

Preparation of Polyethylene/Montmorillonite (MMT) Nanocomposites Through in situ Polymerization Using a Montmorillonite-Supported Nickel Diimine Catalyst

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Properties & Applications of Polyolefin/Layered Silicate Nanocomposites

- Polymer/layered silicate nanocomposites provide the better performance characteristics when compared to virgin polymer or conventional composites.
- Recently, the success on polymer/layered silicate nanocomposites has extended into making high performance polyolefin nanocomposites.

Application



Auto parts



Film

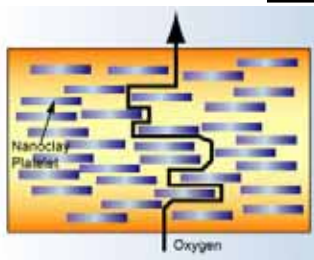
Polyolefin/Layered Silicate Nanocomposites have

Improved Mechanical strength

Improved Thermal Stability

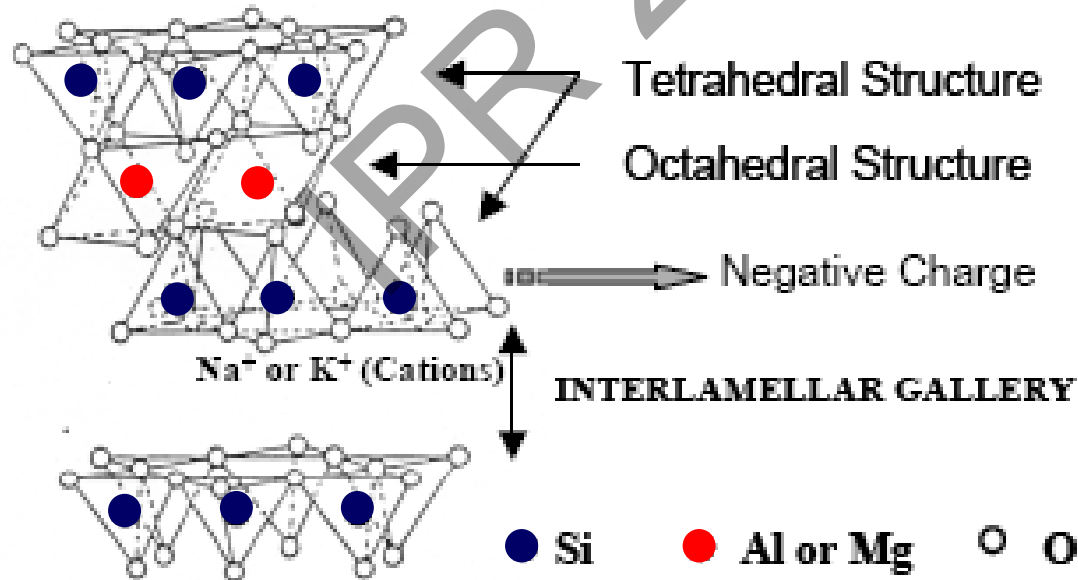
Improved Gas-barrier Properties

Cf.) Tortuous paths

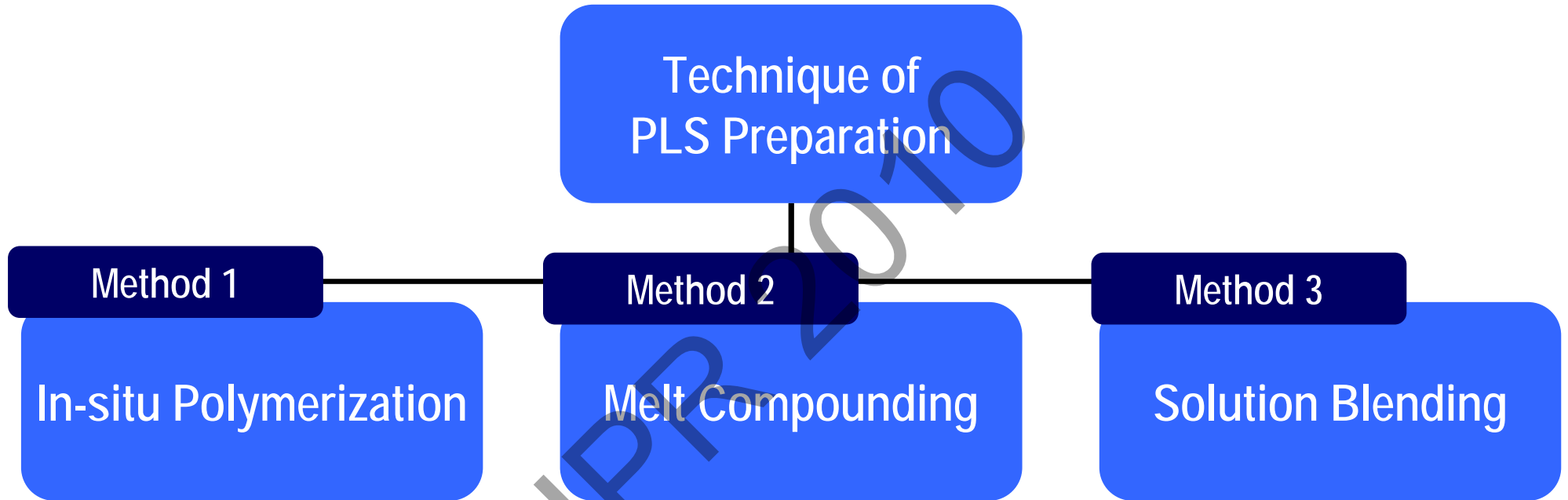


Structure of Layered Silicates- Montmorillonite

- Montmorillonite (MMT) has been used as the main material for polymer/layered silicate nanocomposite due to its remarkable intercalation ability.
- MMT is consisted of stacks of each silica/alumina phase and gallery.
- For preparation of polymer/MMT nanocomposite, single layer of MMT is exfoliated and dispersed into polymer matrix.
- To make it easy dispersion, hydrophilic MMT are converted to the ones with organophilic surface.



Several Techniques for Polymer/Layered Silicate Nanocomposites



◆ Polyolefin/Layered Silicates (MMT) Nanocomposites

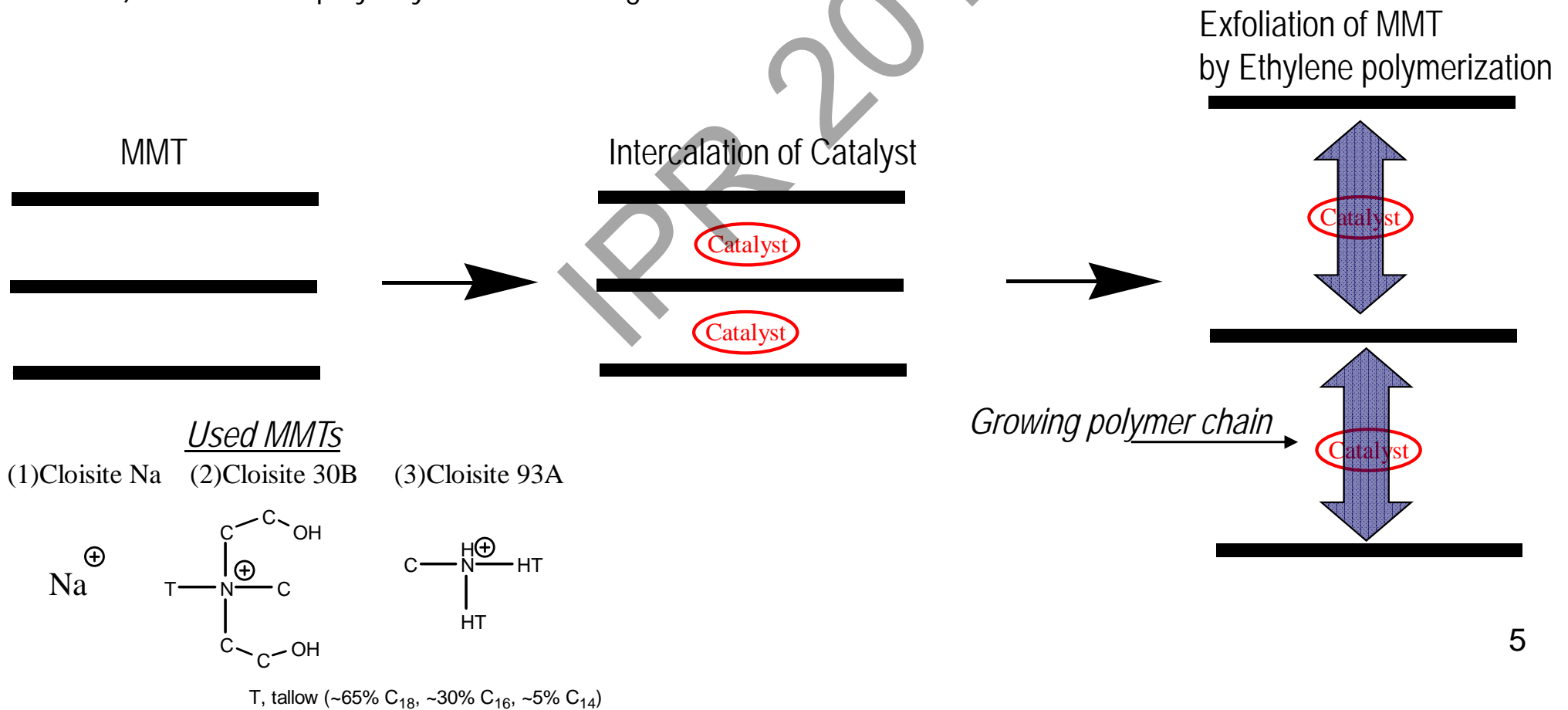
Method 1. Easier intercalation of monomer but it needs understanding of polymerization catalyst and process.

