

**Momentive Performance Materials Inc.
Momentive Specialty Chemicals Inc.**

迈图集团

Global Leader in Specialty Chemicals and Materials
特种化学品和材料的全球引领者

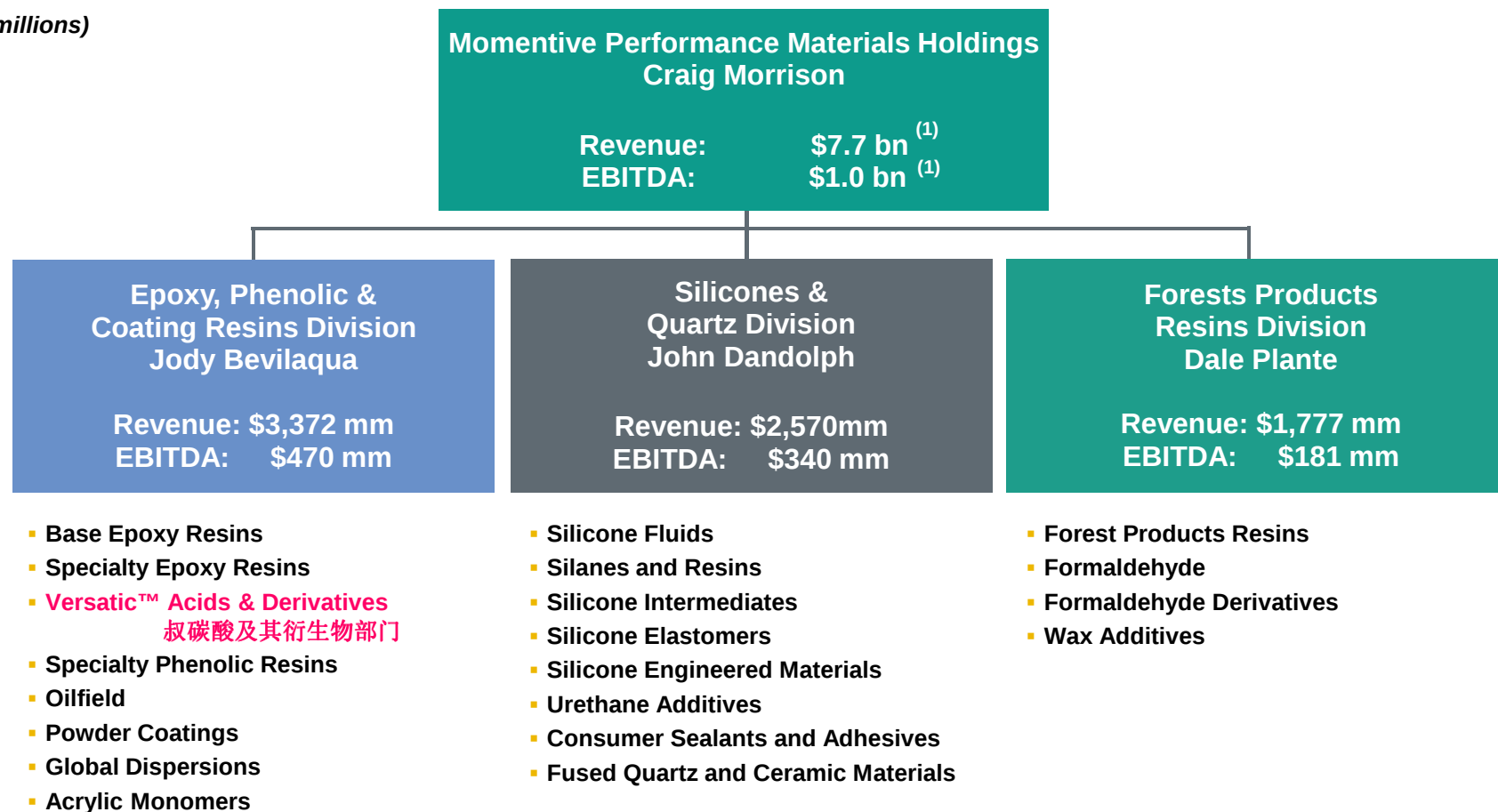


Momentive Creates One Of The Largest Global Specialty Chemical And Materials Growth Platforms

迈图集团创建了全球最大的特种化学品和材料的增长平台之一



(in millions)



Global Leadership Positions Across A Broad Range Of Technologies And Industries 领跑全球多种工业技术领域



Base
Epoxy

Epoxy Resins
Global



Specialty
Epoxy



Quartz
Global



Silicones
Global



Phenolic Specialty
Resins
Global



Versatic Acids &
Derivatives
Global



Forest Product Resins
Global



Oilfield Proppant Resins
Global

LEADING MARKET POSITIONS IN MORE THAN 80% OF ITS REVENUE BASE

超过80%的产品为世界第一

The New Momentive – Forges An Industry Leader

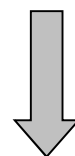
新迈图 – 强强联手铸就工业领导者



迈图高新材料



翰森特种化学品



Pro forma Revenue \$7.5 Billion

Pro forma Adjusted EBITDA \$1.2 Billion

Versatic Acid & Derivatives Business

溯源叔碳酸及其衍生物部业务

MOMENTIVE™



Versatic Acid & Derivatives Applications

叔碳酸及其衍生物应用领域概览



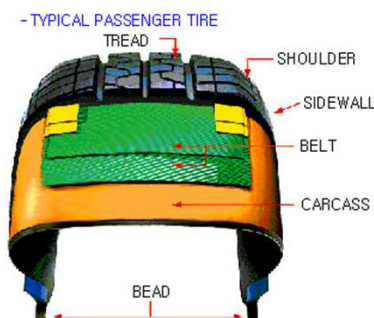
Emulsions (paints & adhesives)
Powder additives (construction)
Fuel additives



Automotive coatings
Coil and Industrial coatings
Reactive diluents (Civ. Eng.)
Pigment Paste

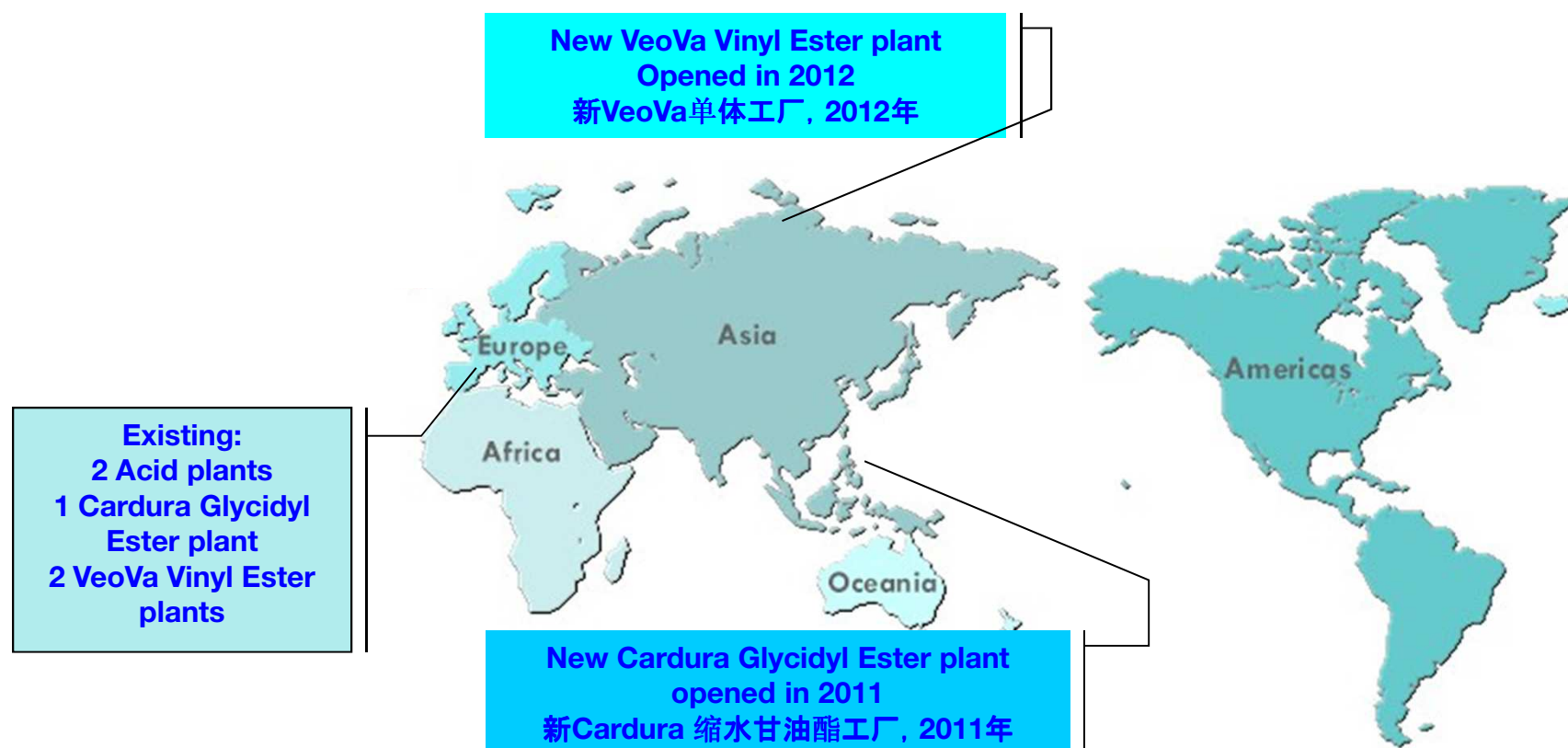


Peroxides
Pharmaceuticals intermediates
Agrochemicals
PVC stabilizers
Paint dryers
Tire adhesives
Lube additives
Metal Working Fluids



Versatic Acid & Derivatives Manufacturing Footprint In Asia

叔碳酸业务部在亚洲的工厂



- Roughly doubling capacity

VERSATIC DERIVATIVES

Unconventional Chemistry

叔碳酸及其衍生物
创造非同寻常的化学作用



Synthesis And Application Of Cardura™ E10P Based Water-borne APO And PUD

基于Cardura™ E10P水性羟基丙烯酸树脂和聚氨酯
分散体的合成和应用



Scott Wang/王丰万

May 15-16, 2013

Agenda 议程

- Introduction 引言
- Synthesis and application of Cardura E10P based water-borne acrylic resin
基于Cardura E10P水性丙烯酸树脂的合成和应用
- Application and application of Cardura E10P based PUD
基于Cardura E10P聚氨酯分散体的合成和应用
- Conclusion 结语

Agenda 议程

➤ Introduction 引言

➤ Synthesis and application of Cardura E10P based water-borne acrylic resin

基于Cardura E10P水性丙烯酸树脂的合成和应用

➤ Application and application of Cardura E10P based PUD

基于Cardura E10P聚氨酯分散体的合成和应用

➤ Conclusion 结语

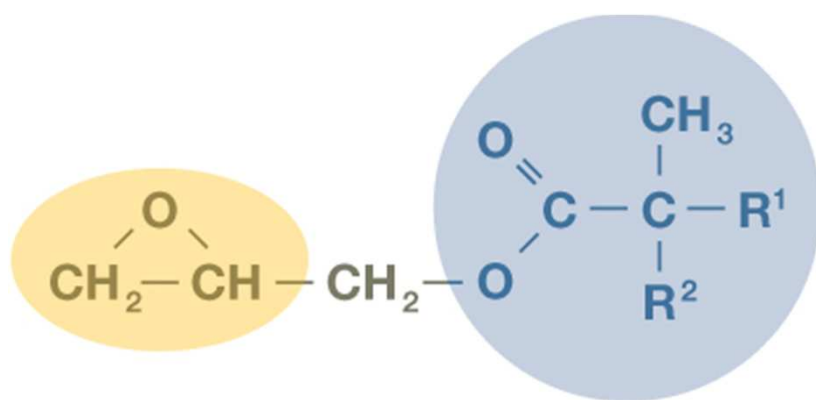
Why Cardura E10P (CE10P) For Waterborne Dispersions

