
6.1.1 The Initiator and Monomer





6.1 Anionic Polymerization

General equation of reaction



B^- : Anionic activated species, normally served by **Nucleophile**;

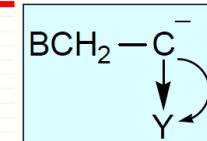
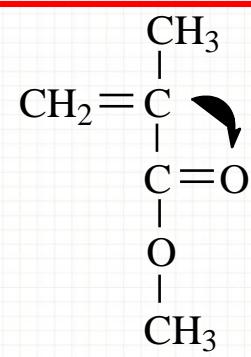
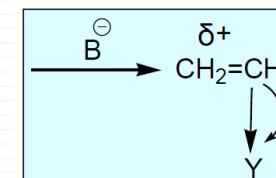
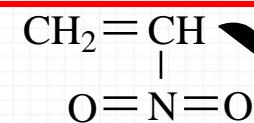
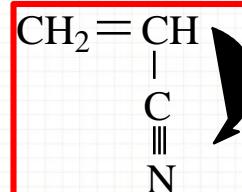
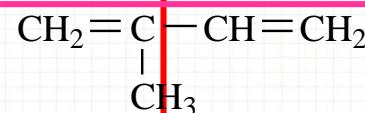
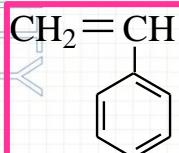
A^+ : Counter-ion, normally was **metallic ion**.

对离子



6.1.1 The Initiator and Monomer

- Typical anionic polymerizable monomers: styrene, MMA and acrylic nitrile etc.
- All types of monomers are π - π conjugated system or that with electron attracting group, making the density of electron cloud of double bond decline.
- The anionic active center reacts with double bond by addition reaction.



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6.1.1 The Initiator and Monomer

6.1.2 阴离子聚合的引发体系

- 阴离子聚合的引发剂是电子给体(亲核试剂), 属碱类物质 (碱金属, 有机金属化合物以及三级胺等) 。
- 根据引发机理可分为电子转移引发和阴离子引发两类。

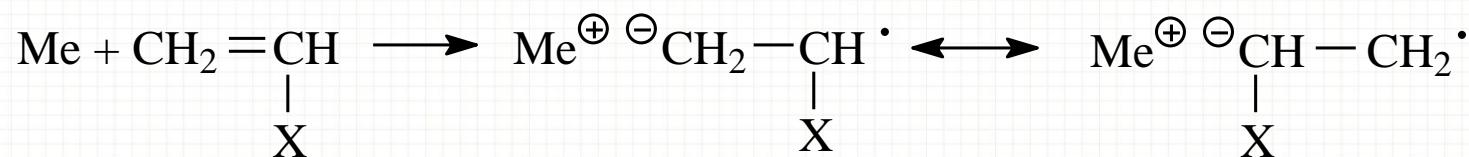


6.1.1 The Initiator and Monomer

电子转移引发

1. 碱金属(Alkali Metal)

Li、Na、K等碱金属原子最外层近一个价电子，容易转移给单体或其他化合物，生成单体自由基—阴离子，并进而形成双阴离子引发聚合。因此属于电子转移引发。

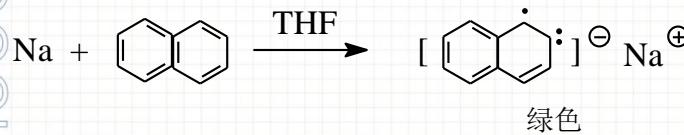


直接转移引发

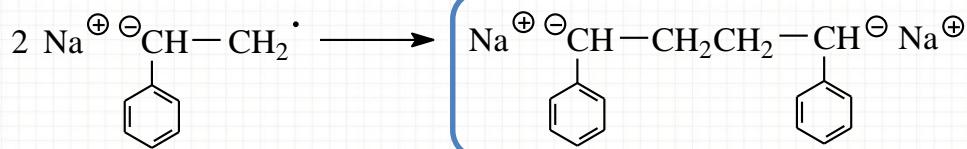
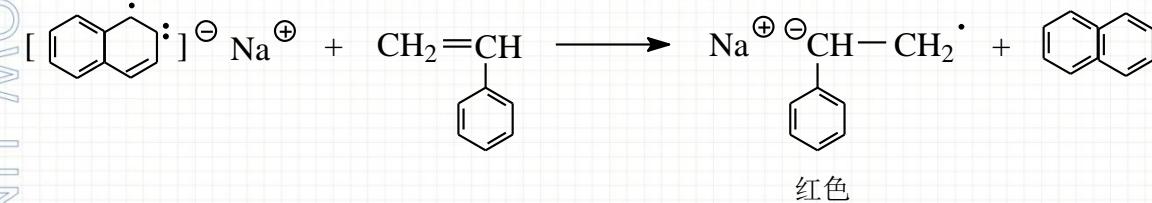


6.1.1 The Initiator and Monomer

碱金属亦可将电子转移给中间体，使中间体转变为自由基—阴离子，然后再将活性转移给单体。这种引发能量较低，反应速度快。如**萘—钠引发体系**在四氢呋喃溶液中引发苯乙烯的聚合。



间接转移引发



碱金属一般不溶于单体和溶剂，是非均相聚合体系，聚合在金属细粒表面进行，效率较低。而**萘—钠体系**在溶剂中溶解，是均相体系，碱金属的利用率增加，聚合效率提高。



6.1.1 The Initiator and Monomer

2. 有机金属化合物

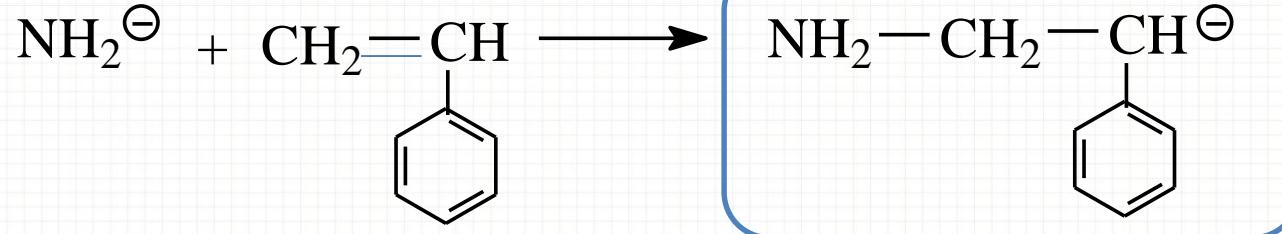
这类引发剂的品种较多，主要有金属胺基化合物、金属烷基化合物和格利雅试剂等。



6.1.1 The Initiator and Monomer

金属胺基化合物

NaNH_2 和 KNH_2 在液氨体系可呈自由阴离子形式引发聚合，是研究得最早的阴离子引发剂。



这类引发剂的活性太高，聚合不易控制，故目前已不使用。



6.1.1 The Initiator and Monomer

金属烷基化合物

金属烷基化合物 RMe 是目前最常用的阴离子聚合引发剂。其活性与金属的电负性有关。金属与碳的电负性相差越大，越容易形成离子。

各种元素的电负性如下：

C(2.5), Mg(1.2), Li(1.0), Na(0.9), K(0.8)



6.1.1 The Initiator and Monomer

RLi、RNa、RK都是引发活性很大的引发剂，其中以RLi最为常用，如丁基锂（Butyl lithium, $C_4H_9\text{-Li}$ ）。

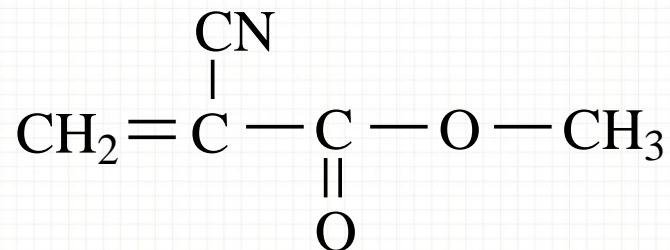
Mg的电负性较大， R_2Mg 不能直接引发阴离子聚合。但制备成格利雅试剂 MgRX 后，Mg—C键的极性增加，也能引发活性较大的单体聚合，如丙烯腈、硝基乙烯等。



6.1.1 The Initiator and Monomer

3. 其他

ROH , H_2O , R_3P , R_3N 等中性亲核试剂中都含有未共用电子对，能引发很活泼的单体阴离子聚合，如硝基乙烯、偏二腈乙烯、 α —氰基丙烯酸酯等等。



α —氰基丙烯酸甲酯



6.1.1 The Initiator and Monomer

4. 阴离子聚合引发剂与单体的匹配

阴离子聚合的单体和引发剂都具有很强的选择性。只有某些引发剂才能引发某些单体。

基本原则为：活性大的引发剂可引发活性活从小至大的种单体；而引发活性小的引发剂，只能引发活性大的单体，见图6—2。

6.1.1 The Initiator and Monomer

引发剂	单体	Q	ϵ	σ	
$\text{SrR}_2; \text{CaR}_2$	α -甲基苯乙烯	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C}_6\text{H}_5$		-0.161	
$\text{Na}; \text{NaR}$	苯乙烯	$\text{CH}_2=\text{CHC}_6\text{H}_5$	1	0	0.009
$\text{Li}; \text{LiR}$	丁二烯	$\text{CH}_2=\text{CHCH}=\text{CH}_2$	1.28	0	
RMgX	丙烯酸甲酯	$\text{CH}_2=\text{CHCO}_2\text{CH}_3$	1.33	1.41	0.385
$t\text{-ROLi}$	甲基丙烯酸甲酯	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2\text{CH}_3$	1.92	1.20	
ROK	丙烯腈	$\text{CH}_2=\text{CHCN}$	2.70	1.91	0.660
ROLi	甲基丙烯腈	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CN}$	3.33	1.74	
强碱	甲基乙烯酮	$\text{CH}_2=\text{CHCOCH}_3$	3.45	1.51	0.502
吡啶	硝基乙烯	$\text{CH}_2=\text{CHNO}_2$		0.778	
NR_3	亚甲基丙二酸二乙酯 $\text{CH}_2=\text{C}(\text{OO}_2\text{C}_2\text{H}_5)_2$				
弱碱	α -氨基丙烯酸乙酯 $\text{CH}_2=\text{C}(\text{CN})\text{CO}_2\text{C}_2\text{H}_5$			1.150	
ROR	α -氨基-2,4-己二烯酸乙酯 $\text{CH}_3\text{CH}=\text{CHCH}=\text{C}(\text{CN})\text{CO}_2\text{C}_2\text{H}_5$				
H_2O	偏二氟基乙烯	$\text{CH}_2=\text{C}(\text{CN})_2$	100	1.256	

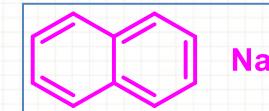
图6—2 阴离子聚合引发给予单体的匹配



6.1.1 The Initiator and Monomer

Common Initiator

Type of Initiator	Molecular Formula or Examples
alkali metals suspension system	Na suspends in THF or fluid chlorine
organic radical anion	naphthalene sodium initiator
alkyl or aryl lithium reagent	$n\text{-C}_4\text{H}_9\text{Li}$
Grignard Reagent	RMgX (R—alkyl or aryl group)
alkyl aluminum	AlR_3