Method 2. Simple but organic modifier of MMT is decomposed by harsh condition, it leads agglomeration of MMT.

Method 3. Impossible method due to poor solubility of polyolefin.

Polyethylene/MMT Nanocomposites Using In-situ Polymerization

- 1) 3 types of montmorillonite (MMT) were used, and modified with trimethyl aluminum.
- 2) Nickel diimine catalyst was intercalated in the MMT galleries.
- 3) Formation of polyethylene inside the galleries leads to the exfoliation of the MMT.



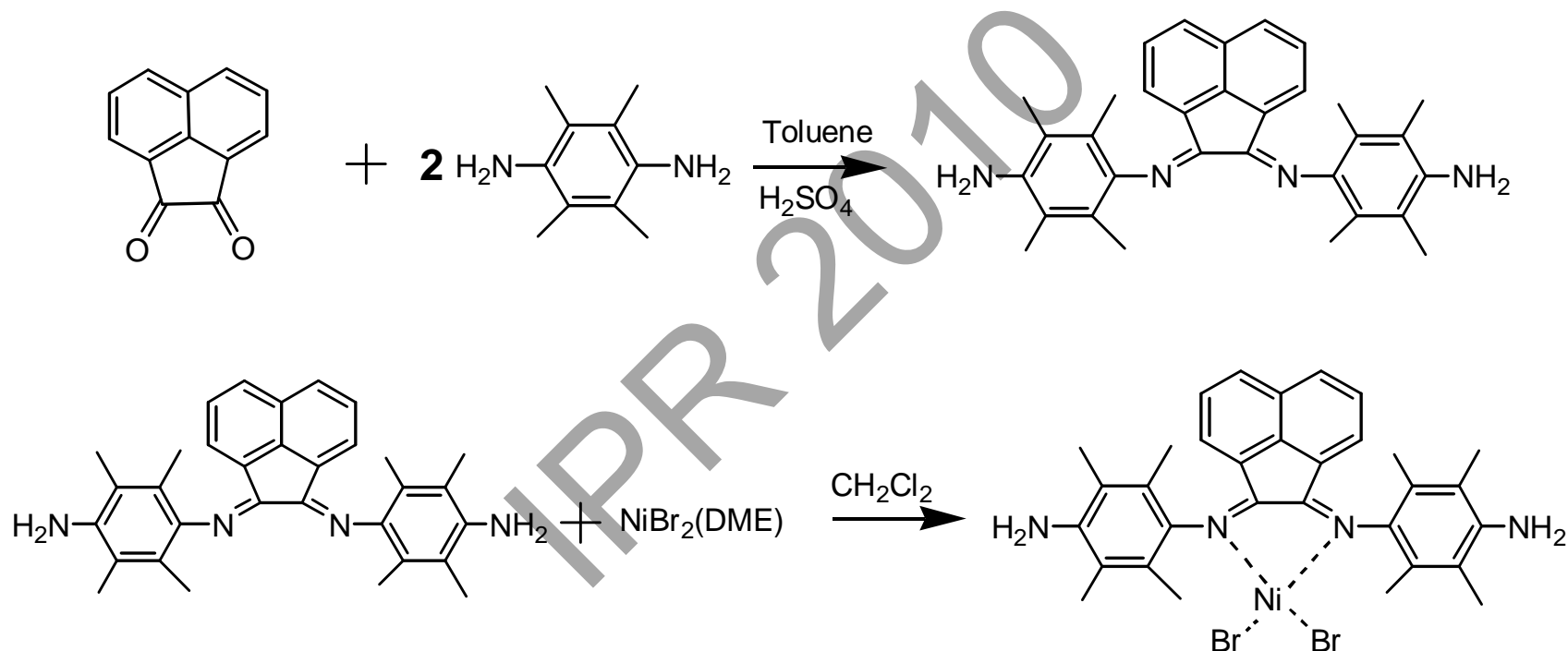
Materials

- ◆ All operations were performed under nitrogen (99.999%, Praxair) using standard Schlenk techniques or inside Glove-box.
- ◆ General Solvents (Toluene, Hexane, Methylene dichloride, etc)
 - Purchased from VWR and purified with activated alumina and 3A/4A mixed molecular sieves.
- ◆ Synthesis of Nickel Diimine Catalyst
 - Purchased from Aldrich or Acros and used without purification
- ◆ MMTs (Cloisite Na, Cloisite 30B and Cloisite 93A) for Catalysts Supporting
 - Purchased from Southern Clay Products and used after drying under vacuum at 60°C overnight.
- ◆ In situ polymerization
 - Ethylene (99.9%, Praxair) was purified with R3-11 copper catalyst, activated alumina and 3A/4A mixed molecular sieves

Nanocomposite Characterization

- Differential Scanning Calorimetry ([DSC](#), Q2000, TA Instruments)
- Thermal Gravimetric Analysis ([TGA](#), Q500, TA Instruments)
- X-ray Diffractometer ([XRD](#), D8-Focus, Bruker)
- Scanning Electron microscope ([SEM](#), LEO 1530 FE-SEM)
- Transition Electron microscope ([TEM](#), CM12, Philips)

Synthesis of Nickel Diimine Catalyst with Functional Group

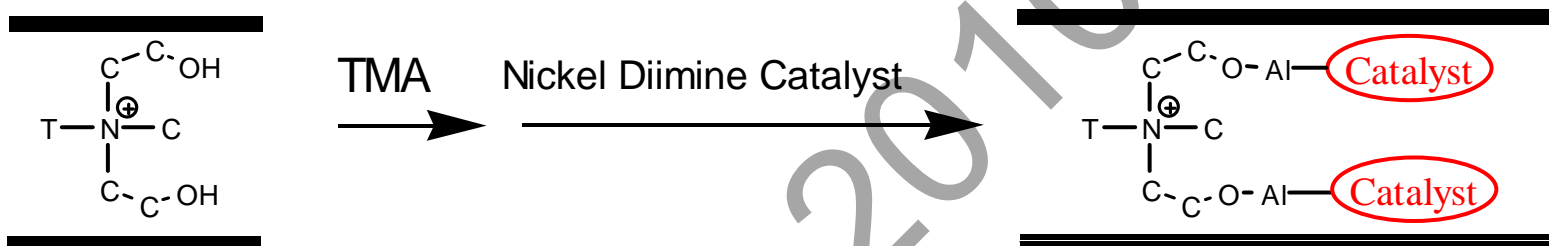


bis(4-amino-2,3,5,6-tetramethylimino)acenaphthene nickel(II) dibromide

P. P. Pflugl, M. Brookhart, *Macromolecules* 2002, 35, 6074

Synthesis of MMT-Supported Nickel Diimine Catalyst -1) C30B

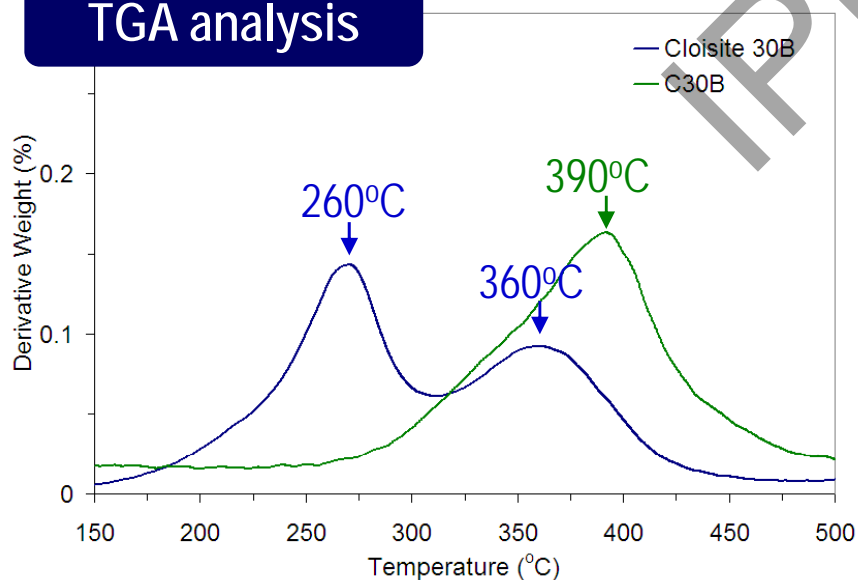
- 1) Cloisite 30B was reacted with TMA for the organic modification and reactive groups generation.
- 2) Amine functionalized nickel diimine catalysts were supported onto Cloisite 30B gallery through chemical bonding.



