UMASS AMHERST

SIRRUS

# Advancing Manufacturing through Chemistry

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*Sirrus Inc.*

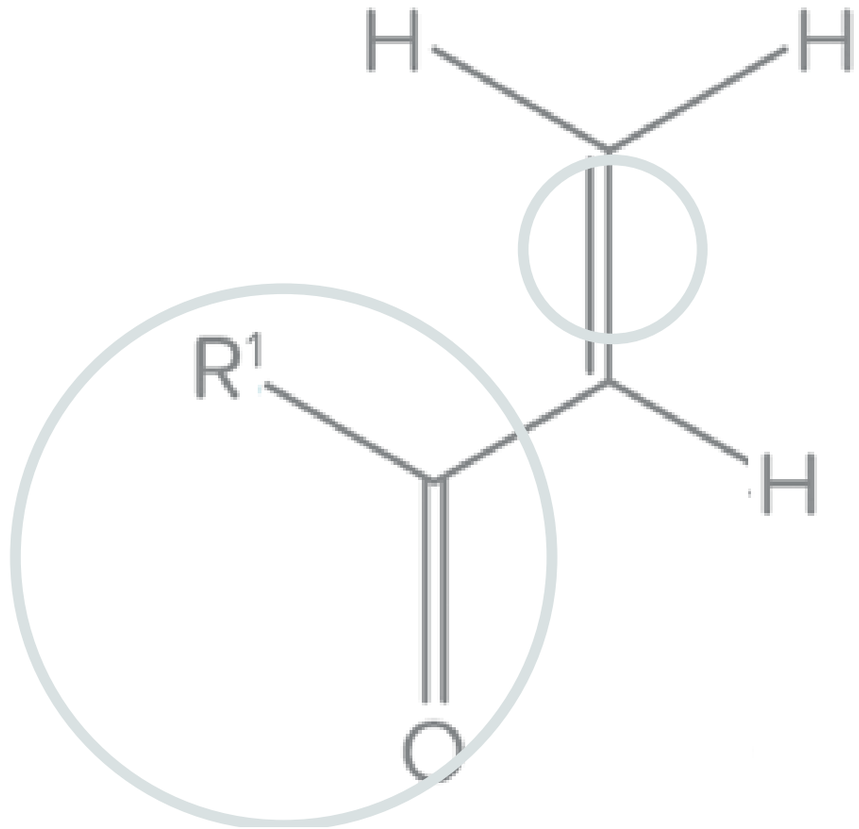
*Subsidiary of Nippon Shokubai Co. Ltd.*

# Introduction to Sirrus Technology

# Core Technology Platform

## Acrylic (~20 billion Pound Market)

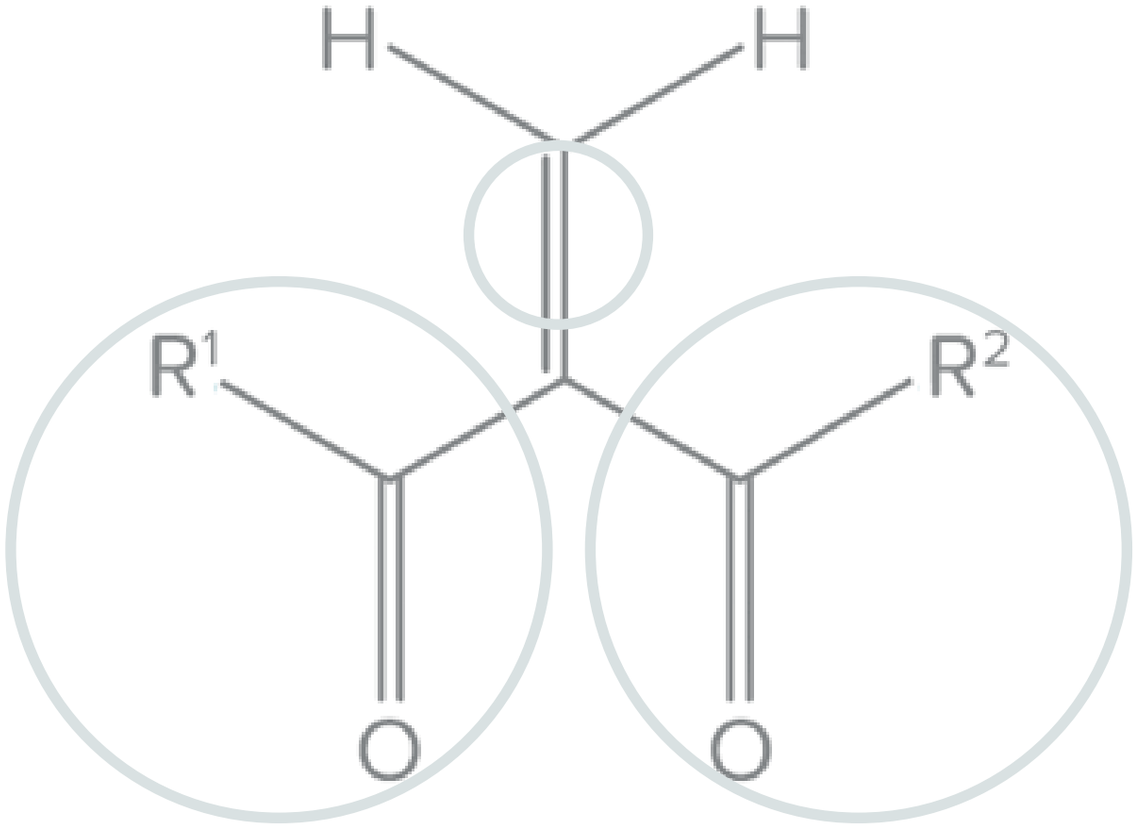
**Alkene requires energy to undergo free radical polymerization**




**Functional group enables unique performance properties**

## Sirrus Monomer – 1,1-Disubstituted Alkene

**The highly reactive electron deficient alkene group promotes fast polymerization at room temperature**




**Two additional functional groups enable physical properties such rigidity, flexibility, crystallinity, thermal and chemical resistance**

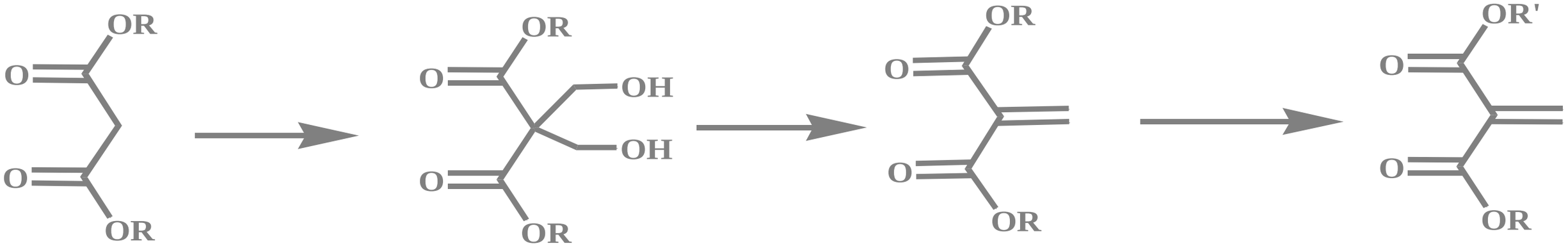
# High Yield & Selectivity

***High molar yielding process eliminates co-product drag***

**Condensation**

**Catalytic Cracking / Fractional Distillation**

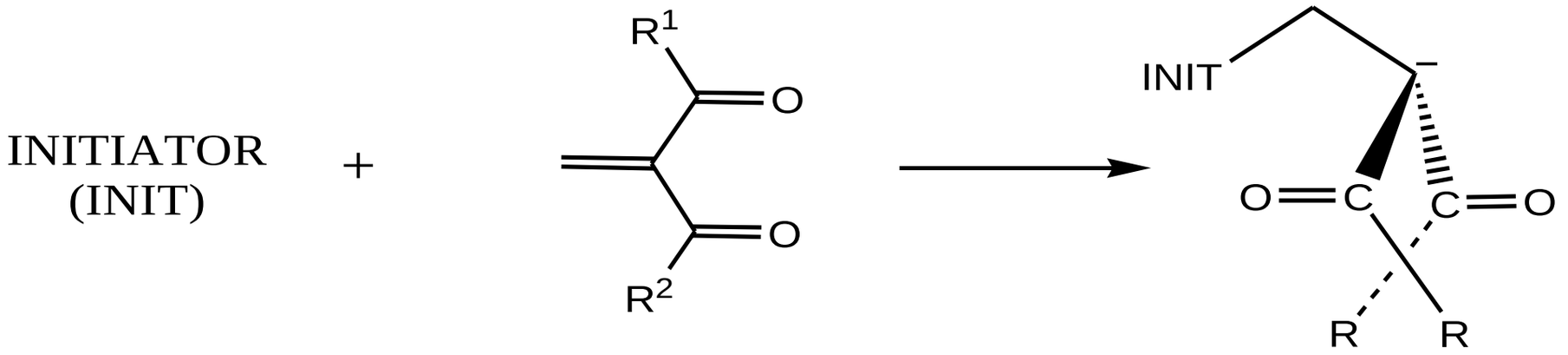
**Transesterification**



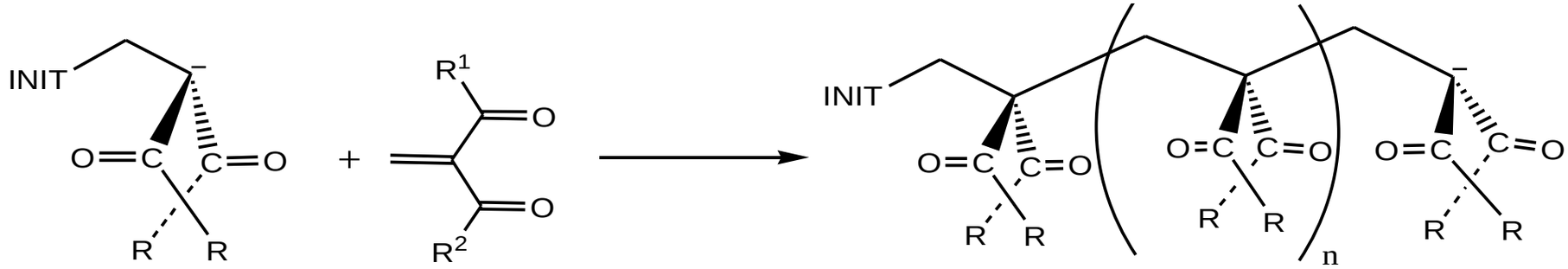

- **Low Raw Material Cost**
- **No Solvents**
- **Minimal Waste**
- **High Yield**
- **Atom Economical**
- **Efficient Catalysis**