为什么研发基于Cardura E10P (CE10P) 的水性分散体

- The need to reduce the emission of VOCs has led to the development of waterborne binders;
出于减少有机挥发物的需要，水性树脂正在被开发；
- Conventional WB dispersions have a solvent removal step which requires high energy and causes side reactions;
常规的水性分散体需要一个除溶剂步骤，常常造成高能耗和副反应。
- Waterborne resins can be prepared in a more convenient and simple process using CE10P as reactive diluent for initial reactor charge.
使用CE10P作为活性稀释剂打底，水性树脂分散体的制备工艺更加便利、简单。

What Is Cardura E10P

Cardura E10P是什么



Reactive epoxy-group 活性环氧基团

- Easy incorporation in polymers due to highly reactive towards amines, acids and alcohols
与胺类、羧酸及醇类反应活性大，易于引入聚合物中；
- Ring opening generates an hydroxyl group for curing
开环产生羟基，可用于固化；
- Enhanced metal adhesion
改善附着力。

of Versatic Acid 10 叔碳酸10 (R¹+R²=7 Carbon atoms)

- Bulky structure 大体积结构
- Reduce intermolecular interaction 减少分子间作用力
- Sterically protected ester group 位阻保护酯键
- Aliphatic Structure 脂肪族结构
- Hydrophobicity 疏水性

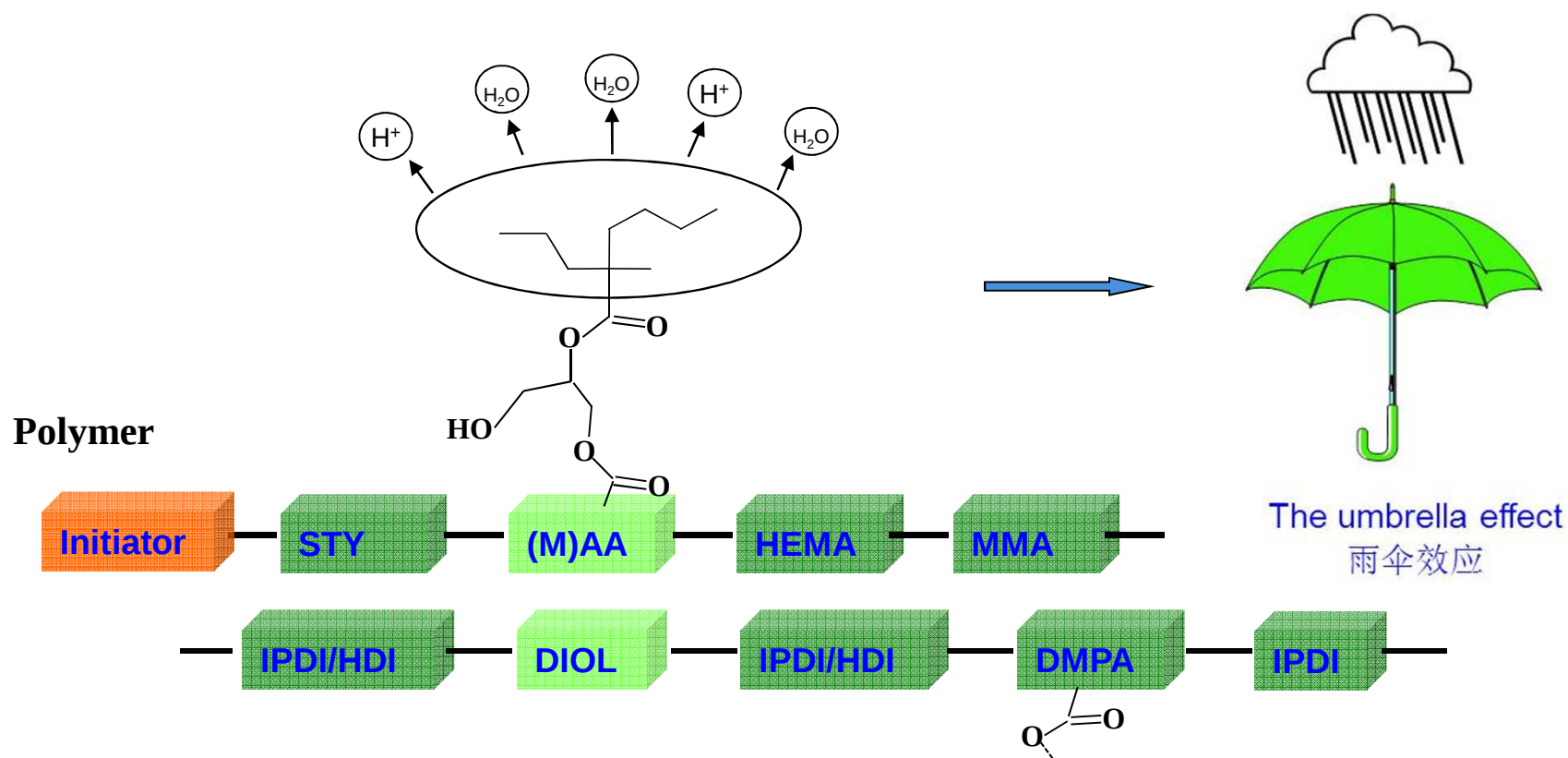
Key Characteristic 主要特性

- Superior appearance, DOI, film build, etc.
极好的外观，如鲜艳性，丰满度等
- A simple polymerization process
简化合成工艺
- Excellent acid and alkali resistance
极好的耐酸碱性能
- Water resistance 耐水
- Enhanced flow and leveling
改善流动和流平
- Good pigment wetting and improve inter-coat adhesion
好的颜料润湿和改善层间附着
- High solid content low viscosity resin
制备高固低粘树脂
- Superior outdoor durability 耐候

The Advantages For CE10P Based Resins

基于Cardura E10P树脂的优势

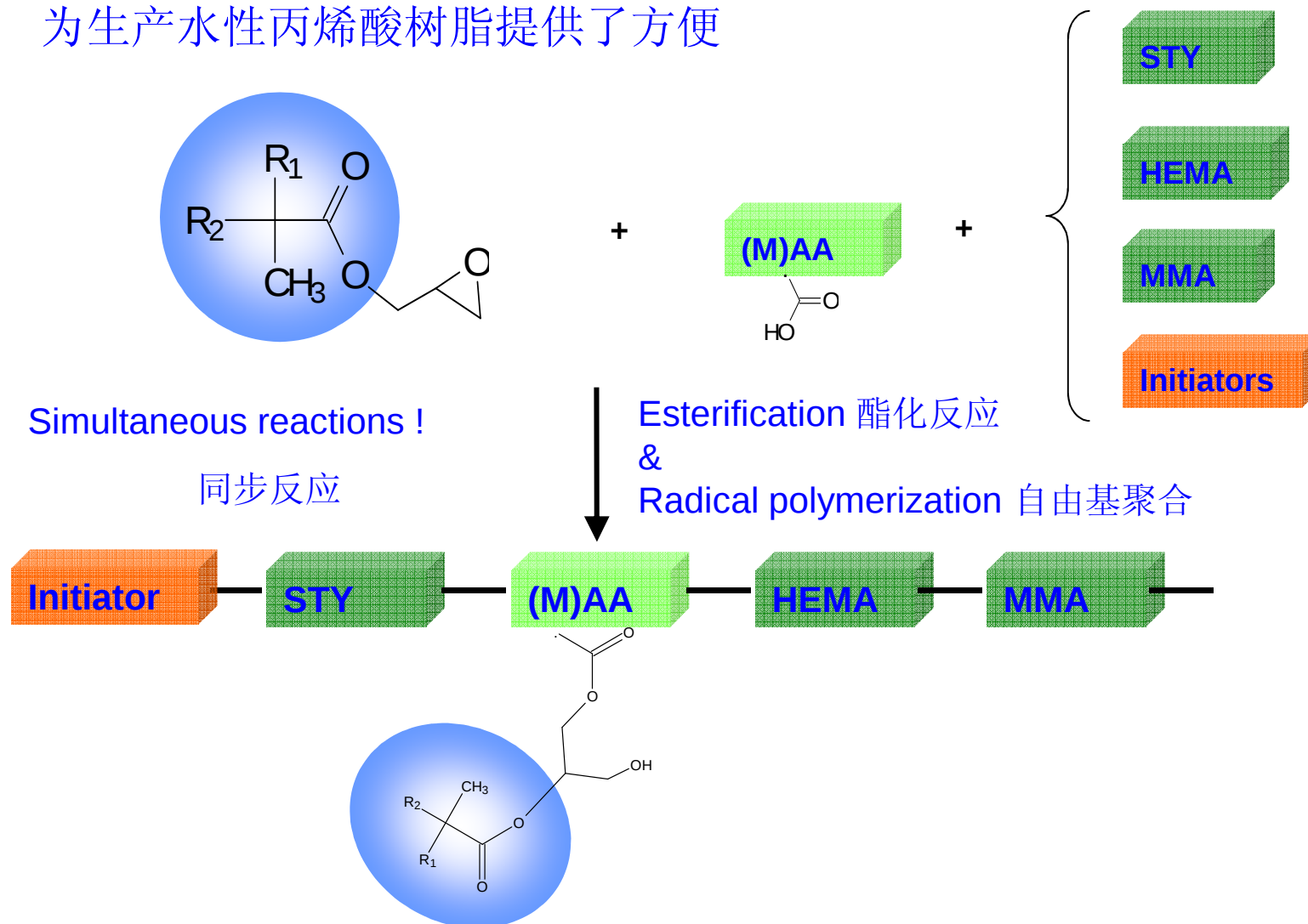
- The steric influence and hydrophobicity of CE10P protect the cross-link from hydrolysis and lead to improve chemical resistance;
CE10P的空间位阻效应和疏水性保护交联的化学键减少水解、改善耐化学品性;



The Advantages For CE10P Based Resins

基于Cardura E10P树脂的优势

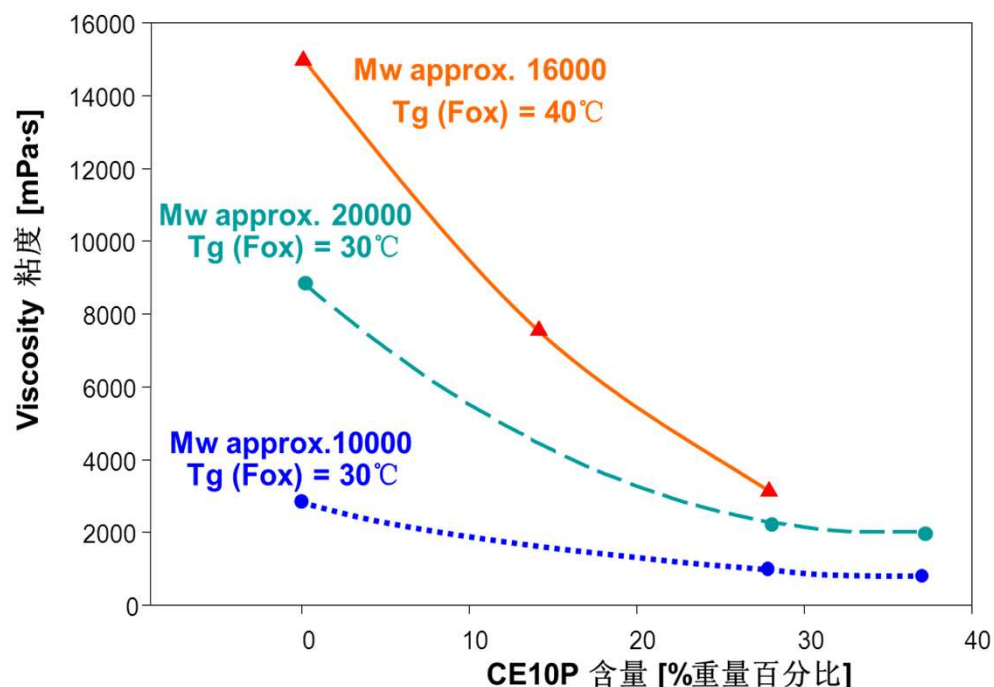
- Offer a considerable processing advantage during the resin production
为生产水性丙烯酸树脂提供了方便



The Advantages For CE10P Based Resins

基于Cardura E10P树脂的优势

➤ Viscosity cutting power of Cardura E10P Cardura E10P的降粘力



- A reasonably low content of Cardura E10P in the polyol structure contributes to **strong viscosity reduction**
在多元醇中适当的Cardura E10P就能强烈地降低粘度
- Cardura E10P produces lower viscosity resins which can be used for **low VOC** applications.
基于Cardura E10P制备的低粘树脂可以制备低VOC涂料

Cardura E10P reduces the resin viscosity because its bulky structure also limits the chain interactions limiting hydrogen bonding.