6.1.2 Mechanism

The Anionic polymerization still belongs to the chain polymerization. It consists of 3 elementary reactions:

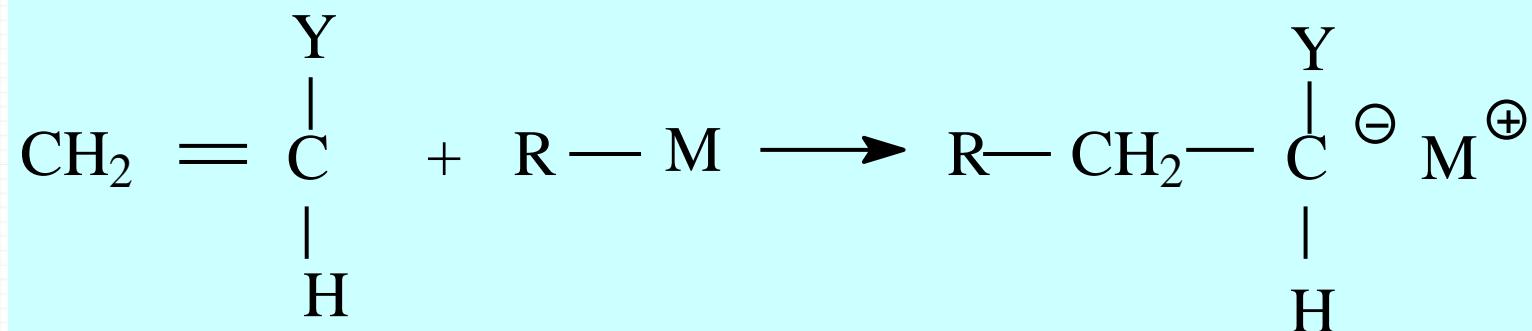
- **Initiation**
- **Propagation**
- **Termination**



6.1.2 Mechanism

(1) Initiation

The initiating progress is that the initiator is added to the monomer double bond to produce an anionic monomer active center:



In the above equation, M represent metal, and Y group is an electron attracting group, which is apt to be attacked by the carboanion of the initiator.



6.1.2 Mechanism

(1) Initiation

an initiator molecule is often in the state of association in the solution. For example:



- Before the initiation, the tetramer must dissociate to produce positive and negative ion pairs.



6.1.2 Mechanism

(1) Initiation

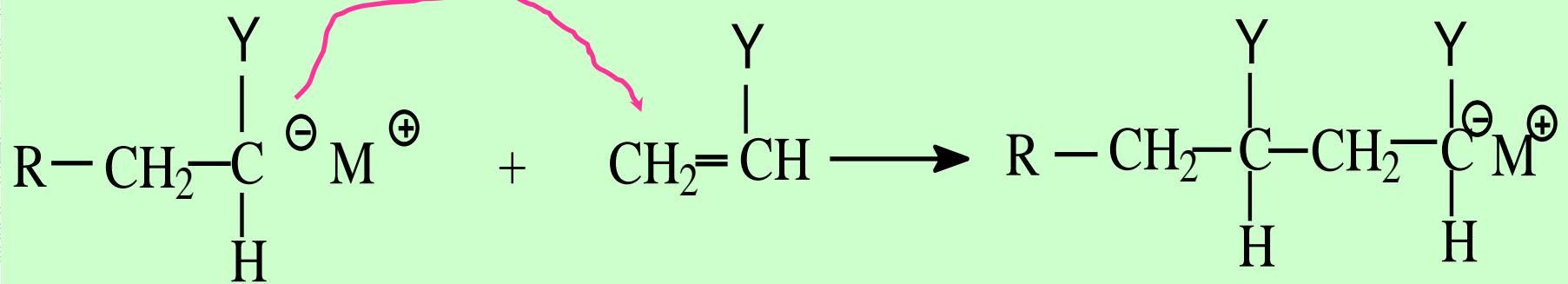
- Carboanion is greatly unstable and have very high reaction activity with the monomer double bond carbon atom, of which the electron cloud density is brought low by the influence of Y.
- Gegenion(反离子), being an ion pair, is always around the active center at the chain end.





6.1.2 Mechanism

(2) Propagation



The chain propagation is that the monomer continuously inserts the ion pairs and adds to the anion at the chain. This progress carries along until the monomer is used up or the chain termination occurs.



6.1.2 Mechanism

(2) Propagation

1. Reaction active centers are of different types, like intimate ion pairs (紧密离子对), loose ion pairs (松散离子对), free ion (自由离子), so that the corresponding propagation reaction activities are greatly different.
2. In the solvents of different polarities, the relative content of each type of the active center differs, which affects the total propagation reaction rate.



6.1.2 Mechanism

In the solvent of strong polarity or solvating power, the content of the incompact or free ion and the propagation reaction rate is high.



6.1.2 Mechanism

(2) Propagation

3. The volume and negativity of the gegenion also affect chain propagation.

The less the volume of the gegenion is, the stronger its electrophilicity is.

In the solvent of low polarity there are more compact ion pairs.



6.1.2 Mechanism

In the solvent of high polarity, for the higher solvated power, more incompact ion pairs gain.

The effect of the gegenion is very complicated.



6.1.2 Mechanism

(3) Transfer

- The chain transfer occurs less in anionic polymerization, especially under low temperature.
- The reason for the hardness of termination in anionic polymerization



6.1.2 Mechanism

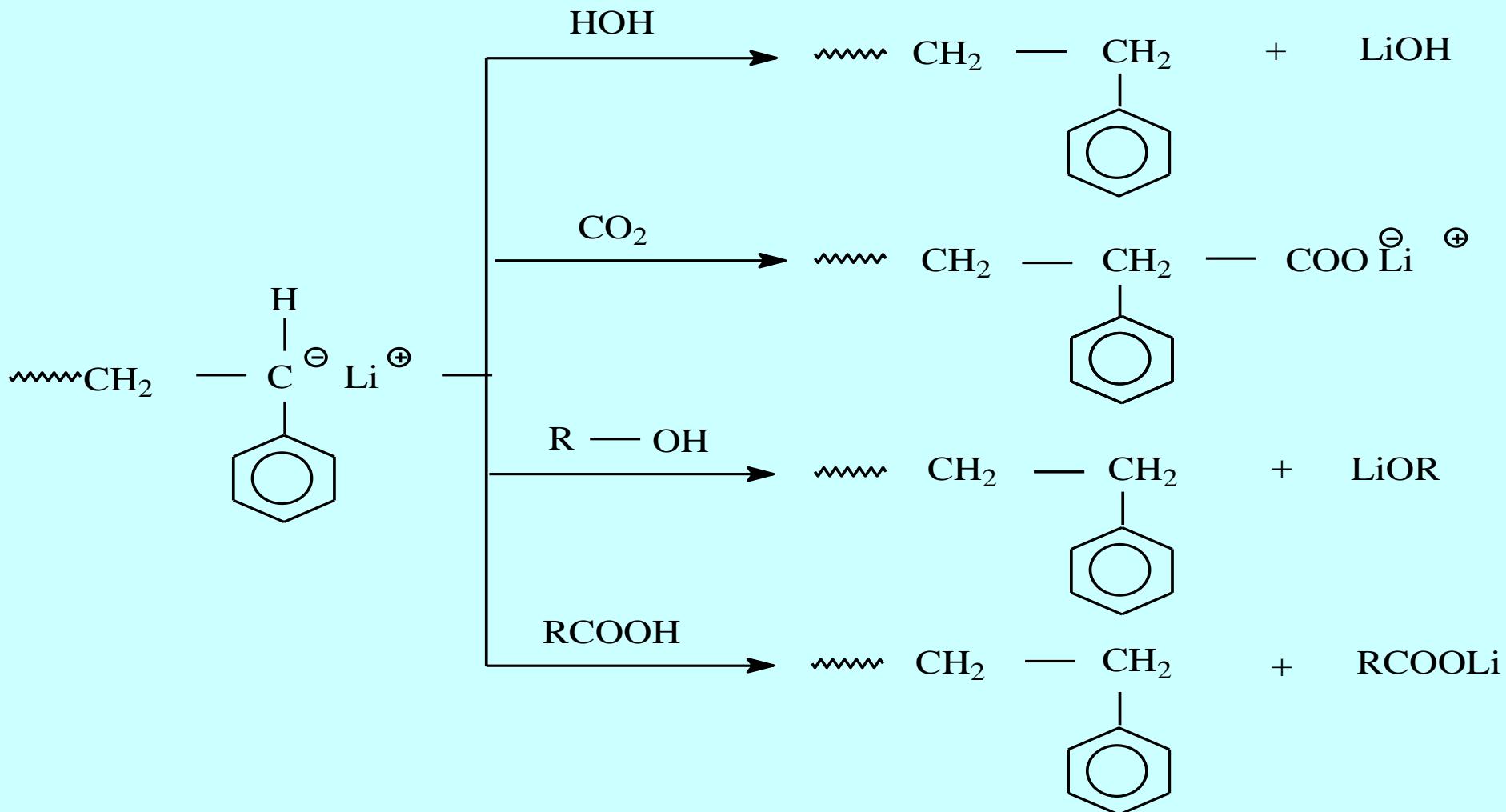
(3) Transfer and Termination

- An Active center is similarly carboanion, where double-group termination cannot occur.
- A Gegenion is a metal ion, not radical;
- Carboanion is hard to take the chain transfer with its self-generating M.



6.1.2 Mechanism

(4) Termination





6.1.2 Mechanism

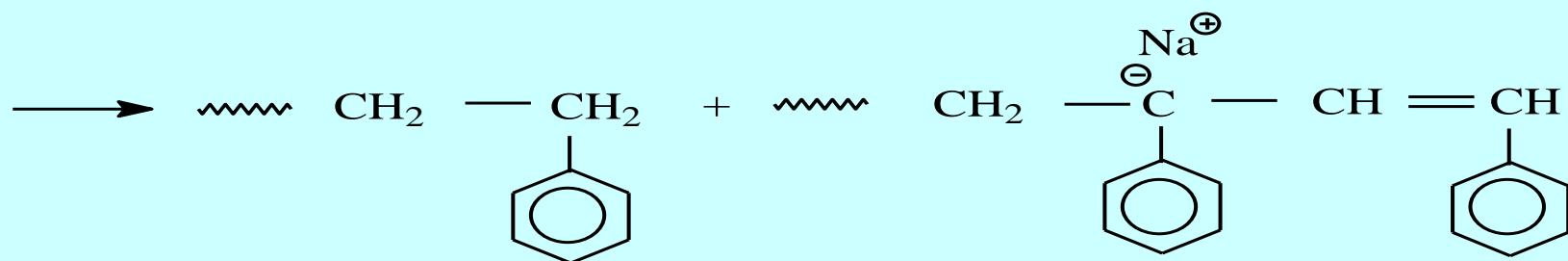
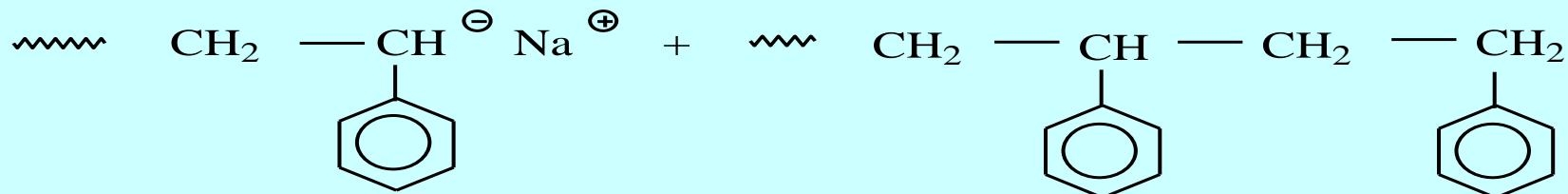
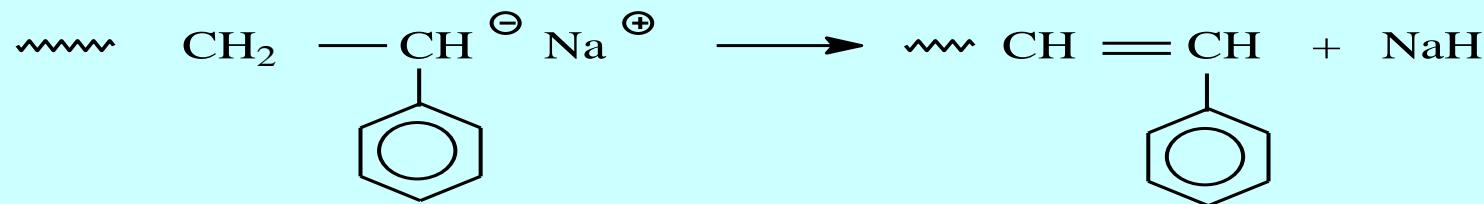
(4) Termination