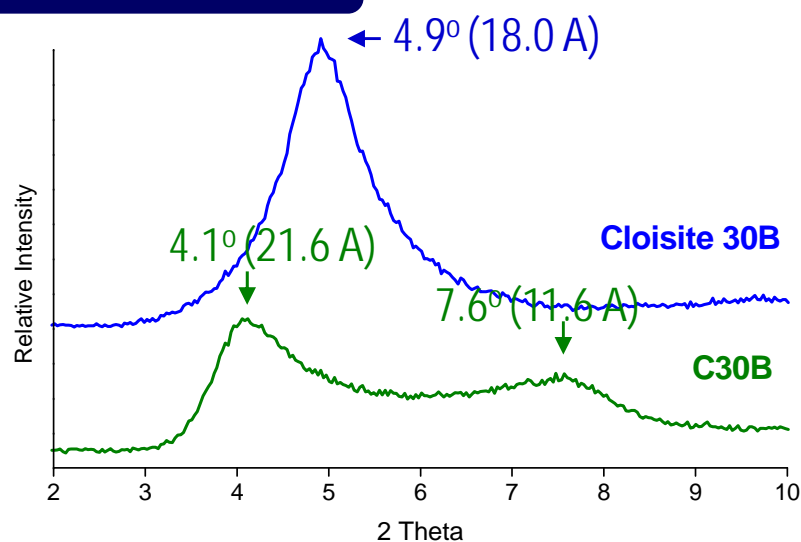
MMT (Cloisite 30B)

Cloisite 30B-Supported Nickel Diimine Catalyst (C30B)

TGA analysis

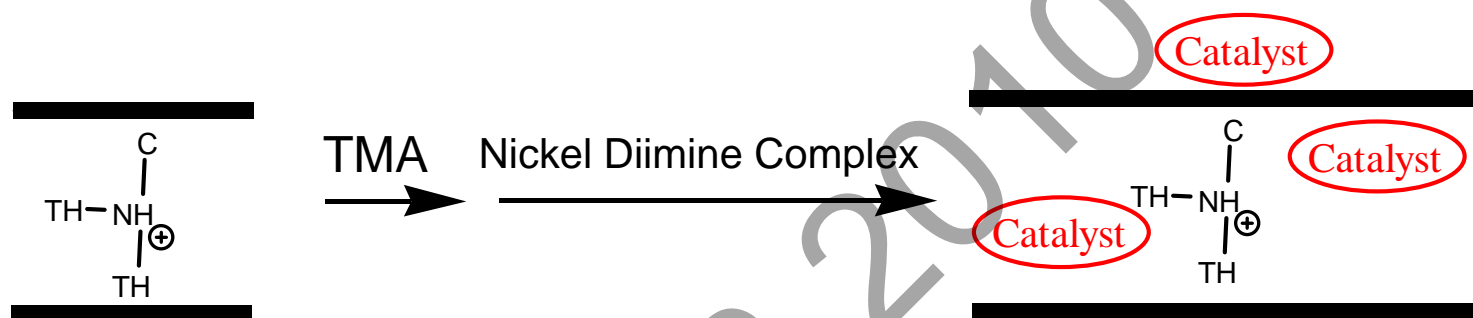


XRD patterns



Synthesis of MMT-Supported Nickel Diimine Catalyst- 2) C93A

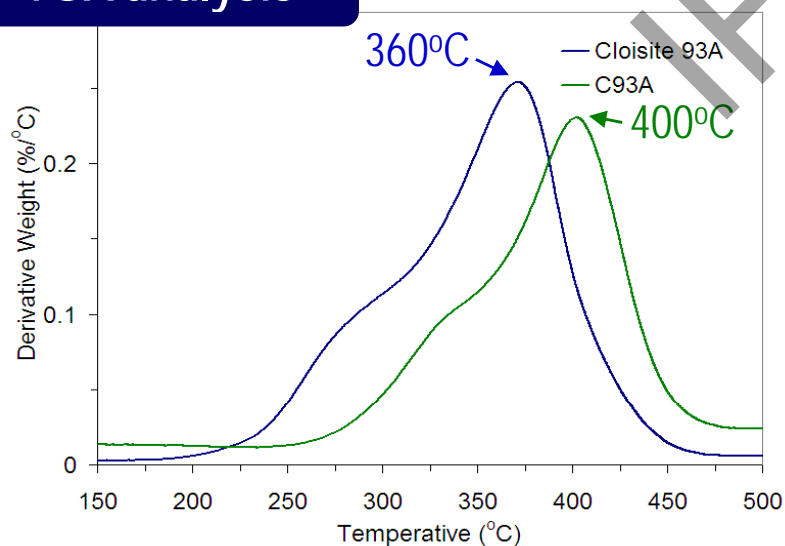
1) Nickel diimine catalyst was physisorbed onto Cloisite 93A surface or gallery.



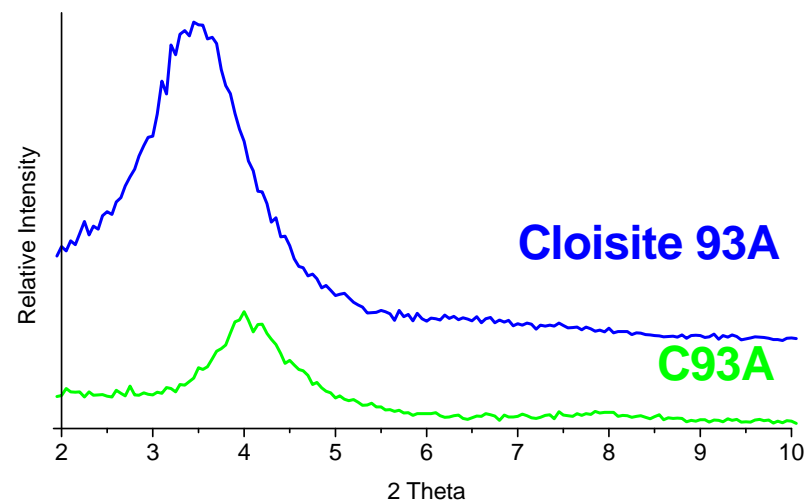
MMT (Cloisite 93A)

Cloisite 93A-Supported Nickel Diimine Catalyst (C93A)

TGA analysis

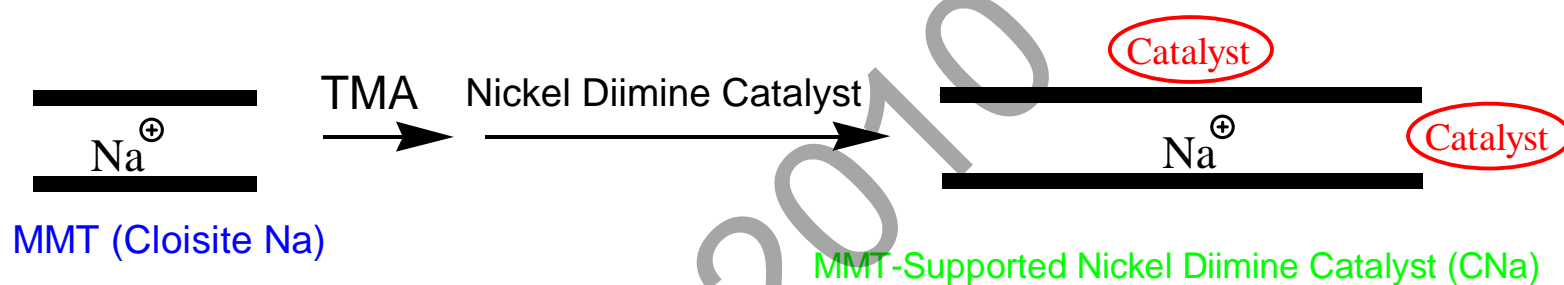


XRD patterns

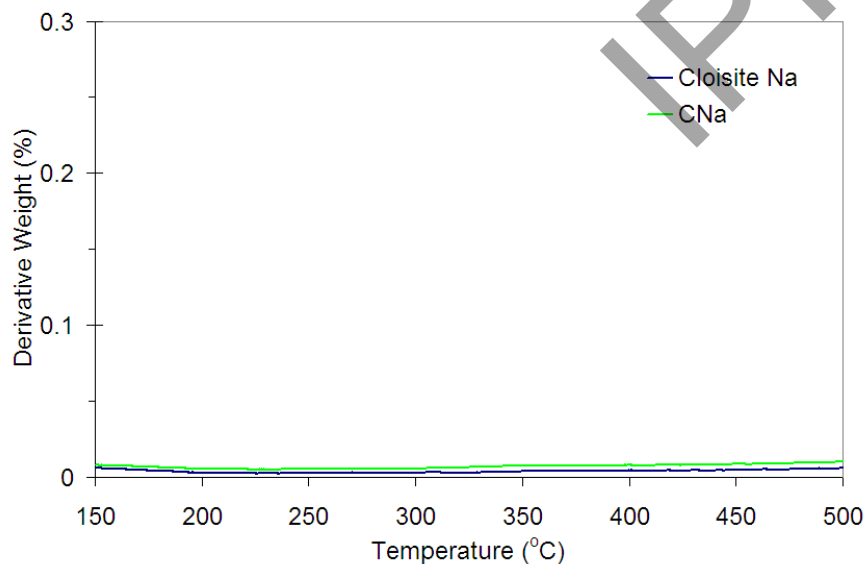


Synthesis of MMT-Supported Nickel Diimine Catalyst- 3) CNa

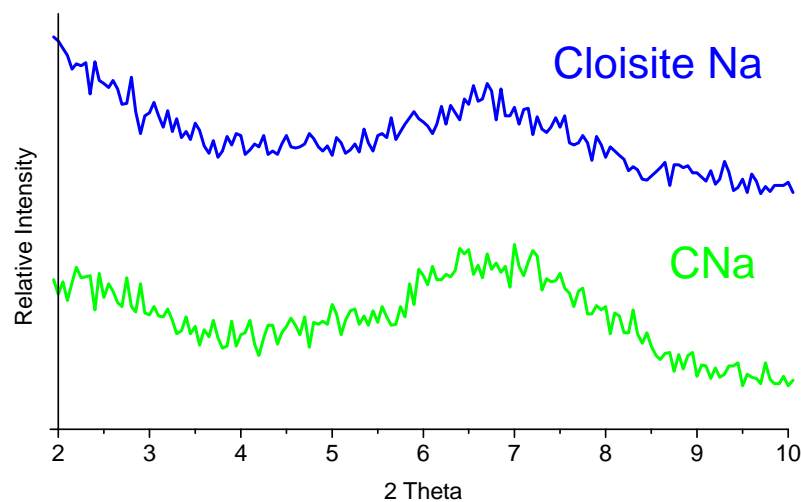
1) Nickel diimine catalyst could be physisorbed onto Cloisite Na surface or gallery.