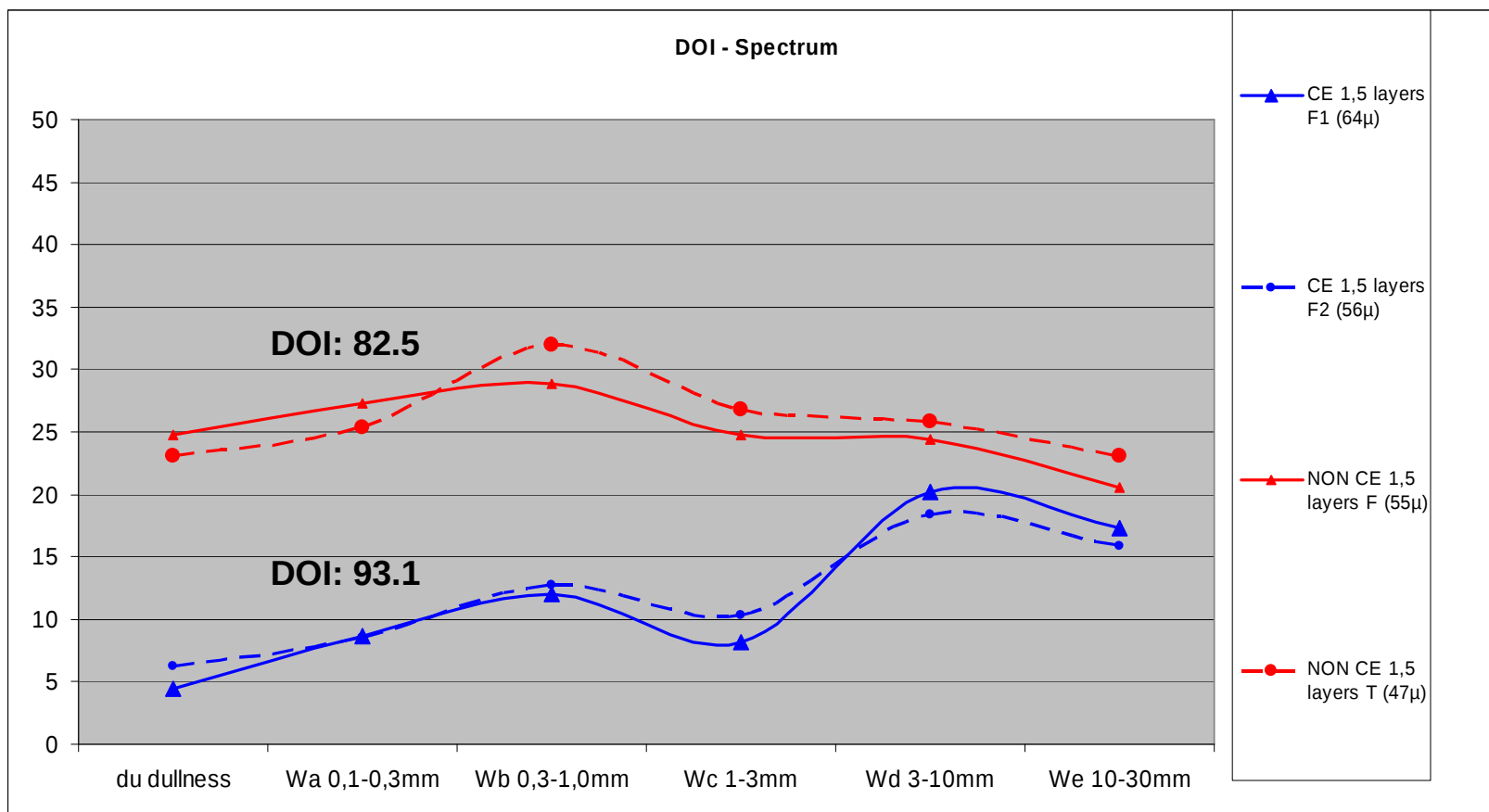
归于大体积结构，降低了分子间的作用力（如氢键、缠绕），从而降低树脂粘度。

The Advantages For CE10P Based Resins

基于Cardura E10P树脂的优势



- Cardura E10P based coatings show a better appearance
基于Cardura E10P涂料制备的涂膜具有更好的外观



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基于Cardura E10P水性丙烯酸树脂的合成和应用

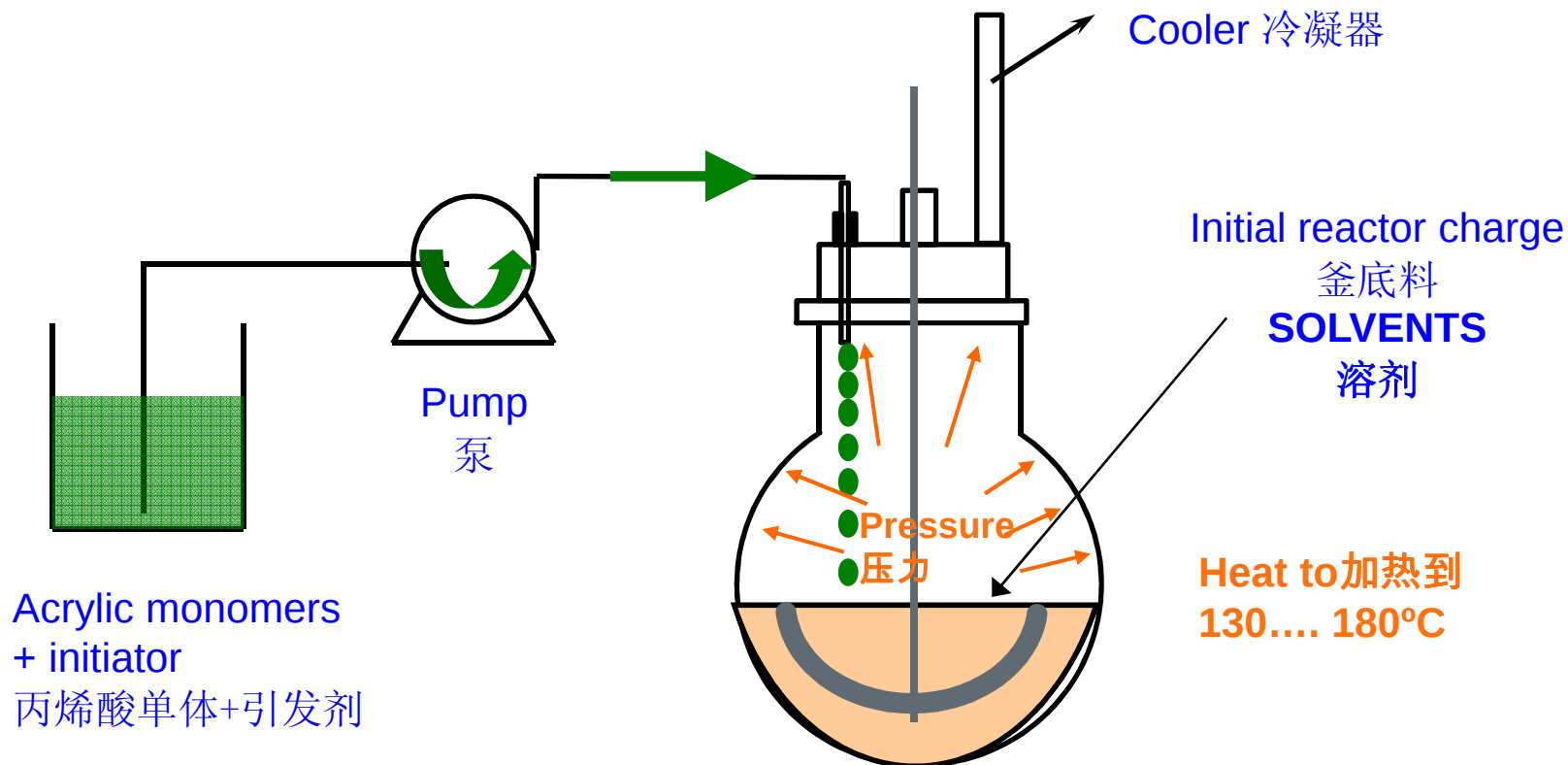
➤ Application and application of Cardura E10P based PUD