- In case the terminator in the reaction system is removed completely, the activity of the living chain end can remain until all monomers are used up.
- When new monomers added, the polymerization can restart. This is so-called living polymerization.
- But in fact the activity can remain only a few days, for a trace amount of proton impurity is difficult to avoid, for example, the Si—OH group on the surface of glass is also a kind of the terminator.



6.1.2 Mechanism

Some kinds of end groups gradually loses activity in isomerization, for example, the **Isomerizatin of the styrene anion** in THF solvent.





6.1.3 The Living Polymer

- As long as no termination occurs, though all monomers are used up, the polymer still remain activity. When new monomer added, the polymerization restart. When another kind of monomers added, a block polymer produces.
- Many initiator can be used in the living polymerization. The most convenient is metal Na and naphthalene sodium initiator.

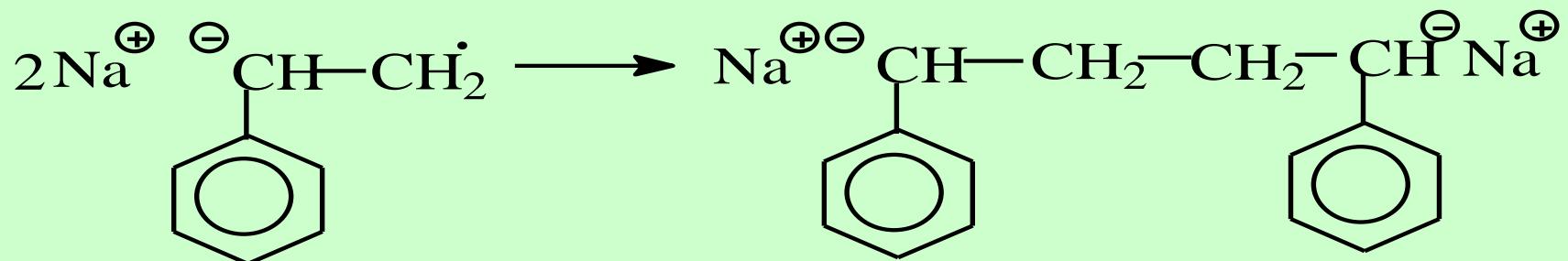
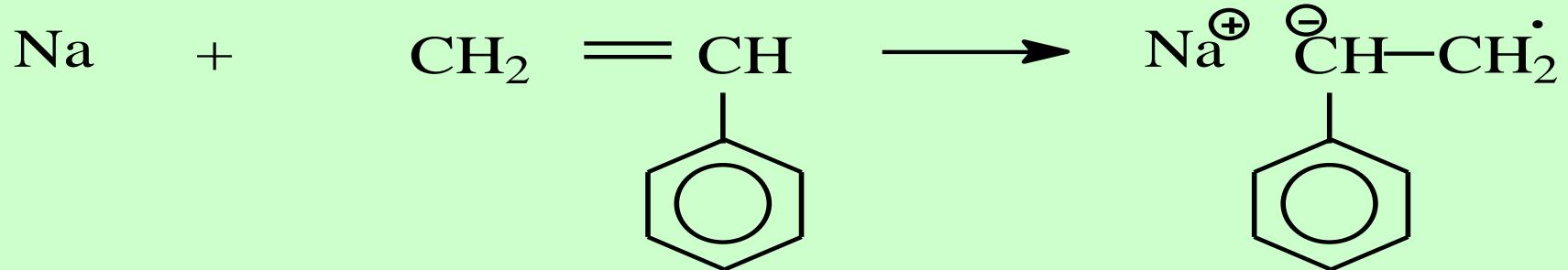


6.1.3 The Living Polymer

Alkali metal Na transfers the electron of the outer layer to the monomer, to form a monomer anion radical, which is produced, through the radical double-group termination, double anion to take on the living polymerization.



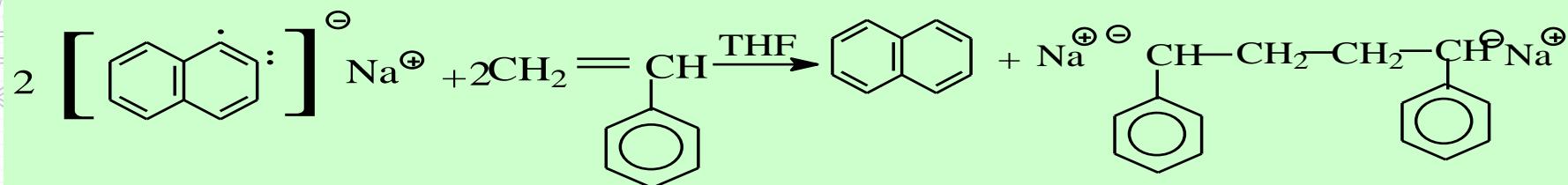
6.1.3 The Living Polymer





6.1.3 The Living Polymer

The polymerization of butadiene initiated by metal Na is one of the living polymerizations. Naphthalene sodium initiator transfer electrons to the monomer to produce double anions. The polymerization propagates in both sides of molecule as the following equation:





6.1.3 The Living Polymer

The feature of the living polymerization is that the MWD of product is quite narrow.

The reasons are:

- (1) The **initiation is very fast**, in which all the initiators immediately join in the initiating progress and are transferred to active centers.
- (2) All chains **propagates at the same rate** until monomers are used up. Every active chain has the same chance to share all of the monomers. The MW of the product is nearly similar.
- (3) **No** chain transfer and chain termination.
- (4) Depolymerization can be overlooked.



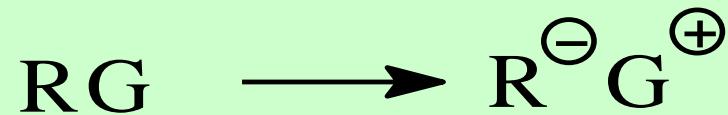
6.1.3 The application of the Living Polymerization

- To synthesis a monodisperse polymer;
- To measure the anionic polymerization rate constant;
- To prepare a block polymer;
- To prepare a telechelic polymer.



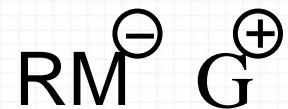
6.1.4 Kinetics

Anionic initiator nearly quantitatively and immediately dissociate into positive and negative ions which have initiation activity. All of the carboanions are added to monomers at once, and at the same time the propagation starts:





6.1.4 Kinetics

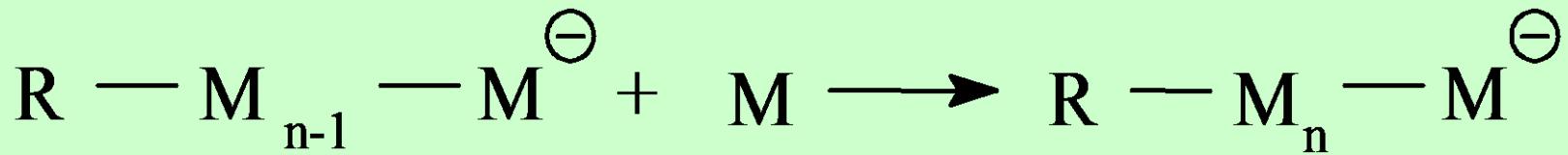
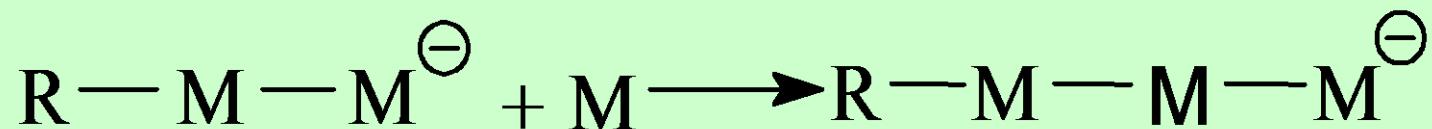
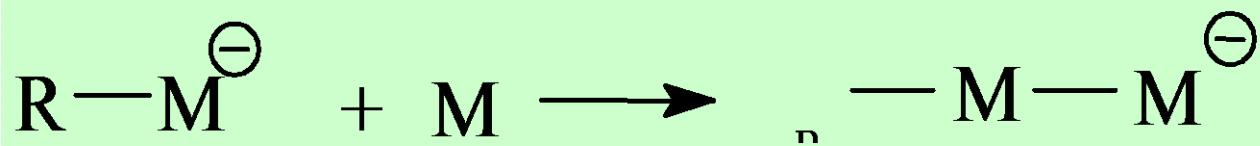


According to the solvating power of the solvent and the character of the gegenion, the active center could be a free ion or an ion pair. Ion pairs differ in compact degree of dissociation. Mostly several kinds of active centers exist proportionally.

Compactly only the primary form is considered, for example, the free ion, so the propagation can be written as:



6.1.4 Kinetics





6.1.4 Kinetics

- Suppose that a cation G^+ is always next to an anion, there is no chain terminator, and the polymerization progresses with no chain transfer and under low temperature, a living polymerization occurs.
- The reaction kinetics, which is quite easy to know, is that during the polymerization no new initiation and termination occurs. That is to say that the concentration of the active center keeps no change.
- The concentration of the active center indicates the total concentration of all active centers produced by initiator at the beginning of the polymerization.



6.1.4 Kinetics

(1) The Polymerization Rate Equation

The total polymerization rate equation is the propagation reaction rate equation (6-1)

$$R_p = -\frac{d[M]}{dt} = k_p [B^-][M]$$

(6-1)

Constant

The total concentration of all chain active centers

=

The concentration of the added initiators $[B^-A^+]_0$

Integrating this equation, the change of monomer concentration with varied time results.

