

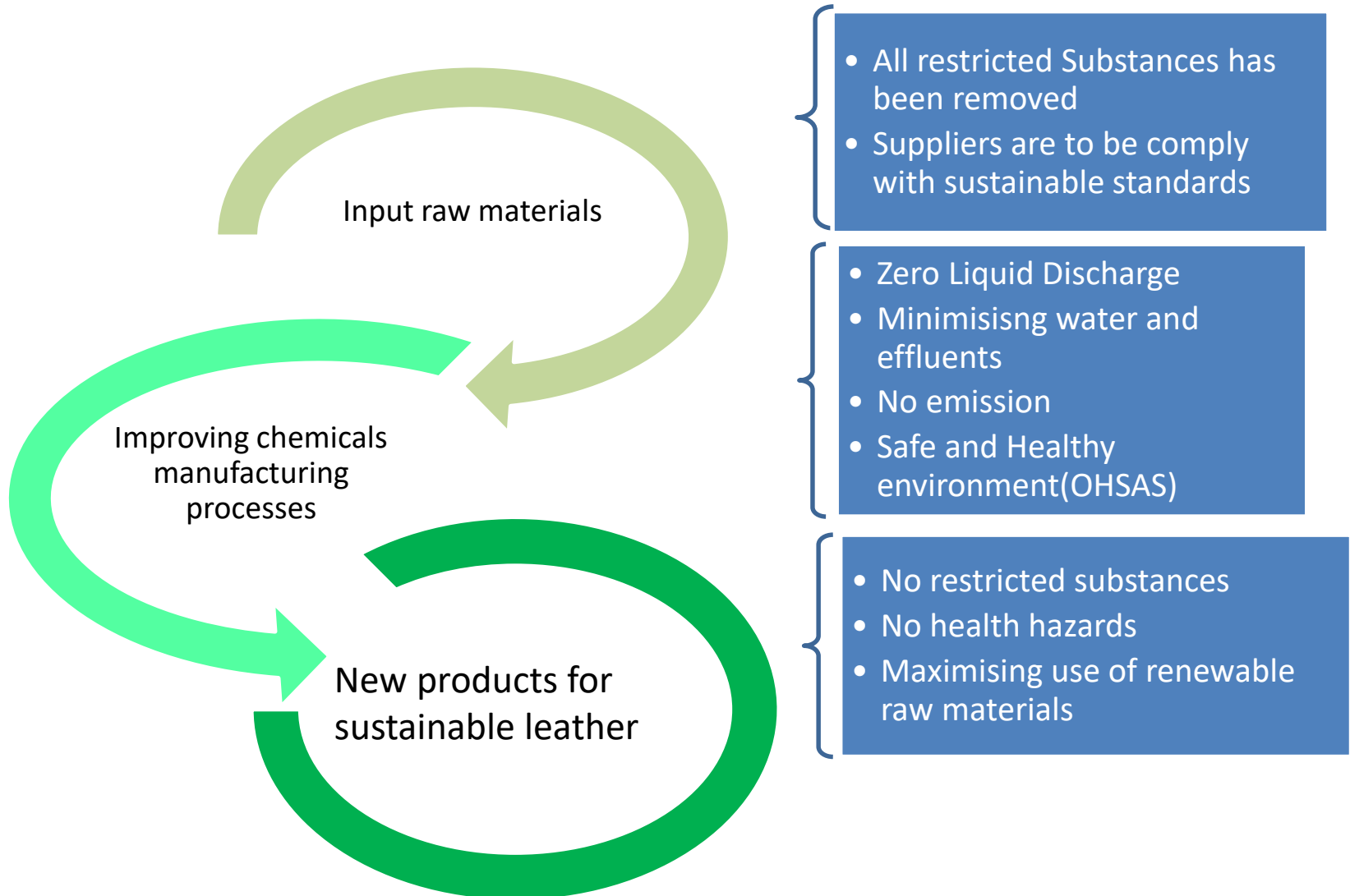
Exploring New Chemistries for Sustainable Leather Processing