基于Cardura E10P聚氨酯分散体的合成和应用

➤ Conclusion 结语

Synthesis Of Acrylic Polyols - free of CE10P

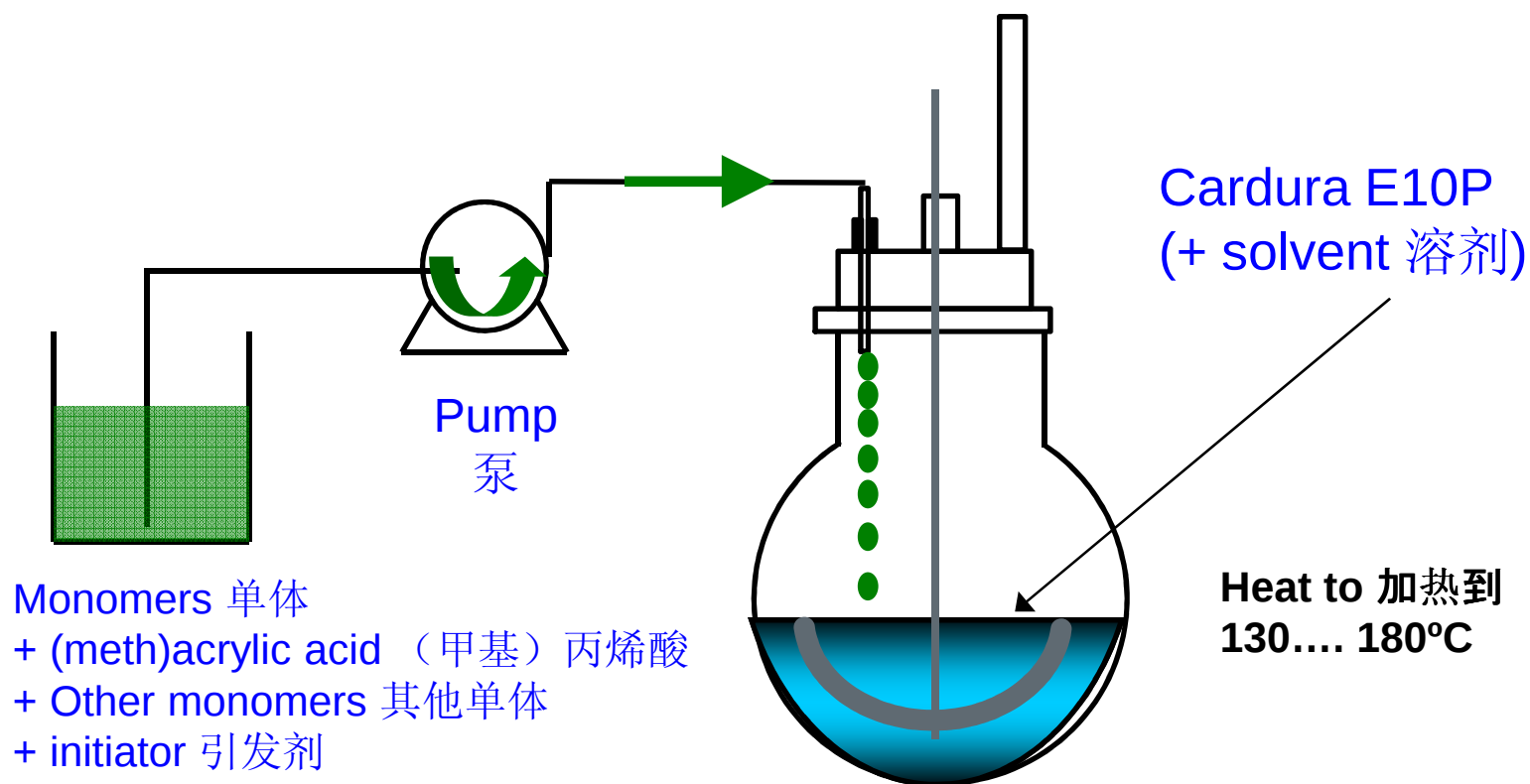
不含CE10P的丙烯酸多元醇合成



☹ Pressure reactor needed
需要使用压力反应釜

High Polymerisation Temperature With Cardura Monomers

使用Cardura 单体可以应用更高的聚合温度

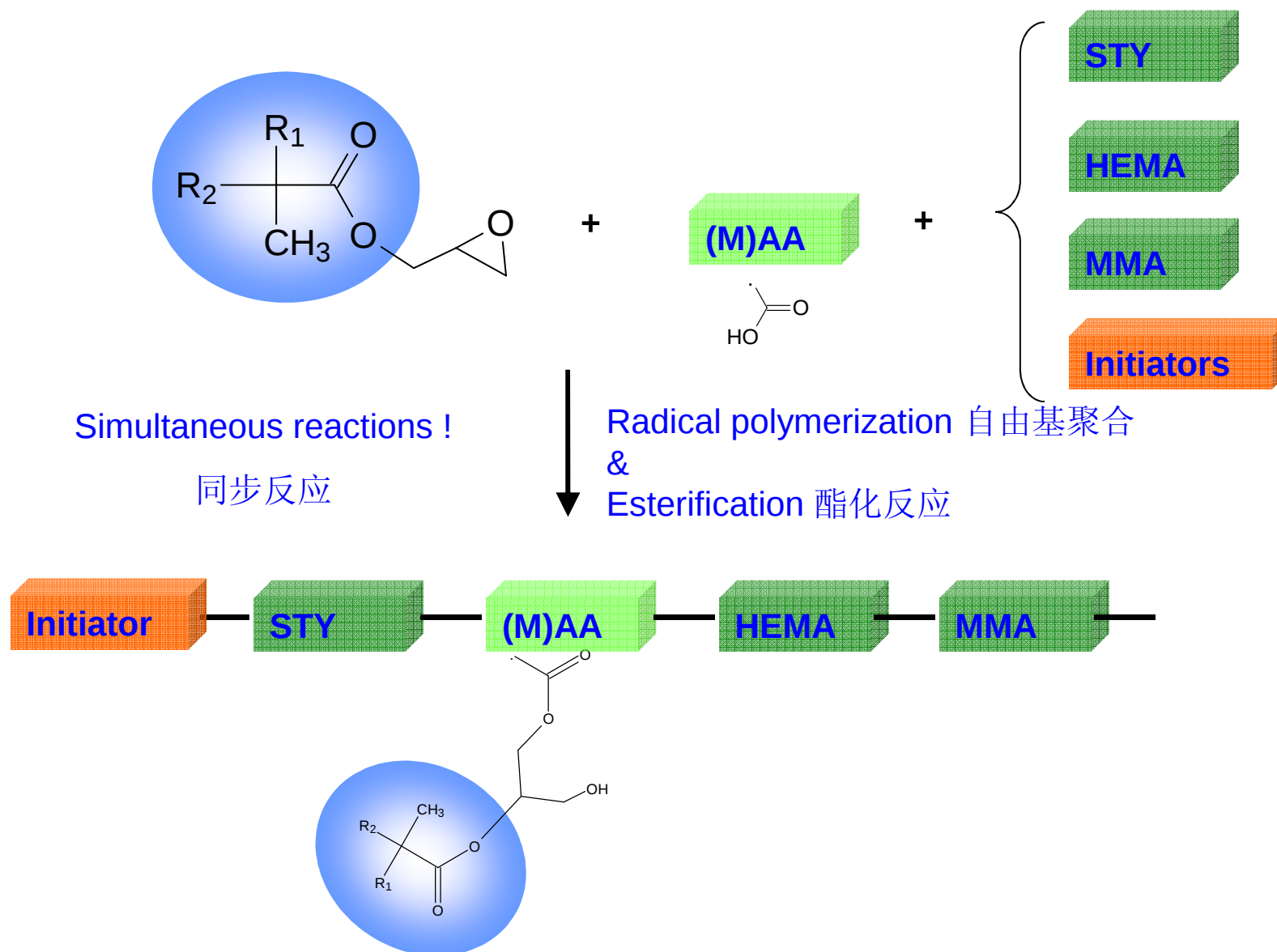


➤ Very high polymerisation temperatures are possible in conventional reactors!

在传统的反应釜中进行高温聚合成为可能！

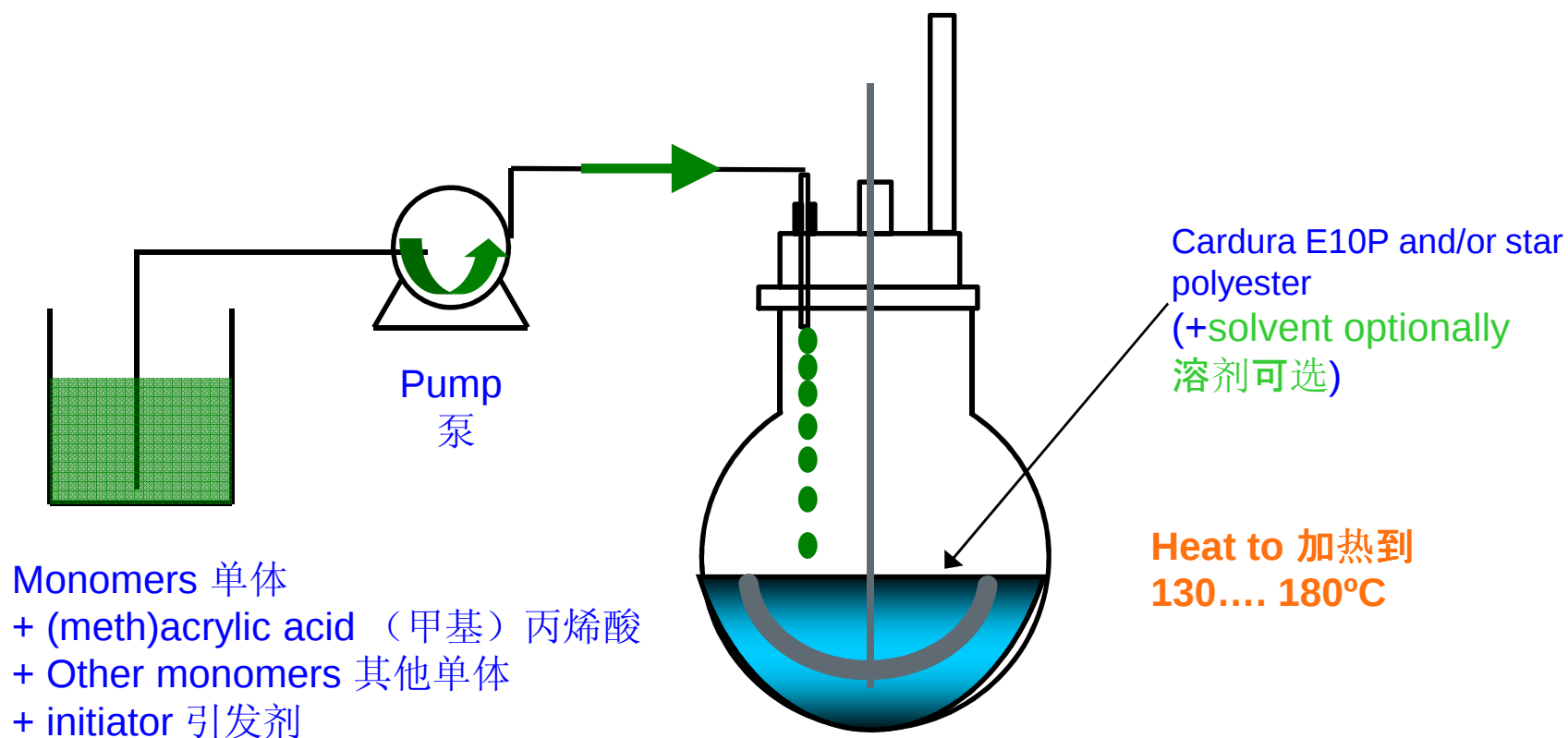
Incorporation Of Cardura E10P In acrylic polyols