It's a first order reaction.

$$\ln \frac{[M]_0}{[M]} = k_p [C]t$$

(6-2)

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6.1.4 Kinetics

(2) The Average Kinetic Chain Length

In the living polymerization, for there is no chain termination, the kinetic chain propagation will not stop until monomers are used up.

The average kinetic chain length is defined as:

$$v = \frac{\text{消耗的单体}}{\text{链活性中心数目}} = \frac{[M]_0 - [M]}{[C]_0 / n} \quad (6-3)$$

When t goes infinite, that is to say the monomers are used up, the longest kinetic chain length is:

$$v_\infty = \frac{n[M]_0}{[C]_0}$$



6.1.4 Kinetics

(3) Average DP

Average DP is the number of monomers consumed by each polymer molecule. If every active center forms one polymer molecule, then:

$$n_x = \frac{N_x}{N} = \frac{e^{-v} e^{x-1}}{(x-1)!} \quad (6-4)$$

$$\frac{\overline{X}_w}{\overline{X}_n} = 1 + \frac{\overline{X}_n}{(\overline{X}_n + 1)^2} \approx 1 + \frac{1}{\overline{X}_n} \quad (6-5)$$

X_n increasing, X_w/X_n close to 1



6.1.4 Kinetics

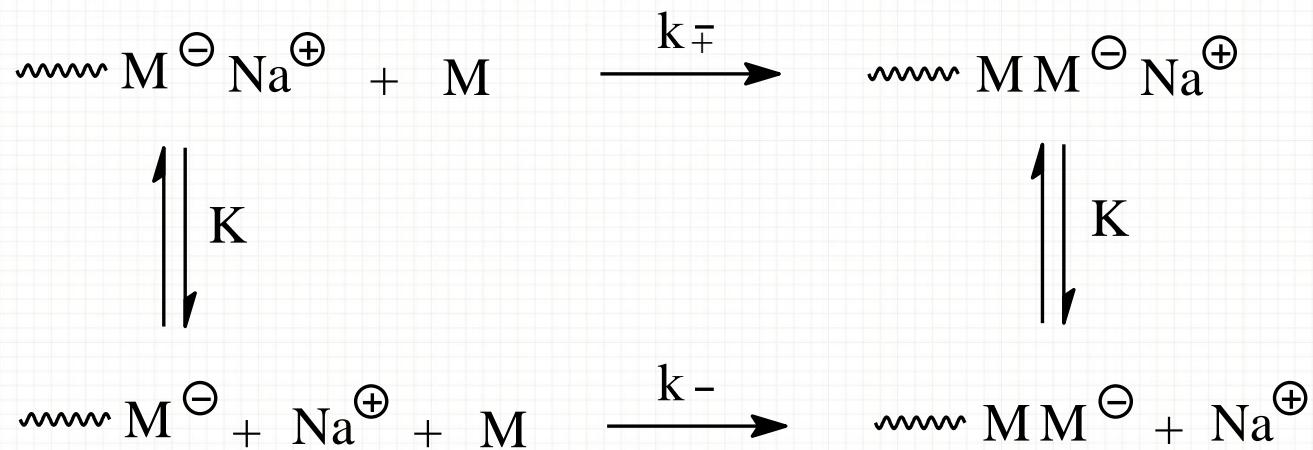
3 影响阴离子聚合速率的因素

(1) 反应介质和反离子性质影响

溶剂和反离子性质不同，离子对的松紧程度可以差别很大，影响到单体插入增长的速率。一般而言，增长活性种可以处于各种状态，如共价键、紧离子对、松离子对、自由离子等，彼此互相平衡。聚合速率是处于平衡状态的离子对和自由离子共同作用的结果。



6.1.4 Kinetics





6.1.4 Kinetics

总聚合速率是离子对 $P\cdot C^+$ 和自由离子 $P\cdot$ 聚合速率之和：

$$R_p = k_{\mp}[P\cdot C^+][M] + k_-[P\cdot][M] \quad (6-15)$$

结合 (6-12) 可得表观速率常数：

$$k_p = \frac{k_{\mp}[P\cdot C^+]+k_-[P\cdot]}{[M^-]} \quad (6-16)$$

其中活性种总浓度：

$$[M^-] = [P\cdot C^+] + [P\cdot] \quad (6-17)$$



6.1.4 Kinetics

两活性种平衡常数：

$$K = \frac{[P^-][C^+]}{[P^-C^+]} \quad (6-18)$$

一般情况下：

$$[P^-] = [C^+]$$

因此可推出：

$$[P^-] = [K(P^-C^+)]^{1/2} \quad (6-19)$$



6.1.4 Kinetics

代入式(6—15)，得

$$\frac{R_p}{[M][P^-C^+]} = k_{\mp} + \frac{K^{1/2} \cdot k_-}{[P^-C^+]^{1/2}} \quad (6-20)$$

在多数情况下，离子对解离程度很低，即

$$[M^-] \approx [P^-C^+]$$

则式(6—20)可改写为：

$$k_p = k_{\mp} + \frac{K^{1/2} \cdot k_-}{[M^-]^{1/2}} \quad (6-21)$$



6.1.4 Kinetics

通常 k_- 比 k_{\mp} 大 $10^2 \sim 10^3$ 倍。在溶剂化能力较大的溶剂中（如四氢呋喃），反离子体积越大，解离程度越低，越易形成紧对，故 k_{\mp} 随反离子半径增加而减小。

而在溶剂化能力小的二氧六环溶剂中，离子对不易电离，也不易使反离子溶剂化，因此离子对增长速率常数很小，同时随反离子半径大，离子对间距增大，单体易插入，结果 k_{\mp} 随反离子半径增加而增大。



6.1.4 Kinetics

(2) 温度对增长速率常数的影响

活性聚合的活化能一般为较小的正值（8~20 kJ/mol），因此聚合速率随温度升高略有增加，但不敏感。

升高温度可使离子对和自由离子的聚合速率常数提高，但使两者的平衡常数降低。



6.1.4 Kinetics

在不同性质的溶剂中，温度对聚合速率常数的影响不同。

在溶剂化能力较弱的溶剂（如二氧六环）中，离子对解离能力较弱，温度对 K 的影响较小，增长速率主要取决于离子对，表观活化能较大，温度对聚合速率影响较大。在溶剂化能力较强的溶剂中，离子对的解离能力较大，温度对 K 的影响也较大。因此温度对 K 和 k_{-} 、 k_{+} 的影响抵消，表观活化能较低，则温度对聚合速率影响较小。



6.1.4 Kinetics

6.3.4 丁基锂的缔合现象和定向聚合作用

丁基锂是目前应用最广的阴离子聚合引发剂。实践中发现若溶剂体系选择不当，丁基锂的引发活性很低，这可能是由于丁基锂的缔合作用引起。

丁基锂在特定条件下对聚合产物具有定向作用。

(1) 丁基锂的缔合现象

丁基锂在非极性溶剂如苯、甲苯、己烷中存在缔合现象，缔合度2 ~ 6不等。缔合分子无引发活性。



6.1.4 Kinetics

一般而言，丁基锂浓度低时，基本不存在缔合现象。在THF等极性溶剂体系中，缔合也不重要。

例如，动力学研究表明，在苯乙烯以丁基锂为引发剂，以苯为溶剂的阴离子聚合中，引发速率和增长速率分别为丁基锂的 $1/6$ 级和活性链浓度的 $1/2$ 级，表明丁基锂的缔合度为6，而活性链的缔合度为2。

丁基锂的缔合现象使聚合速率显著降低。



6.1.4 Kinetics

(2) 丁基锂的定向作用

在阴离子聚合中，溶剂和反离子的性质在一定程度上能控制大分子链的立体规整性。

丁二烯和异戊二烯的自由基聚合只得到10% ~ 20% 顺式1,4 结构；在非极性溶剂中，丁二烯用丁基锂引发，可得 30 ~ 40% 顺式1,4 结构；异戊二烯用丁基锂引发，顺式结构达 93 ~ 94 %。在 THF 等极性溶剂中，丁二烯用丁基锂引发，顺式结构为0。
(参见表6—1和表6—2)



6.1.4 Kinetics

表6—1 溶剂和反离子对聚丁二烯微结构的影响 (T = 0°C)

溶剂和反离子	聚丁二烯微结构, %		
	顺式 1,4	反式 1,4	1,2
在戊烷中聚合			
Li	35	52	13
Na	10	25	65
K	15	40	45
Rb	7	31	62
Cs	6	35	59
在四氢呋喃中聚合			
Li-萘	0	4	96
Na-萘	0	9	91
K-萘	0	18	82
Rb-萘	0	25	75
Cs-萘	0	25	75
自由基聚合, 5°C	15	68	17



6.1.4 Kinetics

表6—2 溶剂和反离子对聚异戊二烯微结构的影响 ($T = 0^\circ\text{C}$)

引 发 剂	溶 剂	聚 合 物 结 构, %		
		顺 式 1,4	反 式 1,4	1,2
C ₄ H ₉ Li	戊 烷	9		
C ₄ H ₉ Li	90 戊 烷 / 10 THF		26	9
C ₄ H ₉ Li	THF			26
Li	戊 烷	94		
Li	(C ₂ H ₅) ₂ O		49	5
Na	戊 烷		743	6
Na	THF			18
Cs	戊 烷	4	51	8



6.1.4 Kinetics

(4) Factors Influencing the Chain Propagation Rate Constant

- If all initiators can quantitatively dissociate into positive and negative ions before chain propagation and no chain termination occurs, then according to kinetic equations
- (6-1) and (6-2), the polymerization rate R_p , can be determined, or the rate constant k_p can be directly determined by the monomer transfer ratio.

$$R_p = -\frac{d[M]}{dt} = k_p [B^-][M]$$

$$\ln \frac{[M]_0}{[M]} = k_p [C]t$$



6.1.4 Kinetics

(4) Factors Influencing the Chain Propagation Rate Constant

- The active center of chain propagation can be free anions, ion pairs or the mixture of both.
- Found by experiment, k_p is affected by the solvent and the property of gegenion.
- If there is only one kind of the active center, free anions, the solvent and the type of gegenion isn't effective.
- So the form of the active center is mainly or totally ion pairs.



6.1.4 Kinetics

(4) Factors Influencing the Chain Propagation Rate Constant

In principle during the polymerization progress the equilibrium between ion pairs and free ions always exists:



k_{\pm}
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6.1.4 Kinetics

(4) Factors Influencing the Chain Propagation Rate Constant

Diluted by a solvent, that is to say, the concentration of $[R-G]_0$ reduces , the dissociation equilibrium moves rightward. Extrapolating the experimental value of k_p to the direction of solution infinite dilution, the chain propagation rate constant of the free ion, k_- , gains. It proved experimentally that the k_- value of the free ion is much larger than that of the ion pair.



6.1.4 Kinetics

(4) Factors Influencing the Chain Propagation Rate Constant

Polarity and solvating of the solvent affect the dissociation degree of the ion pair. So the comprehensive value of the apparent propagation rate constant k_p must be affected, too.

Table 6-6 shows the effect of the solvent on k_p of styrene anionic polymerization.

Determined in styrene polymerization initiated by naphthalene sodium under 25°C

Solvent	Dielectric constant /Debby	K_p (L/mol.s)
Benzene	2.2	2
1,4-dioxane	2.2	5
THF	7.6	550
1,2-dimethoxy ethane	5.5	3800

The property and solvated power of gegenion also affect the dissociation degree of the ion pair, so as to affect value of the propagation rate constant of the ion pair.