# Polymerization Control

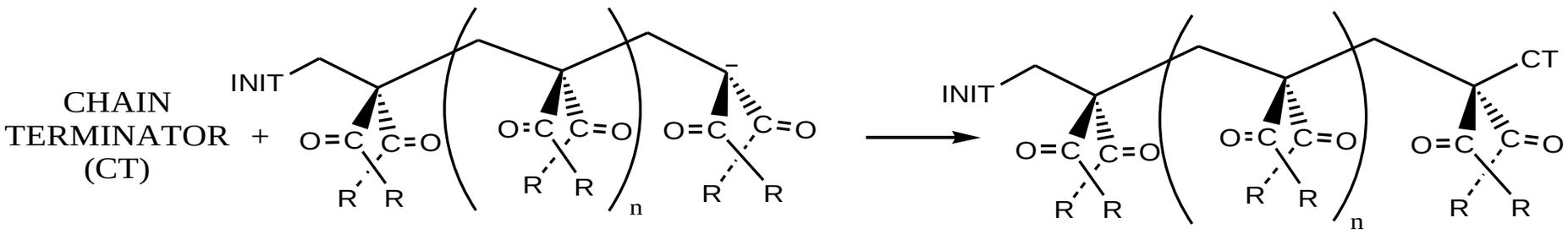
**Initiation**




**Propagation**



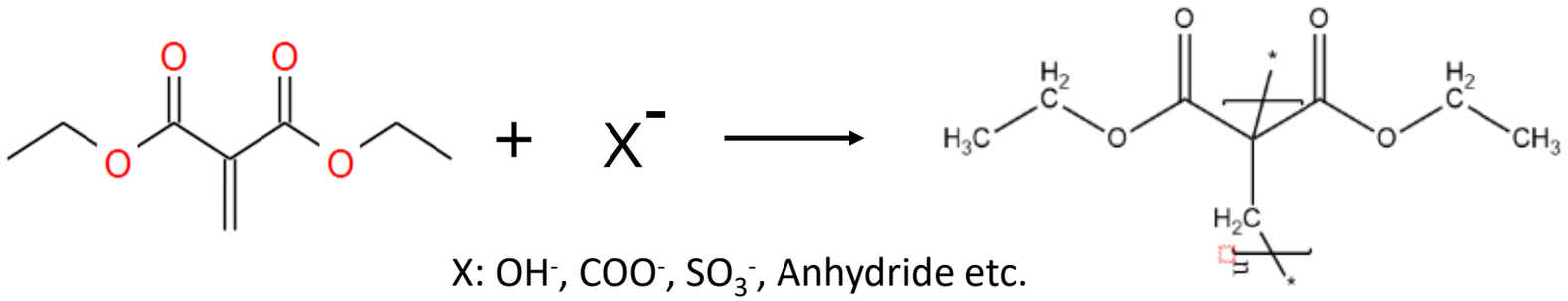

**Termination**



# Polymerization of Methylene Malonates with Various Functionalities

# Chemilian™ M1000 DEMM reacts with various functional monomer salts

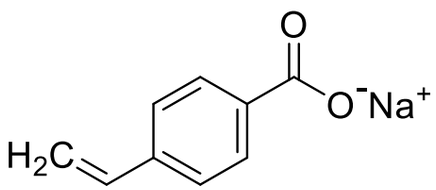
Diethyl 2-Methylenemalonate (DEMM)



X: $OH^-$, $COO^-$, $SO_3^-$, Anhydride etc.

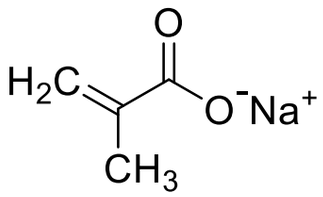
- **Room temperature reaction**
- **Anionic polymerization**
- **Fast reaction rate**

➢ 2-Vinylbenzoic acid (VBA)-DEMM



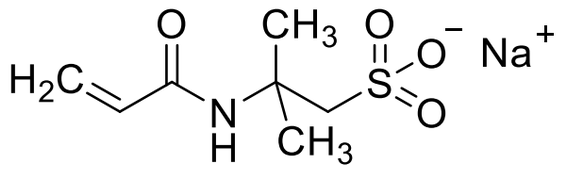
Fast reaction in 5min

➢ Methacrylic acid (MAA)-DEMM

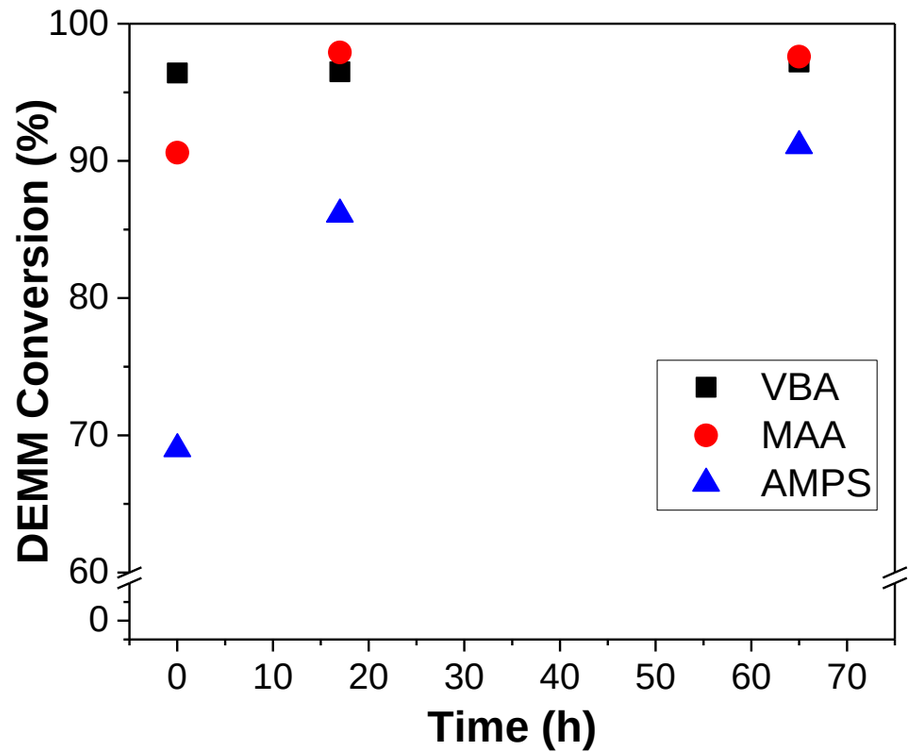


Fast reaction, fully polymerized in 20h

➢ 2-Acrylanmido-2-methyl propanesulfonic acid (AMPS)-DEMM



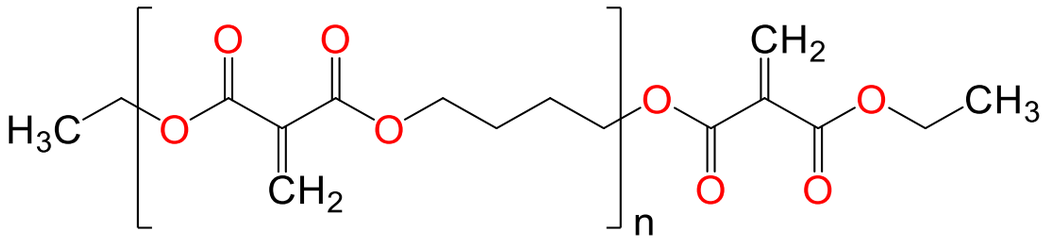
90wt% BDPE polymerized in 70h




Procedure: Mix neutralized monomer salts with DEMM, conduct NMR study

# Polymerization of Forza™ B3100 BDPE with functional groups

BDPE crosslinker




- **Room temperature reaction**
- **Anionic polymerization**
- **React with water under high pH**
- **Viscous, light yellow liquid**