TGA analysis

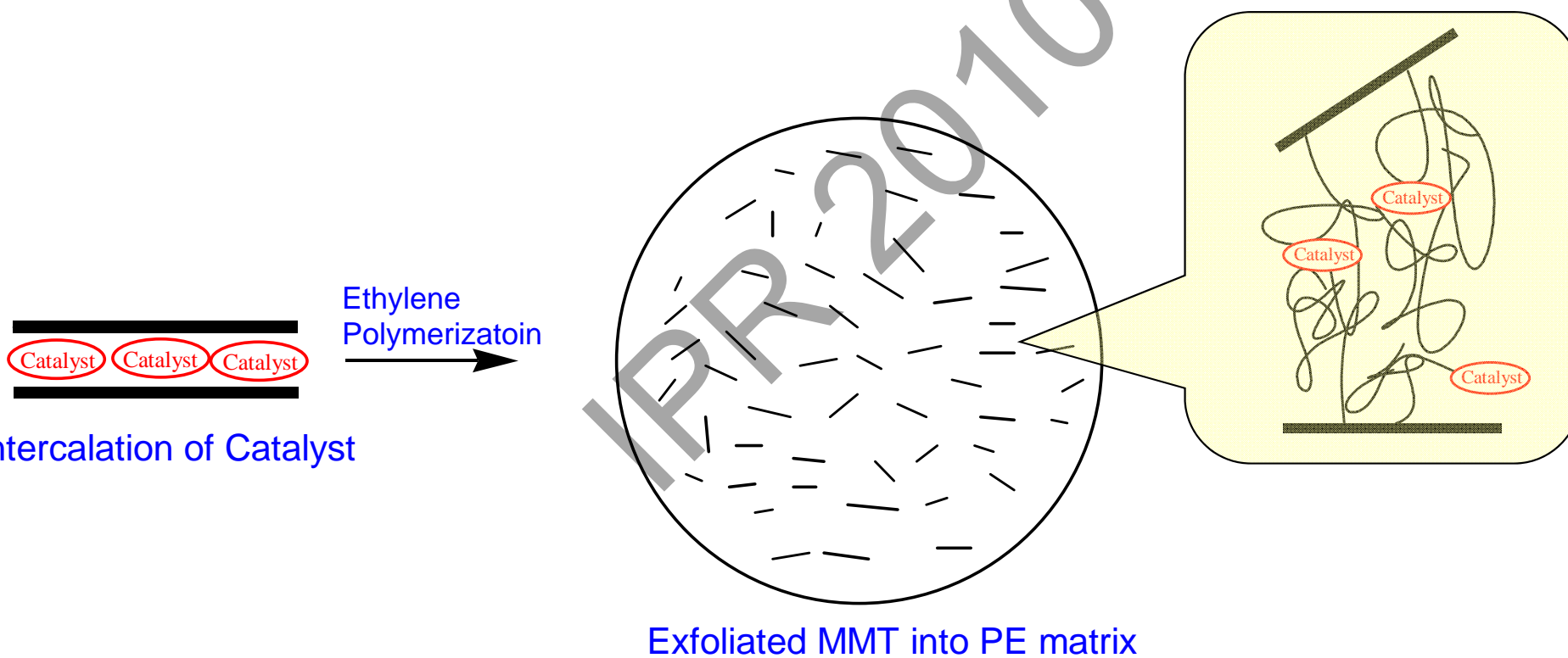


XRD patterns



In Situ Polymerization

- 1) MMT layers are exfoliated by growth of polyethylene, and it means nano size layers are distributed into polyethylene matrix.

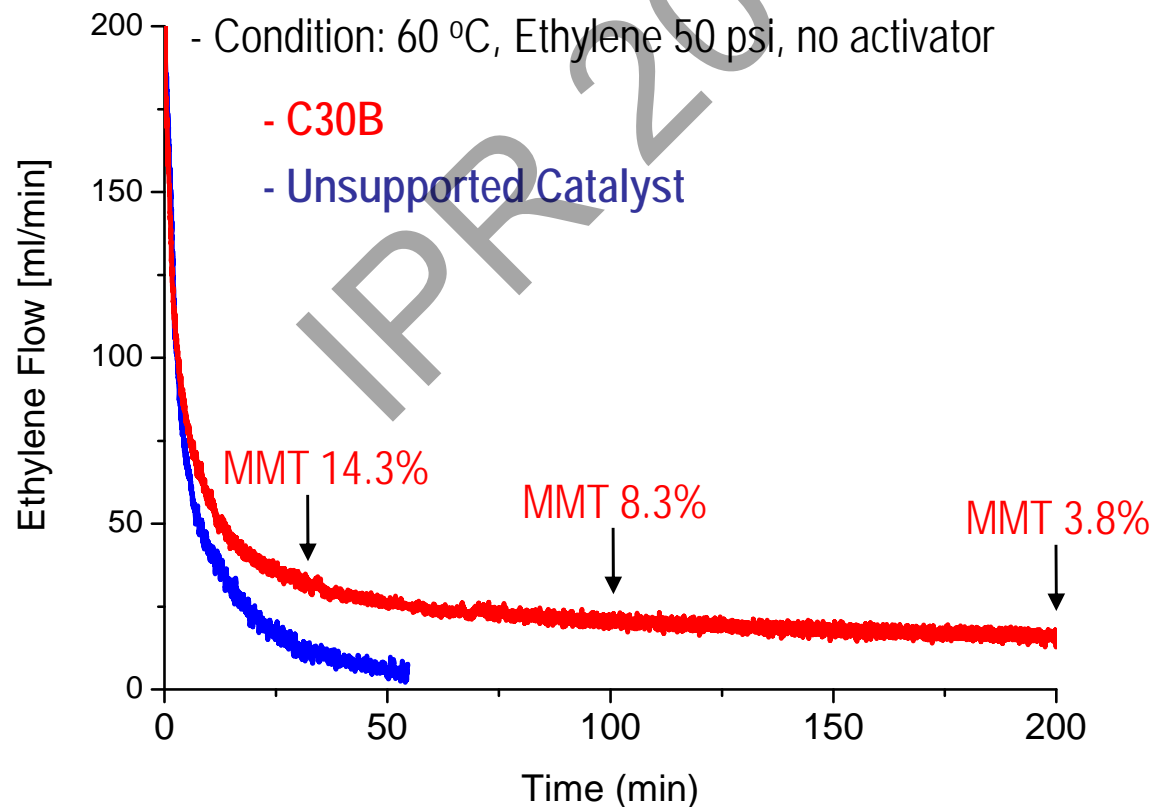


(Slurry batch reactor, Hexane solvent, Continuously ethylene feeding, EASC activator or no activator)

In Situ Polymerization Results - 1) Catalyst Activity Profiles

- 1) MMT supported catalysts systems show very stable activity profile.
- 2) A series of PE/MMT nanocomposites with different MMT fractions were prepared by varying the polymerization time.

Catalyst Activity Profiles (C30B vs. Unsupported Catalyst)