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6.1.4 Kinetics

The effect of the temperature, which varies with different solvents and polymerization systems, can only be determined by experiment.



6.1.4 Kinetics

On the whole, polymerization feature is mainly determined by chain propagation, of which the activation energy is very low, and varies little with the change of **the temperature**.

But dissociation equilibrium of the ion pair, the solvating power, and even the side reaction are affected, where a current rule is hard to be summed up.

Without chain transfer and termination, polymer MW is not easily affected by the temperature.



6.1.4 Kinetics

(5) Association Phenomenon of Alkyl Lithium

- Alkyl lithium, for example, butyl lithium is a kind of the initiator used commonly in the anionic polymerization.
- In the nonpolarity solvent, like benzene, methylbenzene, hexyl — hydride and cyclohexane, there is dissociation phenomenon, which makes effective initiator concentration reduced. As a result, polymerization rate obviously lowers.



6.1.4 Kinetics

Fox example:

Styrene polymerization in benzene solvent initiated by butyl lithium is several orders of magnitude lower than that by naphthalene sodium.



6.1.4 Kinetics

(5) Association Phenomenon of Alkyl Lithium

- When the concentration of the initiator is very low(lower than $10^{-4} \sim 10^{-5}$), the association of ortho butyl lithium occurs litter. Both the initiation rate and the propagation rate are proportional to the concentration of ortho butyl lithium.
- When the concentration of the initiator increase, R_i and R_p are directly proportional to the sixth root and square root of the concentration of ortho butyl lithium,respectively.



6.1.4 Kinetics

(5) Association Phenomenon of Alkyl Lithium

- The dissociation phenomenon also exists in other kind of alkyl lithium initiator, but dissociation number is not always same.

For example:

Dissociation number of butyl lithium could be 6, and that of secondary and tertiary butyl lithium are 4.



6.1.4 Kinetics

(5) Association Phenomenon of Alkyl Lithium

- All of the above association phenomena, besides disappear in a highly dilute solution, completely disappear in a polar solvent, for example, THF. The Polymerization rate is greatly enhanced. Adding polybasic amine , for example, N, N, N', N'—tetramethylethylene diamine (TMEDA), polyether, which is a comparatively strong complexing agent, can destroy the association of alkyl lithium, too.

Elevating polymerization temperature can also weaken association.



6.2 Cationic Polymerization

1. Monomer and Initiator

Monomer:

push-electron group, the activity of M depends on the push-election ability of substitute.

Initiator:

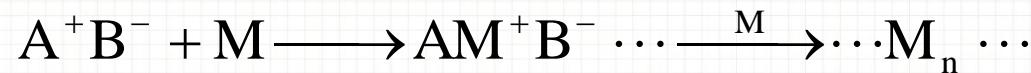
**proton acids or Lewis acids (coinitiators)
the substances which supply protons or carbocations**



6.2 Cationic Polymerization

阳离子聚合 (Cationic polymerization)

阳离子聚合通式可表示如下：



式中 B^- 为反离子，又称抗衡离子（通常为引发剂碎片，带反电荷）。 A^+ 为阳离子活性中心（碳阳离子，氧鎓离子），难以孤立存在，往往与反离子形成离子对。



6.2 Cationic Polymerization

6.2.1 阳离子聚合的单体

(1) α - 烯烃

能用于阳离子聚合的单体有烯类化合物、羧基化合物、含氧杂环化合物等，以烯类单体为重点。

原则上，具有推电子取代基的烯类单体都可进行阳离子聚合。但实际上能否进行阳离子聚合取决于取代基推电子能力的强弱和形成的碳阳离子是否稳定。



6.2 Cationic Polymerization

乙烯无取代基，不能进行阳离子聚合。

丙烯和丁烯上的甲基和乙基都是推电子基团，但仅一个烷基，推电子能力太弱，增长速率很低，实际上只能得到低分子量油状物。

异丁烯含两个推电子的甲基，双键电子云密度大，易受阳离子进攻。聚合物链中— CH_2 —受到四个甲基保护，减少了副反应，因此产物稳定，可得高分子量的线性聚合物。



6.2 Cationic Polymerization

更高级的 α - 烯烃，由于空间位阻效应较大，一般不能通过阳离子聚合得到高分子量聚合物。

异丁烯：唯一一个具有实际工业价值的能进行阳离子聚合的 α - 烯烃单体



6.2 Cationic Polymerization

(2) 烷基乙烯基醚

烷氧基的诱导效应使双键电子云密度降低，但是氧原子上的未共有电子对与双键形成 p - π 共轭效应，双键电子云增加。与诱导效应相比，共轭效应对电子云偏移的影响程度更大。事实上，烷氧基乙烯基醚只能进行阳离子聚合。

但当烷基换成芳基后，由于氧上未共有电子对也能与芳环形成共轭，分散了双键上的电子云密度，从而使其进行阳离子聚合的活性大大降低。



6.2 Cationic Polymerization

(3) 共轭单体

苯乙烯，丁二烯等含有共轭体系的单体，由于其 π 电子云的流动性强，易诱导极化，因此能进行阳离子、阴离子或自由基聚合。但聚合活性较低，远不及异丁烯和烷基乙烯基醚，故往往只作为共聚单体应用。

基本原则：

由于离子聚合的工艺要求较高，故能用自由基聚合的，尽可能不采用离子聚合。



6.2 Cationic Polymerization

6.2.2 阳离子聚合的引发体系

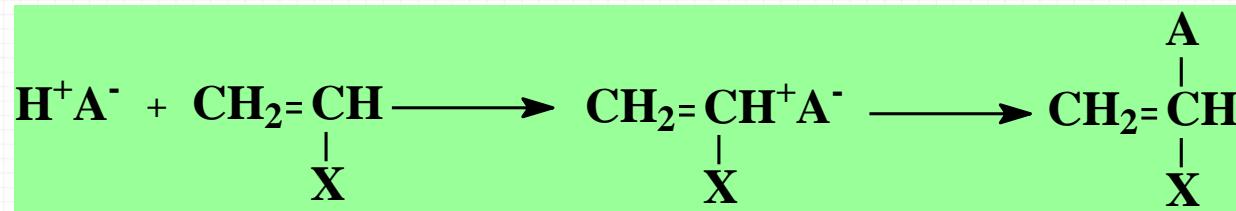
阳离子聚合的引发方式有两种：一是由引发剂生成阳离子，进而引发单体，生成碳阳离子；二是电荷转移引发。碳阳离子引发剂包括质子酸、Lewis酸等，电荷转移引发剂有乙烯基咔唑和四腈基乙烯等。其中Lewis酸是最重要的阳离子聚合引发剂。



6.2 Cationic Polymerization

1. 质子酸

H_2SO_4 、 H_3PO_4 、 HClO_4 、 Cl_3CCOOH 等强质子酸在非水介质中离解出部分质子，使烯烃质子化，从而引发烯烃的阳离子聚合。但要求既有足够的酸强度，同时酸根的亲核性又不能太强，以免与质子或阳离子结合形成共价键，造成链终止。





6.2 Cationic Polymerization

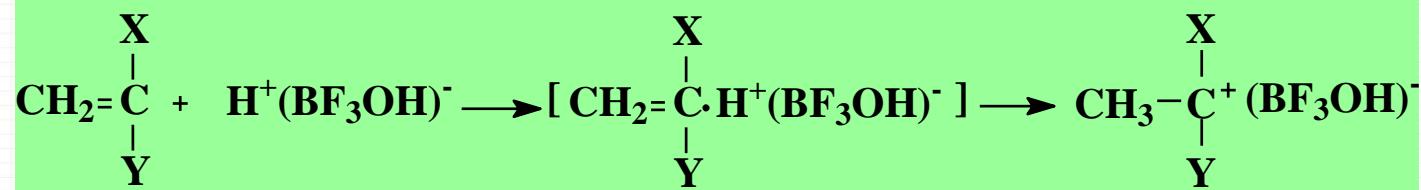
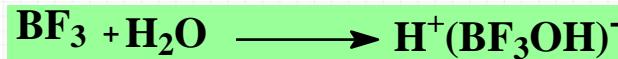
2. Lewis酸

AlCl_3 , BF_3 , SnCl_4 , ZnCl_2 , TiBr_4 等是最常见的阳离子聚合引发剂（俗称Friedel-Grafts催化剂），聚合大多在低温下进行。

Lewis酸单独使用时活性不高，往往与少量共引发剂（如水）共用，两者形成络合物离子对，才能引发阳离子聚合，例如 $\text{BF}_3\text{-H}_2\text{O}$ 引发体系。



6.2 Cationic Polymerization



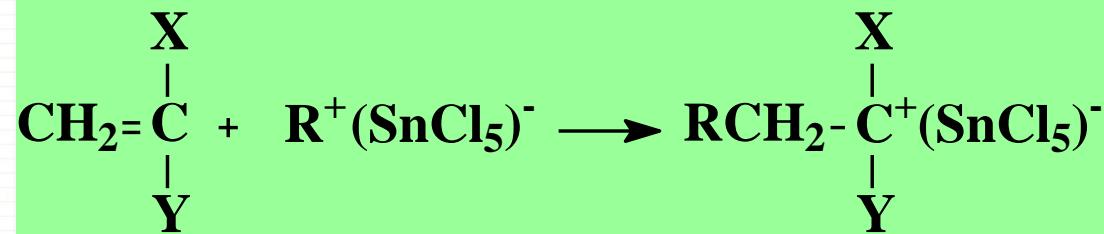
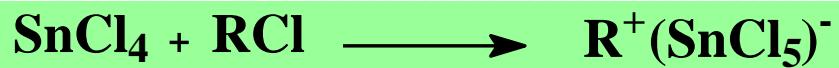
BF₃-H₂O引发体系的引发机理