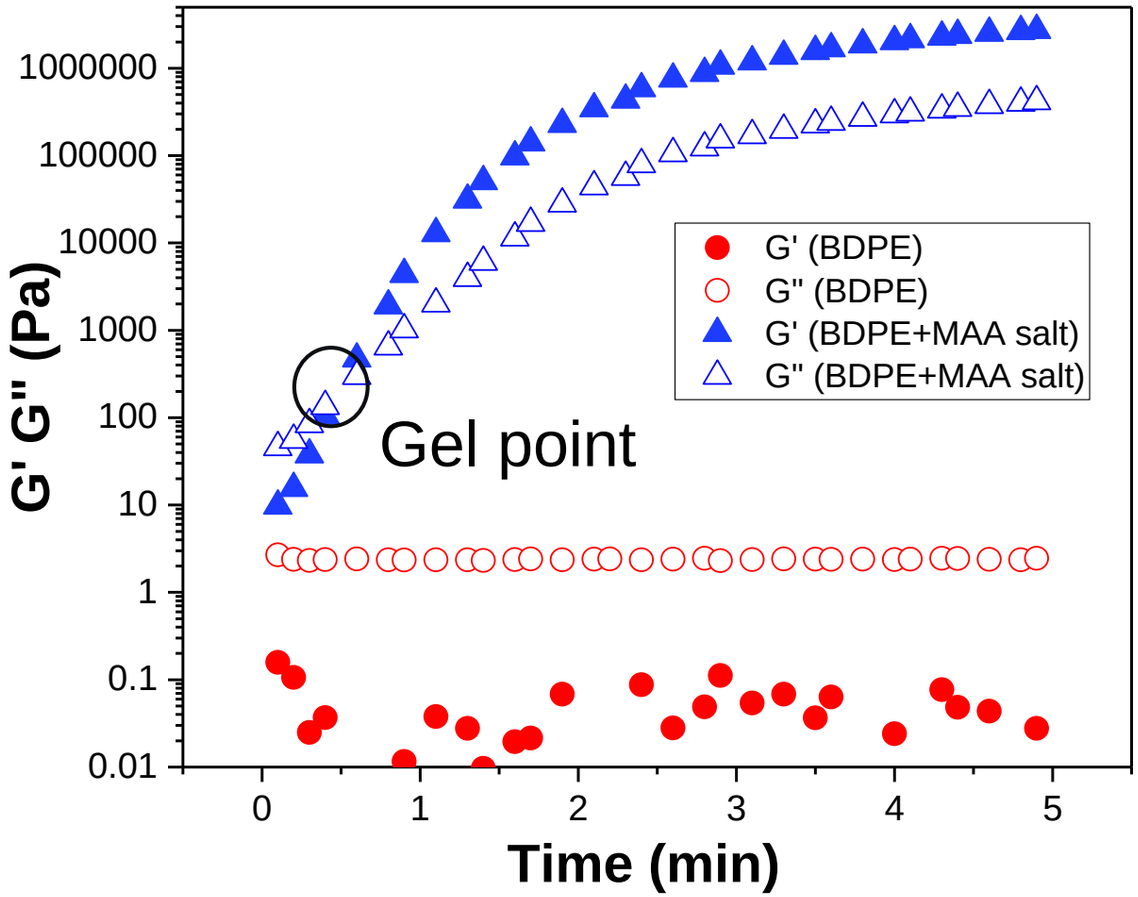
➢ **Experimental procedure:**

(1) Neutralize Methacrylic acid pH7

(2) Blow with $N_2$ and get dry MAA sodium salt

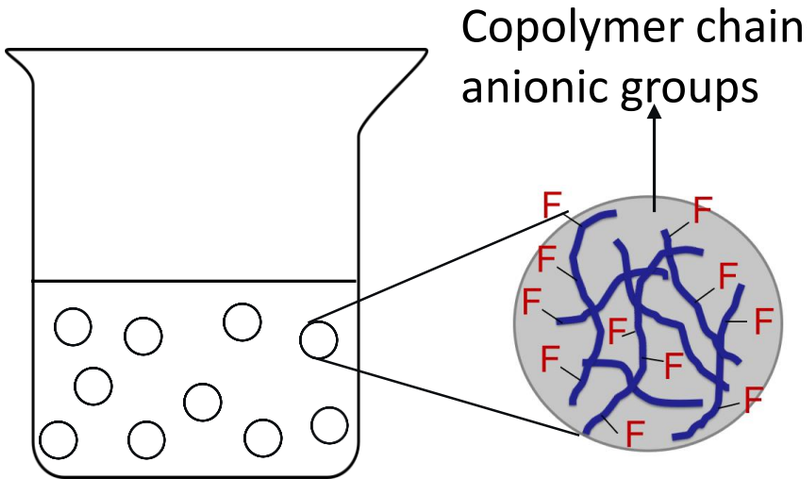
(3) Mix MAA salt with BDPE with weight ratio 1:2

(4) Measure the modulus with rheometer

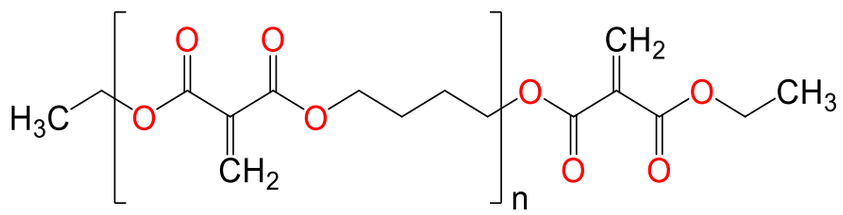

- Carboxylate group can initiate BDPE polymerization in a short period of time

# Crosslinking Functional Latex with Forza™ B3100 BDPE

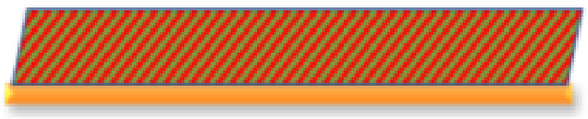



**Functional latex**

-F: functional group, eg COO-, $SO_3$-, -$NH_2$, -OH




**BDPE crosslinker**

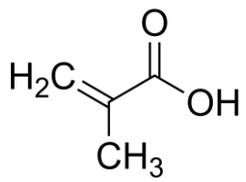


**Crosslinked coating**

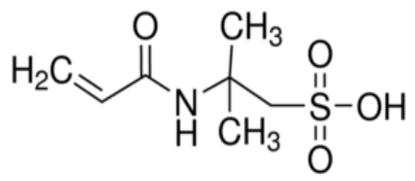
- Matrix monomer of latex: Methyl Methacrylate and Butyl Acrylate
- Co-polymerize with functional monomers
- No volatile organic Compounds

- **Room temperature cure**
- **Excellent Material performance**
- **Solvent and corrosion resistant**

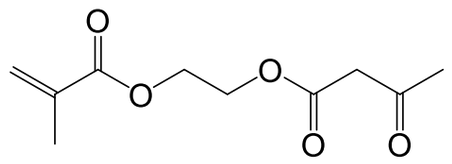
➢ Functional monomers that were investigated:



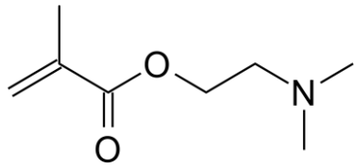
Methacrylic acid



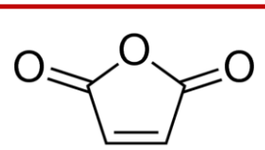
2-Acrylanmido-2-methyl propanesulfonic acid



