paintistanbul TURKCOAT CONGRESS

The Effects of Chain Rigidity of Hyper Branched Polymer based Dispersion Agents for Carbon Black Dispersion Systems

Assoc. Prof Ümit Hakan YILDIZ

İzmir Institute of Technology
&
Denge Kimya

densurf

The Effects of Chain Rigidity of Hyper Branched Polymer based Dispersion Agents for Carbon Black Dispersion Systems

Assoc. Prof Ümit Hakan YILDIZ
İzmir Institute of Technology
&
Denge Kimya

PRODUCT RANGE

DA Dispersing Agents

AF Defoamers and Air Release Agents

SM Surface Modifiers

HR Silicone Resins

DISPERSING AGENTS

Talk Plan/Outline

- Gray/Green Chemistry
- Strategies in Green Conversion

densurf

Talk Plan/Outline

- Gray/Green Chemistry

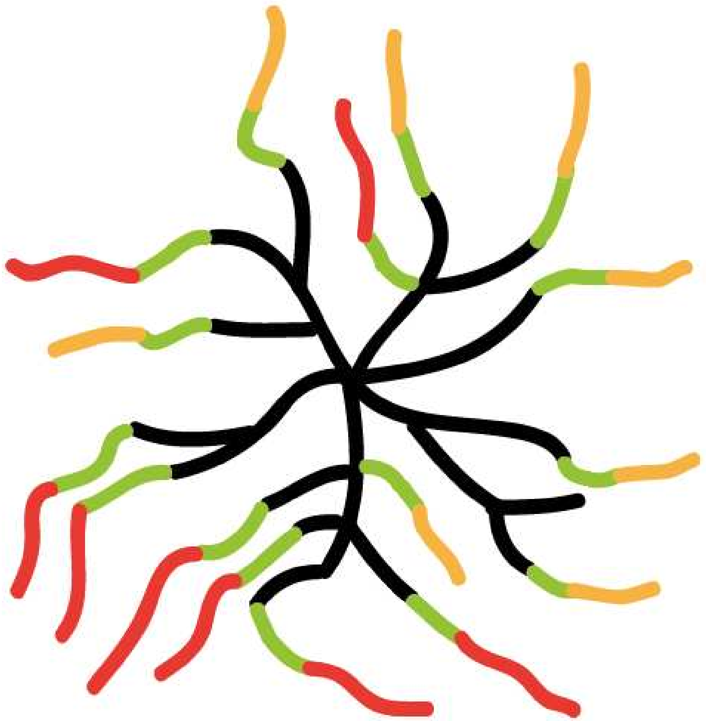
1. Prevent Waste

2. Maximize Atom Economy

11. Prevent Pollution

Talk Plan/Outline

- Gray/Green Chemistry
- Strategies in Green Conversion
- Hyper-branched Polymers



densurf

Talk Plan/Outline

- Gray/Green Chemistry
- Strategies in Green Conversion
- Hyper-branched Polymers
- Synthetic details of Hyper-branched Polymers based dispersion agents
  - Green catalyst for Polyesters
  - Natural Feedstocks of Polyesters
- Near Future Projections
- Road Map for 100% Green Product
- Conclusive Remarks

densurf

Twelve Principles of Green Chemistry

GREEN CHEMISTRY

1. Prevent Waste
2. Maximize Atom Economy
3. Less Hazardous Chemicals
4. Safer Chemicals Products
5. Safer Solvents & Rxn Cond.
6. Increase Energy Efficiency
7. Use Renewable Feedstocks
8. Avoid Chemical Derivatives
9. Use Catalyst
10. Degrading Products After Use
11. Prevent Pollution
12. Prevent Accidents

Gray to Green Conversion

Green Chemistry: Conducting chemical reactions and processes via natural products without hazardous solvents and by products at room temperature

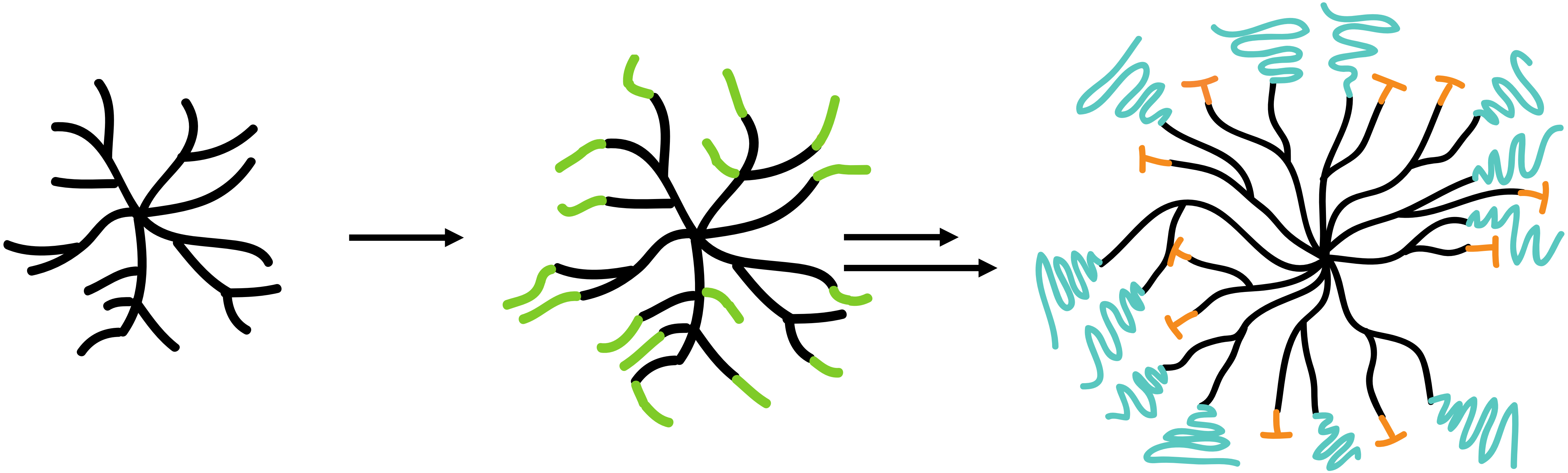
Gray Chemistry is the current practice in which oil based reactants and solvents are involved for production.

Green Transformation Plan: Starting point is 10% with current settings, in 36 months our commitment is 50% and following in 24 months 90% green transformation is projected

Gray to Green Conversion

10% 90%

Hyper-Branched Polymer based Dispersion Agent



DA-4115

Hyper-Branched Polymer based Dispersion Agent

Detailed discussion of hyper-branched polymer based dispersion agent were presented in ….
As highlighted polyester as well as viscosity modifying units are necessary.

Macromol. Symp. **187**, 683–693 (2002) 683

Hyperbranched Polymers as a Novel Class of Pigment Dispersants

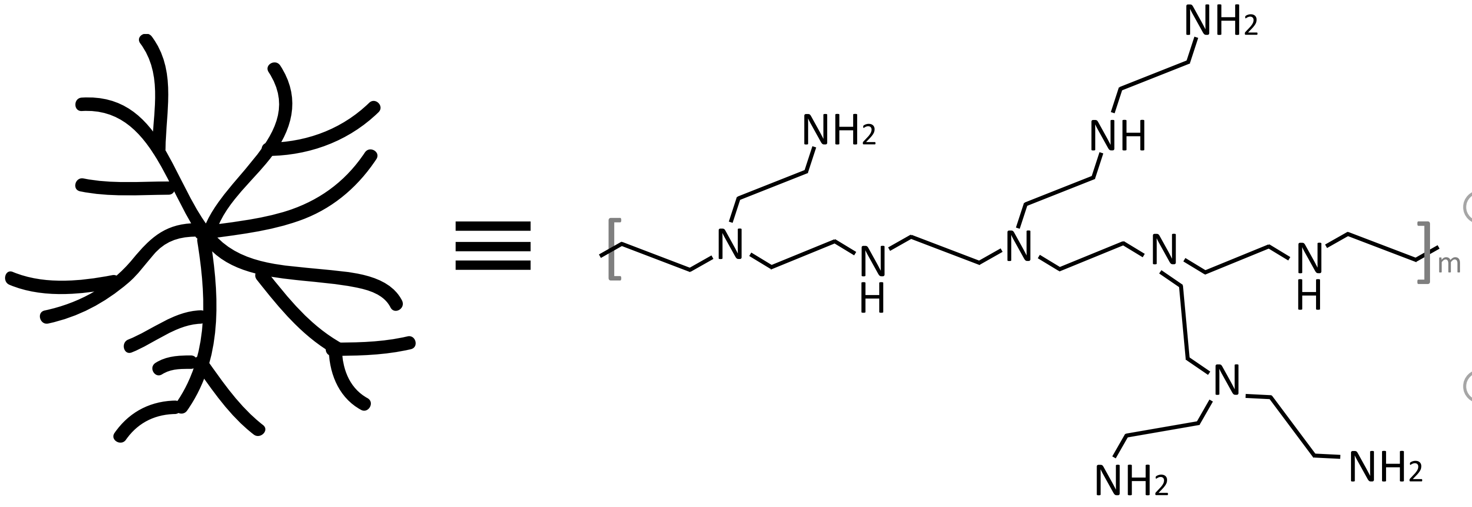
*F.O.H. Pirrung, E.M. Loen and A. Noordam**

EFKA Additives B.V., Innovatielaan 11, 8466 SN Nijehaske, The Netherlands

PEI-Core

10% 90%

Hyper-Branched Polymer based Dispersion Agent



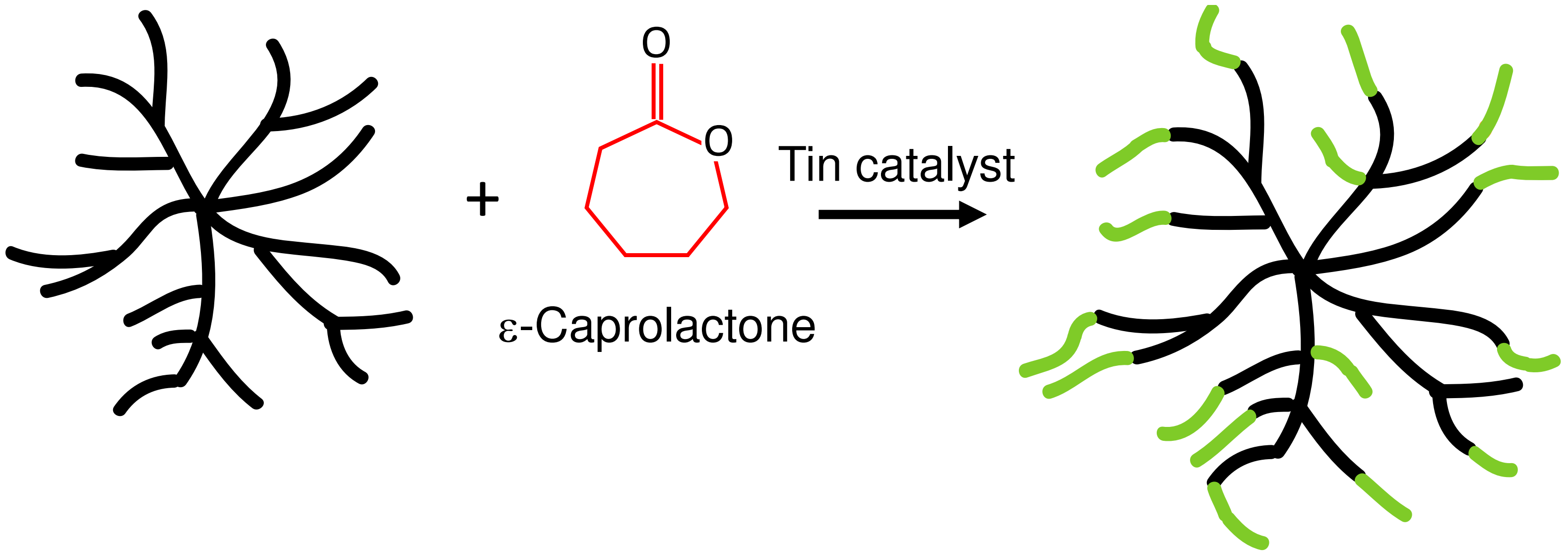
- Core of the dispersion agent is hyper-branched Polyethyleneimine of Mw: 2000 g/mol.
- It is a ring opening of product of Aziridine.
- PEI_{2000} is colorless, liquid reactant containing 60% reactive amine.

PEI hyper branched polymers is 7.5 % of the end product

densurf

Is Green Functionalization Possible ?

Hyper-Branched PEI with Polyester arms



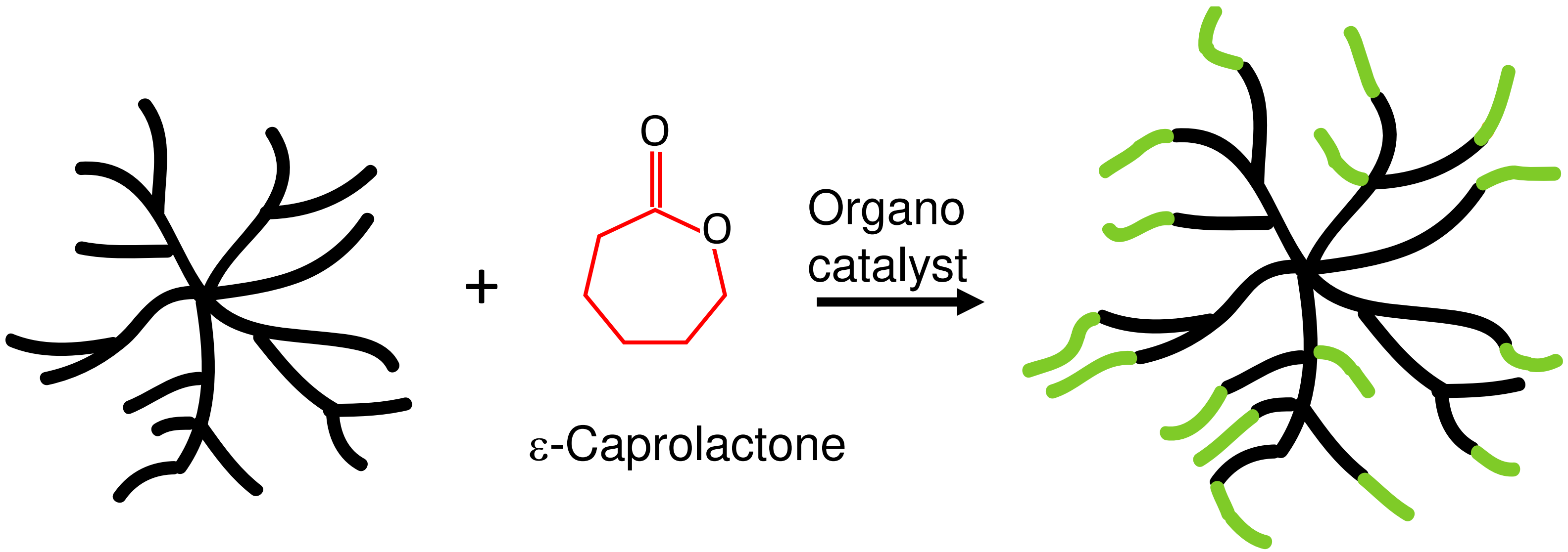
- Reactive amines used as initiator of ring opening reaction of cyclic ester monomers
- Conventional method suggest use of "Tin" catalyst.