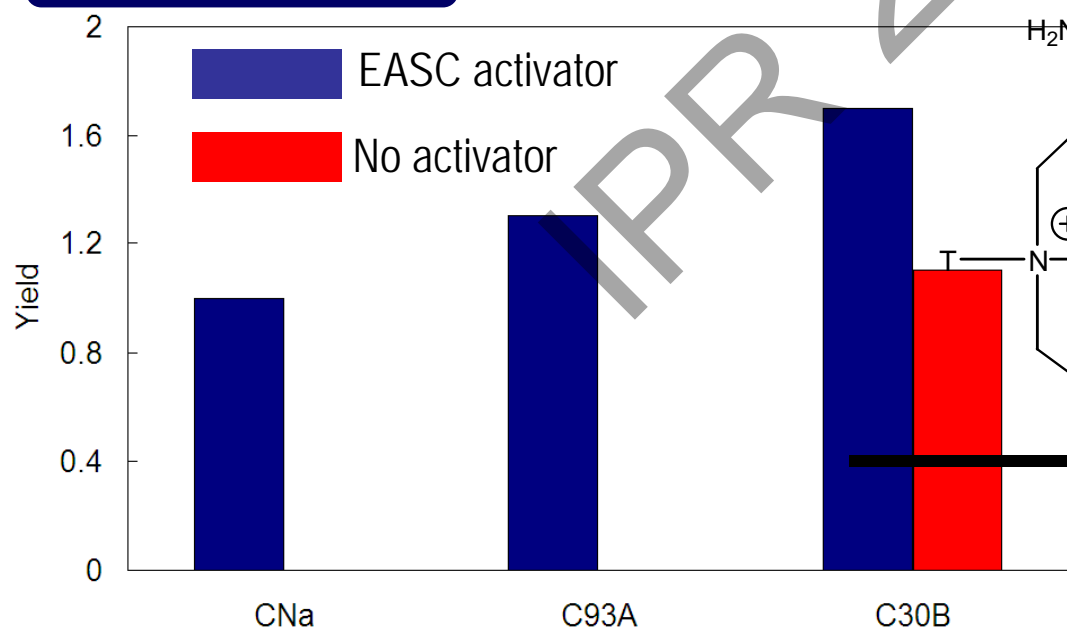


In Situ Polymerization Results- 1) Catalyst Activity

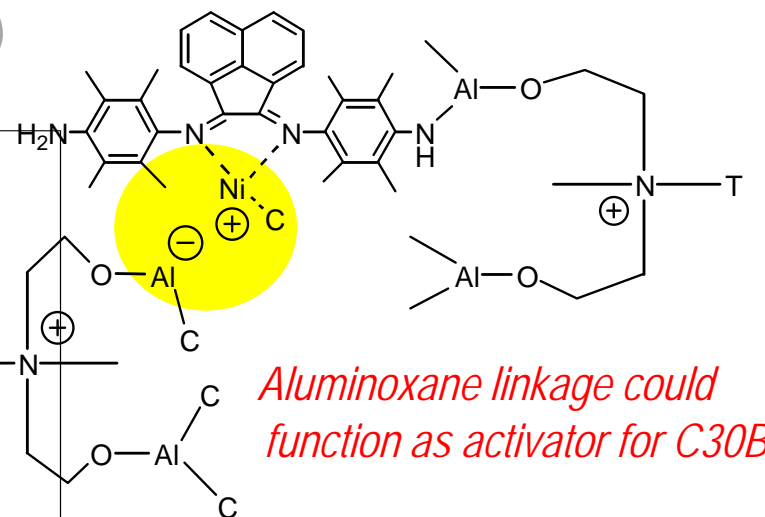
- 1) C30B shows the highest yield.
- 2) C30B comparable catalyst activity in the absence of EASC activator, but CNa and C93A had not catalyst activity without EASC activator.

Structure of C30B

Catalyst Activity



- Condition: 60 °C, Ethylene 50 psi,

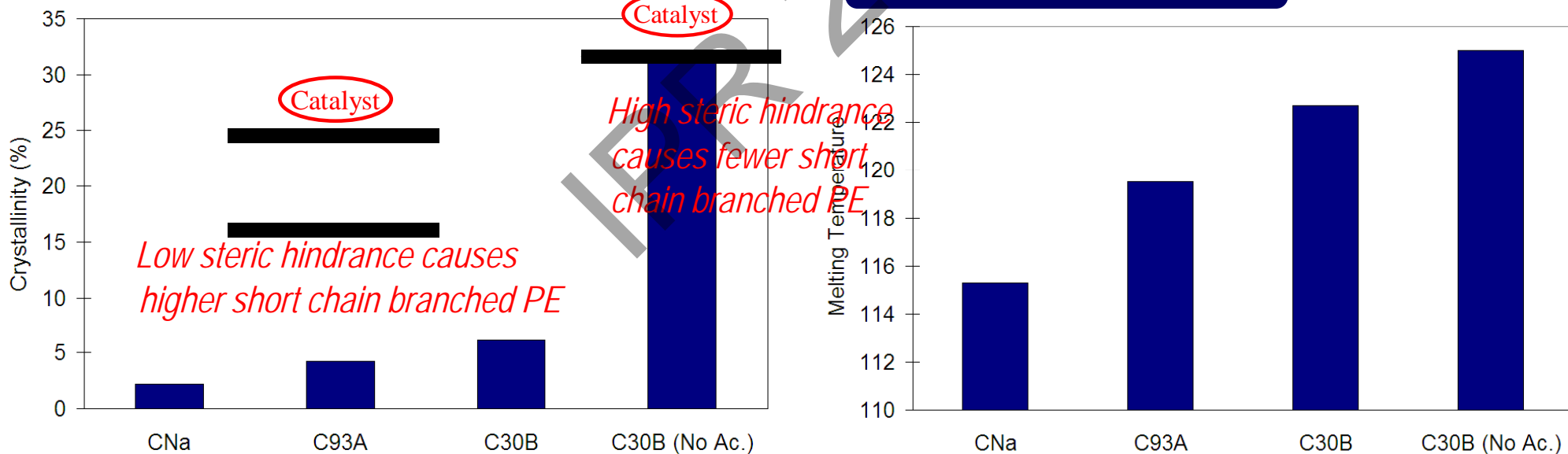


In Situ Polymerization Results- 2) Crystallinity & Melting Temperature of Nanocomposites

- C30B without activator made nanocomposite with the highest T_m and crystallinity.

Crystallinity

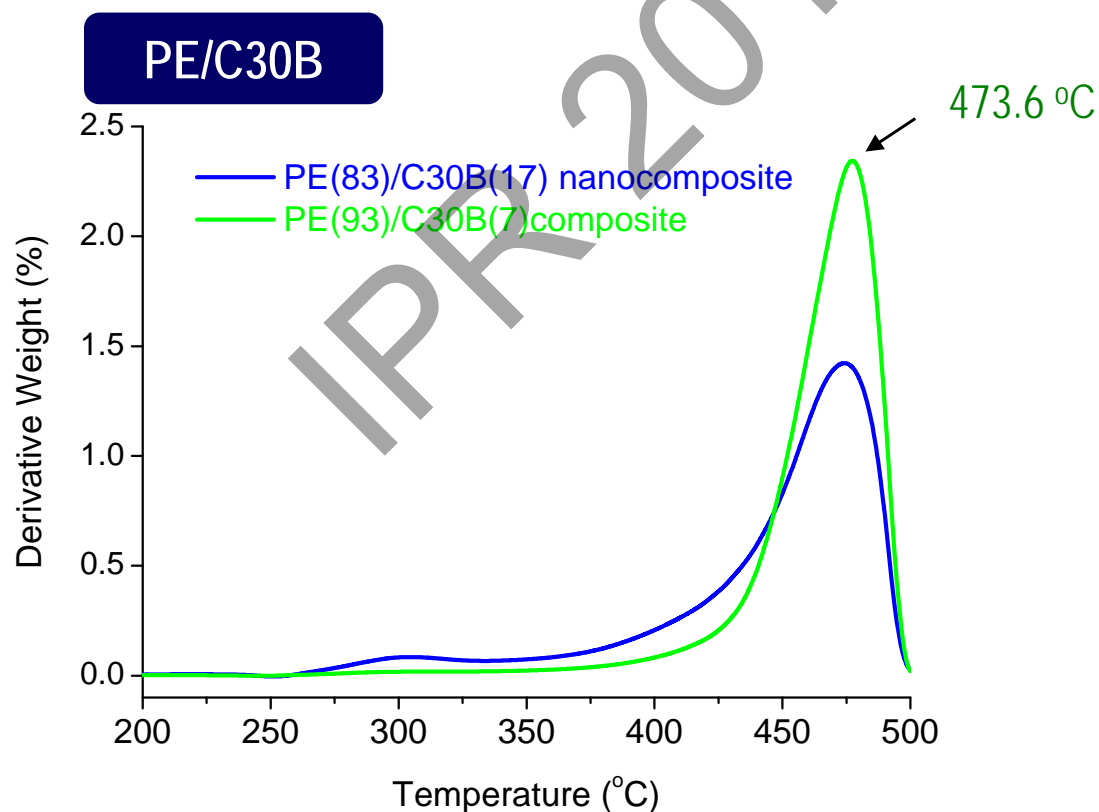
Melting Temperature



- Polymerization Conditions: 60 °C, Ethylene 20 psi, EASC activator or no activator