在丙烯酸多元醇中引入叔碳酸缩水甘油酯



CE10P Based APO For Waterborne Clearcoats

基于CE10P的丙烯酸多元醇用于水性清漆



➤ No need to remove (strip) the excess solvents

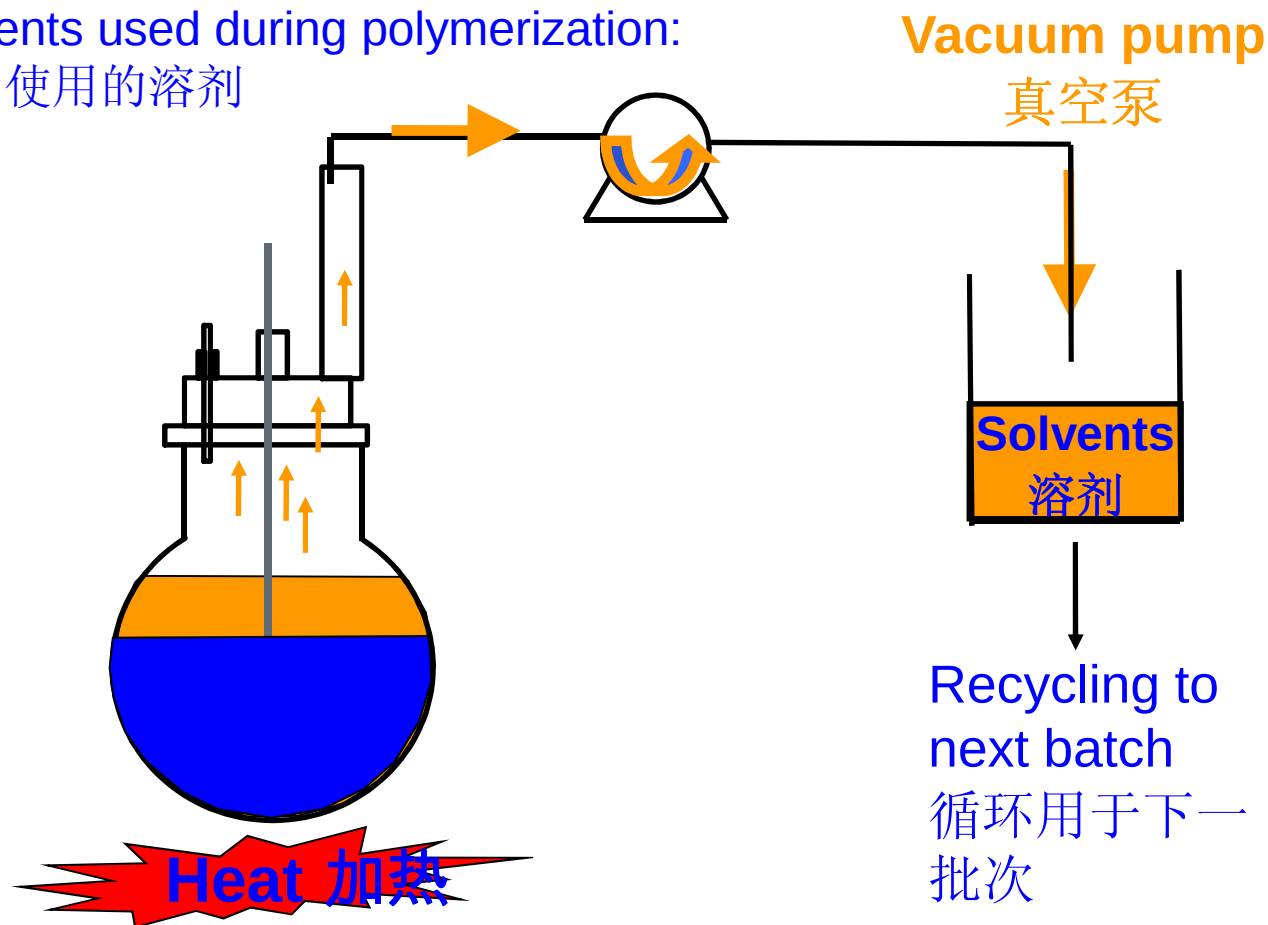
无需除去过量的溶剂

APO For Waterborne Clearcoats – free Of CE10P

不含CE10P的丙烯酸多元醇用于水性清漆

Removal of the solvents used during polymerization:

需要除去聚合过程中使用的溶剂



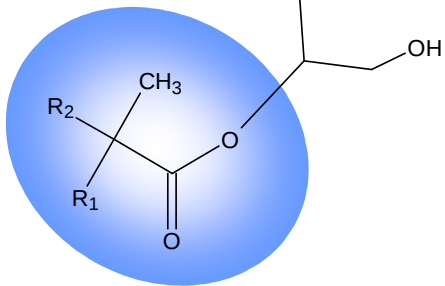
☹ Time and energy consuming 消耗时间和能源

☹ Side reactions during solvent removal 除去溶剂时的副反应

基于CE10P水性丙烯酸树脂的关键设计要点

- The distribution of the acid groups may be random, but better results are obtained by introducing poly-acrylic acid blocks.

丙烯酸在聚合物中的分布也许是随机的，但是如果这些丙烯酸在聚合物中是封端排布的话，效果会更好。



Formulation Of CE10P Based Waterborne Acrylic Resin



基于Cardura E10P的水性丙烯酸树脂的制备

Ingredients/process 组份/工艺	Weight, g 重量, 克
Solvent-borne acrylic resin 溶剂型丙烯酸树脂	496.7
Di-methyl ethanolamine 二甲基乙醇胺	19.5
First water addition 第一次加水量	273.2
Second water addition 第二次加水量	74.5
Third water addition 第三次加水量	136.1
Total 总量	1000.0

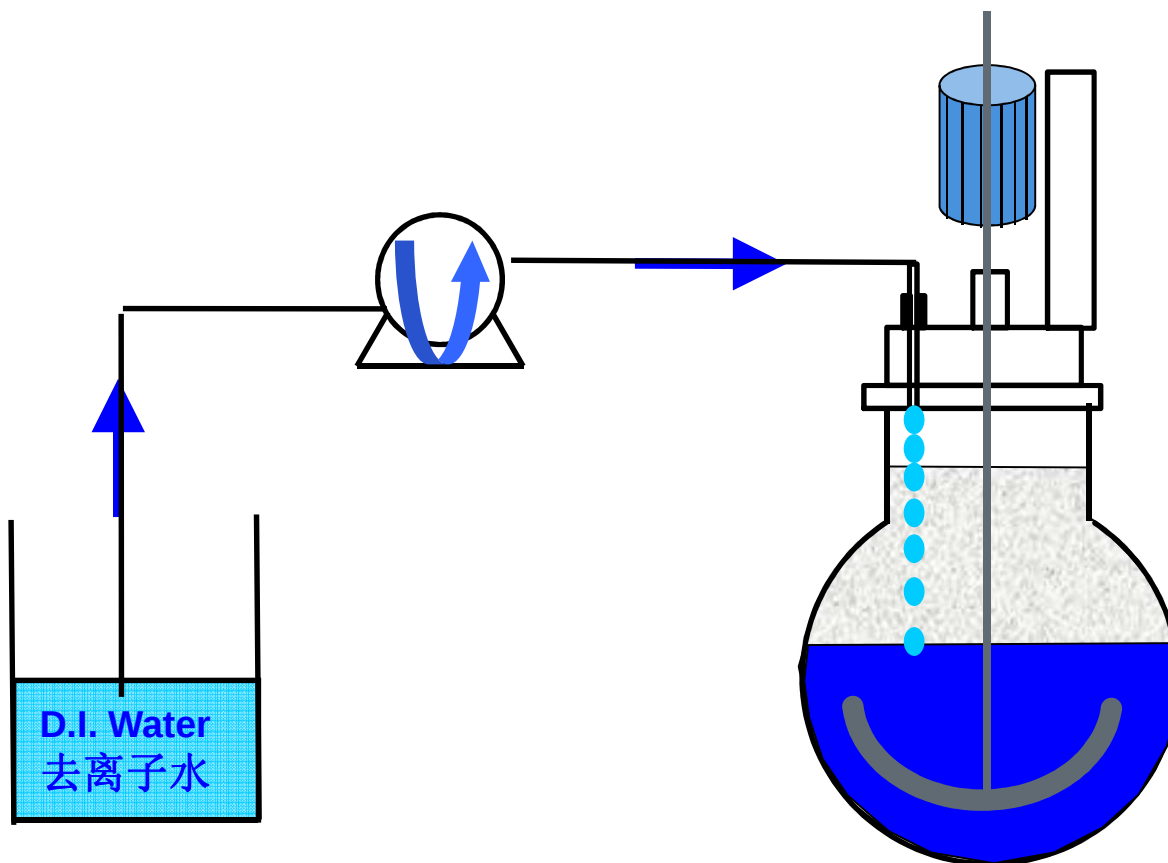
Preparation Procedure For Aqueous Dispersions

丙烯酸树脂的水性化制备工艺

➤ Heat solvent-borne acrylic resin to 70°C
加热溶剂型丙烯酸树脂至70°C

➤ Add DMEA to the resin solution at 70°C to neutralise about 80% of the acid groups, and stir well for 15 minutes.

在70 °C，滴加二甲基乙醇胺中和80%的羧基基团，并搅拌15分钟左右；

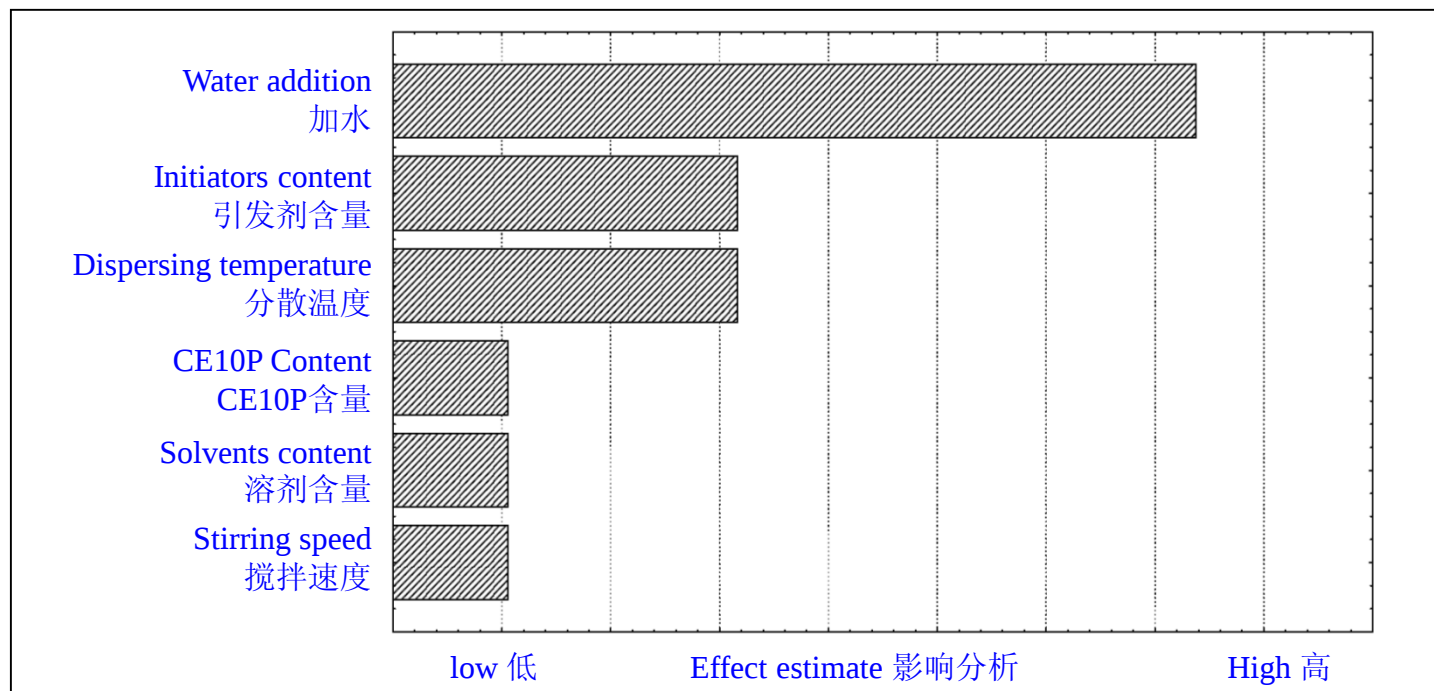


The Major Factors To Particle Size And Stability Of WB Acrylic

水性丙烯酸分散体稳定性的影响因素

- Average particle size, which is related primarily to the addition rate of water to the neutralised resin. It is therefore recommended that sufficient time is allowed for the dispersion process;

平均粒径：在完全转水前，加水到被中和聚合物的速率对粒径是非常关键的，我们推荐使用足够的时间进行分散。



Formulation Of Cardura E10P Waterborne Acrylic Coating

基于Cardura E10P的水性丙烯酸涂料的制备

Ingredients 组份	Weights, g 重量, 克
Acrylic dispersion 丙烯酸分散体	100
Melamine resin 氨基树脂 (Cymel 303)*	19.3
Acid catalyst (1%) 酸催化剂	1.3
Additives 助剂	1.0
D. I. Water 去离子水	7.0
Total 总计	128.6

* 氰特工业公司的氨基树脂

Application And Cure Conditions Of Water-borne Coatings

水性涂料的应用及固化条件

- Spray it to produce a dry film thickness of about 40 microns.