Green Chemistry: Conventional rxn carried out at 110-130 ^{o}C and yield 98 %

densurf

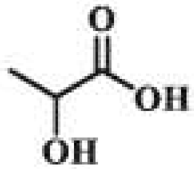
Is Green Functionalization Possible ?

Hyper-Branched PEI with Polyester arms

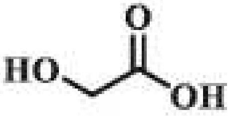


ε-Caprolactone

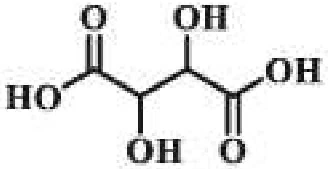
- Instead conventional method we suggest use of acid catalyst.
- Lactic Acid, Glycolic Acid, Tartaric Acid, Citric Acid have been employed



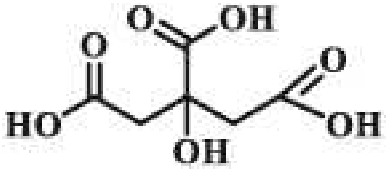
Lactic Acid



Glycolic Acid



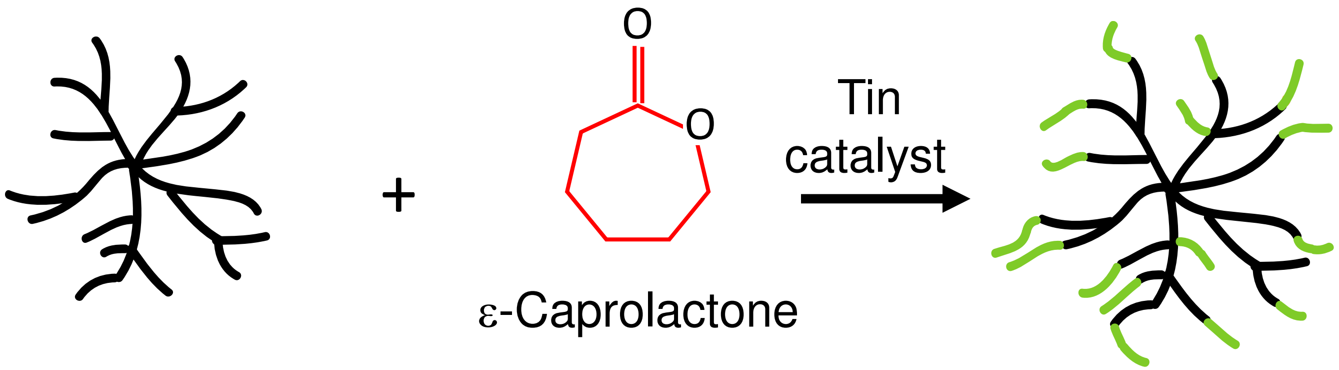
Tartaric Acid



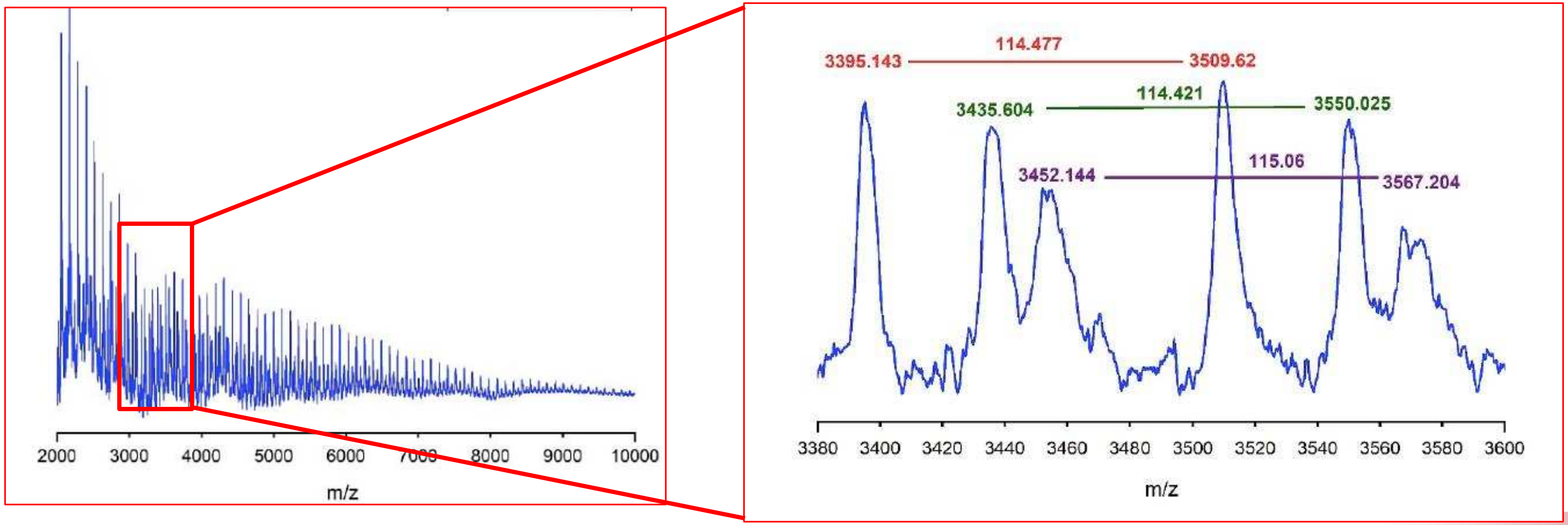
Citric Acid

Green Chemistry: Organo catalyst rxn carried out at 85 ^{o}C and yield 95 %

Molecular Weight of Tin Catalyzed ROP



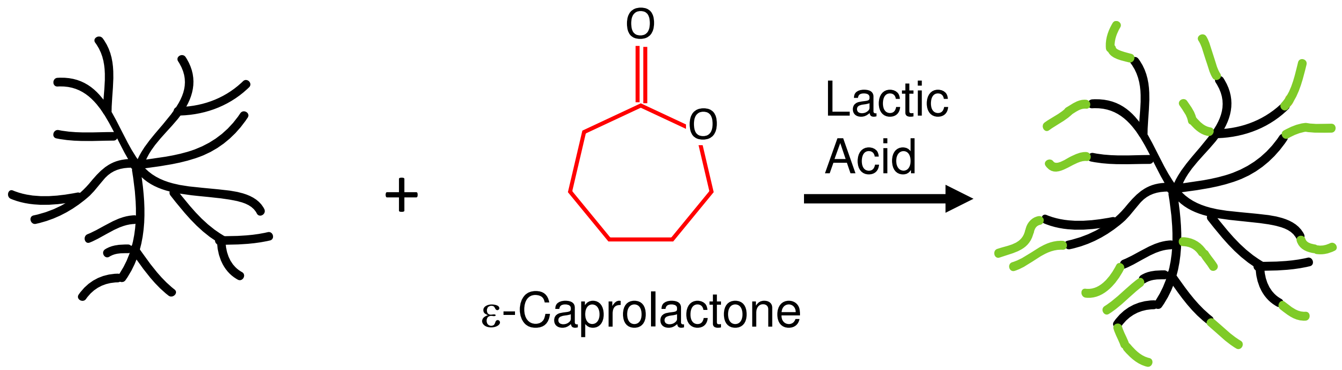
- Tin catalyzed rxn exhibits polydisperse molecular weight.



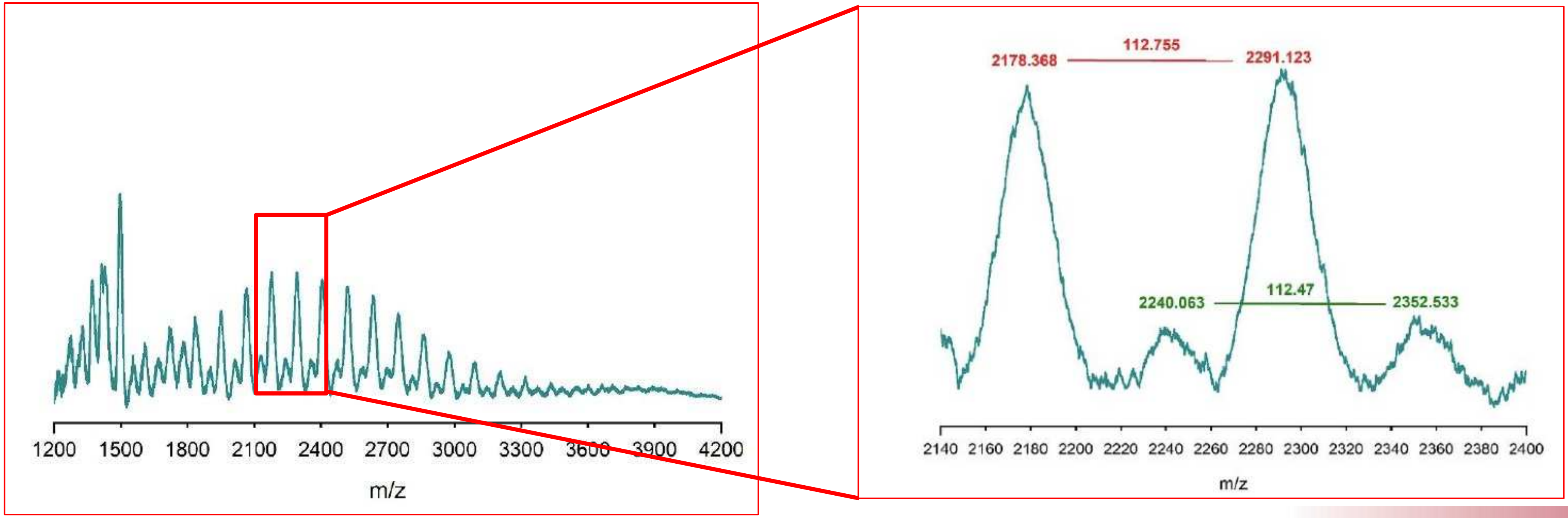
Mass spectrum of PEI-PCL (Tin Catalyzed Rxn.)

densurf

Molecular Weight of LA. Catalyzed ROP



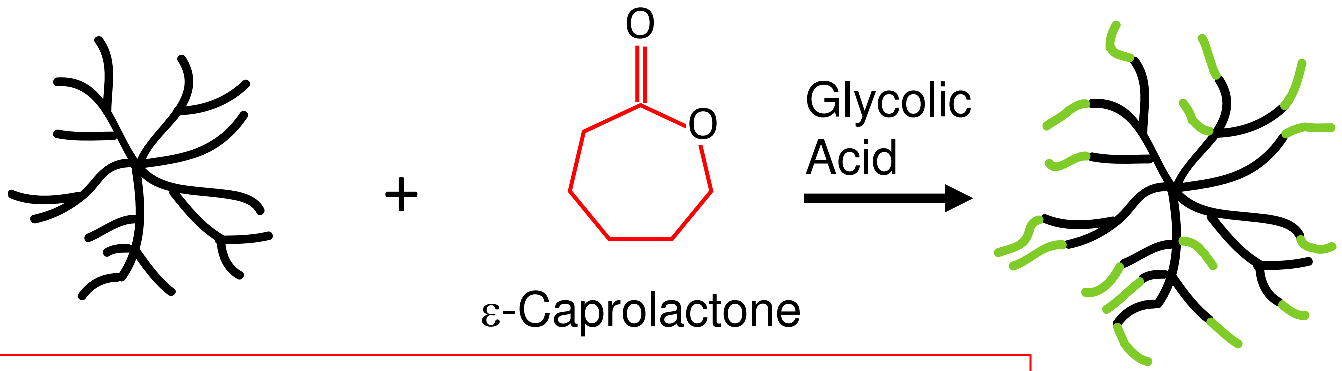
- LA catalyzed rxn exhibits Gaussian type polydisperse molecular weight.(1500-3300 Da)



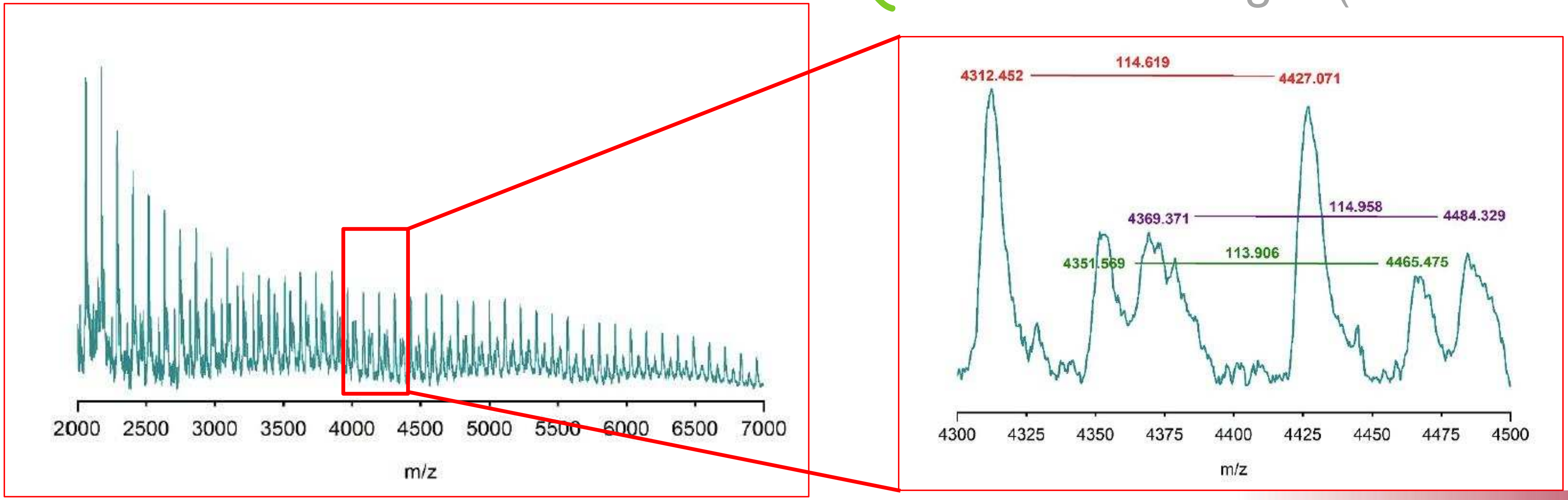
Mass spectrum of PEI-PCL (Lactic Acid Catalyzed Rxn.)