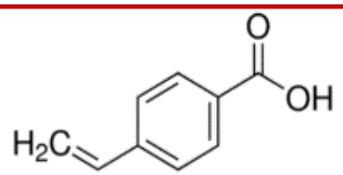
Acetoacetoxyethyl methacrylate



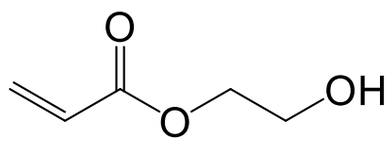
2-(Dimethylamino)ethyl methacrylate



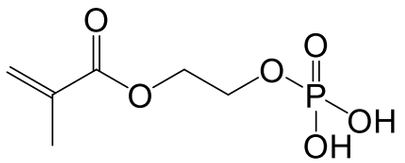
Maleic anhydride



4-Vinylbenzoic acid



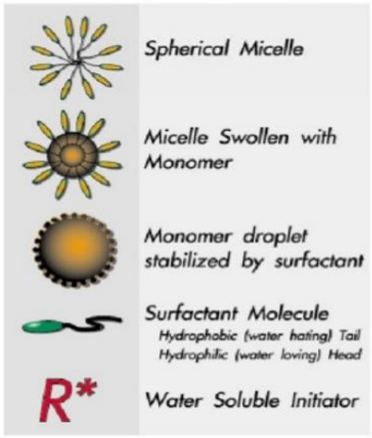
2-Hydroxyethyl acrylate

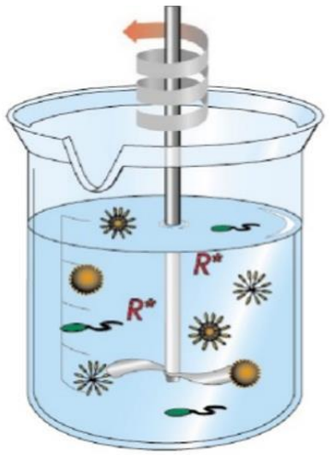


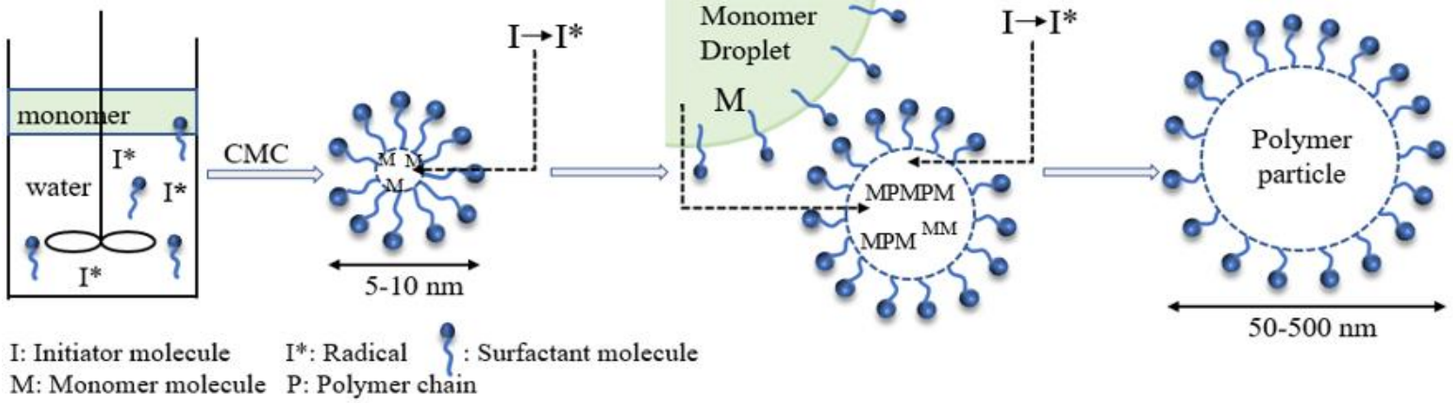
Phosphoethyl methacrylate

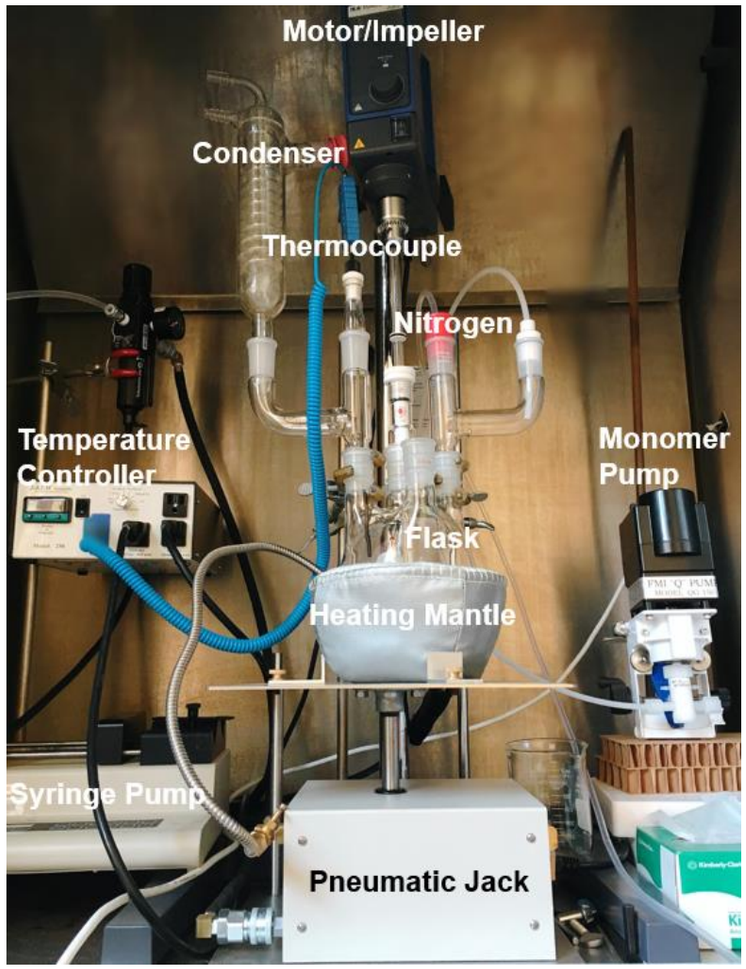
# Crosslinking of Model Latexes

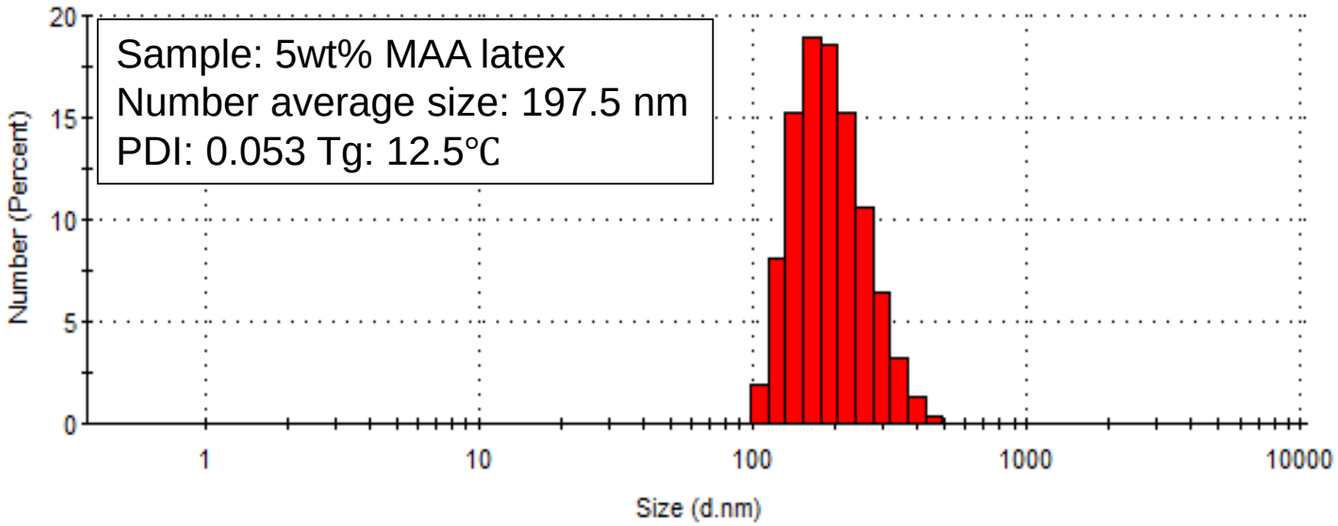
# Functional Latex by Emulsion Polymerization



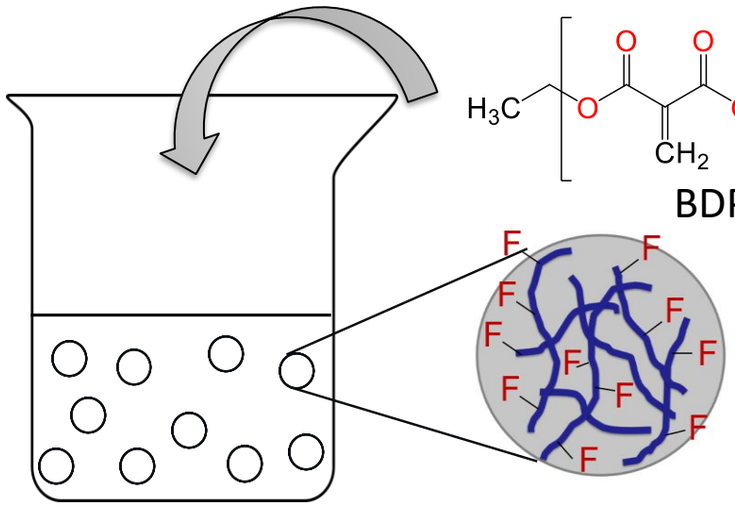



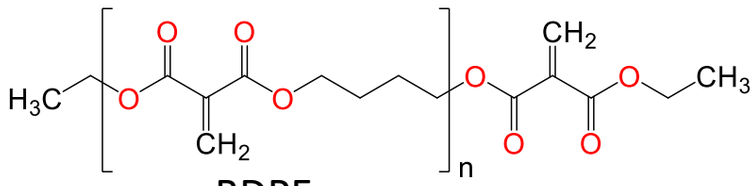




- Emulsion polymerization can synthesize stable latex with narrow particle size distribution
- A widely used approach in industry due to its convenience