- 喷涂，漆膜大致40 μm ;

1

- Panels are left to dry 15 min at room temperature.

- 样板在室温下放置15分钟;

2

- A flash-off of 5 minutes at 70 °C is applied.

- 70 °C 下预烤（流平）15分钟;

3

- The panel is baked for 30 minutes at 140°C.

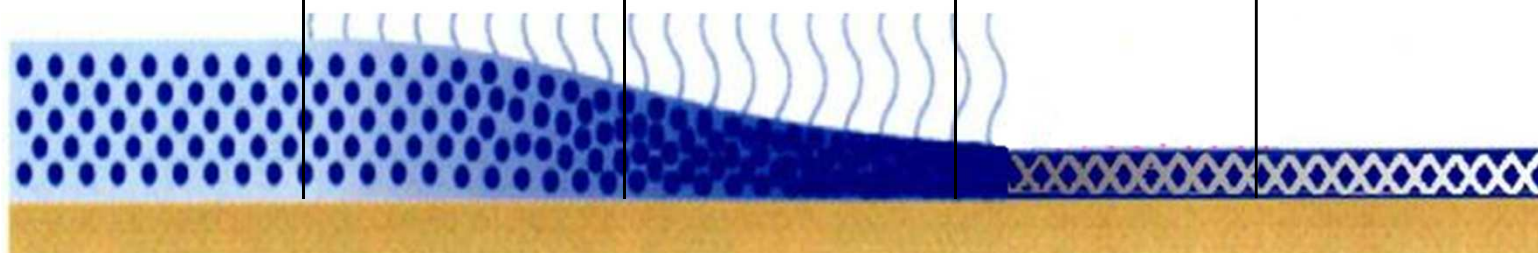
- 样板在140 °C下烘烤30分钟;

4

- Cured systems are tested after 1 day at 23 °C.

- 烘烤后样板放置一天后测试。

5



Poroperties Of The Film Of WB Acrylic Coating

水性丙烯酸清漆的漆膜性能

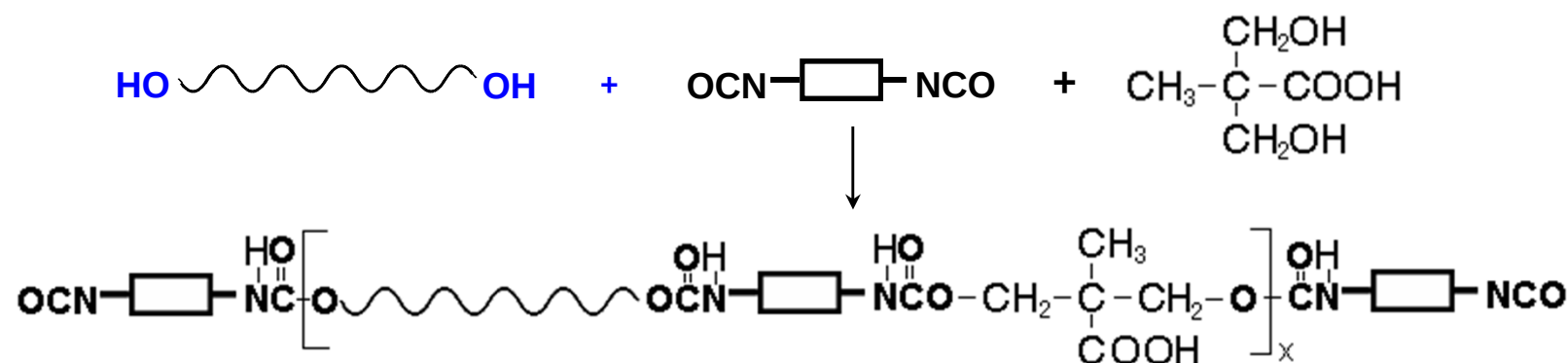
Test items 测试项目	Unit 单位	Results 结果
Film thickness 膜厚	μm, 微米	30~40
Gloss 光泽 (20/60°)	%	91/94
Pendulum hardness 摆杆硬度	s, 秒	203
Pencil hardness 铅笔硬度		2H
BA resistance 耐醋酸丁酯		OK
Xylene resistance 耐二甲苯		OK
Petrol resistance 耐汽油性		OK
MEK resistance (Double rub 来回)	Cycles 循环	>100
Fingernail scratch resistance 耐指甲划伤		OK

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- **Application and application of Cardura E10P based PUD**
基于Cardura E10P聚氨酯分散体的合成和应用
- Conclusion 结语

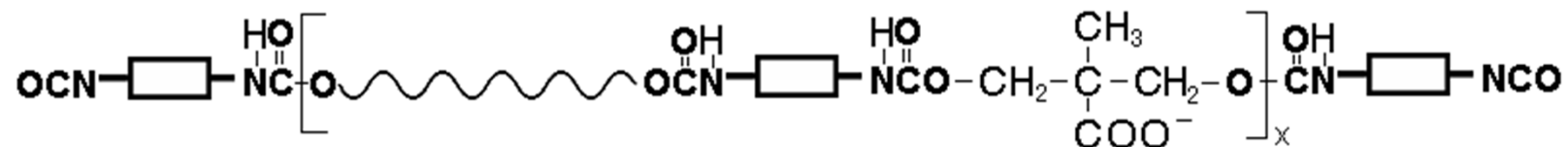
The Synthesis Process Of PUD---(DMPA)