densurf

Molecular Weight of GA. Catalyzed ROP

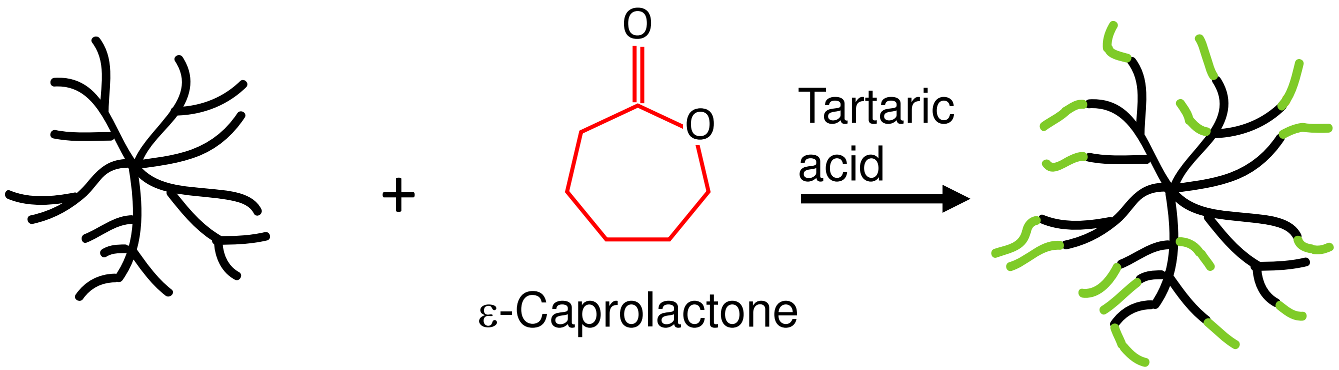


- GA catalyzed rxn exhibits irregular type polydisperse molecular weight.(2000-7700 Da)

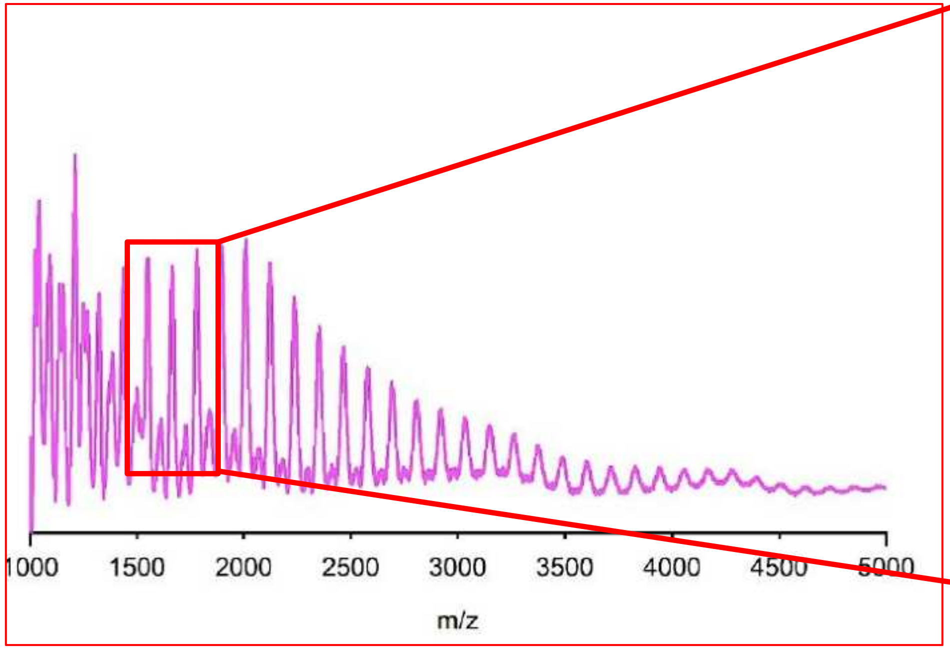


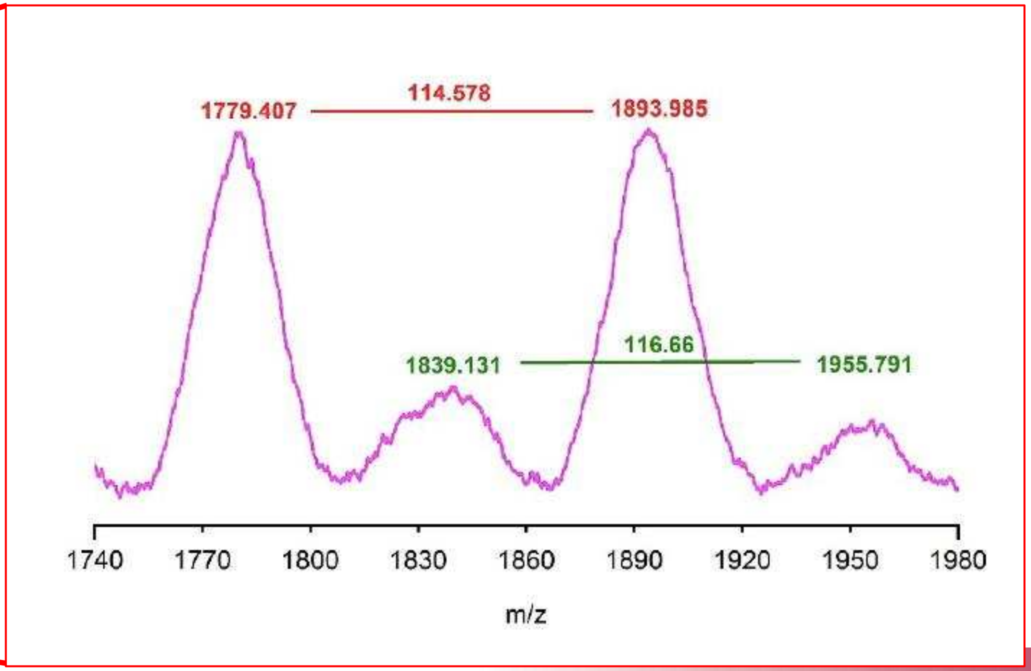
Mass spectrum of PEI-PCL (Glycolic acid Catalyzed Rxn.)

Molecular Weight of TA. Catalyzed ROP



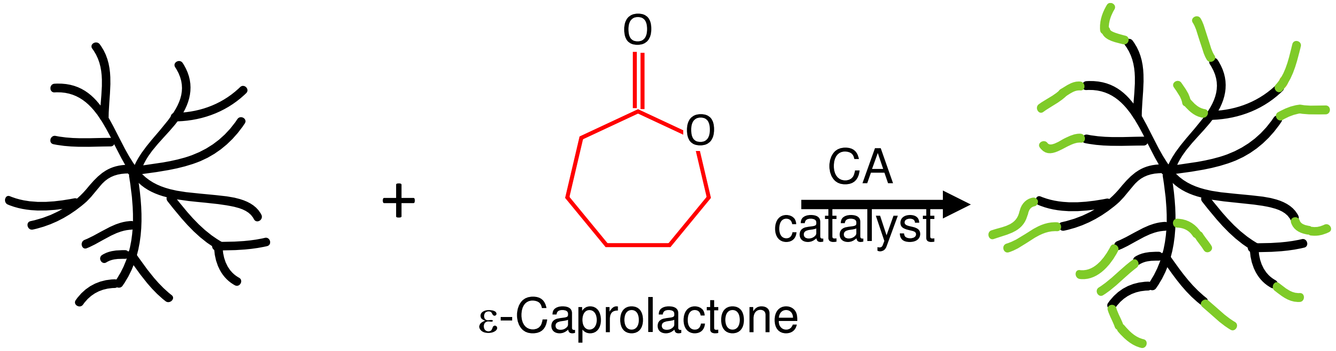
- TA. catalyzed rxn exhibits distorted Gaussian type polydisperse molecular weight.(1000-5000 Da)



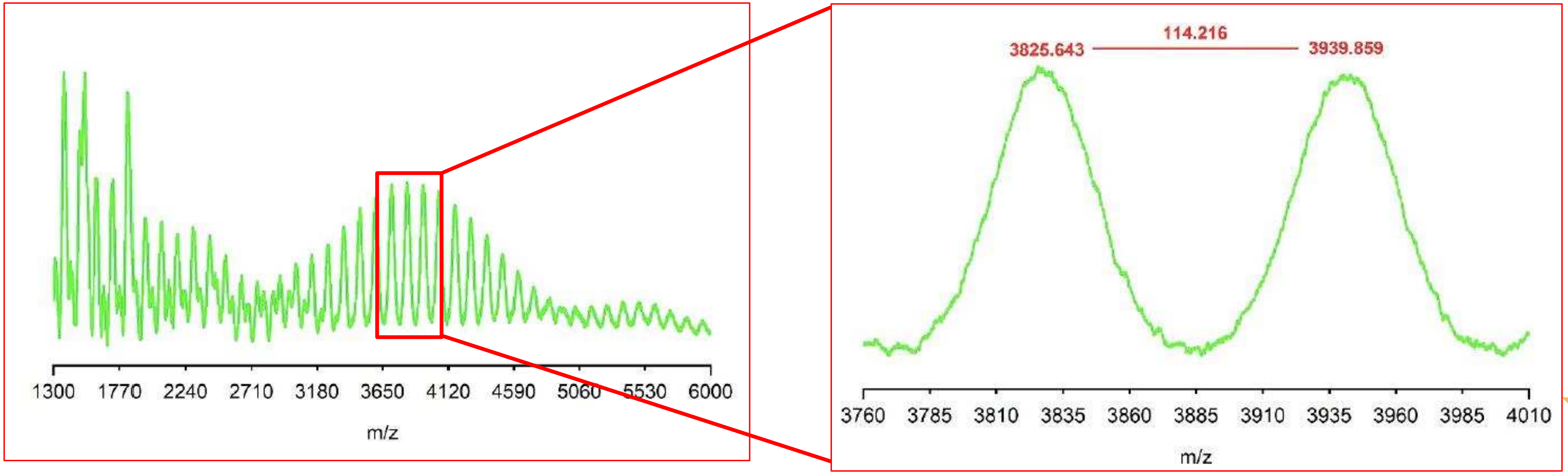


Mass spectrum of PEI-PCL (Tartaric Acid Catalyzed Rxn.)

Molecular Weight of CA. Catalyzed ROP

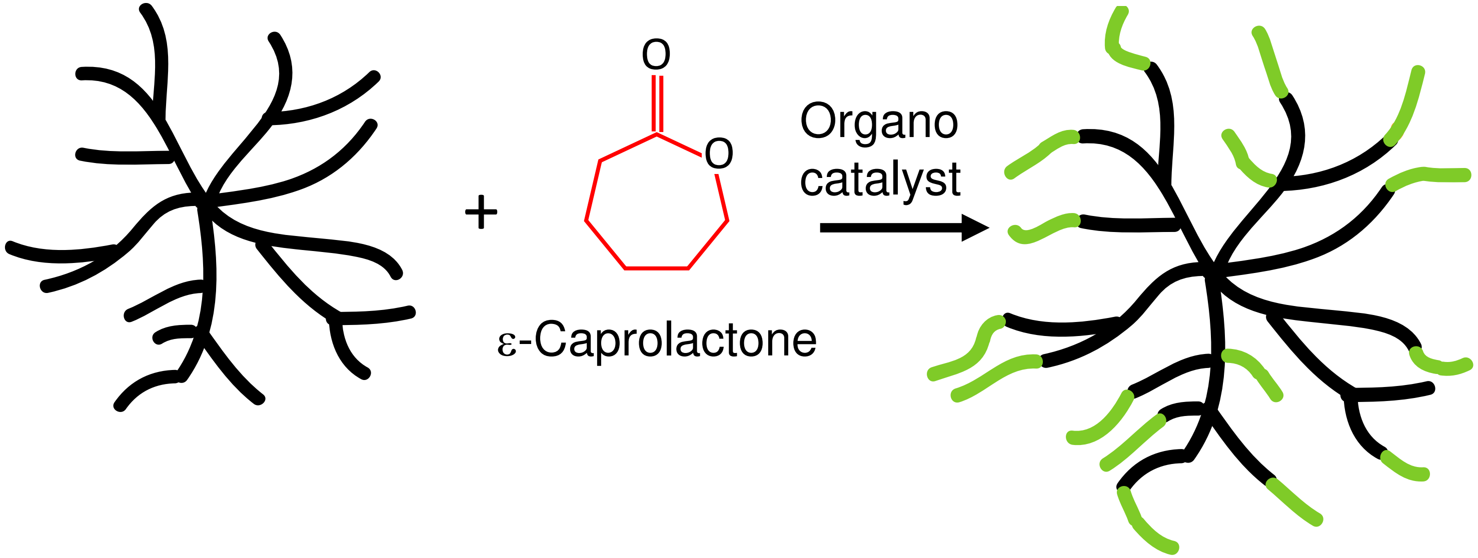


- CA. catalyzed rxn exhibits perfect Gaussian type polydisperse molecular weight.(2700-5000 Da)



Mass spectrum of PEI-PCL (Citric Acid Catalyzed Rxn.)