In Situ Polymerization Results- 3) Decomposition Temperature of PE/C30B

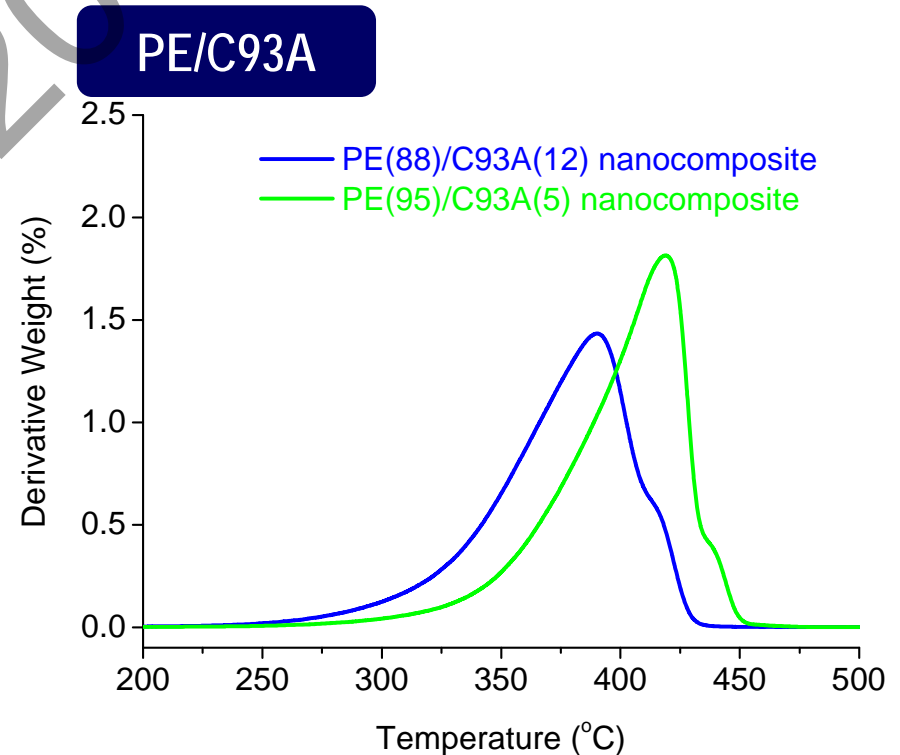
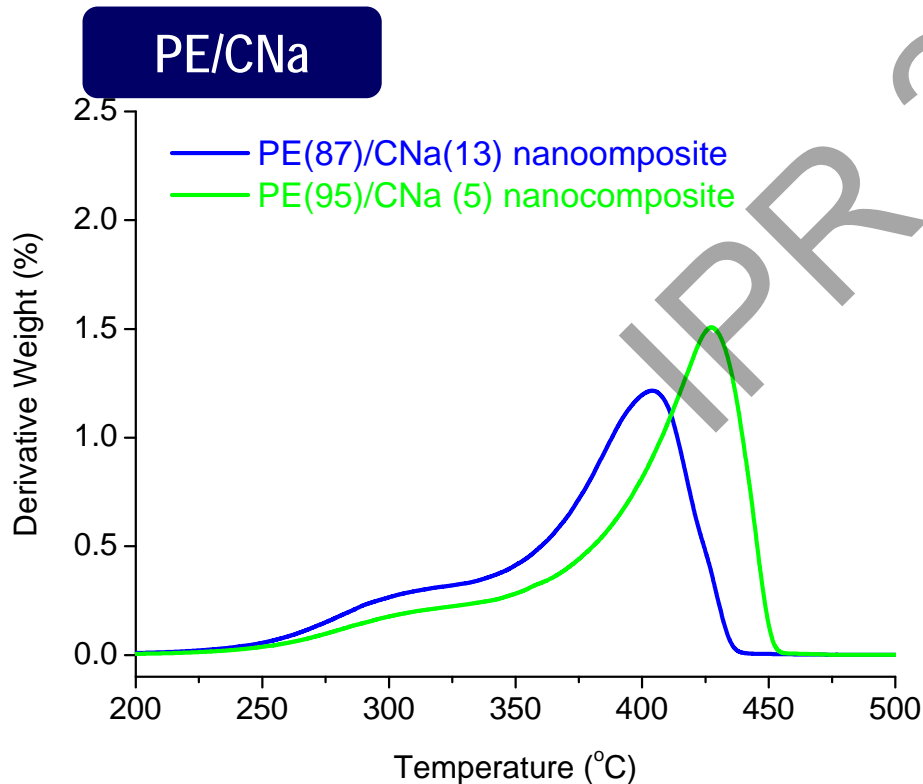
- T_d of nanocomposites with C30B were similar with reference homogeneous PE resin (473.4 °C).
- Good dispersion of the MMT layers in the polymer matrix, resulting in enhanced thermal stability of the nanocomposites.



- Polymerization Conditions: 60 °C, Ethylene 50 psi, no activator

In Situ Polymerization Results- 3) Decomposition Temperature of PE/C93A and CNa

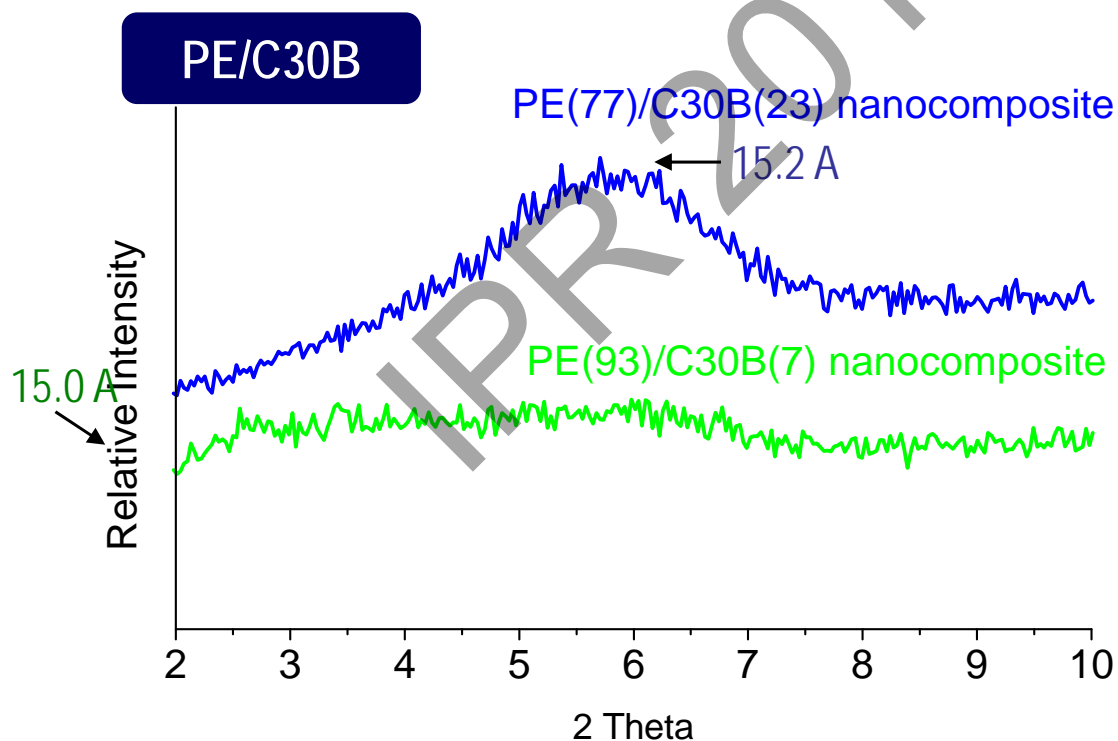
- 1) T_d of nanocomposites using CNa and C93A were lower than that of the reference homogeneous PE resin (473.4 °C)
- 2) As MMT contents increase, T_d of nanocomposites decreases.
- 3) MMT and/or alkyl modifier accelerate the degradation of PE.



- Polymerization Conditions: 60 °C, Ethylene 50 psi, EASC activator

In Situ Polymerization Results- 4) XRD Patterns of PE/C30B

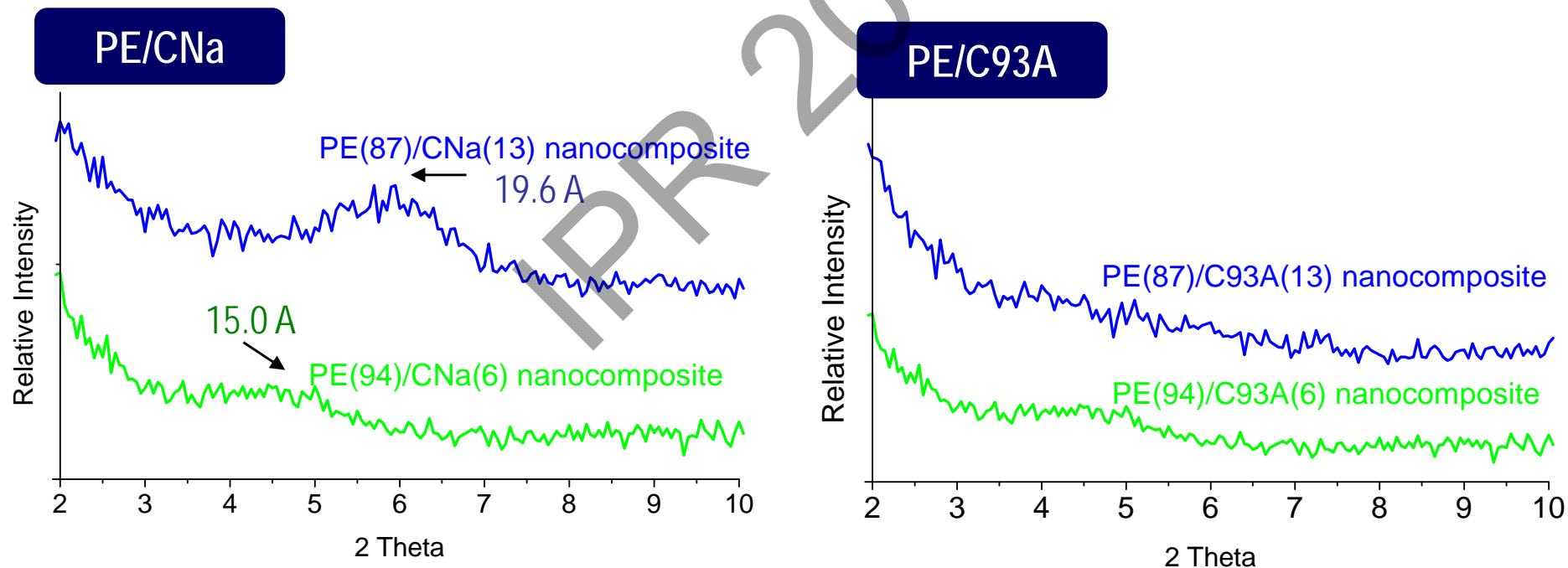
- As increased polymerization time (lower C30B contents), the MMT layers were exfoliated.



- Polymerization Conditions: 60 °C, Ethylene 20 psi, EASC activator

In Situ Polymerization Results- 4) XRD Patterns of PE/CNa and C93A

- As increased polymerization time (lower MMT content), the MMT layers were not fully exfoliated.