PUD的合成工艺 ---（二羟甲基丙酸）



stabilization by incorporated anionic groups

+ Acetone+TEA



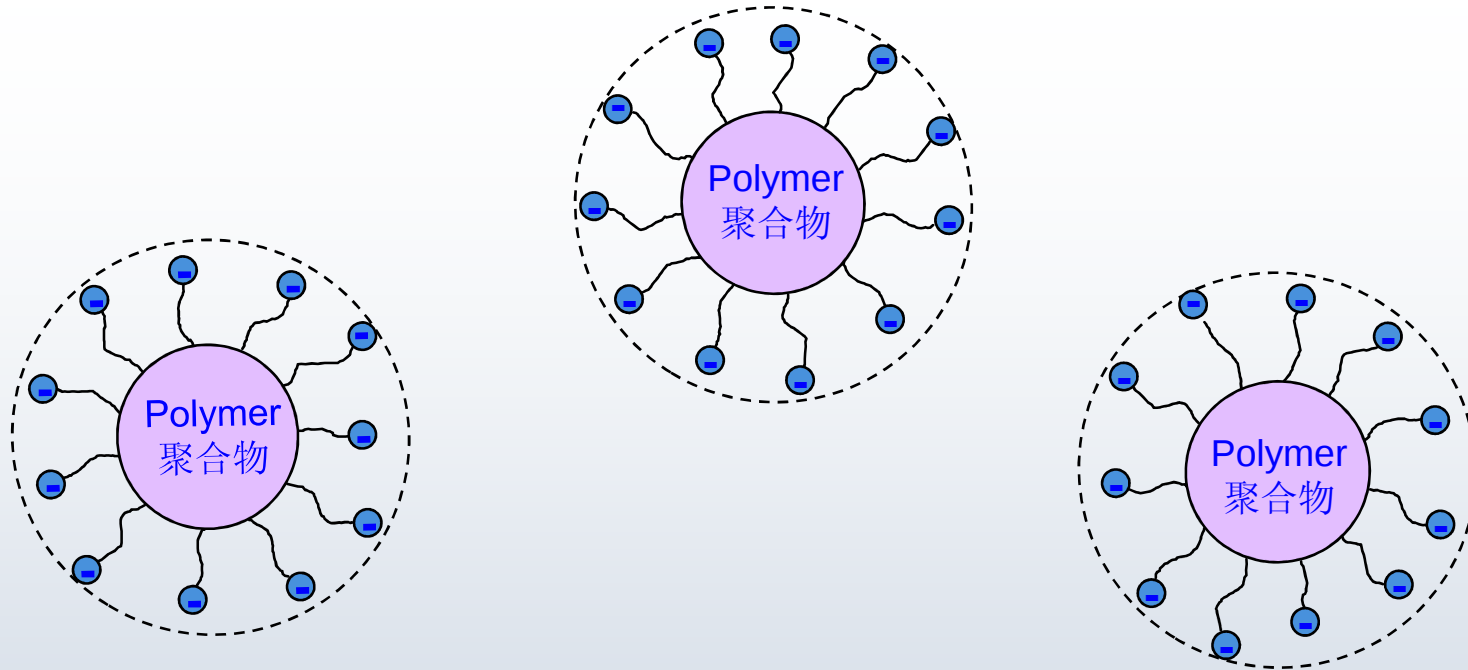
+ Water

+ EDA

Polyurethane dispersion
聚氨酯分散体

Principle Of The Stability Of PUD

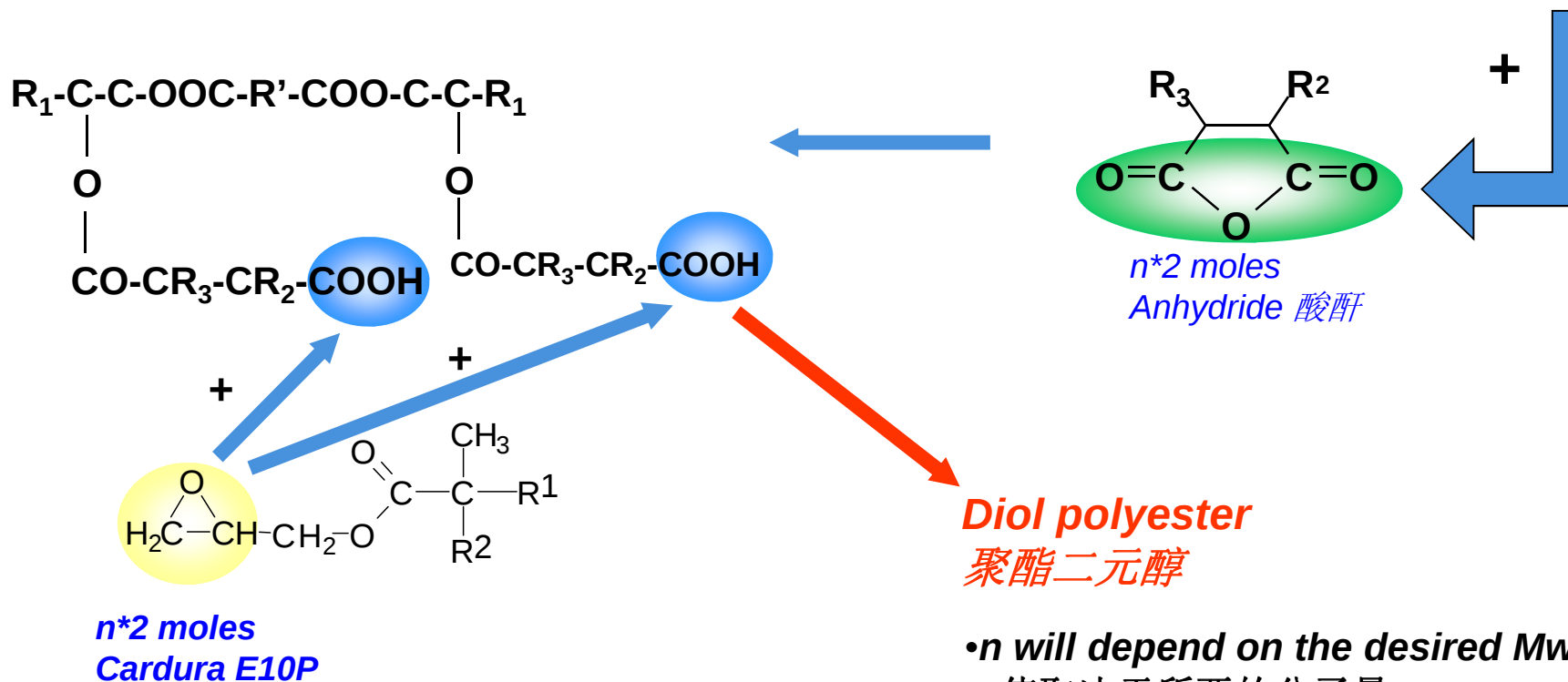
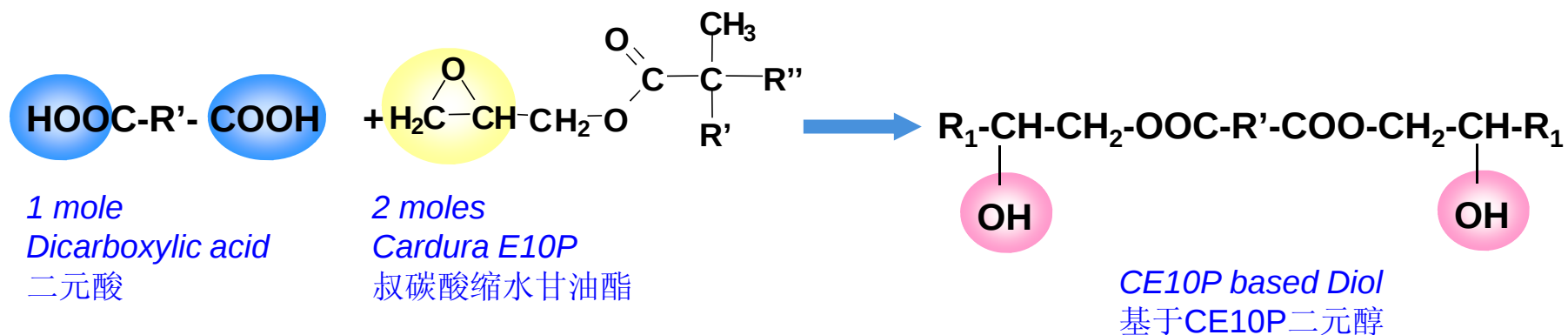
PUD的稳定性原理



- Dispersed particles are surrounded by a stabilizing hydrophilic core
分散的聚合物粒子由稳定的亲水基团包覆
- Hydrophilic core is composed of anionic groups in the polymer
亲水核是由在聚合物上的阴离子组成

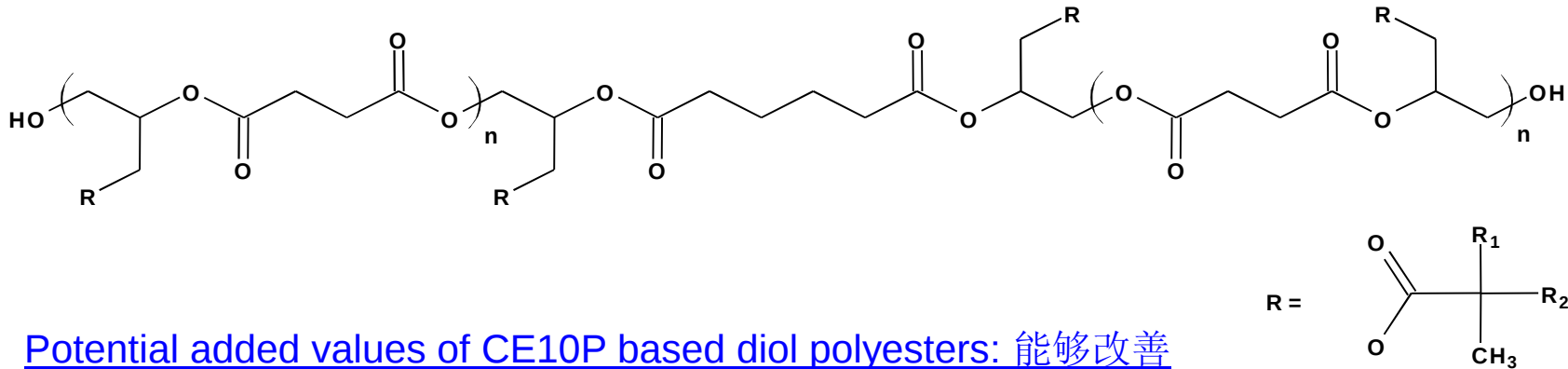
The Preparation Of The CE10P Based Diol

基于CE10P二元醇的制备



The Structure Of The Diol

二元醇的结构



Potential added values of CE10P based diol polyesters: 能够改善

- Step process 反应过程
 - narrow molecular weight distribution 分子量分布
 - polymer with low viscosity 聚合物粘度低
 - Ideal balance between viscosity and mechanical properties
对机械性能与粘度的良好平衡
- Can modulate molecular weight via the n factor 通过调节n值来控制分子量
- Hydroxy function at both ends of the chain 端羟基
- Hydrophobicity 增水性
 - Improved chemical and water resistance 改善耐水、耐化学品
 - Helps wetting of apolar substrates 帮助润湿非极性底材

Two Cases

例子



Typical properties 典型性能

OH (%)	5.4
Mn (g/mol)	643
Mw (g/mol)	666
Mw / Mn	1.04
Solids content (%)	
固含	100
Viscosity (mPa·s)	
粘度	3000



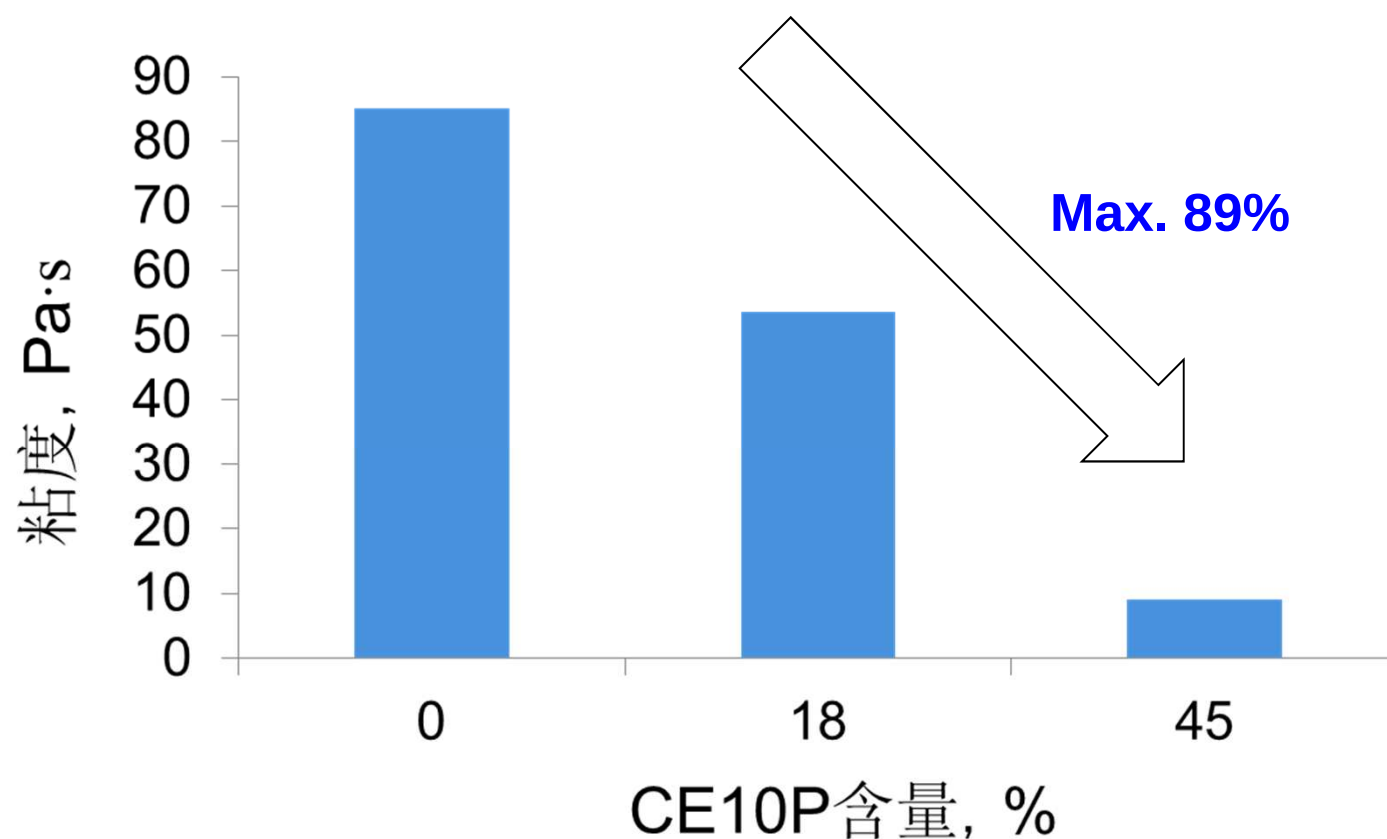
The Viscosity Comparison Of Prepolymer For PUD

用于PUD的预聚物粘度比较

Ingredients 组份	No.1	No.2	No.3
PBA 2000 聚己二酸丁二醇酯二醇	22.04	14.51	-
CEP10 based Diol 626	-	8.1	-
CE10P based Diol 2000	-	-	22.04
DMPA 二羟甲基丙烷	1.50	1.50	1.50
IPDI/HDI	9.35	9.35	9.35
Catalyst(1% in Acetone) 催化剂	0.3	0.3	0.3
Co-solvent 共溶剂	4.26	4.26	4.26
Glycol 乙二醇	0.60	0.03	0.60
React them to the calculated value or about 3~4 hours NCO反应至理论值或反应大约3-4个小时			
Acetone 丙酮	4.18	4.18	4.18
Results 结果			
Viscosity, 粘度 mPa·s	85000	53600	9000