Tin vs. Acid Catalyzed ROP
Gray to Green Conversion

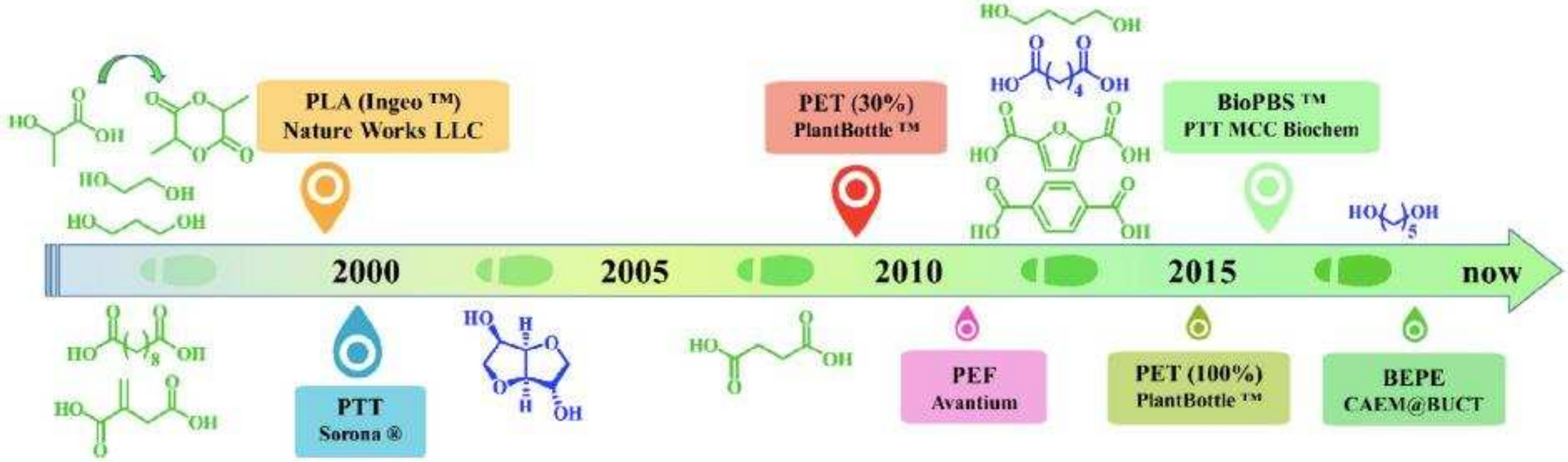


- By employing organic acid 0.5 % Gray-Green conversion provided. NOT ENOUGH… Looking from birght side: Reaction temperature reduced from 110 to 85 ^{o}C that generate energy saving up to 10 %.

Green Chemistry: Organo catalyst rxn carried out at 85 ^{o}C and yield 95 %

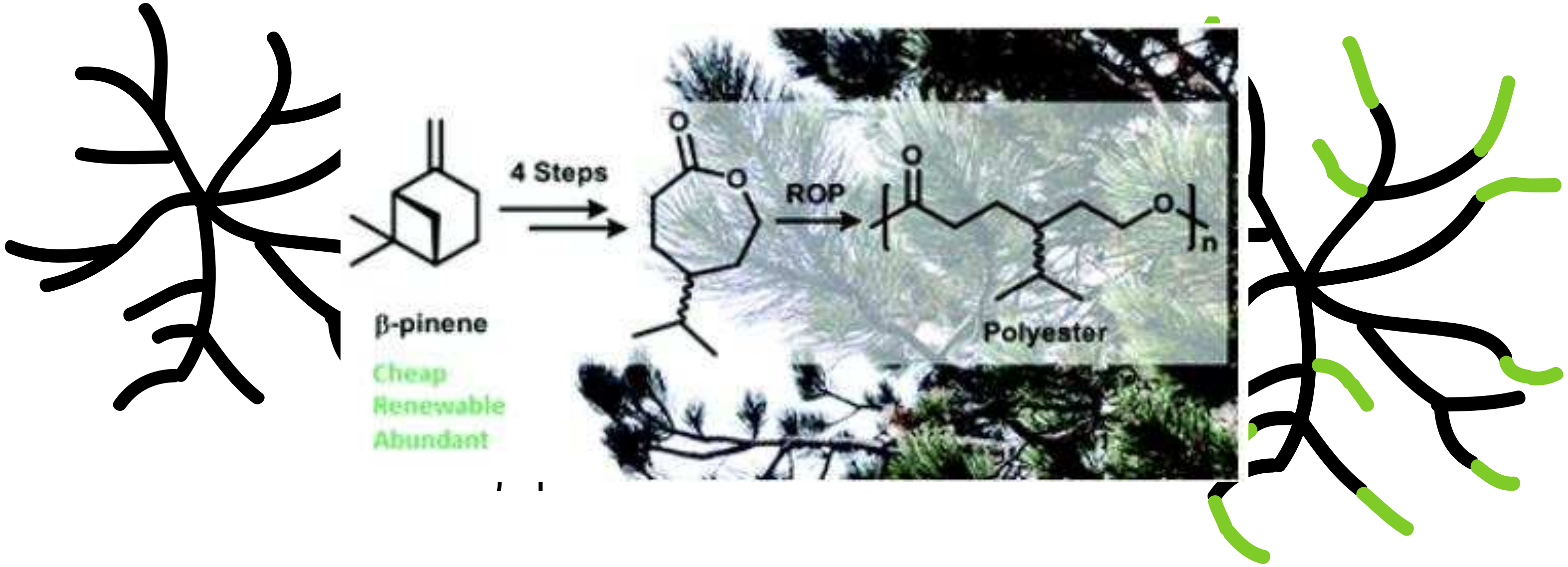
Ring Opening Polymerization with Natural Cyclic Esters

- Linear, cyclic, aromatic natural esters have been heavily employed over the years



Green Chemistry: Natrual esters can improve Gray-Green up to 30%

Ring Opening Polymerization with Natural Cyclic Esters Conversion



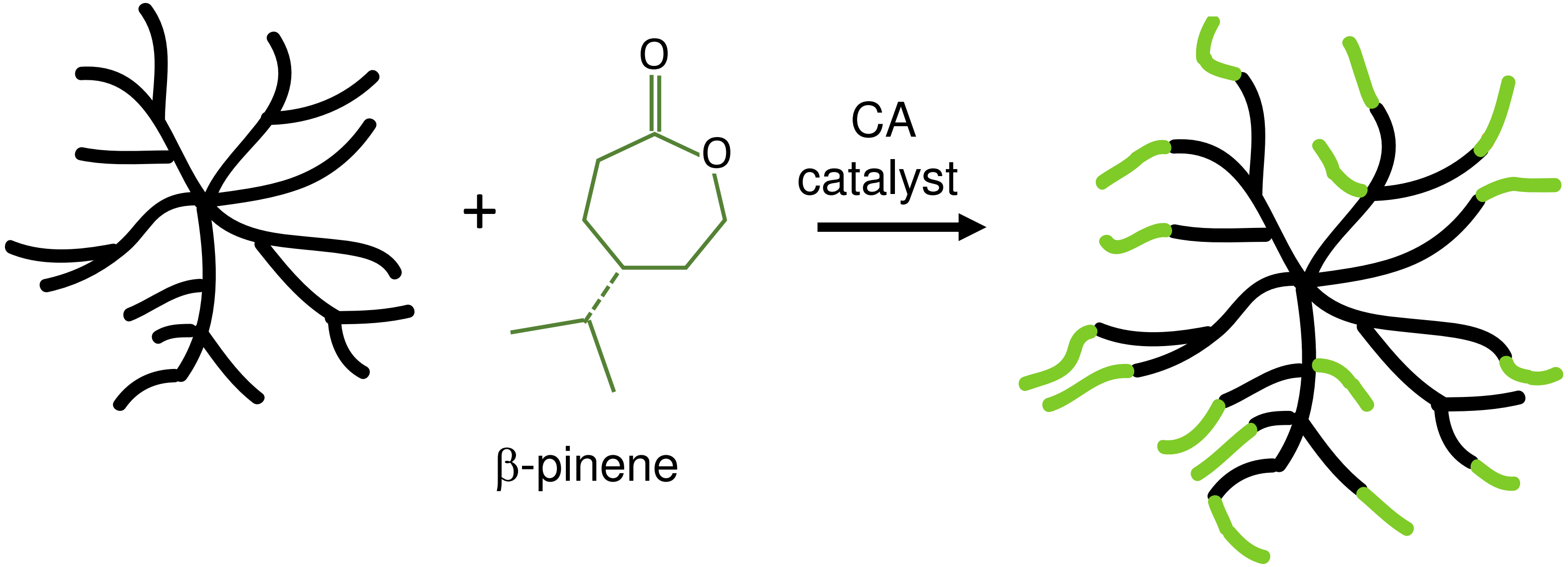
- Natural cylic ester have been used by Quilter et al. Zinc catalyzed conversion were suggested to provide 90-95 % polymerization.

10.5% 89.5%

Helena Quilter et al., Polym. Chem., 2017,**8**, 833-837 (DOI: https://doi.org/10.1039/C6PY02033J)

densurf

Ring Opening Polymerization with Natural Cyclic Esters Conversion



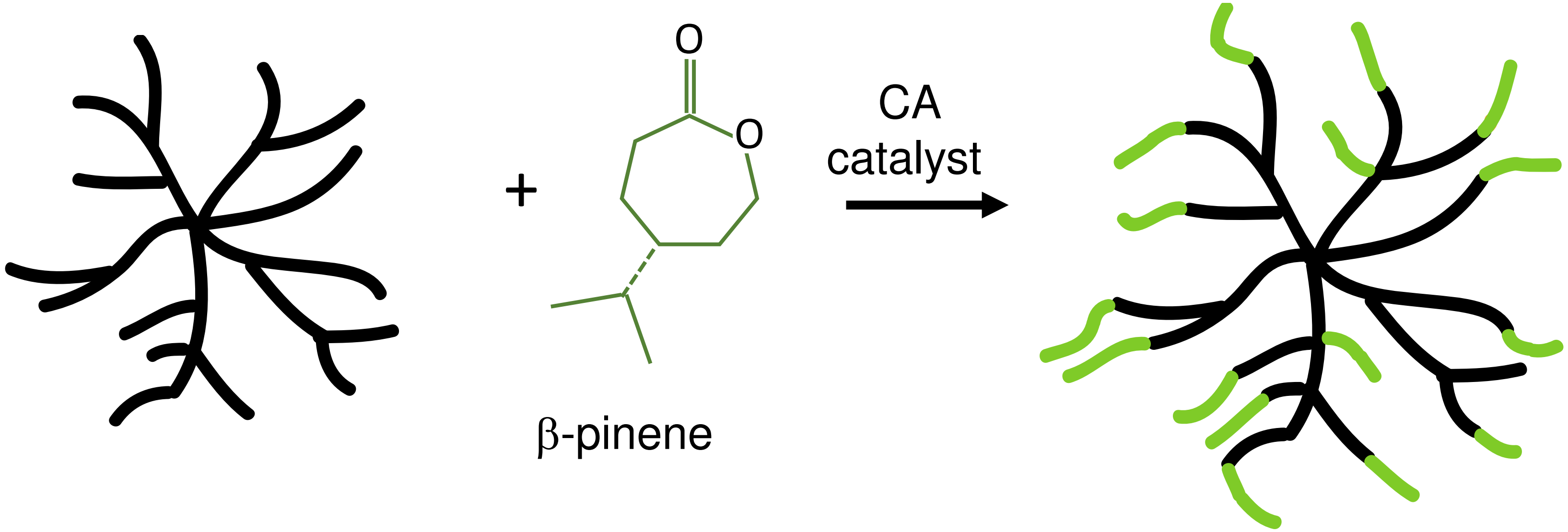
- β–pinene cyclic ester have been replaced with ε caprolactone to and similar protocol have been utilized .
- Polymerization yield is 85%...

30 % 70%

Helena Quilter et al., Polym. Chem., 2017,**8**, 833-837 (DOI: https://doi.org/10.1039/C6PY02033J)