6.2 Cationic Polymerization

共引发剂共有两类：一类是质子供体，如H₂O, ROH, RCOOH, HX等；另一类是碳阳离子供体，如RCl, RCOX, (RCO)₂O, ROR等。

引发剂和共引发剂的共引发作用如下：





6.2 Cationic Polymerization

引发剂和共引发剂的不同组合，可得到不同引发活性的引发体系。

主引发剂的活性与接受电子的能力、酸性强弱有关，顺序如下：





6.2 Cationic Polymerization

异丁烯以 SnCl_4 为引发剂时，共引发剂的活性顺序为：



异丁烯以 BF_3 为引发剂时，共引发剂的活性比为：
：

水: 醋酸: 甲醇 = 50 : 1.5 : 1



6.2 Cationic Polymerization

通常引发剂和共引发剂有一最佳比，此时聚合速率最快，分子量最大。最佳比还与溶剂性质有关。

共引发剂过量可能生成氧鎓离子，其活性低于络合的质子酸，使聚合速率降低。





6.2 Cationic Polymerization

在工业上，一般采用反应速率较为适中的 AlCl_3 — H_2O 引发体系。

对有些阳离子聚合倾向很大的单体，可不需要共引发剂，如烷基乙烯基醚。



6.2 Cationic Polymerization

3. 其他引发剂

其它阳离子引发剂有碘、高氯酸盐、六氯化铅盐等。如碘分子歧化成离子对，再引发聚合：

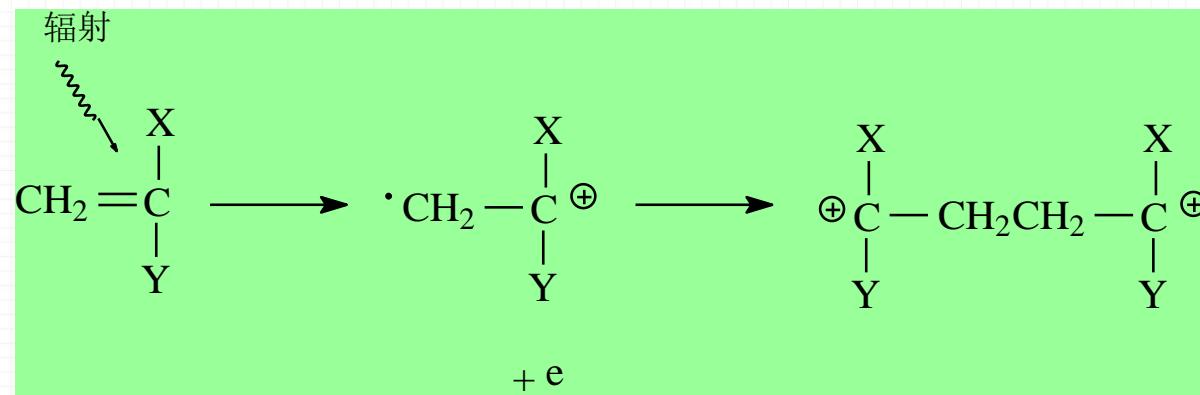


形成的碘阳离子可引发活性较大的单体，如对甲氧基苯乙烯、烷基乙烯基醚等。



6.2 Cationic Polymerization

阳离子聚合也能通过高能辐射引发，形成自由基阳离子，自由基进一步偶合，形成双阳离子活性中心：



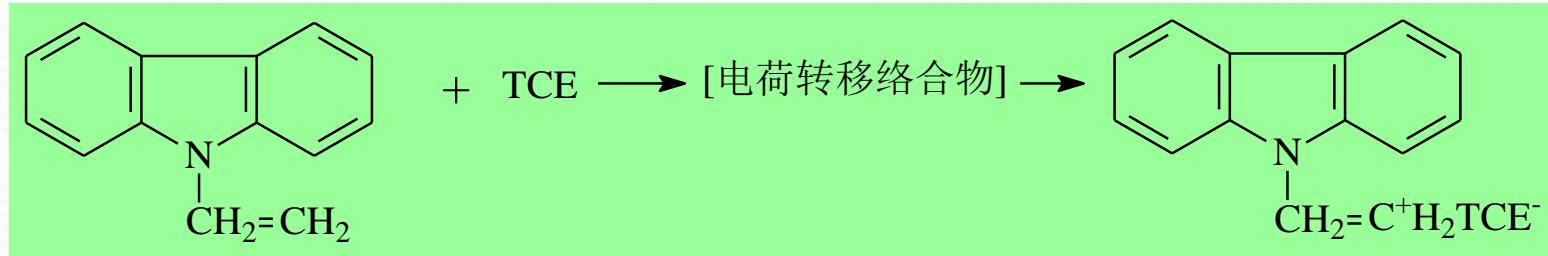
辐射引发阳离子聚合的特点是无反离子存在。



6.2 Cationic Polymerization

4. 电荷转移引发剂

能进行阳离子聚合的单体都是供电体，当与适当的受电体配合时，能形成电荷转移络合物。在外界能量的作用下，络合物会解离形成阳离子而引发聚合。如乙烯基咔唑和四腈基乙烯（TCE）的电荷转移引发：





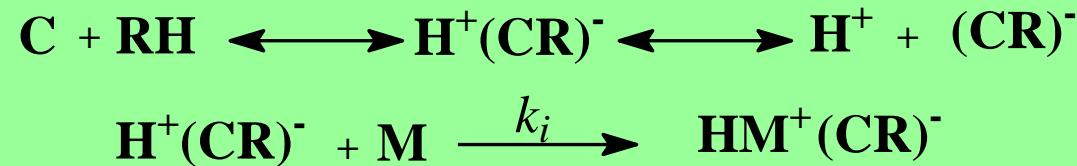
6.2 Cationic Polymerization

6.2.3 阳离子聚合机理及动力学

1. 阳离子聚合机理

阳离子聚合也是由链引发、链增长和链终止等基元反应组成的。与自由基聚合相比，阳离子聚合有其自身的特点，如快引发、快增长、易转移、难终止，链转移是终止的主要的方式等。

1) 链引发





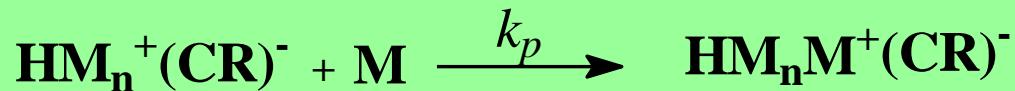
6.2 Cationic Polymerization

引发剂首先与质子给体（RH）反应，形成络合离子对，小部分离解成质子和自由离子，两者之间建立平衡。然后引发单体聚合。阳离子引发活化能为 $E_i = 8.4\sim21 \text{ kJ/mol}$ （自由基聚合的 $E_i = 105\sim150 \text{ kJ/mol}$ ），引发极快，瞬间完成。



6.2 Cationic Polymerization

2) 链增长



引发反应生成的碳阳离子活性中心与反离子始终构成离子对，单体分子不断插入其中而增长。其特点为：

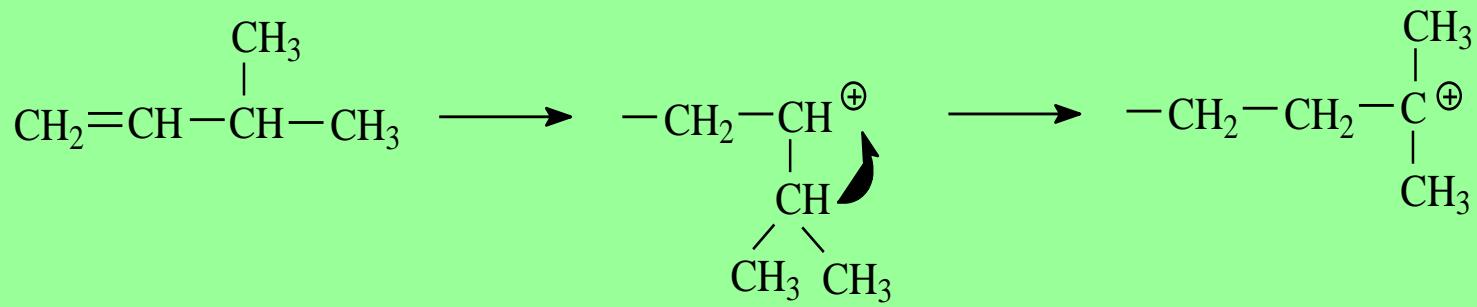


6.2 Cationic Polymerization

- a. 增长反应是离子和分子间的反应，活化能低，速度快，几乎与引发同时完成 ($E_p=8.4\sim21\text{ kJ/mol}$)。
- b. 离子对的紧密程度与溶剂、反离子性质、温度等有关，对聚合速率、分子量和构型有较大影响。
- c. 常伴有分子内重排，异构成更稳定的结构，例如3-甲基-1-丁烯聚合，先形成二级碳阳离子，然后转化为更稳定的三级碳阳离子。因此分子链中可能含有两种结构单元。



6.2 Cationic Polymerization



二级碳阳离子（仲碳阳离子）

三级碳阳离子（叔碳阳离子）



6.2 Cationic Polymerization

6.2.4 链转移和链终止

离子聚合的活性种带有电荷，无法双基终止，因此只能通过单基终止和链转移终止，也可人为添加终止剂终止。

自由基聚合的链转移一般不终止动力学链，而阳离子聚合的链转移则有可能终止动力学链。因此阳离子聚合的链终止可分为动力学链不终止的链终止反应和动力学链终止的链终止反应两类。

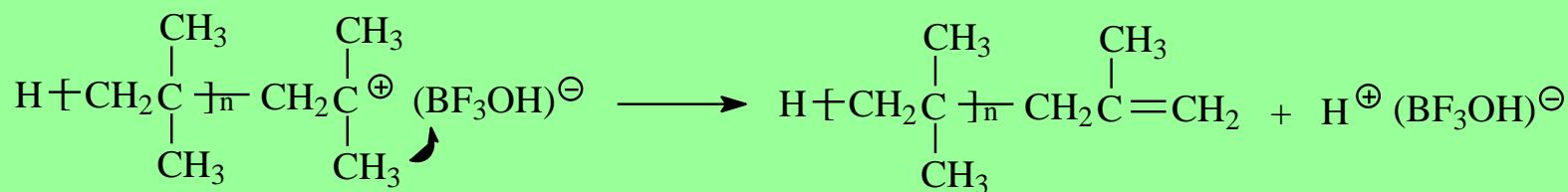


6.2 Cationic Polymerization

(1) 动力学链不终止

(i) 自发终止（向反离子转移终止）

增长离子对重排导致活性链终止成聚合物，再生出引发剂—共引发剂络合物，继续引发单体，动力学链不终止。

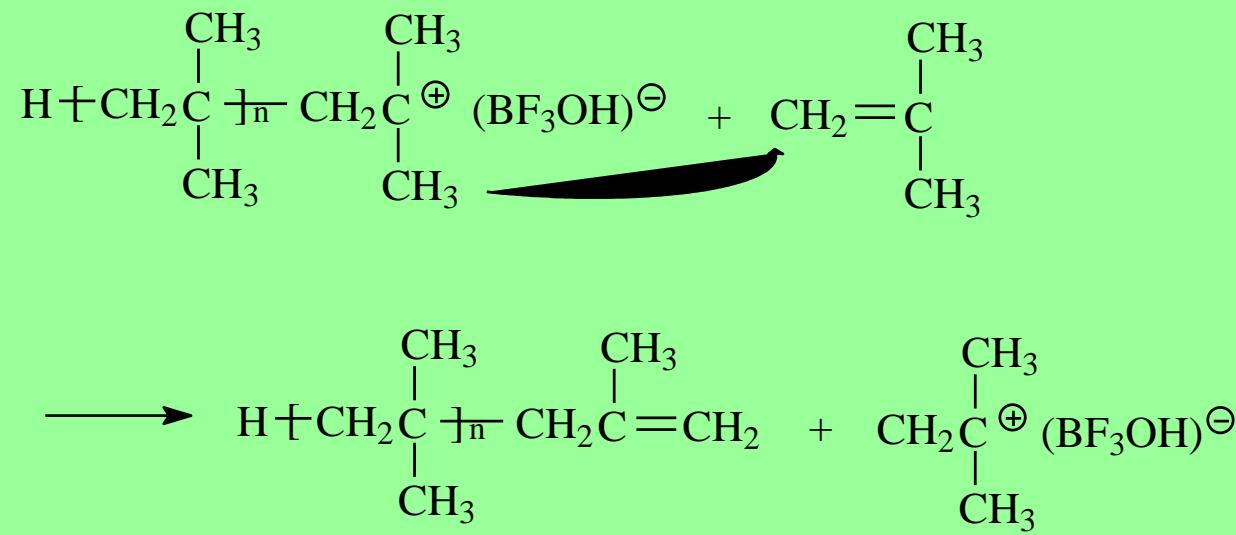




6.2 Cationic Polymerization

(ii) 向单体转移终止

活性种向单体转移，形成含不饱和端基的大分子，同时引发剂再生，动力学链不终止。





6.2 Cationic Polymerization

向单体链转移是阳离子聚合最主要终止方式之一。 C_M 约 $10^{-2} \sim 10^{-4}$ ，比自由基聚合的 C_M 大（ $10^{-4} \sim 10^{-5}$ ），因此是控制分子量的主要因素。