Dr. V.Vijayabaskar

SBU – Leather Chemicals



Balmer Lawrie 's efforts towards sustainability



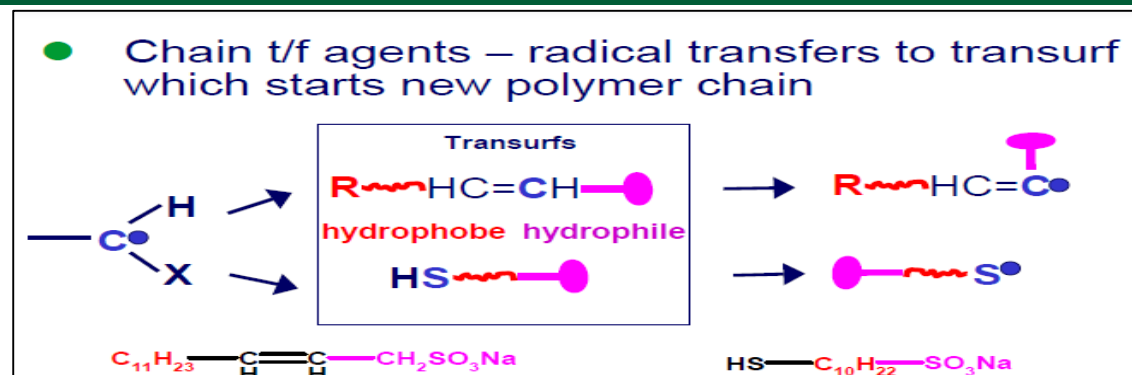
- ❖ This presentation will highlight some of the new approaches not pertaining to just change of substrates but new reactions with possible different outcomes-BL inhouse works
- ❖ **Technological Translations** , new chemistries from other research institutions in various fields with an intention to be adoptable is highlighted