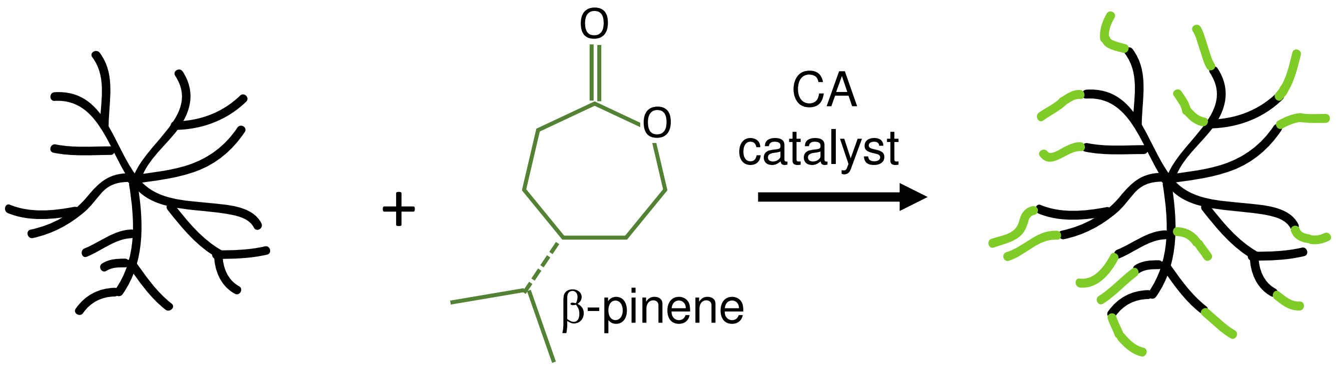
densurf

Ring Opening Polymerization with Natural Cyclic Esters Conversion

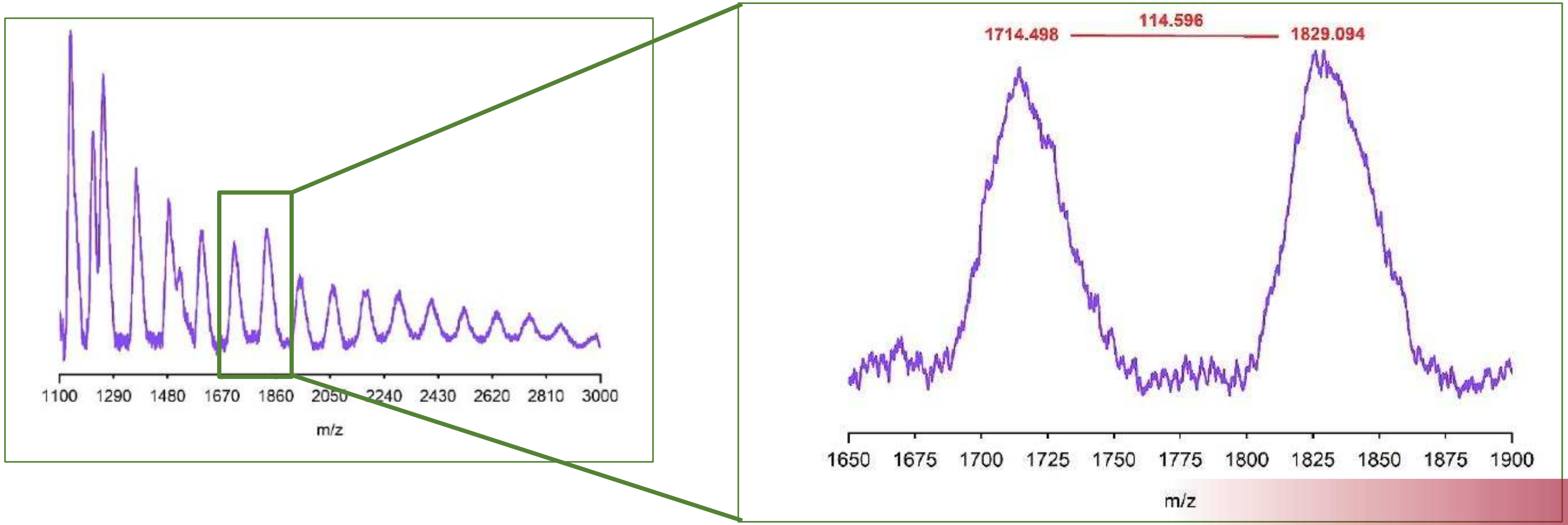


densurf

Molecular Weight of PEI-Poly β– Pinene



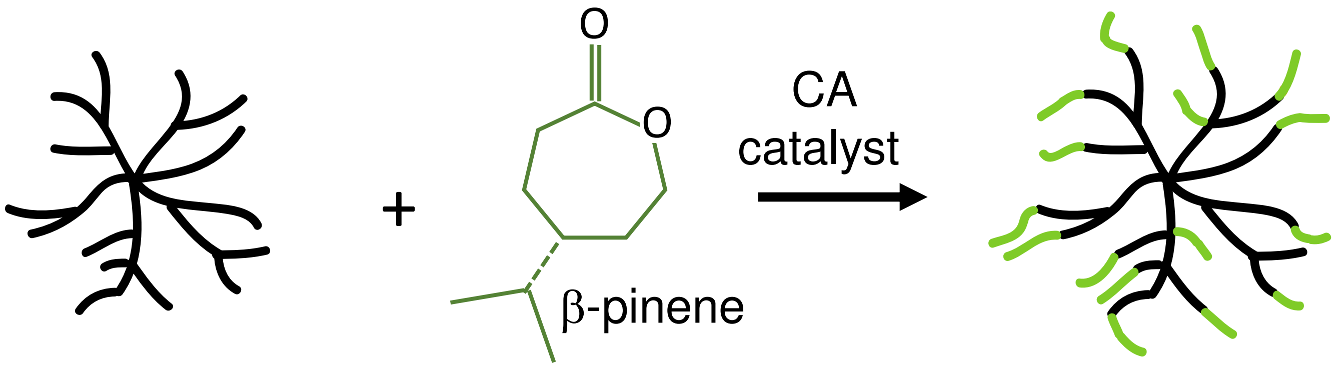
- CA. catalyzed β-pinene exhibits non-Gaussian type polydisperse molecular weight.(1100-3300 Da)



Mass spectrum of PEI-poly β–pinene (Citric Acid Catalyzed Rxn.)

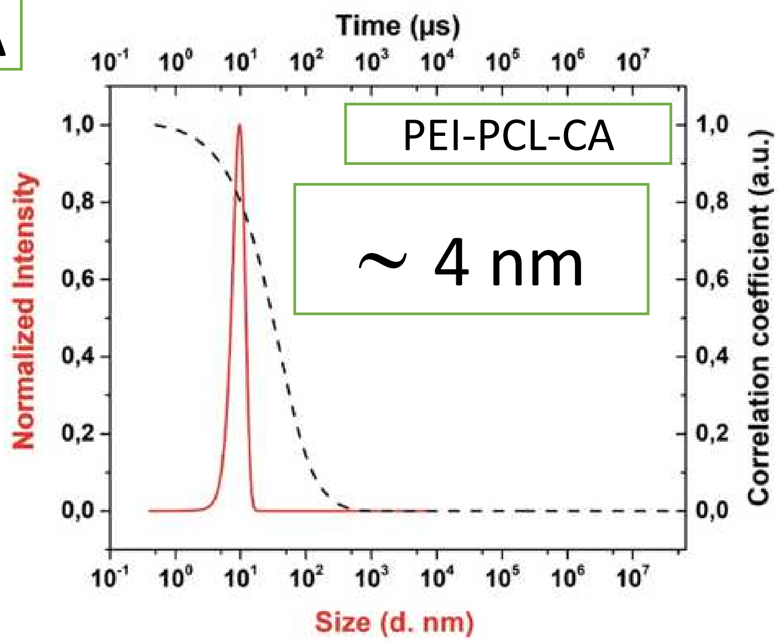
densurf

Hydrodynamic Radii of PEI-Poly β– Pinene

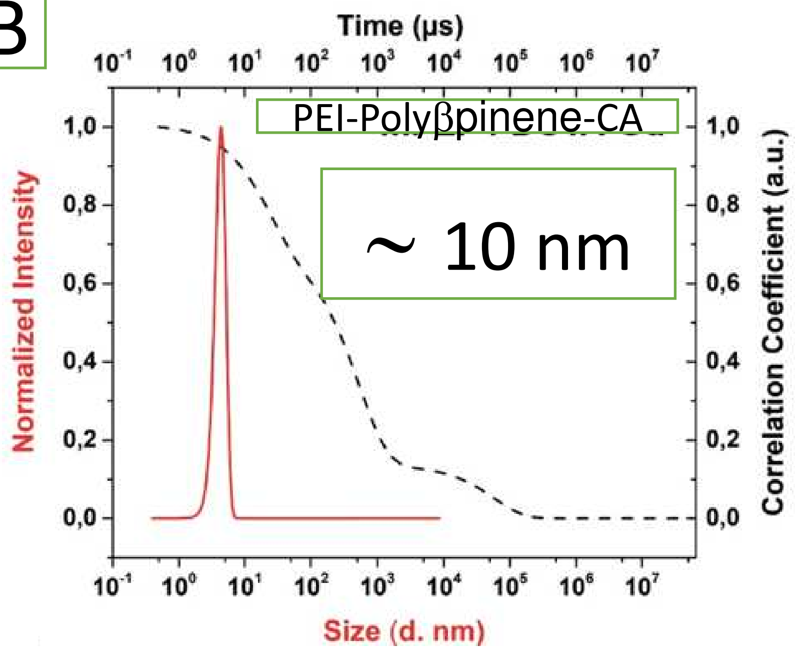


- CA. catalyzed β-pinene exhibits multi modal delay profile in DLS showing variation in size of particles.

A

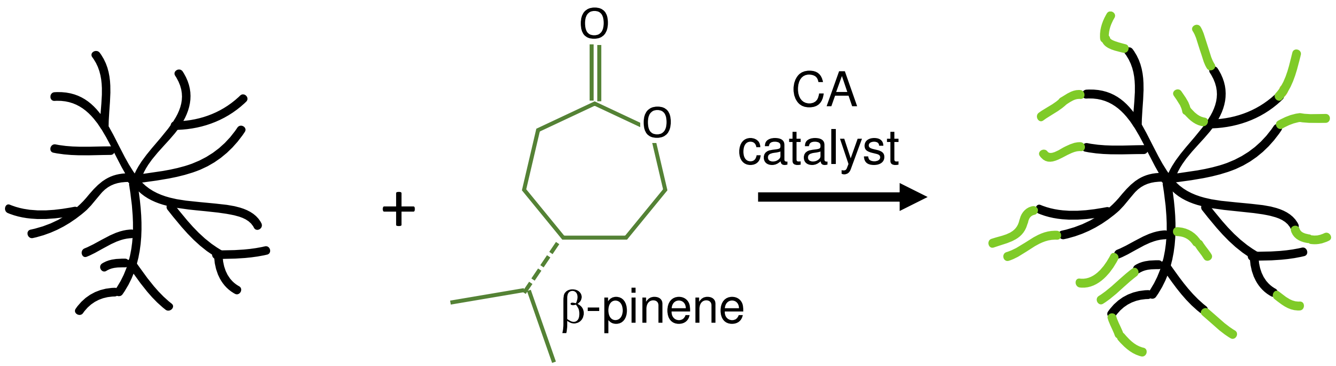


B

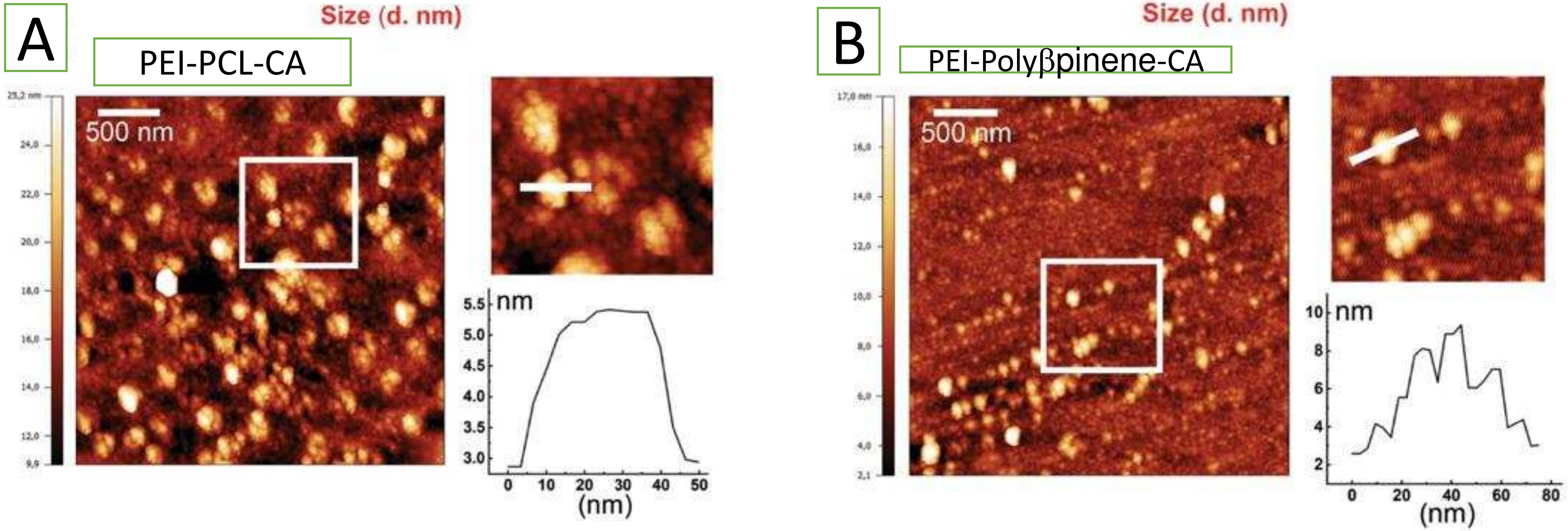


Multi Angular Dynamic Light Scattering of PEI-poly β–pinene (Citric Acid Catalyzed Rxn.)

Particle Shape of PEI-Poly β– Pinene

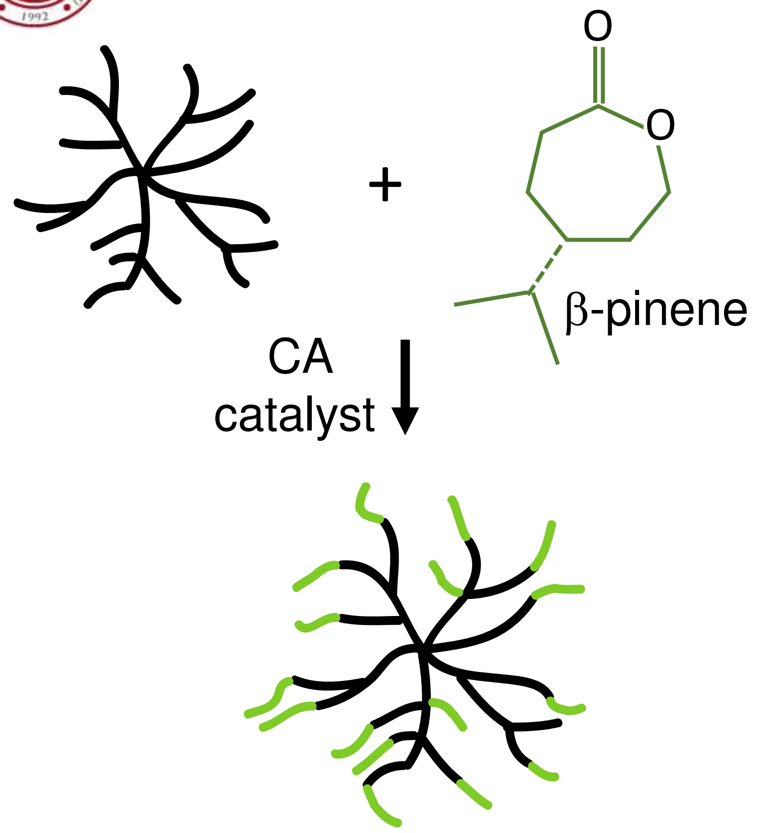


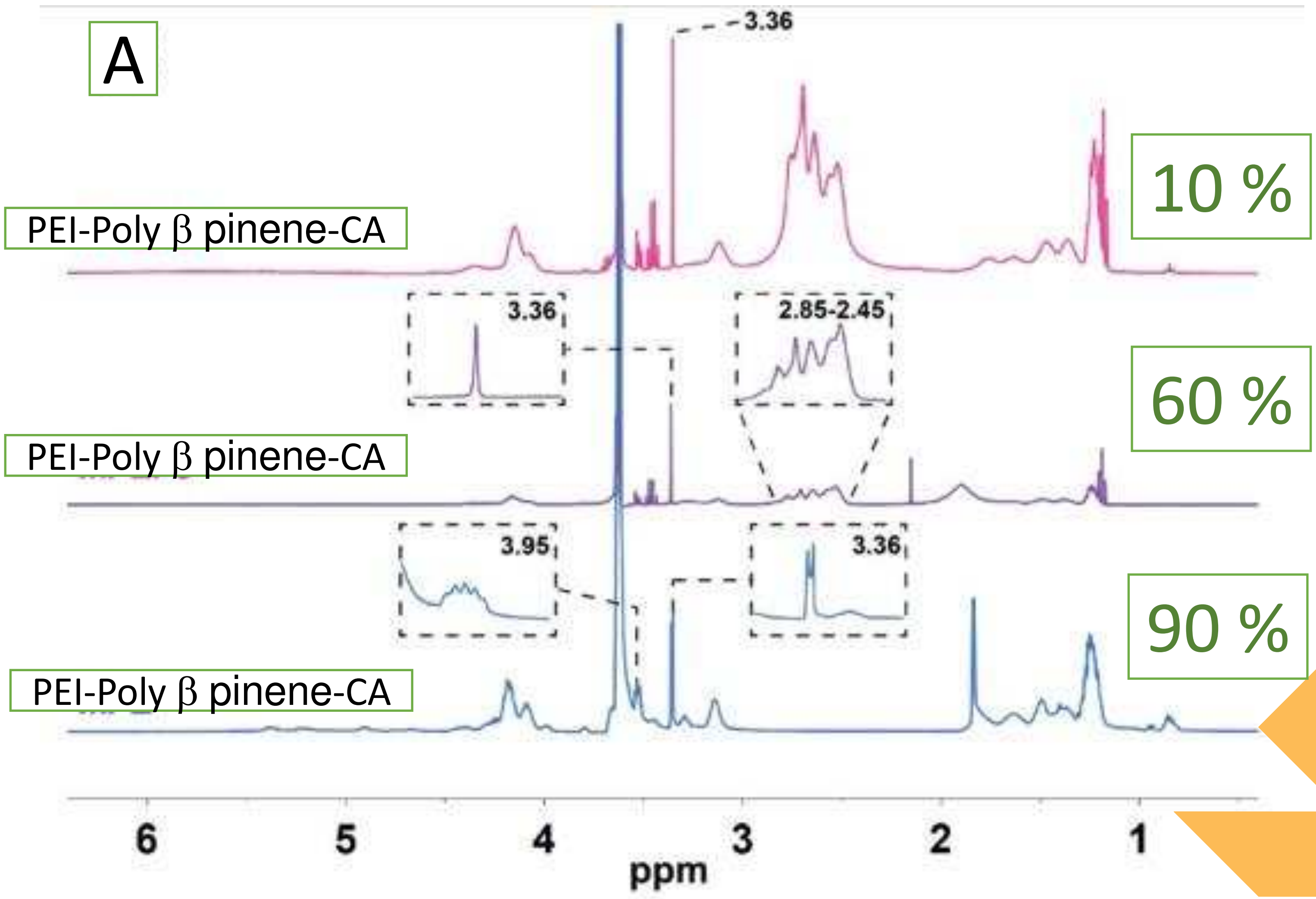
- CA. catalyzed β-pinene DLS profile were confirmed via AFM analysis.