# Side Reactions with Water



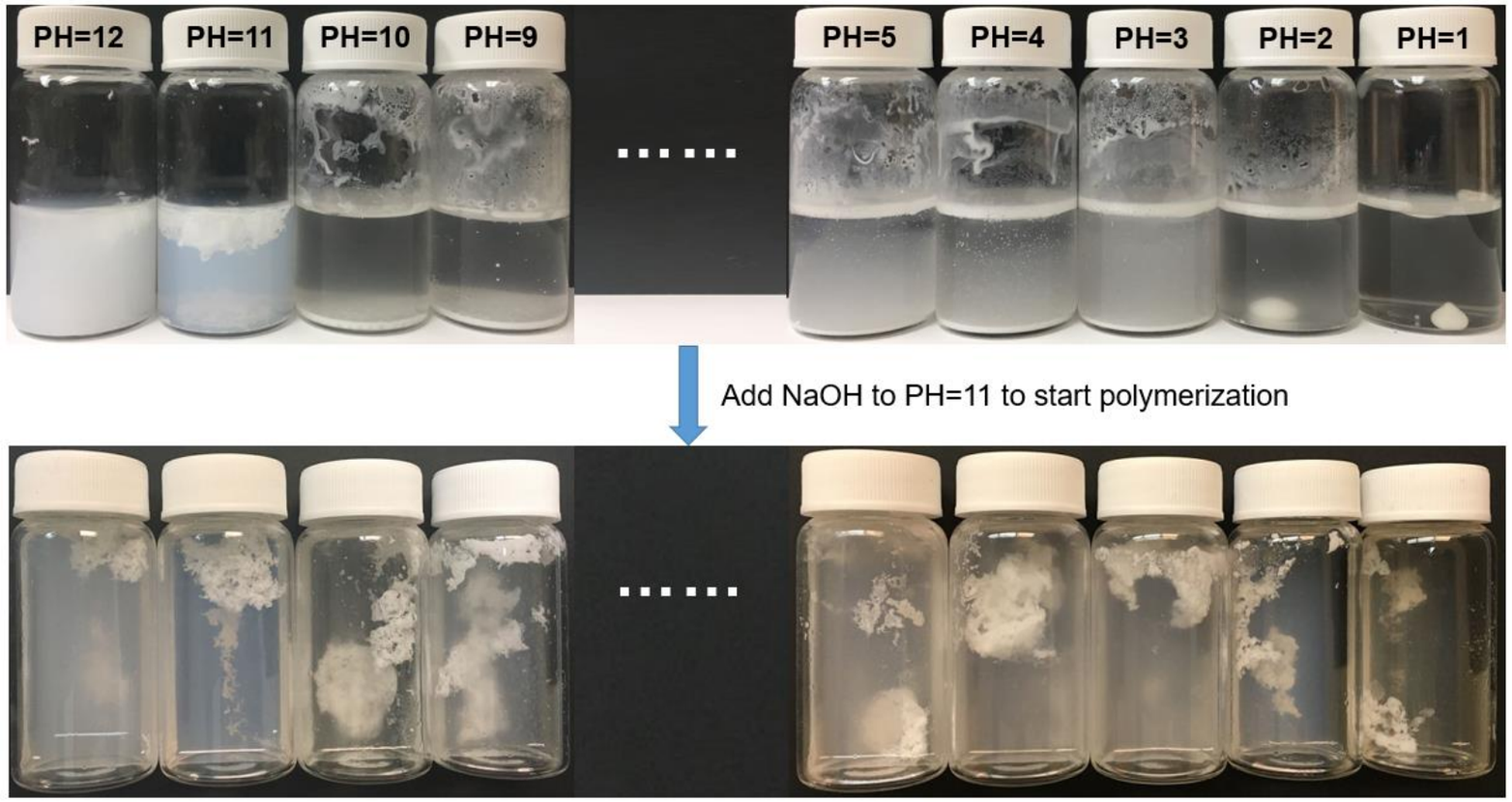



BDPE




- BDPE reacts with $H_2O$

Increasing pH



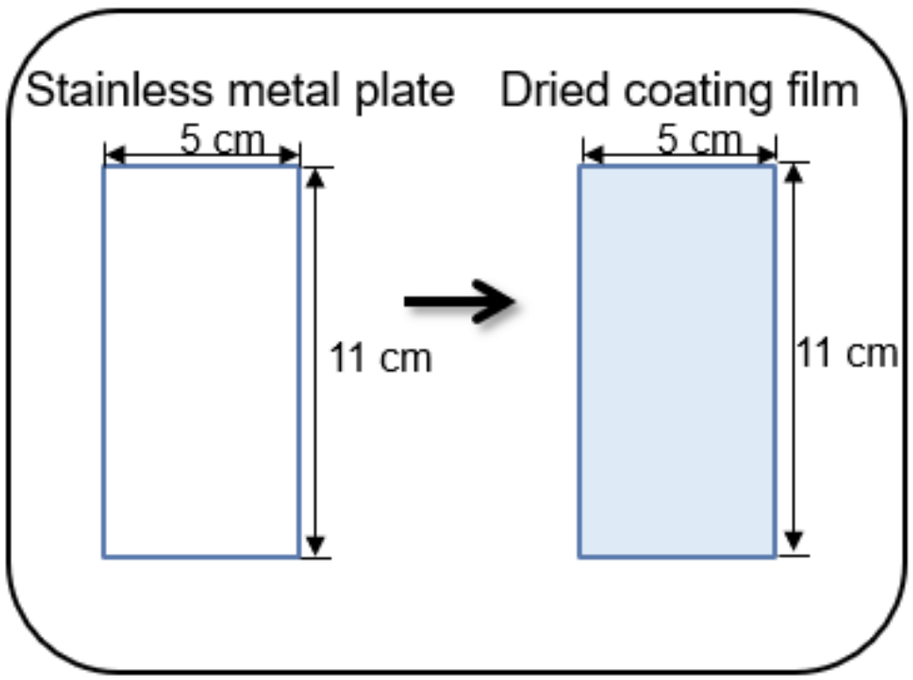

BDPE can react with water, but this side reaction can be suppressed by the control over pH.

# Performance after Crosslinking

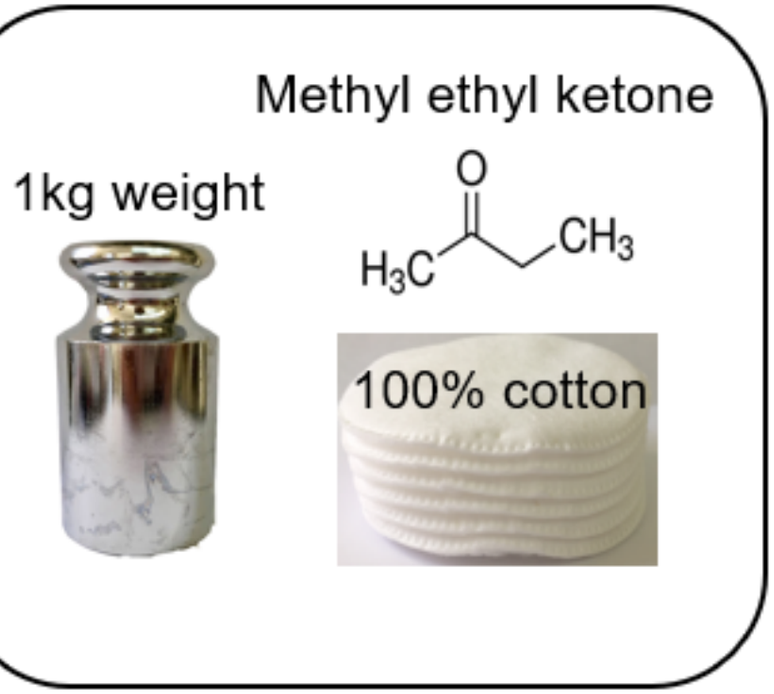
# MEK Double Rub Test Procedure (ASTM D4752)