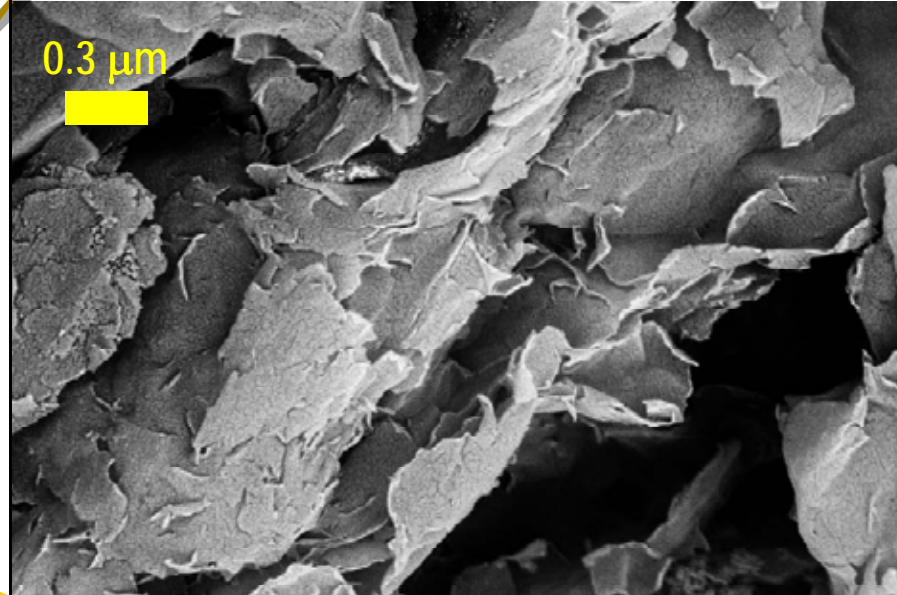
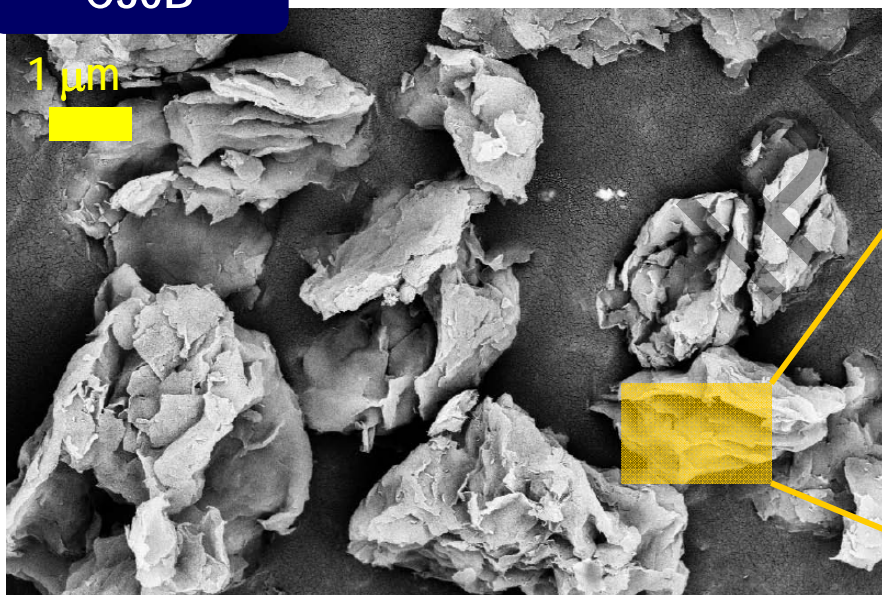


- Polymerization Conditions: 60 °C, Ethylene 20 psi, EASC activator

In Situ Polymerization Results- 5) SEM Micrographs of Supported Catalyst

- C30B shows irregular particles in the 2-3 μm width.
- The edge of the C30B particles are "curly", indicating that MMT layers have been intercalated and exfoliated by diffusion of the reactants from their edges to their centers during supporting process.

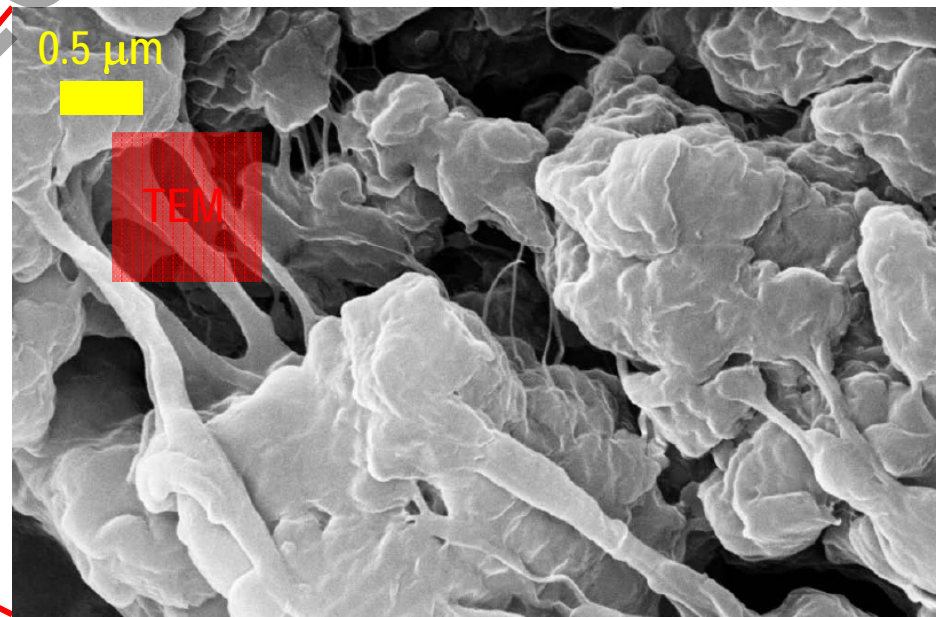
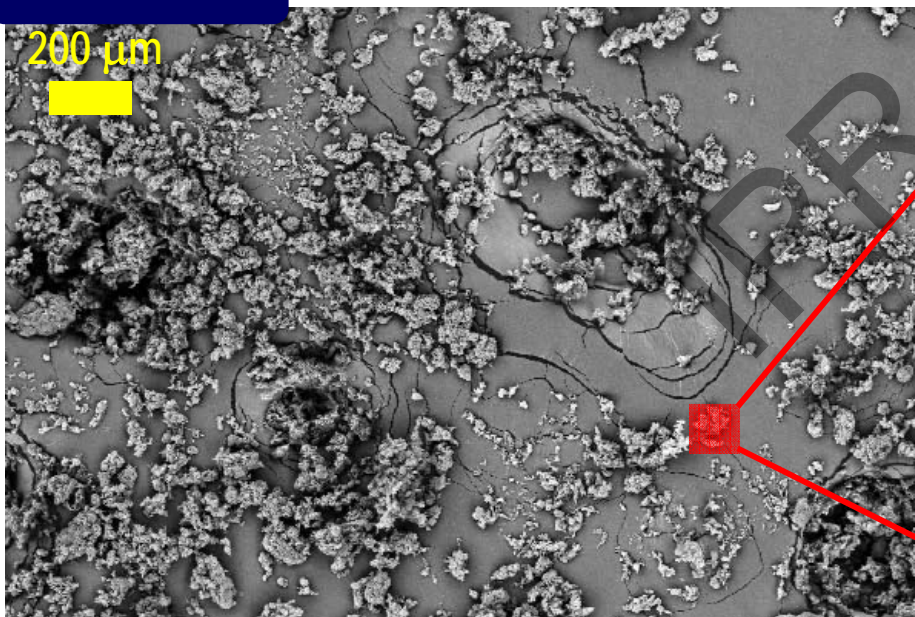
C30B



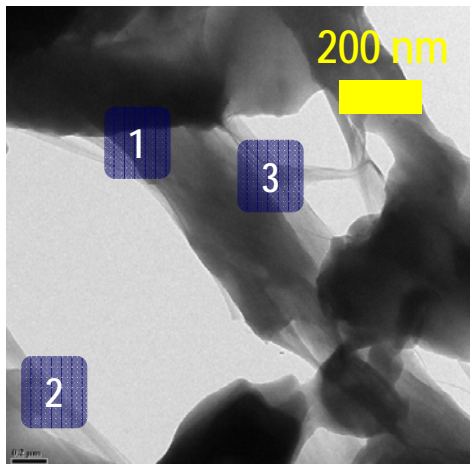
In Situ Polymerization Results - 5) SEM Micrographs of Nanocomposites

- Free-flowing nanocomposite particles were obtained without reactor fouling.
- The MMT layers appear as stacks connected by polymer strips and fibrils of different lengths and width.