Atomic Force Microscopy analysis of PEI-poly β–pinene (Citric Acid Catalyzed Rxn.)

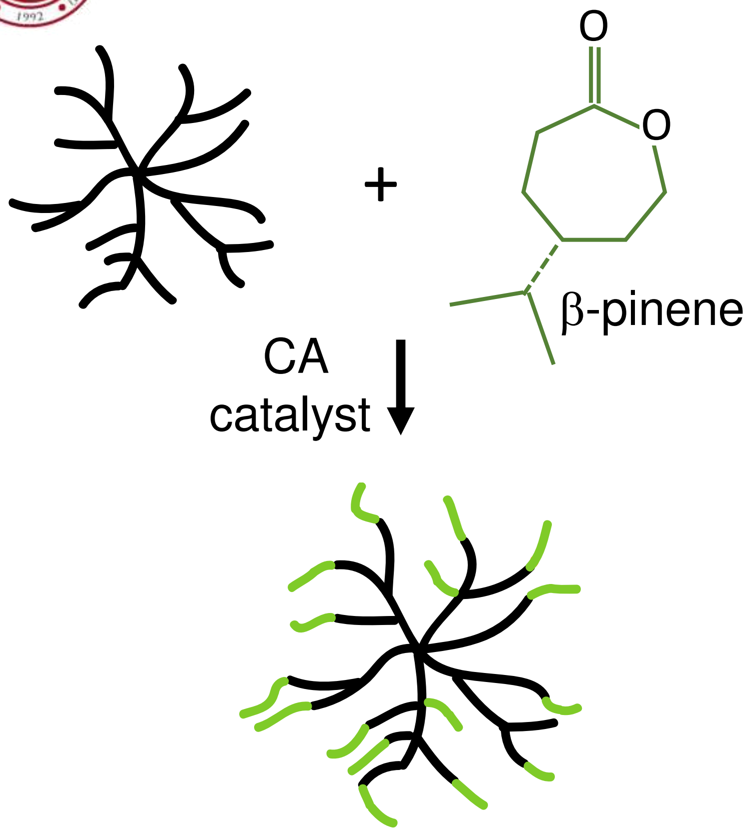
Structural Analysis of PEI-Poly β– Pinene

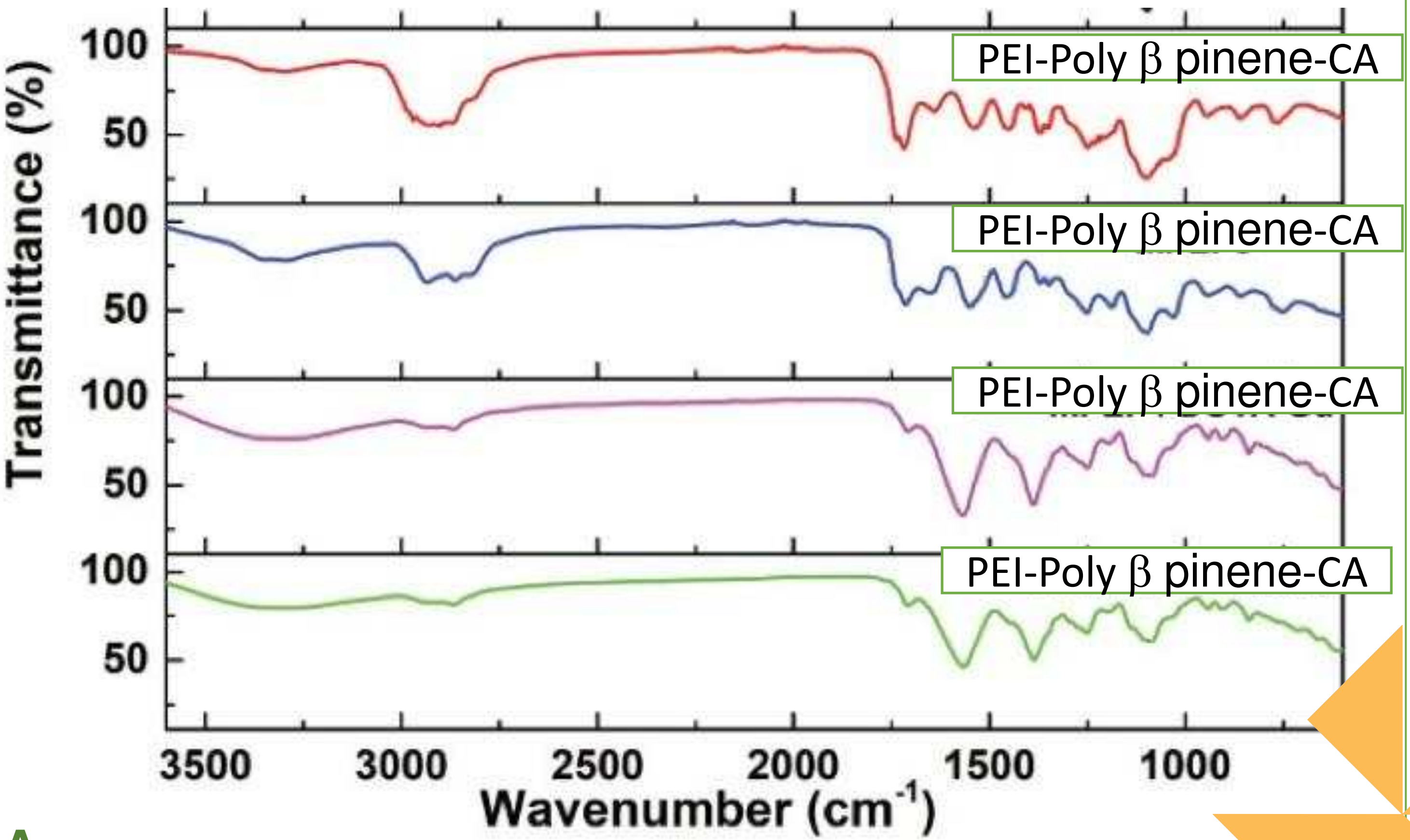




- Monomer Conversion of CA. catalyzed β-pinene

Structural Analysis of PEI-Poly β– Pinene





- Monomer Conversion of CA.

catalyzed β-pinene

densurf

Scattering Intensity Profile of Sol&Gel

Accounts

Gel Formation Analyses by Dynamic Light Scattering

Mitsuhiro Shibayama* and Tomohisa Norisuye†

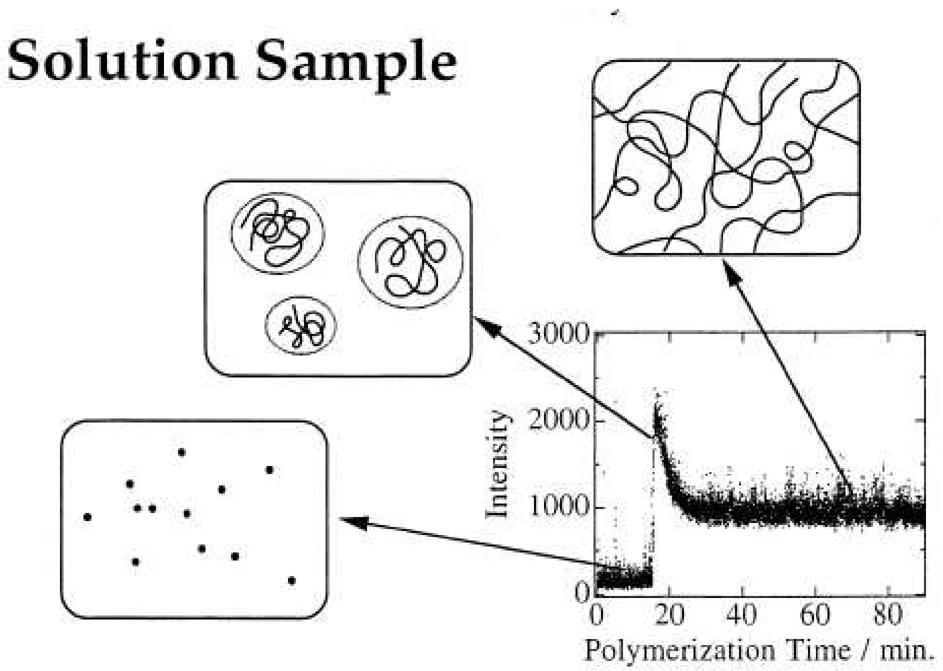
Neutron Scattering Laboratory, Institute for Solid State Physics, The University of Tokyo, Tokai, Ibaraki 319-1106

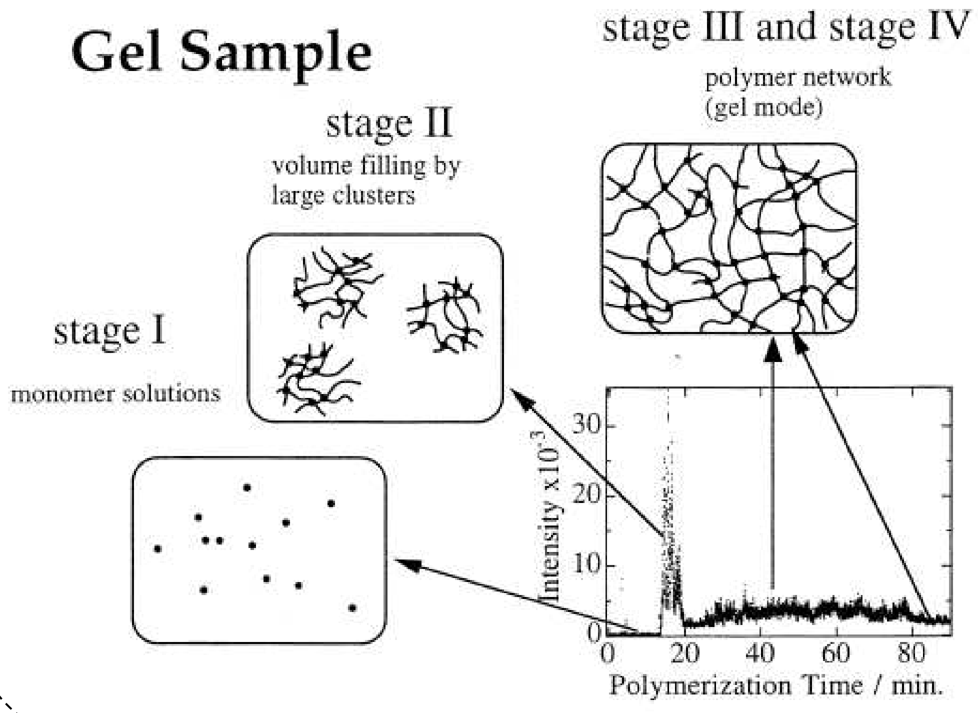
†Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585

(Received August 14, 2001)

A novel methodology for non-destructive and real-time determination of the gelation threshold for both chemical and physical systems has been proposed. This method i.e., a *time-resolved dynamic light scattering* (TRDLS) measurement, allows one not only to determine the gelation threshold but also to investigate critical dynamics near gelation threshold, mechanism of gelation, and architecture of gelling cluster. The gelation threshold was found to be characterized by (1) the appearance of a speckle pattern in the scattering intensity, (2) a power-law in the intensity–time correlation function (ICF), (3) a specific broadening of the distribution function, and (4) a noticeable suppression of the initial amplitude of ICF. All of these features originate from some unique aspects of gels: *nonergodicity, frozen inhomogeneities*, and *divergence of connectivity correlation*. As an application of these concepts, we propose four methods for determination of gelation threshold and examine their validity and usefulness for various types of gels; these include chemical gels of *N*-isopropylacrylamide, a gelling system of silica gel in a reaction batch, thermoreversible physical gels of poly(vinyl alcohol)–Congo Red complex, and biological gels of gelatin and globular protein.