为了保证聚合物有足够大的分子量，阳离子聚合一般在低温下进行。

例如，异丁烯的聚合， $T = 0 \sim -40^\circ\text{C}$ ， $M_n < 5$ 万， $T = -100^\circ\text{C}$ ， $M_n = 5$ 万~ 500 万。



6.2 Cationic Polymerization

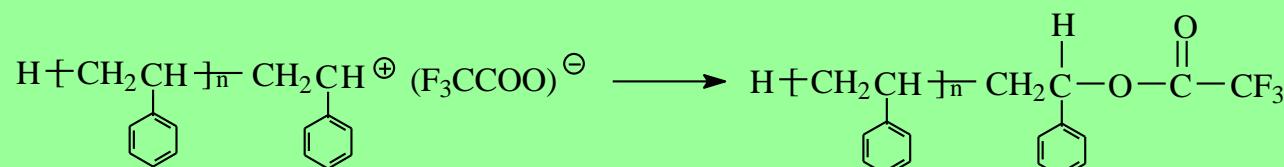
(2) 动力学链终止

(i) 反离子向活性中心加成终止

反离子亲核性足够强时会与增长的碳阳离子以共价键结合而终止。



例如三氟乙酸引发的苯乙烯聚合：



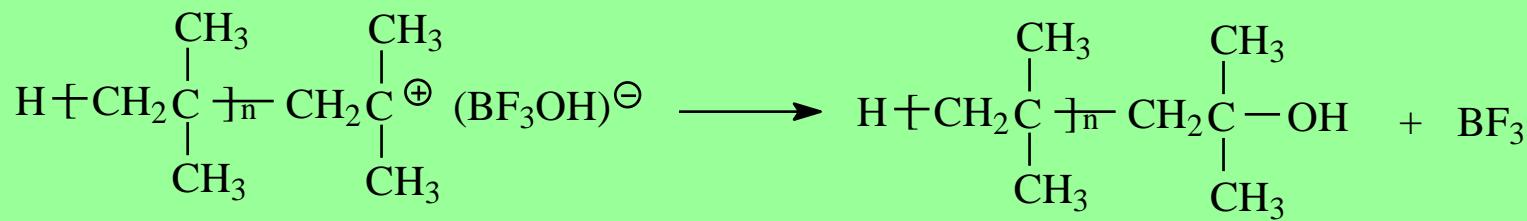


6.2 Cationic Polymerization

(ii) 活性中心与反离子中的阴离子碎片结合终止

活性中心与反离子中的阴离子碎片结合而终止，从而使引发剂—共引发剂比例改变。

例如用 $\text{BF}_3-\text{H}_2\text{O}$ 引发的异丁烯聚合。





6.2 Cationic Polymerization

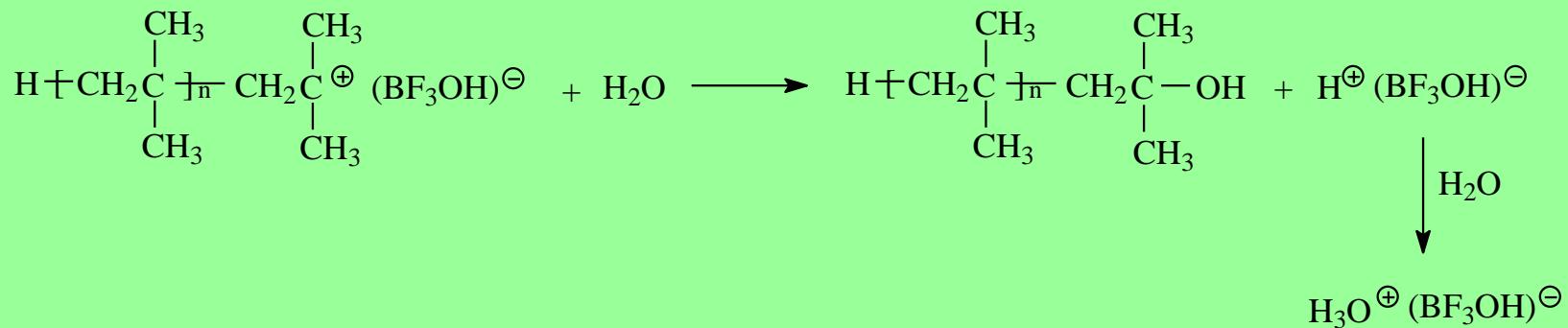
(iii) 添加链终止剂

阳离子聚合自身不容易终止，通过添加水、醇、酸、醚、胺、醌等终止剂可使聚合终止。





6.2 Cationic Polymerization



形成的氧鎓离子活性低，不能再引发聚合。

阳离子聚合的特点：

快引发，快增长，易转移，难终止



6.2 Cationic Polymerization

6.2.5 阳离子聚合动力学

阳离子聚合速率快，对环境条件苛刻，微量杂质对聚合速率影响很大，实验重复性差；引发速率很快，而真正的终止反应实际上不存在，稳态假定很难成立等等，使得其动力学研究复杂化。因此只能在特定条件下做动力学研究。



6.2 Cationic Polymerization

(1) 聚合速率

离子聚合无双基终止，无自动加速现象，往往以低活性的 SnCl_4 为引发剂，向反离子转移作为终止方式时的聚合作为典型进行讨论。各基元反应的动力学方程为：

链引发：

$$\begin{aligned} R_i &= k_i [\text{H}^+ (\text{CR})^\ominus][\text{M}] \\ &= \text{K}k_i[\text{C}][\text{RH}][\text{M}] \end{aligned} \quad (6-1)$$

链增长：

$$R_p = k_p [\text{HM}^+ (\text{CR})^\ominus][\text{M}] \quad (6-2)$$

链终止：

$$R_t = k_t [\text{HM}^+ (\text{CR})^\ominus] \quad (6-3)$$



6.2 Cationic Polymerization

其中 $[HM^+(CR)^{\ominus}]$ 为所有增长离子对的总浓度；
 K 为引发剂和共引发剂络合平衡常数。

为便于处理，仍作稳态假定， $R_i = R_t$ 。

则有：

$$[HM^+(CR)^{\ominus}] = \frac{Kk_i[C][RH][M]}{k_t} \quad (6-4)$$

聚合速率方程为：

$$R_p = \frac{Kk_i k_p [C][RH][M]^2}{k_t} \quad (6-5)$$



6.2 Cationic Polymerization

由此可见，速率对引发剂和共引发剂均呈一级反应，对单体浓度则呈二级反应。自发终止时，引发剂浓度为常数，而向反离子加成时，引发剂浓度下降。



6.2 Cationic Polymerization

(2) 聚合度

在阳离子聚合中，向单体转移和向溶剂转移是主要的终止方式，虽然转移后聚合速率不变，但聚合度降低。转移速率方程为：

$$R_{tr,M} = k_{tr,M} [HM^+ (CR)^\ominus] [M]$$

$$R_{tr,S} = k_{tr,S} [HM^+ (CR)^\ominus] [S]$$

参照自由基聚合，可将阳离子聚合物的聚合度表达为：

$$\frac{1}{\overline{X}_n} = \frac{k_t}{k_p[M]} + C_M + C_S \frac{[S]}{[M]} \quad (6-6)$$



6.2 Cationic Polymerization

单基终止时：

$$\overline{X_n} = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t} \quad (6-7)$$

向单体转移终止时：

$$\overline{X_n} = \frac{R_p}{R_{tr,M}} = \frac{k_p}{k_{tr,M}} = \frac{1}{C_M} \quad (6-8)$$

向溶剂转移终止时：

$$\overline{X_n} = \frac{R_p}{R_{tr,S}} = \frac{k_p[M]}{k_{tr,S}[S]} = \frac{1}{C_S} \cdot \frac{[M]}{[S]} \quad (6-9)$$

6.2 Cationic Polymerization

例如，聚异丁烯的制备采用在 CH_3Cl 溶剂中的阳离子聚合，终止方式有向单体链转移和向溶剂链转移两种，取决于温度的影响。聚合温度低于 -100°C ，主要向单体转移终止；聚合温度高于 -100°C ，主要向溶剂转移终止。见图5—1。

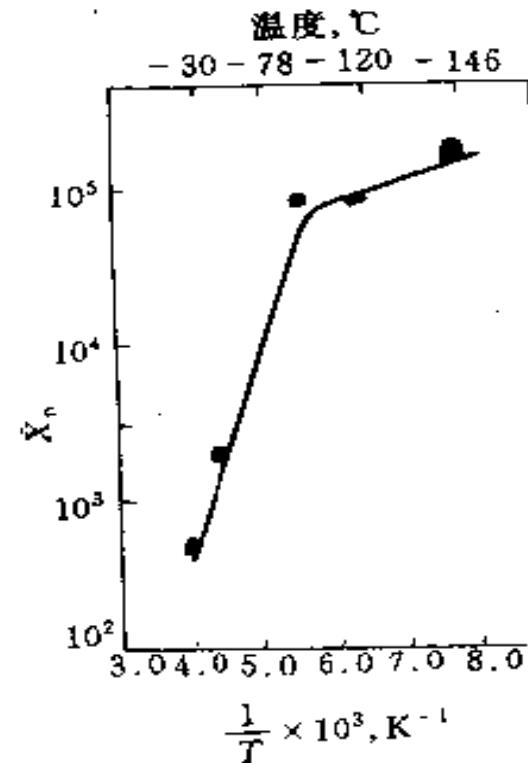


图6—1 AlCl_3 引发异丁烯聚合时温度与聚合度的关系

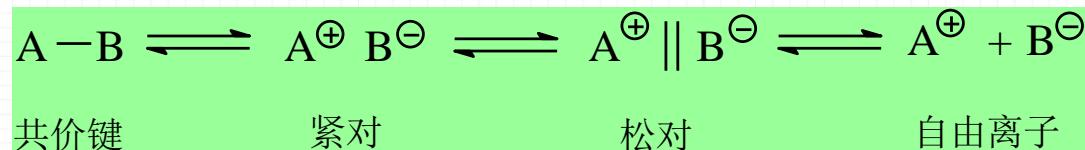


6.2 Cationic Polymerization

6.2.6 影响阳离子聚合的因素

1. 反应介质（溶剂）的影响

在阳离子聚合中，活性中心离子与反离子形成离子对，增长反应在离子对中进行。溶剂的极性大小影响离子对的松紧程度，从而影响聚合速率。



一般情况下，离子对为松对时的聚合速率和聚合度均较大。溶剂的极性越大，松对比例越高，因此聚合速率和聚合度都较大。



6.2 Cationic Polymerization

2. 反离子的影响

反离子的亲核性强，易与活性中心离子结合，使链终止。如 Cl^- 一般不宜作为反离子。

其次，反离子的体积越大，离子对越疏松，聚合速率越大。

例如，用 I_2 、 $\text{SnCl}_4-\text{H}_2\text{O}$ 、 HClO_4 引发苯乙烯在1,2—二氯乙烷中25°C下的阳离子聚合，聚合速率