Drawdown the latex

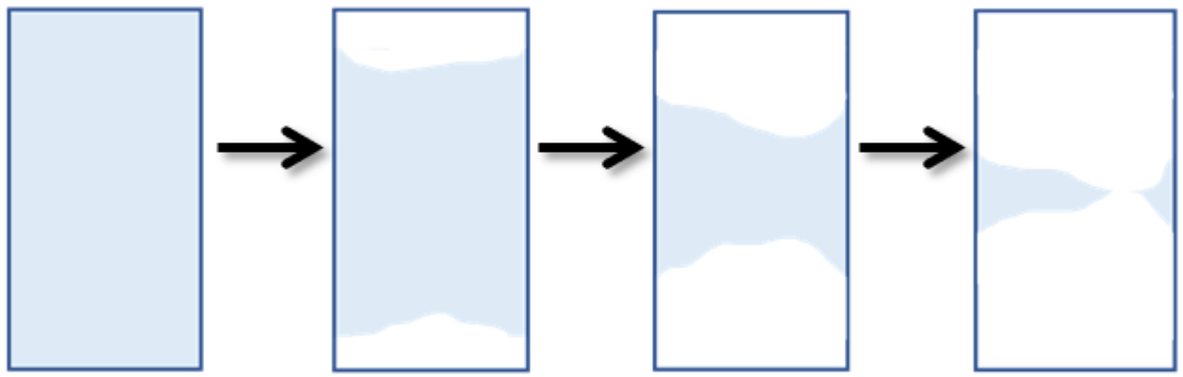

Curing with water evaporation




MEK double rub test



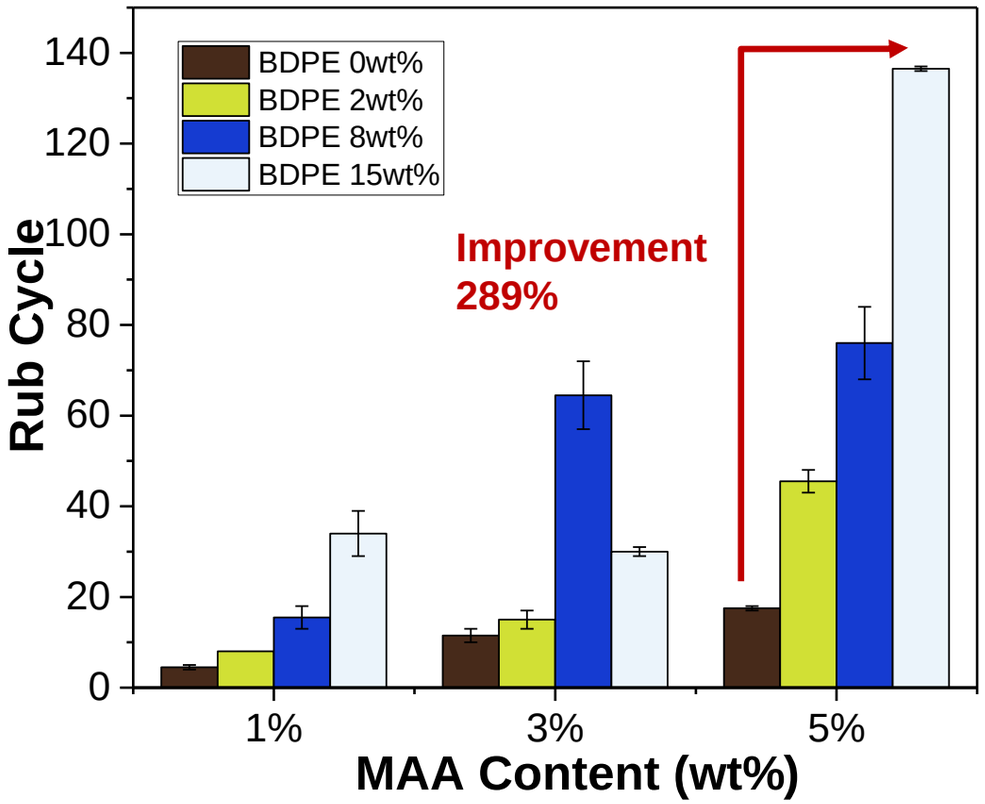

Rubbing procedure



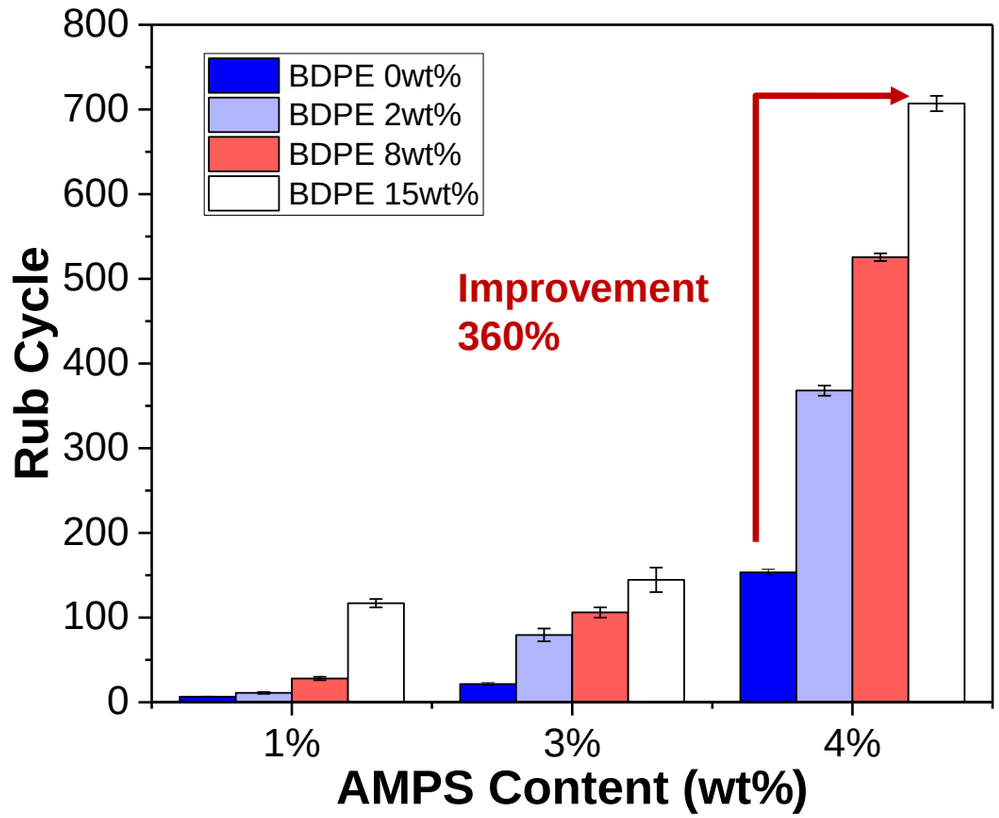
# MEK Rub-Resistance with Forza™ B3100 BDPE Addition

**Preparation : Add BDPE directly to latex (pH 7), mix for 2h, drawdown and cure at room temperature for 3 days before rub test.**

MAA latex




AMPS latex

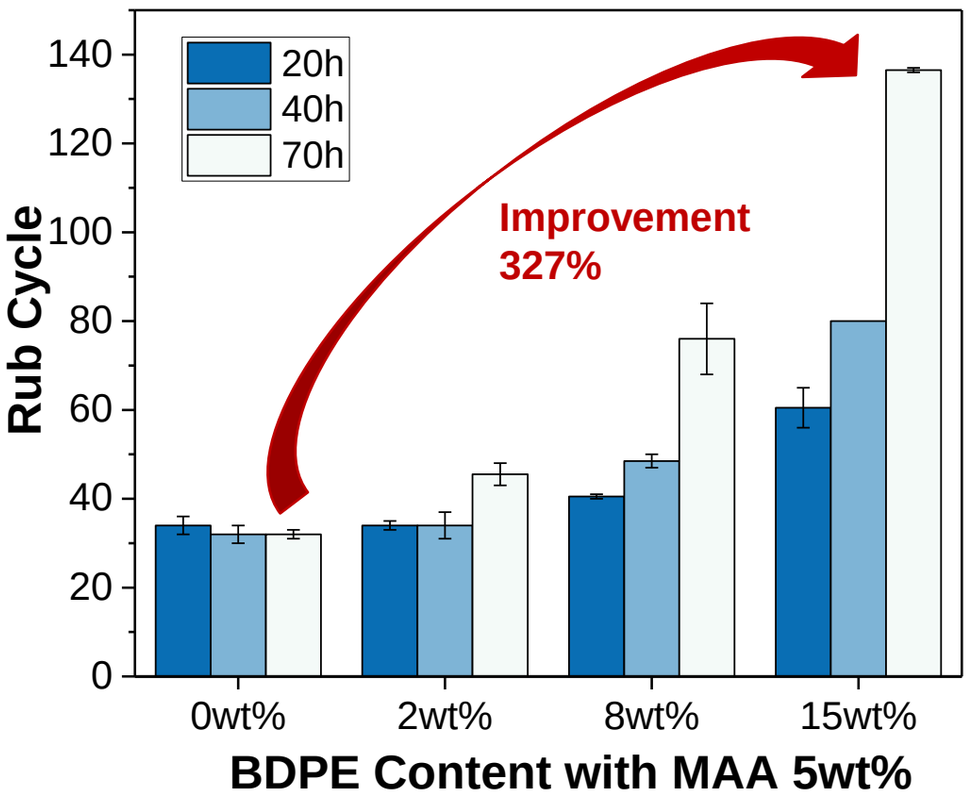



- Rub-resistant performance is improved by increasing the content of functional monomers and BDPE crosslinker
- In this experiment, AMPS might be less protonated than MAA, resulting in higher activity

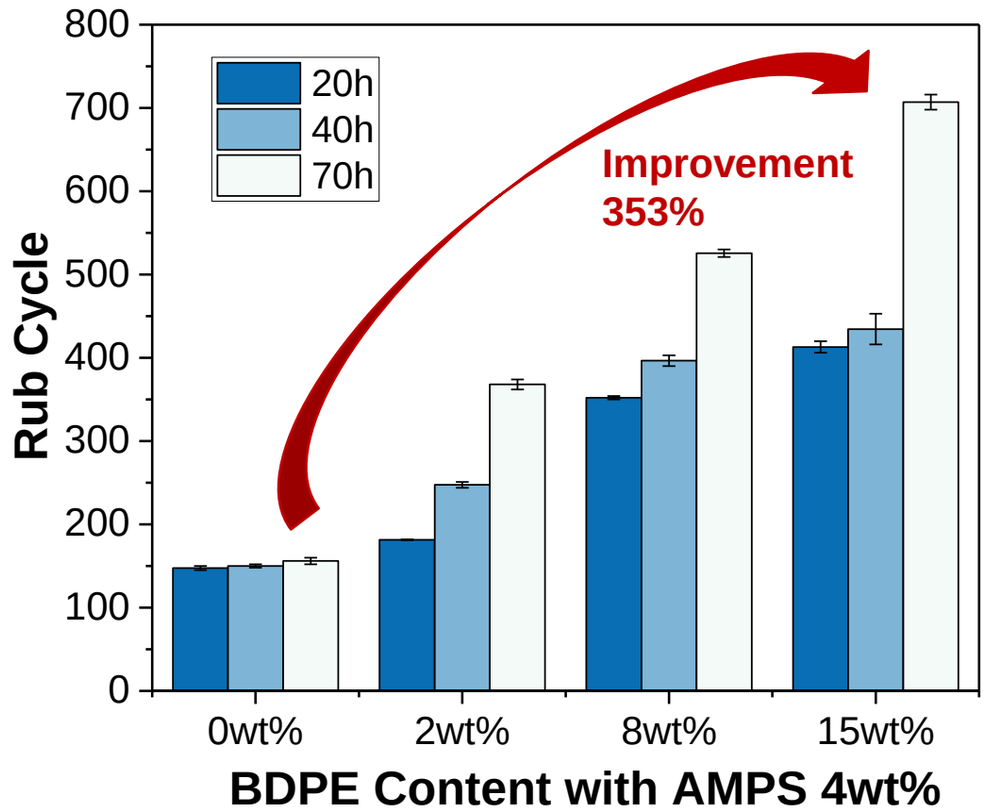
# Curing Time Dependence

**Preparation : Add BDPE directly to latex, mix for 2h, drawdown and cure at room temperature for various curing time then conduct rub test.**