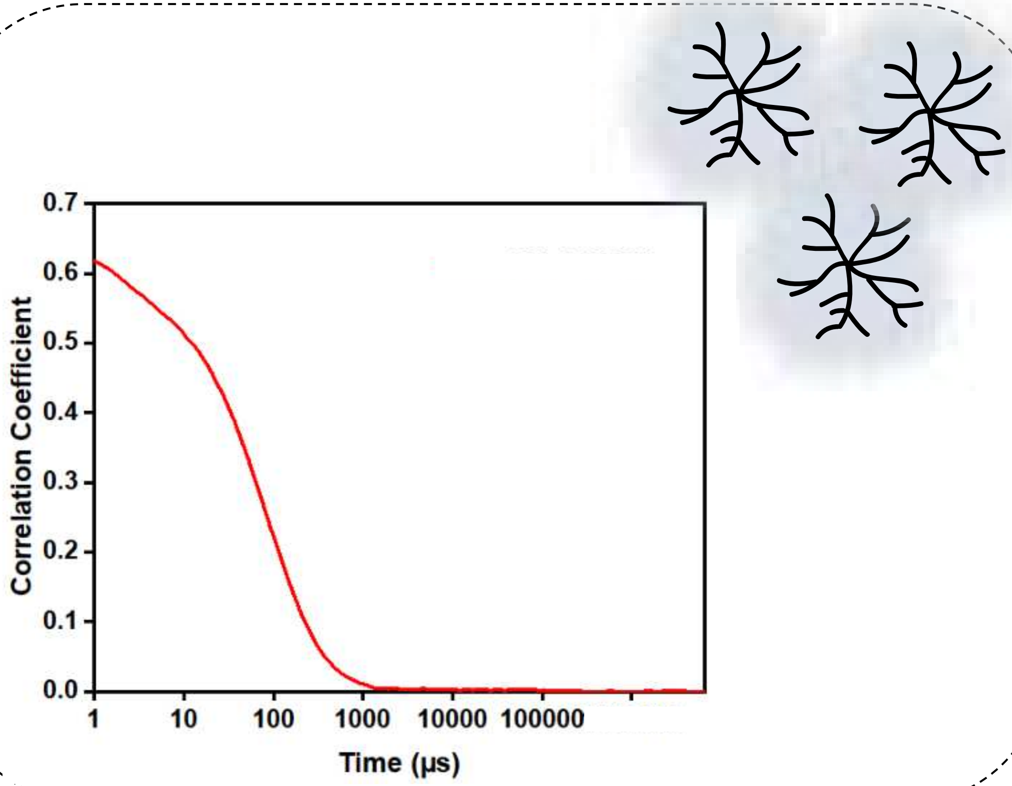
Scattering Intensity Profile of Sol&Gel

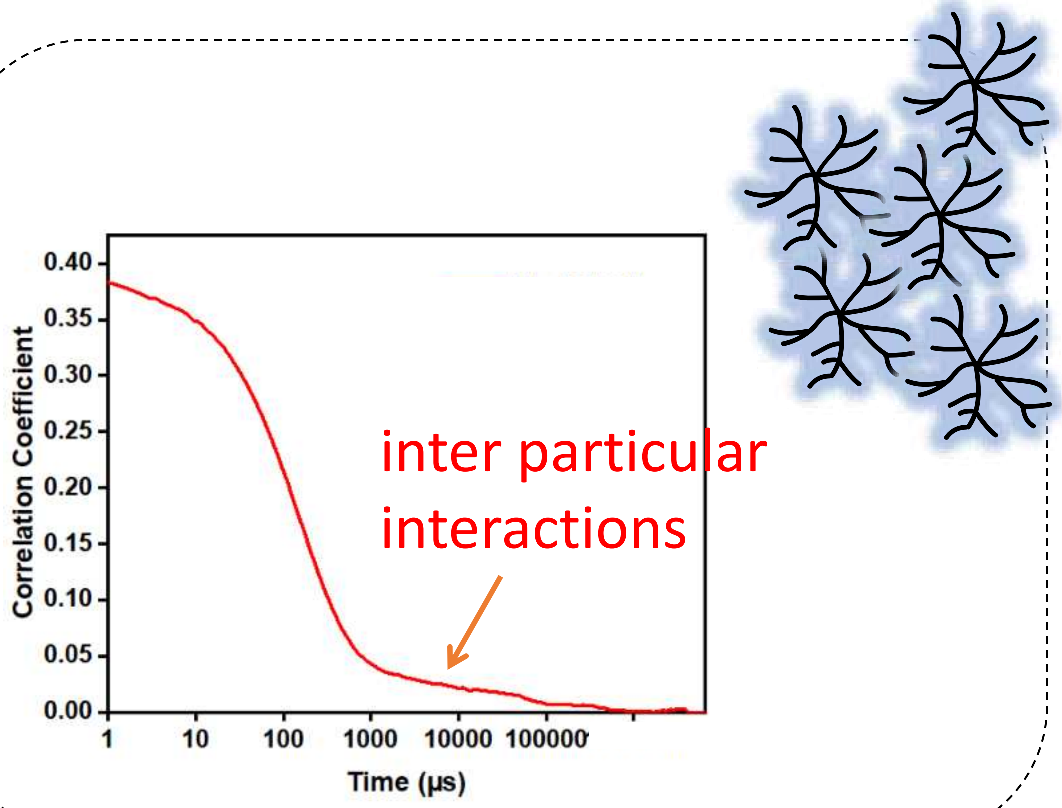




Scattering intensity profile of Gels are typically low due to multi-scattering loss. Polymer, 39, 2769–2775 (1998). Copyright 1998 Elsevier Science

Autocorrelation Function (ACF) of PEI



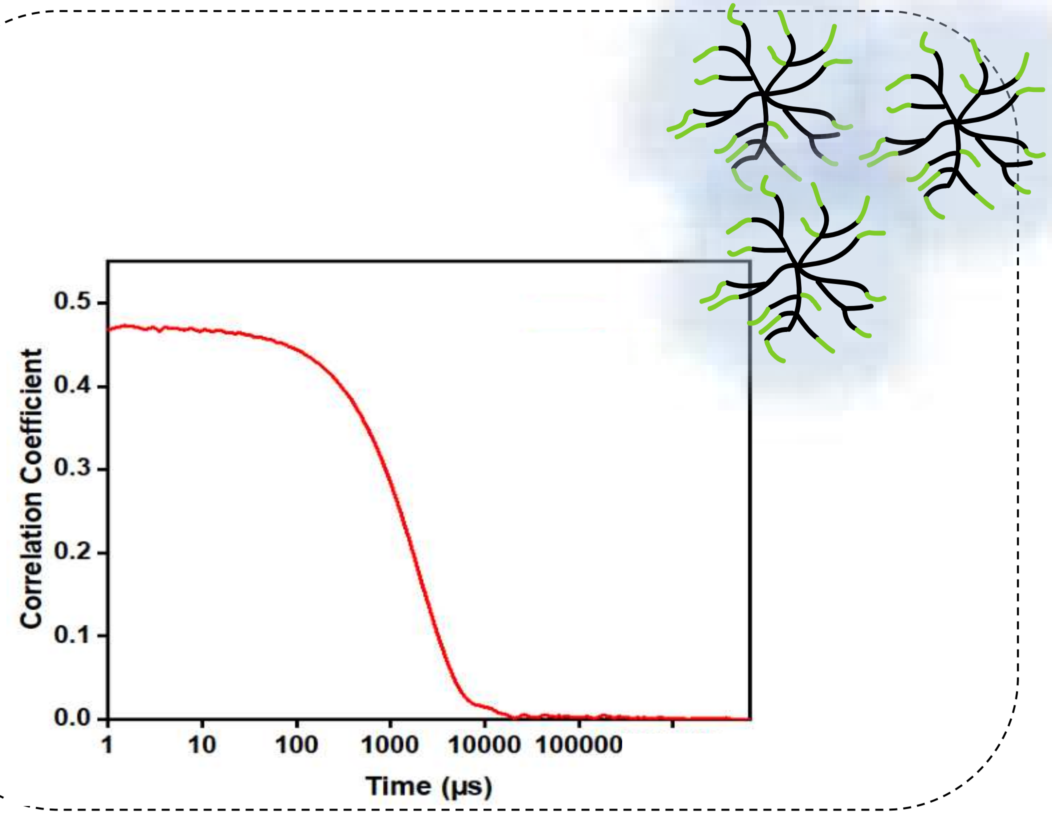


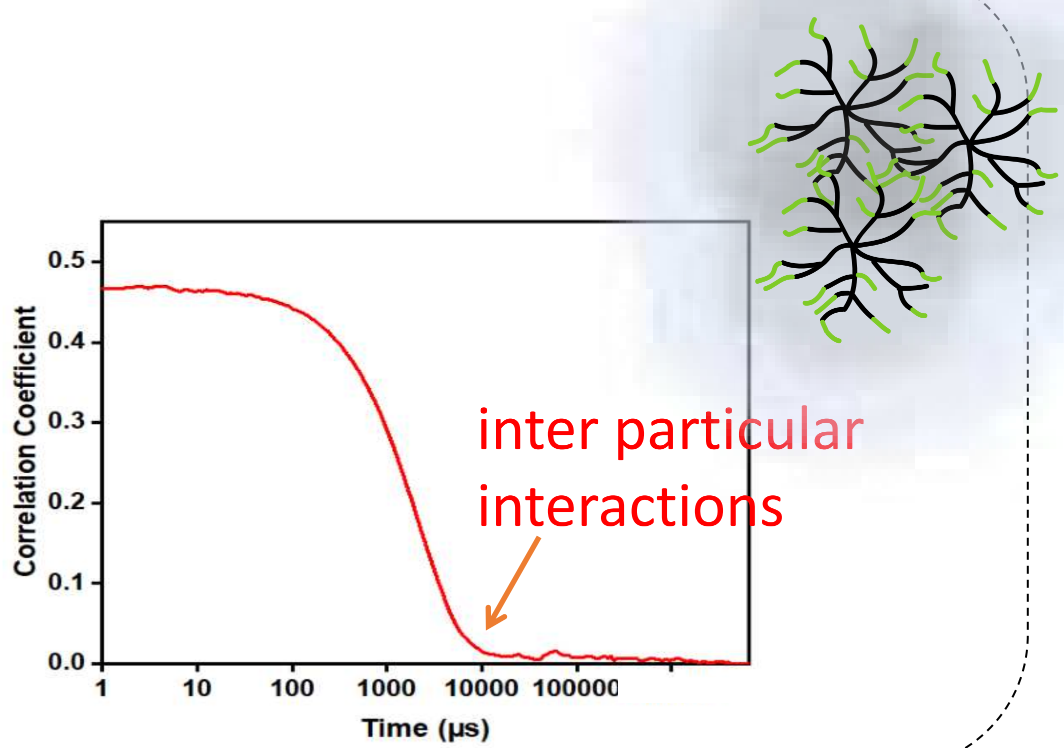
τ= relaxation time of PEI was determined as 23 µs in dilute conditions

τ= relaxation time of PEI was determined as 67 µs in concentrated conditions

densurf

ACF of PEI-PCL



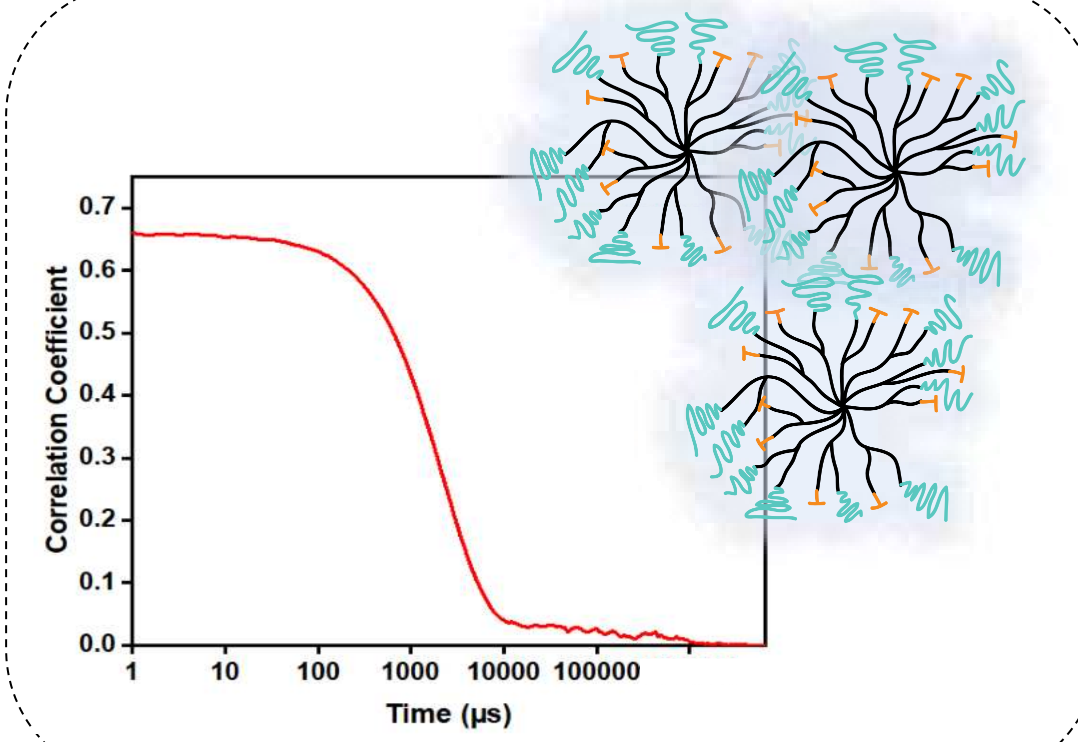


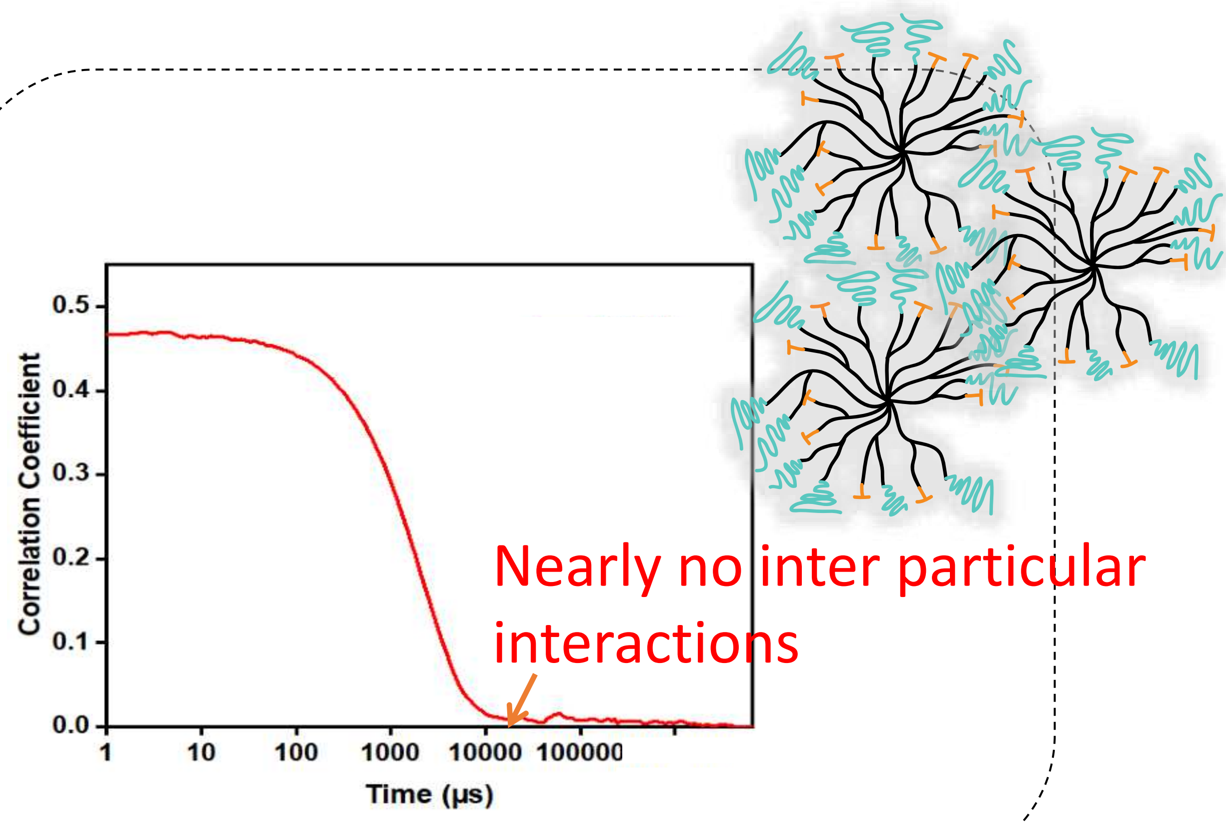
τ= relaxation time of PEI-PCL was determined as 200 μs in dilute conditions