常数分别为0.003、0.42、1.70 L/mol.s。



6.2 Cationic Polymerization

3. 聚合温度的影响

根据Arrhenius公式，从式(6—5)和(6—7)可知，聚合速率和聚合度的综合活化能分别为：

$$E_R = E_i + E_p - E_t \quad (6-10)$$

$$\bar{E}_{X_n} = E_p - E_t \quad (6-11)$$



6.2 Cationic Polymerization

通常，聚合速率总活化能：

$$E_R = -21 \sim -41.8 \text{ kJ/mol}$$

因此往往出现聚合速率随温度降低而增加的现象。

E_{Xn} 一般为 $-12.5 \sim -29 \text{ kJ/mol}$ ，表明聚合度随温度降低而增加。这也是阳离子聚合一般在低温下进行的原因，同时低温下进行聚合还可以减弱副反应。



6.2 Cationic Polymerization

举例一：异丁烯聚合

AlCl_3 为引发剂，氯甲烷为溶剂，在 $0 \sim -40^\circ\text{C}$ 聚合，得低分子量（<5万）聚异丁烯，主要用于粘结剂、密封材料等；在 -100°C 下聚合，得高分子量产物（5万~100万），主要用作橡胶制品。



6.2 Cationic Polymerization

聚例二：丁基橡胶制备

异丁烯和少量异戊二烯(1~6%)为单体， AlCl_3 为引发剂，氯甲烷为稀释剂，在 -100°C 下聚合，瞬间完成，分子量达20万以上。

丁基橡胶冷却时不结晶， -50°C 柔软，耐候，耐臭氧，气密性好，主要用作内胎。



6.2 Brief Summary of the Cationic Polymerization

Requirement: of which the ability to supply protons or carbocations is strong and the gegenion nucleophilicity is weak.



6.2 Brief Summary of the Cationic Polymerization

2. Mechanism

Initiation: $E_i = 8.4 \text{ -- } 21 \text{ KJ/mol}$

Propagation: more complicated than the radical polymerization

- a) Diversiform spike;
- b) Carbocation being apt to isomerize



6.2 Brief Summary of the Cationic Polymerization

Transfer: mainly to monomer, solvent and gegenion

Cationic polymerization is apt to transfer, and its CM is larger than that of the radical polymerization

Termination: single-group termination, mainly to the gegenion reaction

Summary: fast initiation, rapid propagation, greatly easy transfer and comparatively hard termination



6.2 Brief Summary of the Cationic Polymerization

3. Kinetics

a. R_p :

$$R_p = \frac{Kk_p k_i}{k_t} [C][RX][M]^2$$

b. \overline{X}_n

$$\overline{X}_n = \frac{R_p}{R_t + R_{trM}}$$



6.2 Brief Summary of the Cationic Polymerization

A. The property of solvent

The solvability increases with increase of the solvent between polarity, increasing the distance between ion pairs, the amount of loose ion pairs, the concentration of the free ion and hence the rate of polymerization.



6.2 Brief Summary of the Cationic Polymerization

B. The effect of the solvent and gegenion

When Solvent polarity increases, the incompact ion pairs multiply, and the polymerization rate enhances

The gegenion with nucleophilicity, polymerization rate reduces; the volume of gegenion enhances, the incompact ion pairs multiply and the polymerization rate increases.



6.2 Brief Summary of the Cationic Polymerization

C. Temperature

$$E_R = E_p - E_t < 0:$$

The temperature increased , polymerization reduces.

$$E_{\bar{X}_n} = E_p - E_t \text{ or } E_{\bar{X}_n} = E_p - E_{trM} < 0:$$

The temperature increased, polymerization reduces.



6.3 Comparison between radical polymerization and ionic polymerization

- (1) the type of the initiator*
- (2) the monomer structure*
- (3) the effect of the solvent*
- (4) the polymerization temperature*
- (5) the polymerization mechanism*



6.3 Comparison between radical polymerization and ionic polymerization

(1) the type of the initiator

- Radical polymerization usually uses reagents easy to thermally decompose into a peroxide, or azo compound as the initiator. The property of initiator merely affects the process of initiation.
- Ionic polymerization uses reagents apt to produce active ions as the initiator.



6.3 Comparison between radical polymerization and ionic polymerization

(1) the type of the initiator

- A cationic initiator is an electrophilic reagent , mainly Lewis acid;
- An anionic initiator is a nucleophilic reagent , mainly alkali metals and their organic compounds;



6.3 Comparison between radical polymerization and ionic polymerization

- Because a gegenion always exists around the active center, the property of an ionic initiator affects not only the elementary reaction of initiation, but also the propagation and termination;
- Gegenion affects polymerization all the way.



6.3 Comparison between radical polymerization and ionic polymerization

(2) The Monomer Structure

The ionic polymerization have high selectivity of the monomer.

- Vinyl monomers with push-electron groups, of which the density of electron cloud on double bond increases, are apt to the cationic polymerization.
- Vinyl monomers with attract-electron groups are apt to the anionic polymerization.
- Vinyl monomers with weak attract-electron groups are apt to the radical polymerization.



6.3 Comparison between radical polymerization and ionic polymerization

(2) The Monomer Structure

- Conjugated alkene monomers can be polymerized by three mechanisms.
- Annular monomers and carbonyl compounds, for their comparatively high polarity, commonly are not able follow the radical polymerization, but apt to polymerize in ionic or stepwise ways.



6.3 Comparison between radical polymerization and ionic polymerization

(3) the Effect of the Solvent

In the radical polymerization a solvent only takes part in the chain transfer and can affect the initiator decomposition rate.

- In the ionic polymerization the polarity and solvating power of the solvent greatly affect the state of active centers of the initiation and propagation. The state can be from covalent association, compact ion pairs, incompact ion pairs to ion free.



6.3 Comparison between radical polymerization and ionic polymerization

(3) The Effect of the Solvent

The Ionic polymerization can use a nonpolar hydrocarbon solvent , and other solvents can only be used selectively.

- The Cationic polymerization can use alkyl halide , CS_2 , liquid SO_2 and CO_2 as the solvent.
- The anionic polymerization can use liquid ammonia , liquid chlorine and ether as the solvent.

The rules cannot be used inversely, otherwise the chain transfer or termination will occur.



6.3 Comparison between radical polymerization and ionic polymerization

(4) The Polymerization Temperature

- The radical polymerization temperature , which is around or more than $50\sim 80^{\circ}\text{C}$, depends on the requirement of the initiation.
- The initiating activation energy of the ionic polymerization is quite low. To prevent side reaction , like chain transfer and rearrangement , the ionic polymerization often occurs under low temperature , where the reaction can also get a rapid enough rate.



6.3 Comparison between radical polymerization and ionic polymerization

(5) The Polymerization Mechanism

- The inhibitor of radical polymerization commonly is oxygen , benzopuinone and substances that stabilizes radicals. They usually have no inhibitive effect.
- Polar substances , like water and alcohol , are all inhibitors of the ionic polymerization.
- Acids are inhibitors of the anionic polymerization.
- Alkali are inhibitors of the cationic polymerization.



6.3 Comparison between radical polymerization and ionic polymerization

6.3.5 离子聚合与自由基聚合的比较

表6—3 离子聚合和自由基聚合特点的比较

聚 合 反 应	自由 基 聚合	离 子 聚 合	
		阳离子聚合	阴离子聚合
聚合方法	本体,溶液,悬浮,乳液	本体,溶液	
引发剂(催化剂)	过氧化物,偶氮化物。本体,悬浮聚合可用溶于单体的引发剂;乳液聚合可用水溶性引发剂;溶液聚合可用溶于溶剂的引发剂	Lewis 酸,质子酸,阳离子生成物,亲电试剂	碱金属,有机金属化合物,碳阴离子生成物,亲核试剂
单体聚合活性	弱电子基的烯类单体共轭单体	推电子取代基的烯类单体, 易极化为负电性的单体	吸电子取代基共轭的烯类单体, 易极化为正电性的单体
活性中心	自由基 $C\cdot$	碳阳离子 C^+	碳阴离子 C^-
阻聚剂	生成稳定自由基和稳定化合物的试剂	亲核试剂	供给质子的试剂
水、溶剂的影响	水有除去聚合热的作用	要防湿,溶剂的介电常数有影响	
聚合速度	$k[M][I]^{1/2}$	$k[M]^2[C]$	
聚合度	$k'[M][I]^{-\frac{1}{2}}$	$k'[M]$	
活化能	一般较大	小	



6.4 Ionic copolymerization

6.4 离子共聚

自由基共聚物组成方程也适用于离子共聚，但在以下几方面存在差异。

(1) 离子共聚对单体有较高的选择性，能进行离子共聚的单体相对较少。且同一对单体采用不同机理的引发体系共聚时，竟聚率和共聚组成会有很大差别。例如苯乙烯和甲基丙烯酸甲酯在采用不同机理聚合时的竟聚率见表6—4。



6.4 Ionic copolymerization

表6—4 苯乙烯和甲基丙烯酸甲酯共聚的竟聚率

共聚类型	引发剂	聚合温度 /°C	r_1	r_2
阳离子	SnCl_4	20	10.5 ± 0.2	0.1 ± 0.05
自由基	BPO	60	0.52 ± 0.26	0.46 ± 0.025
阴离子	N_a (液氨中)	-30	0.12 ± 0.05	6.4 ± 0.05

(2) 离子共聚单体极性往往相近，因此有理想共聚倾向。较难合成两种单元含量都很高的共聚物。

(3) 溶剂和反离子的性质和温度对单体活性和竞聚率有很大影响，从而影响共聚物的组成。



现有DPPH和苯醌两种试剂，用其如何区别自由基聚合反应、阳离子聚合和阴离子聚合这三种反应？

解：已经知道：三种聚合反应的阻聚剂如下：

自由基聚合：氧、DPPH、苯醌

阳离子聚合：极性物质水、醇，碱性物质，苯醌

阴离子聚合：极性物质水、醇，酸性物质，二氧化碳

阻聚剂DPPH和苯醌对这三种反应所表现的阻聚作用不同：

DPPH(1,1-二苯基-2-三硝基苯肼)是高效自由基捕获剂，它能非常有效的捕获初级自由基，常称为自由基捕获剂。DPPH通过链转移反应消灭自由基，一个DPPH分子能够按化学计量消灭一个自由基，因此可以用来测定引发速率。亦即DPPH是自由基的阻聚剂，但它对离子聚合无阻聚作用，故借助DPPH对自由基聚合产生阻聚作用、而对离子聚合不产生阻聚作用的原理，可将自由基聚合和离子聚合区分开来。而苯醌是阳离子聚合的阻聚剂，可据此区分阳离子聚合和阴离子聚合。



课前练习

- 合成相对分子质量窄分布聚合物的聚合反应条件有哪些？
- 在离子聚合反应过程中，能否出现自动加速现象？为什么？