Viscosity Cutting Power Of The CE10P For Prepolymer

CE10P对预聚物的降粘力

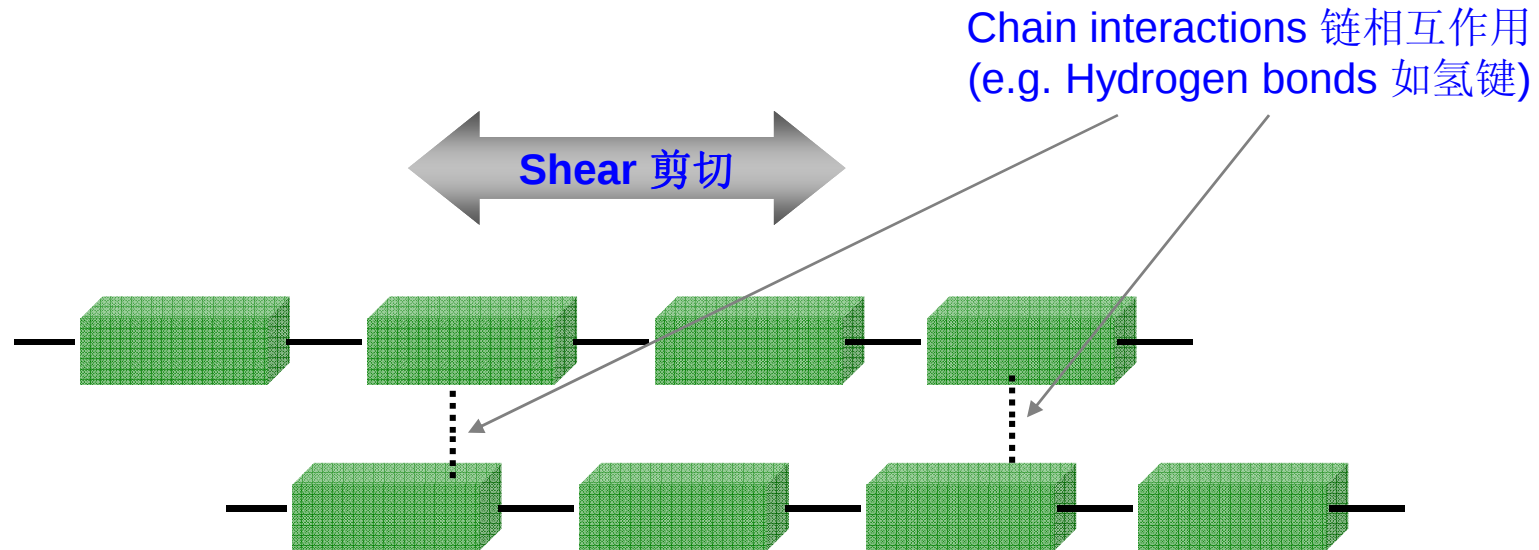


Viscosity cutting power allows for prepolymer with lower VOC or bigger molecular weight

降粘力可以制备更低VOC或更大分子量的预聚物

A Standard Polymer Structure

常规的聚合物结构



- The polymer chains are more prone to interactions, i.e. hydrogen bonds, resulting in building up with an impact to the final resin viscosity

聚合物链更倾向于分子相互作用，如氢键，从而导致更高的树脂粘度

A Cardura E10P Based Polymer Structure

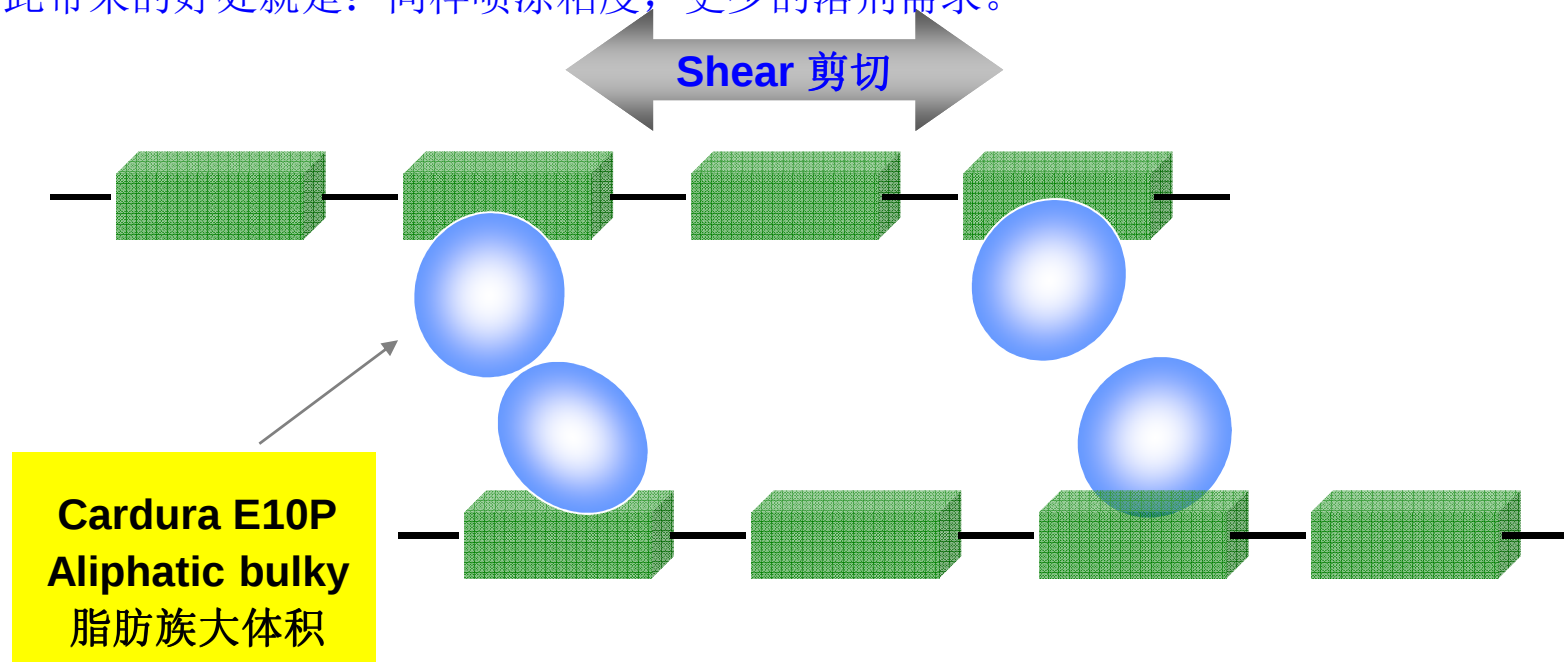
基于Cardura E10P的聚合物结构

- With Cardura E10P bulky group there is more space between polymer chains hence the hydrogen bonding is reduced;

归于Cardura E10P的大体积结构，分子链间作用力减少，尤其氢键；

- As a positive effect, less solvent is needed to reach the good spraying viscosity (lower VOC)。

由此带来的好处就是：同样喷涂粘度，更少的溶剂需求。



The low viscosity property allows for prepolymers with higher solids
低粘度特性可以制备更高固含的预聚物

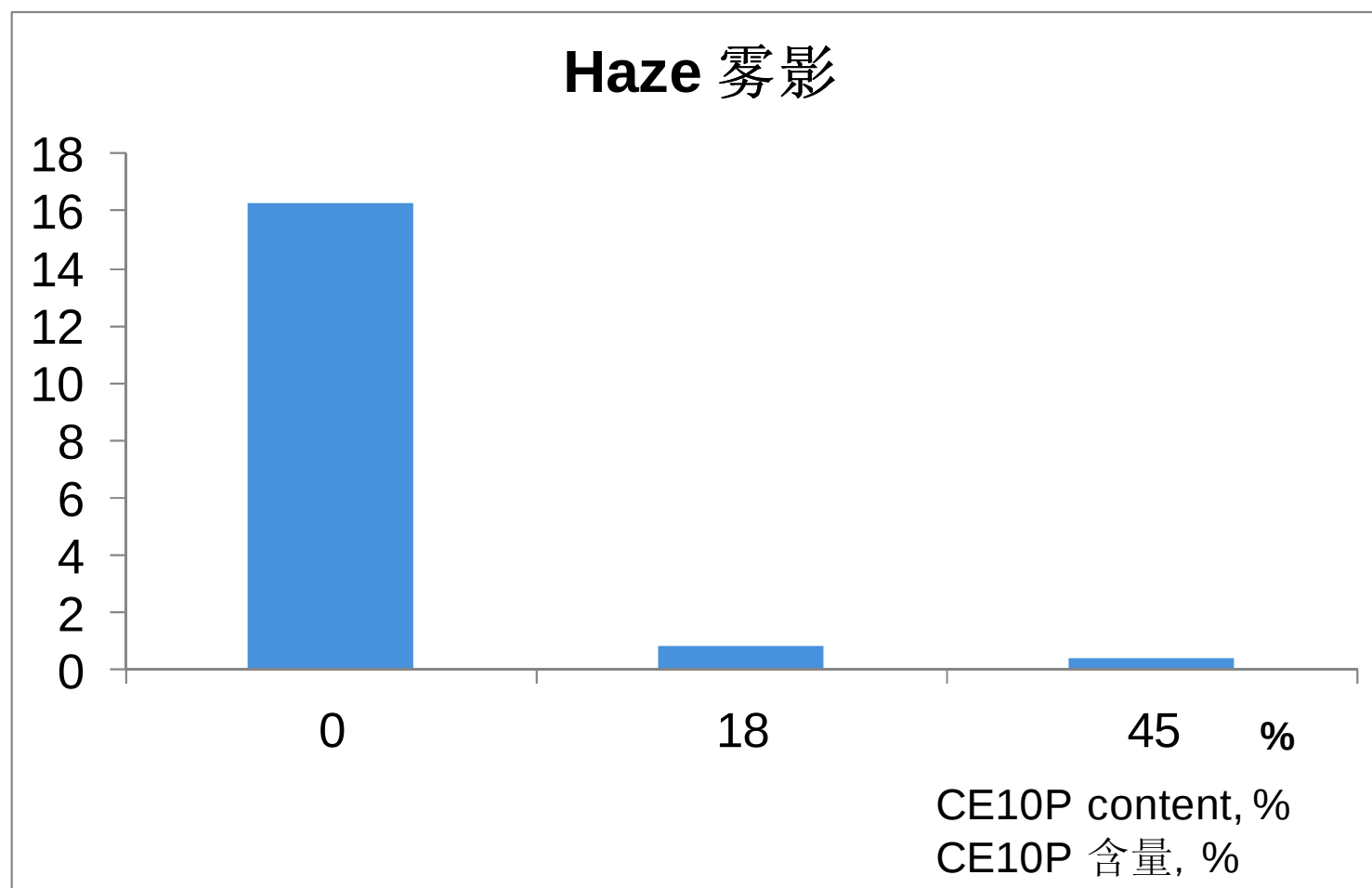
The Properties Comparison Of The PUDs

聚氨酯分散体的应用性能对比

		No.1 PBA 2000	No.2 PBA 2000 + Diol 626	No.3 Diol 2000	Benchmark 参考
Specular gloss 光泽	20°	30.5	81.0	81.5	81.0
	60°	65.9	87.0	86.8	87.0
Transparency 透过率		88	90	90	90
Haze 雾影		16.3	0.8	0.4	0.7
Clarity 清晰度		98.4	99.3	99.6	99.0
Pendulum hardness, s 摆杆硬度, 秒		40	38	-	40
Tensile strength, MPa 拉伸强度		40.0	32.5	-	25.3
Elongation at break, % 断裂伸长率		345	440	-	214

The Effect Of CE10P Content To Transmittance Haze Of The PUDs

CE10P含量对聚氨酯膜的透射雾影的影响



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Conclusions

结论

- ✓ CE10P can be conveniently synthesized to water-borne resins with excellent performance by introducing preparation conditions and process;

详细介绍了水性树脂的设计和制备工艺，CE10P能够更加便利的用于水性树脂分散体中，且性能优异；

- ✓ CE10P based polymer has lower viscosity, which is helpful to convert the phase of the solution and reduce VOC;

基于CE10P的聚合物具有更低的粘度，有利于转相，降低VOC；

- ✓ Water-borne coatings based on CE10P gives the film with a good gloss level, low haze, etc.

基于CE10P的水性涂料给予漆膜非常好的外观和性能，如高光泽、低雾影等性能。



Thanks For Your Attention

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