τ= relaxation time of PEI-PCL was determined as 450 μs in concentrated conditions

densurf

ACF Profile of DA 4115

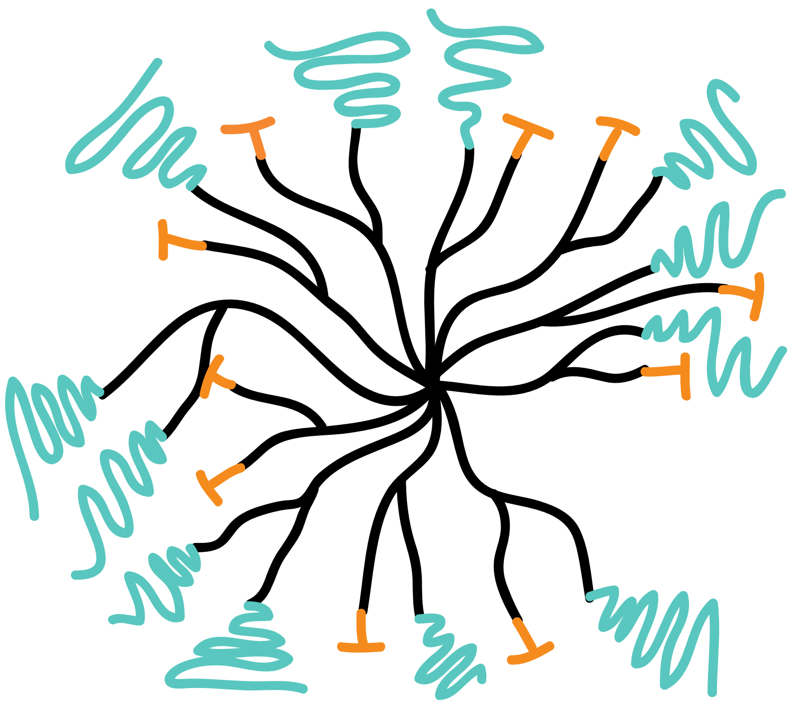


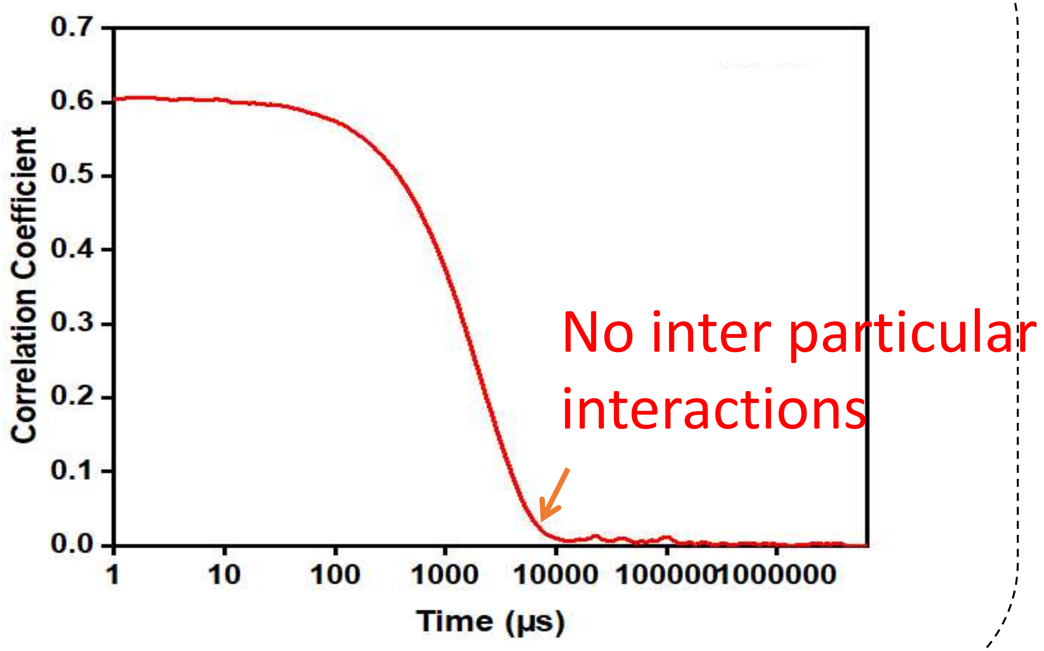


τ= relaxation time of DA-4115 was determined as 350 μs in dilute conditions

τ= relaxation time DA-4115 was determined as 300 μs in concentrated conditions

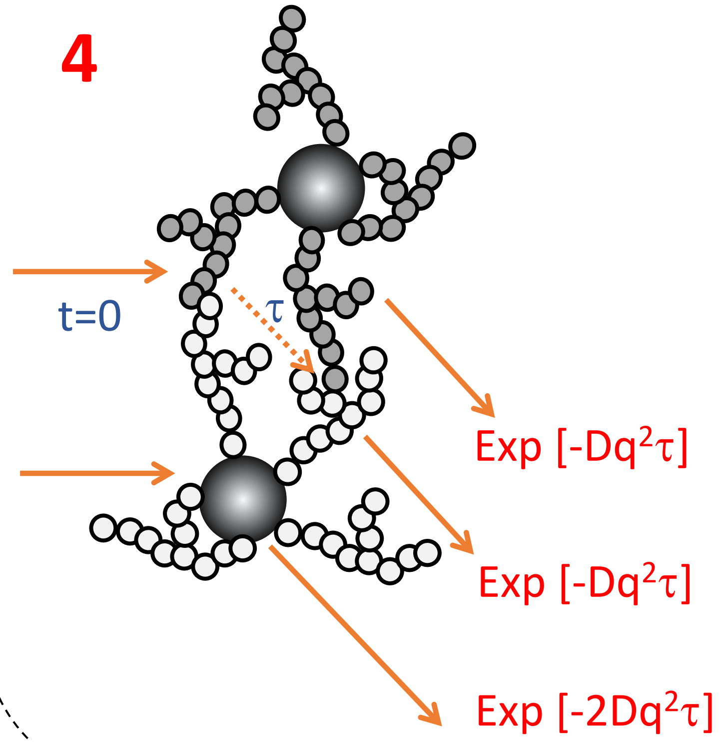
Scattering Intensity Profile of Sol&Gel





τ= DA-4115 was determined as 450 μs in concentrated conditions

Scattering Profile



Homodyne
$\text{Exp}\,[-2Dq^2\tau]$

Heterodyne
$\text{Exp}\,[-Dq^2\tau]$

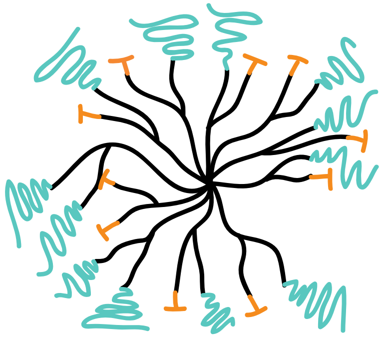
Homodyne and heterodyne Scattering reveals inter particular interactions !!!

Homodyne:: $g^2(\tau)-1 = \text{Exp}\,[-2Dq^2\tau]$

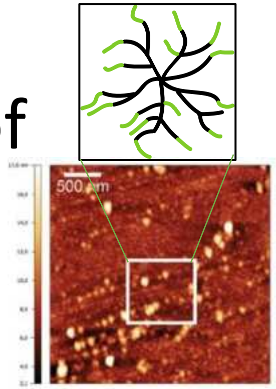
Partial Heterodyne:: $g^2(\tau)-1 = X^2\,\text{Exp}\,[-2Dq^2\tau]+2X(1-X)\,\text{Exp}\,[-Dq^2\tau]$

Conclusions

1 Synthesis of hyperbranched polymer based dispersion agent (DA-4115)

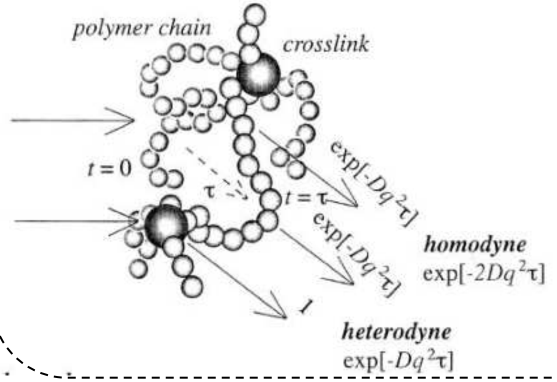


2 Colloidal properties of Dispersion Agents



3 Determination of Chain Rigidity via DLS: Scatering Vector "**q**"

4 Homodyne and heterodyne Scattering



densurf

Gray to Green Conversion

Green Chemistry: Conducting chemical reactions and processes via natural products without hazardous solvents and by products at room temperature

Green Transformation Plan: Starting point is 20% with current settings, in 24 months our commitment is 50% and following in 24 months 90% green transformation is projected

Gray to Green Conversion

- Tin catalysis is required for PEI-PCL hyper-branched DA. but organo-catalyst replacement (in particular Citric Acid) can even increase polymerization yield up to 90 %,
- β–pinene cyclic ester have been replaced with ε caprolactone. Polymerization yield is 85%...

densurf

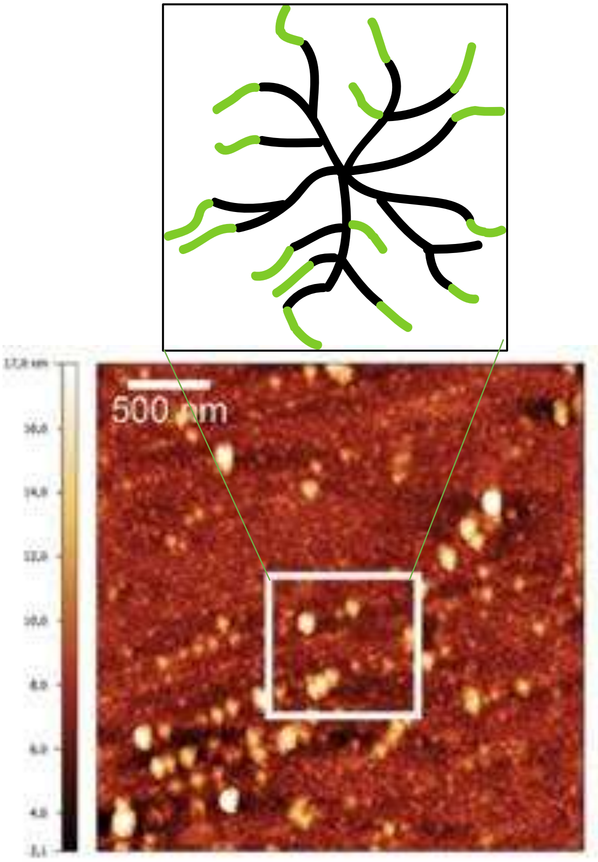
Gray to Green Conversion

- Mass spectrum analysis confirmed that CA. catalyzed polymerization has perfect Gaussian type of molecular weight distribution.
- Dynamic Light Scattering analysis revealed that CA. catalyzed PEI-PCL has monomodal delay profile

densurf

Gray to Green Conversion

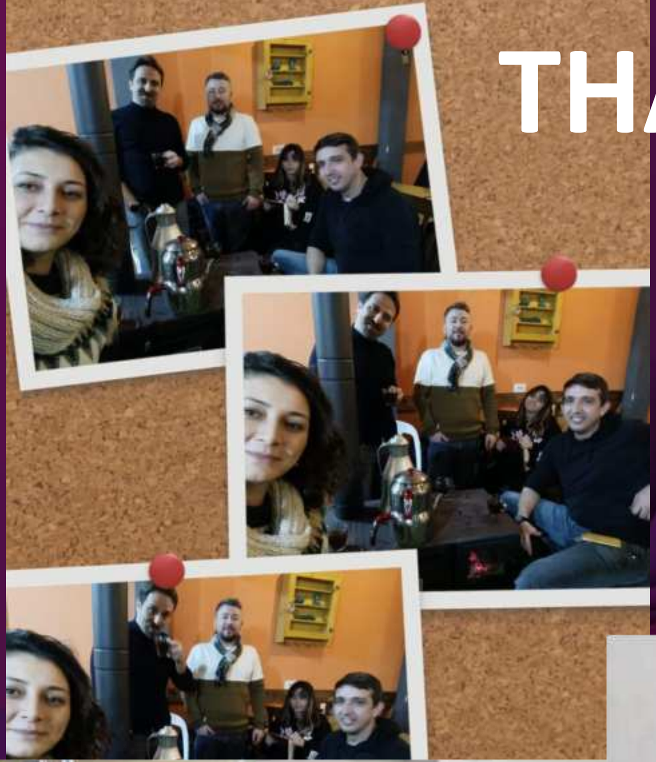
- AFM analysis confirmed that CA catalyzed PEI-Poly β– Pinene has 70-80 nm in size.
- Hyper-branched polymer based dispersion agents are readily synthesized by using green components.
- Total conversion could be increase up to 30 %



30% 70%

densurf

THANKS YOU FOR ATTENDANCE








densurf


densurf
Coating
Additives
&
Silicone Resins
Come visit us at:
5-265
we make it
perform
better.
Powered by
denge


dens
HUNTSMAN
densurf


vynax
bonding sparkling ideas
ANSTEEL
G VANADIUM AND TITANIUM
TiO2