MAA latex




AMPS latex

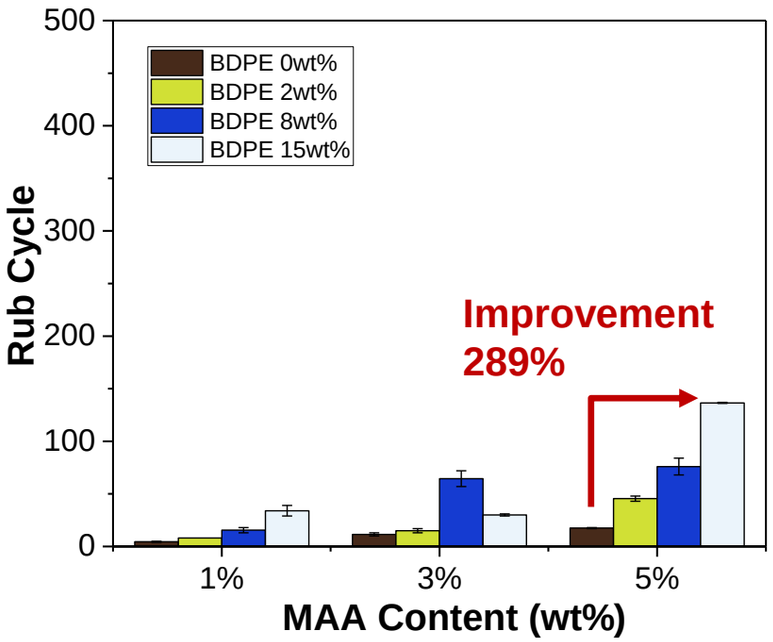


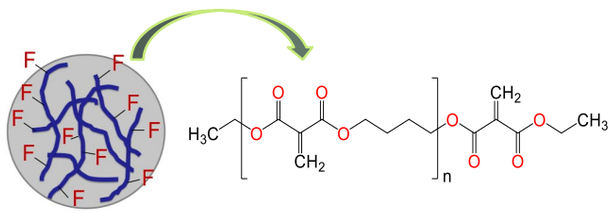

- The performance of MAA and AMPS latex crosslinked by BDPE is greatly improved with longer curing time.

# Comparison of Different Sample Preparation Techniques

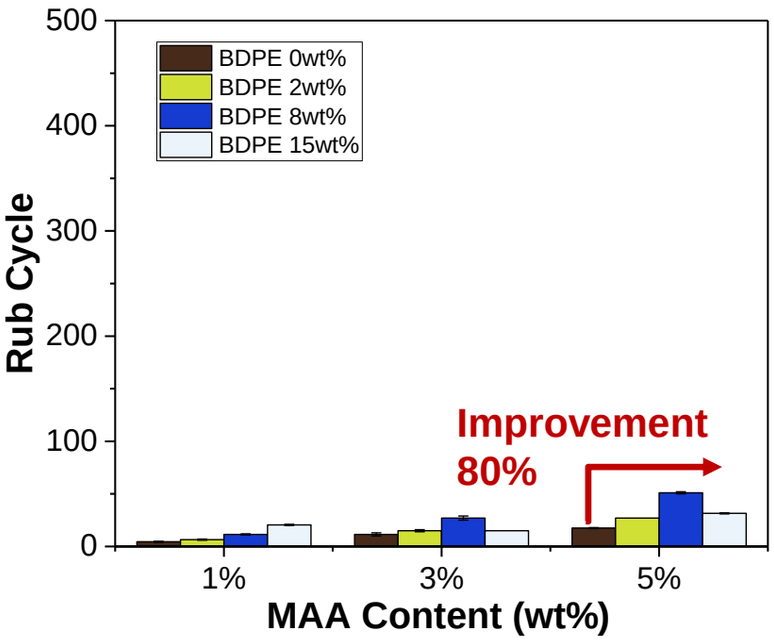
- **Three other methods applied for MAA latex**