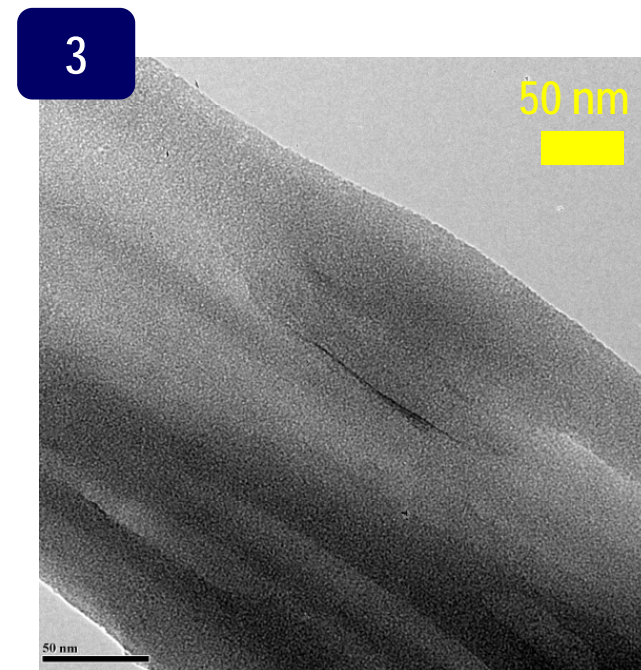
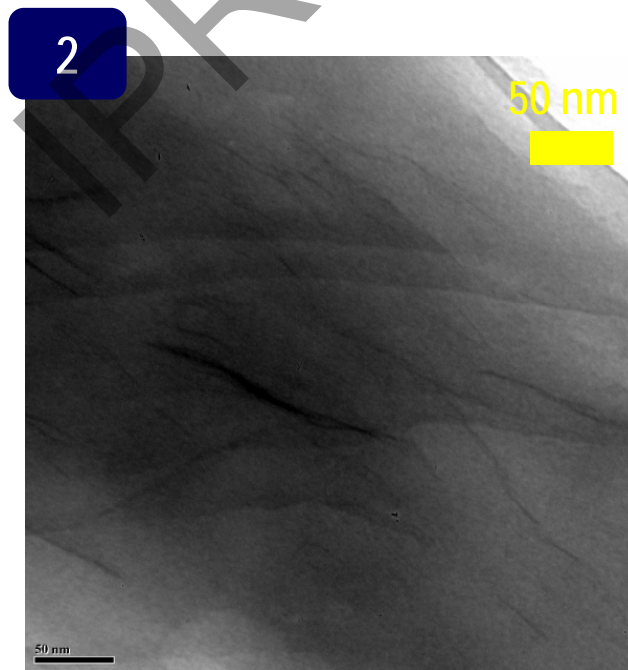
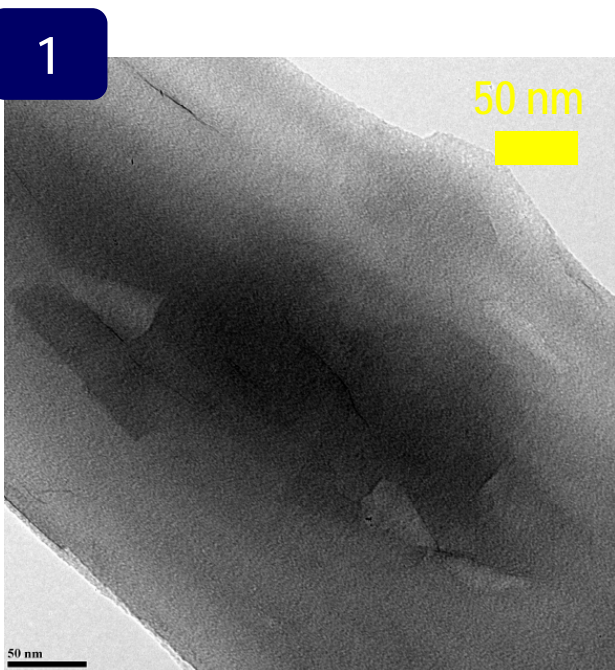
PE/C30B



In Situ Polymerization Results- 5) TEM Micrographs of Nanocomposites



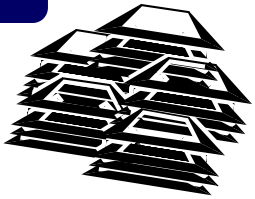
1. The MMT layers are oriented in planes that are parallel to the slicing plane, appearing as dark regions.
2. The MMT layers are oriented perpendicularly to the slicing plane, showing very good exfoliation.
3. Several layers of MMT appear to be completely exfoliated and seem to “flow” with the polymer.



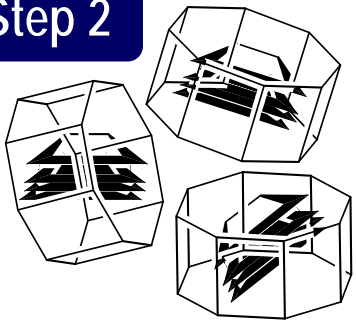
- Particle Fragmentation Mechanism

1. Large MMT particles are broken into several smaller particles.
2. The MMT layers are exfoliated by growing polymer.
3. Nanophase distribution of MMT layers on the polymer matrix.

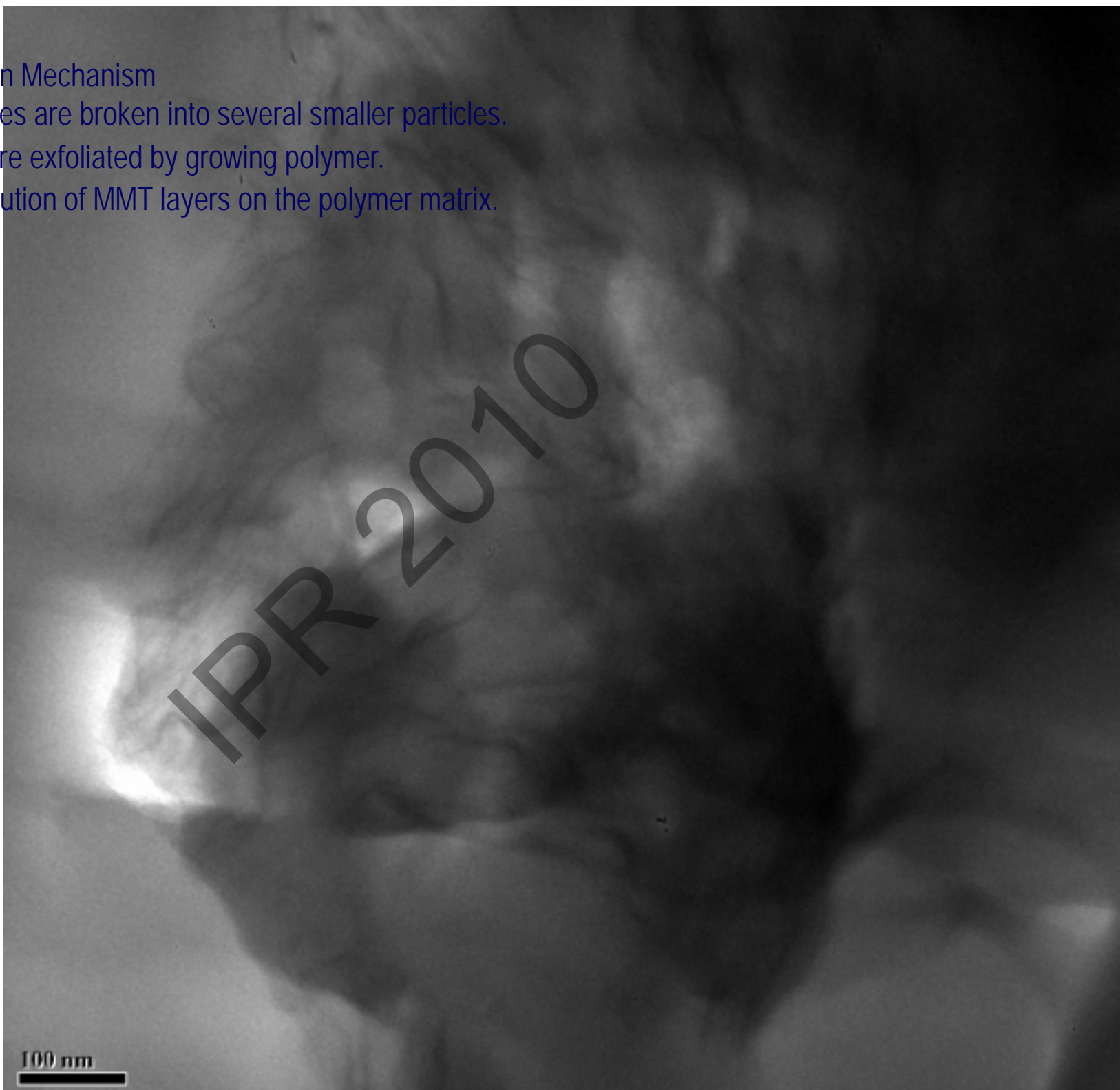
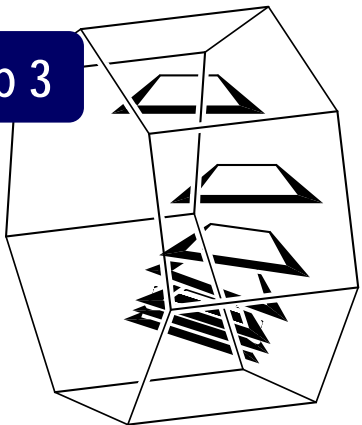
Step 1



Step 2



Step 3



A decorative graphic consisting of a vertical stack of three squares (dark blue, yellow, green) on the left, followed by a horizontal line of seven squares (yellow, green, dark blue, yellow, dark blue) extending to the right.

Conclusion

1. PE/MMT nanocomposites were prepared by in situ polymerization with a functionalized nickel diimine catalyst on Cloisite Na and two organically modified MMTs, Cloisite 93A and Cloisite 30B.
2. The particle intercalation and exfoliation was initiated by the insertion of the nickel diimine catalyst into TMA-modified MMT galleries, and continued even further during the polymerization by the formation of polymer chains within the clay galleries.
3. C30B made nanocomposites with better thermal properties than those made with CNa and C93A.
4. C30B was active for ethylene polymerization even in the absence of the EASC activator.
5. SEM and TEM micrographs confirmed the formation of a nanophase of MMT layers distributed in the polymer matrix.

Yiyoung Choi, Sang Young A. Shin, João B.P. Soares, *Macromol. Chem. Phys.* 2010, 211,1026

Thank you!