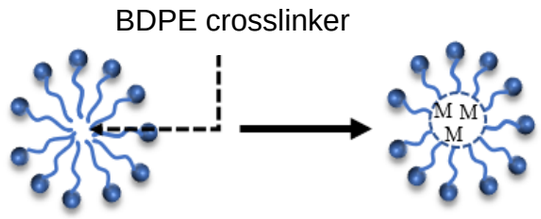
**Add BDPE directly**



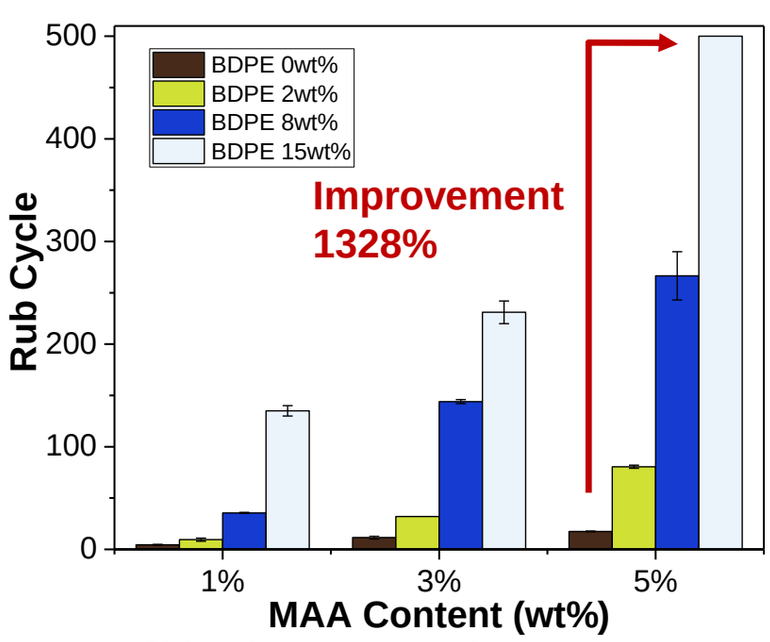



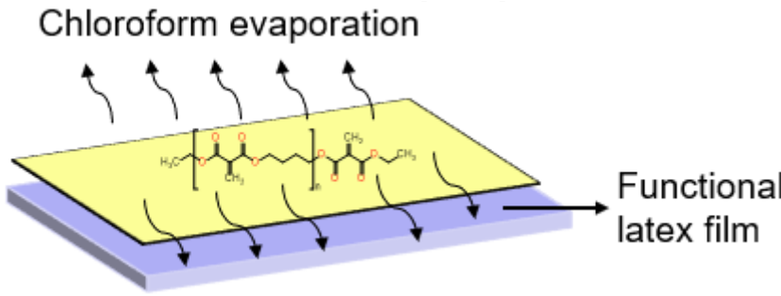

**Pre-emulsified BDPE in surfactant in water first**




**Dissolve BDPE in Chloroform then apply to dry film**

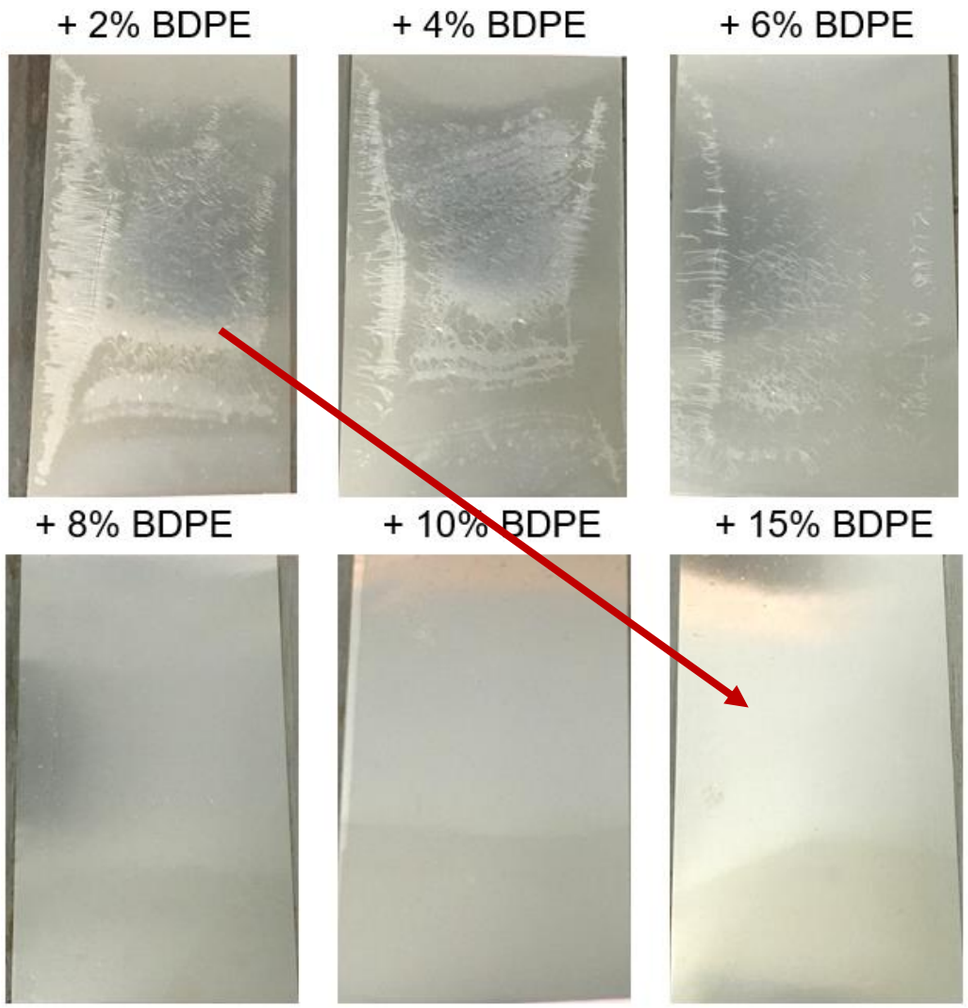


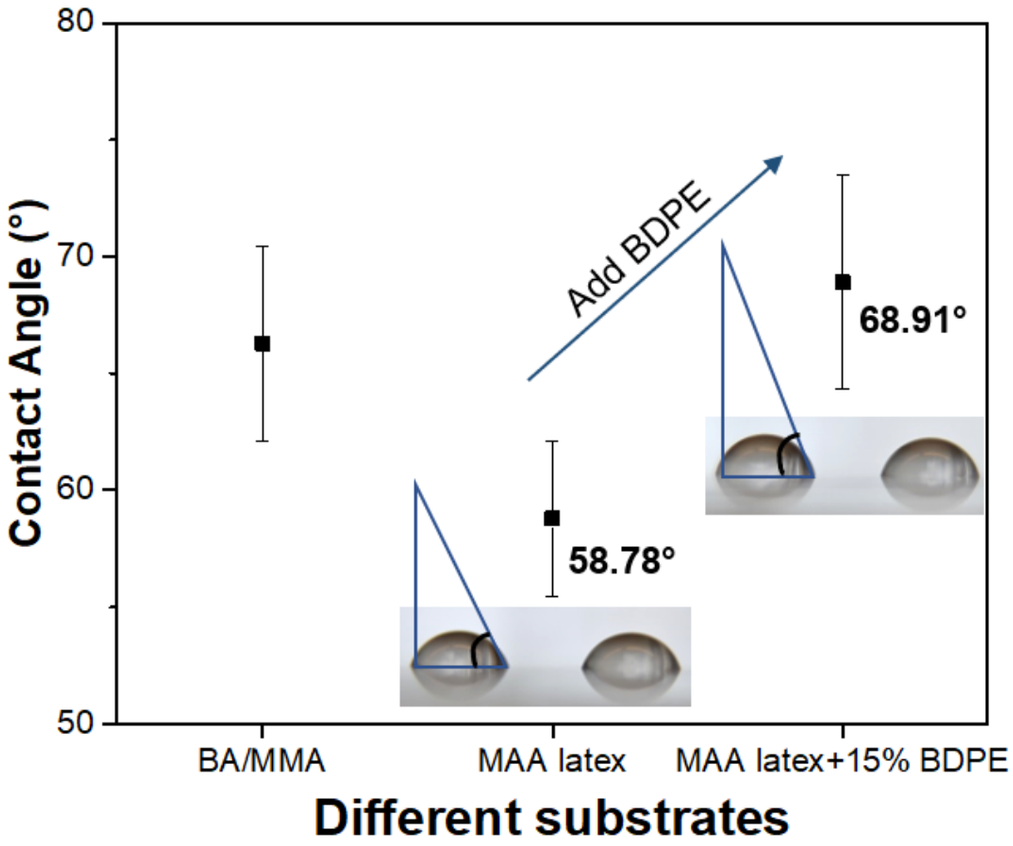

- The introduction of surfactant molecular might wrap BDPE into micelles
- Organic solvent allows penetration of BDPE across the coating layer

# Improvements in Film Formation

- Film formation of 5wt% MAA latex with BDPE




- Contact angle experiment

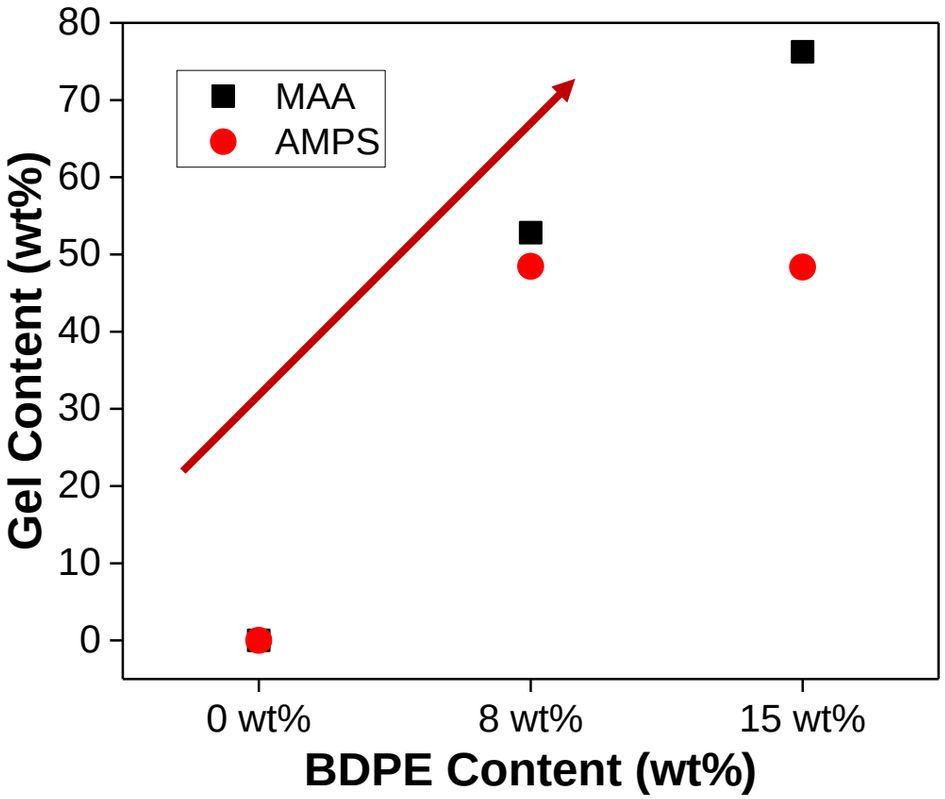



Preparation : Drop 4ul water onto 5wt% MAA latex film with and without BDPE.

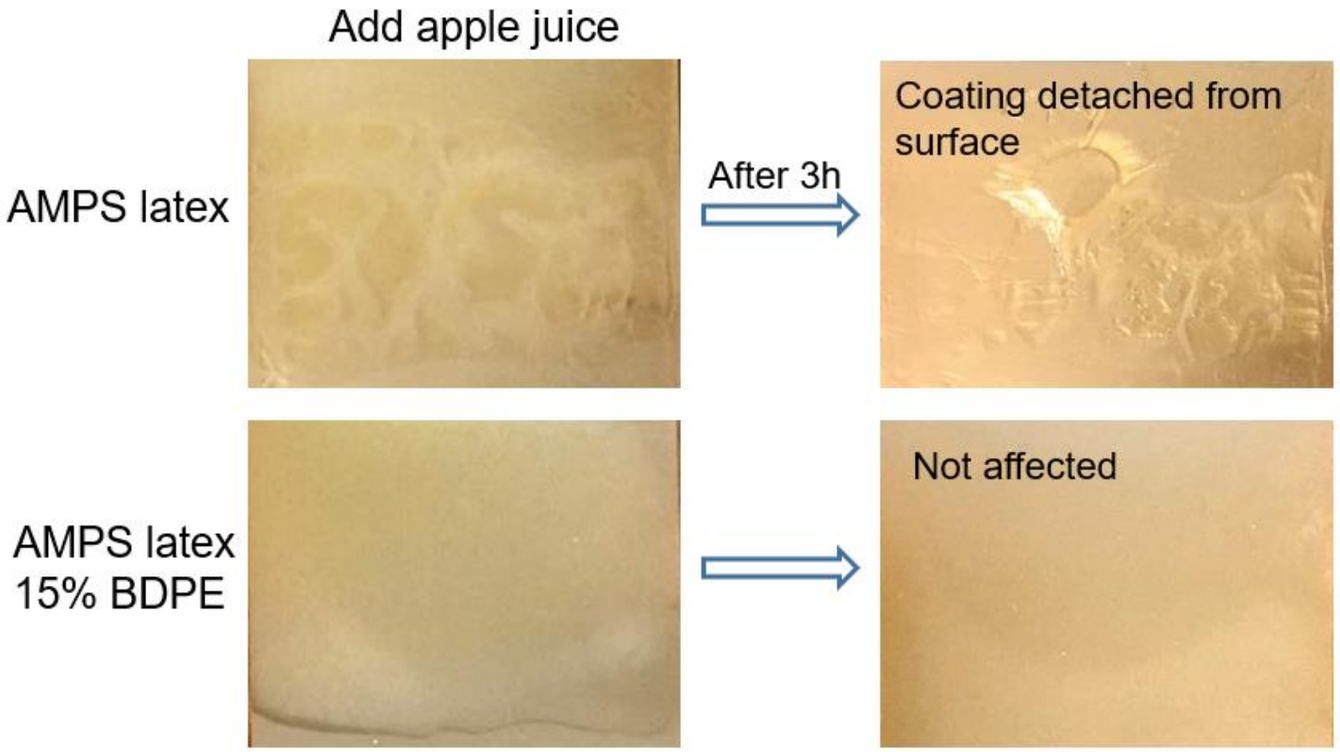
- Addition of BDPE improves film forming capabilities
- Addition of BDPE results in higher hydrophobicity

# Stain-Resistance and Gel Content of Forza™ B3100 BDPE-Containing latex

## ➢ Gel content experiment




## ➢ Apple juice test




Procedure:

1. BDPE and functional latex react for 2h, get solid product
2. Dissolve solid latex in dimethylformamide for two days
3. Dry the mixture again, and measure gel content

- The addition of BDPE causes gelation, indicating the formation of network
- BDPE increased the hydrophobicity of the latex film

# Conclusions

- Chemilian™ M1000 (DEMM) and Forza™ B3100 (BDPE) exhibit rapid reaction rate with anionic groups on polymer latexes at room temperature reaction
- pH impacts the anionic initiation through neutralization of acid functionality
- Evidence of crosslinking is based on
  - Improved resistance to solvent, rub and stain
  - Good film formation
- Multifunctional methylene malonates can provide a new crosslinking technology for latexes

# Acknowledgements



**Advisor:**
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Dr. Yuan Liu

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Irene Kurtz
Xiangxi Meng
Juanfeng Sun
Kelsi Skeens
Shane Taylor
Nicholas Hight-Huf
Yen Tran
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Samuel Trevenen

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