Fatliquor- some new Ideas

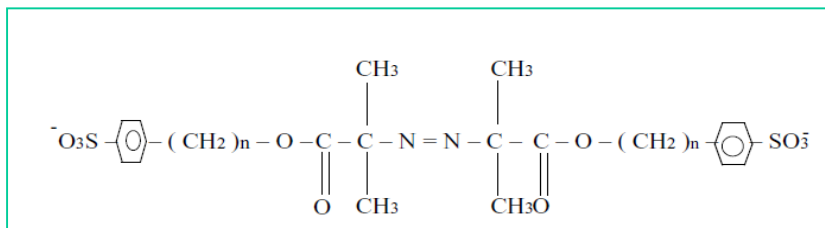


Reactive Surfactants

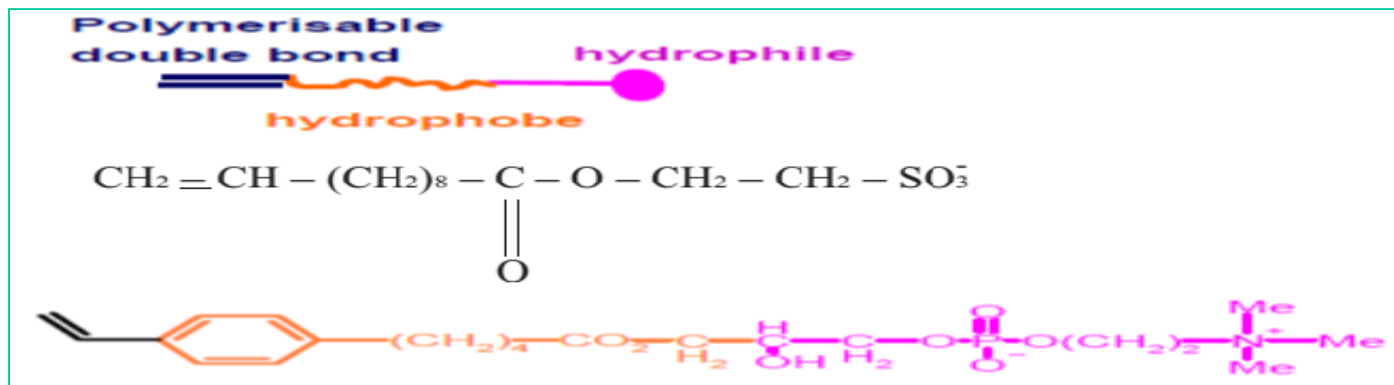
1. Transurfs



2. Inisurfs



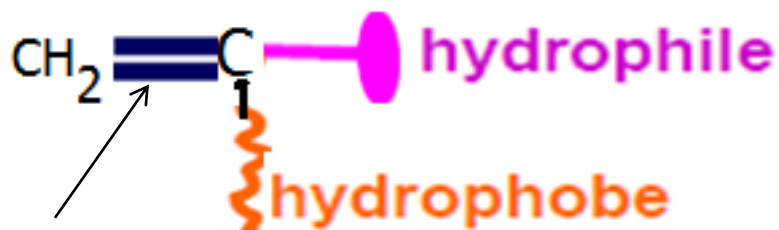
3. Surfmers



Chemically bound surfactants to Latexes – for enhanced stability and performance .

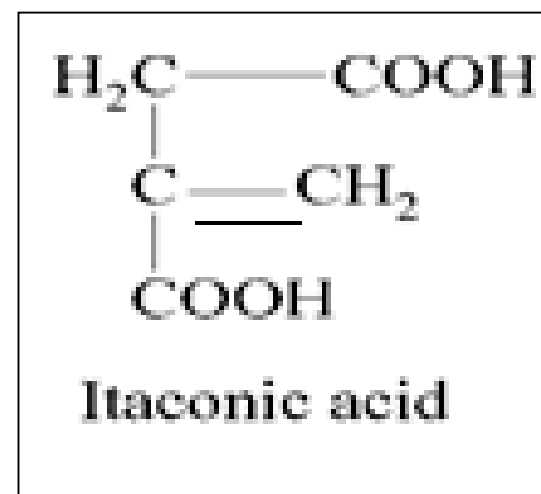
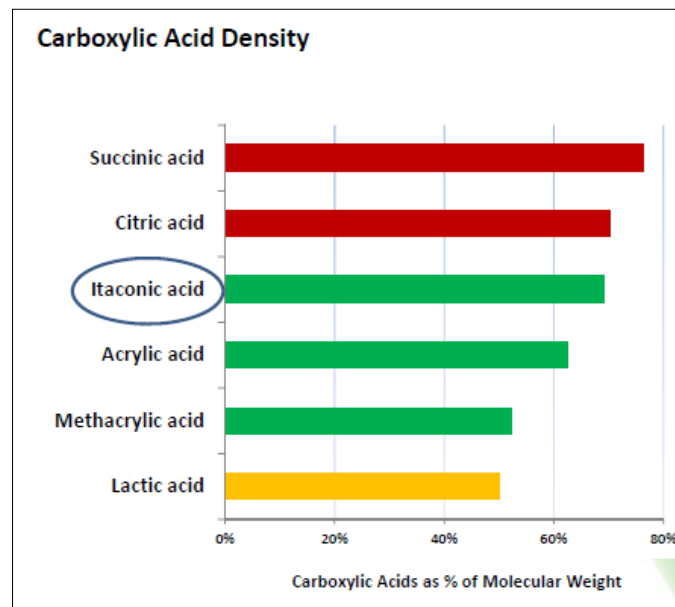
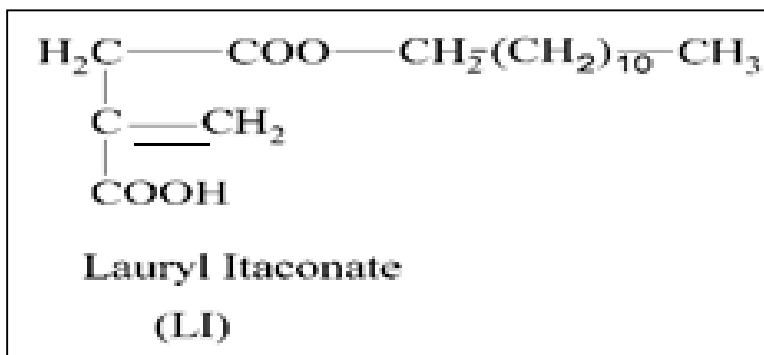
Polymeric Fat through Polymerisable Surfactant

1. Preparation of polymerisable surfactant/Surfmer

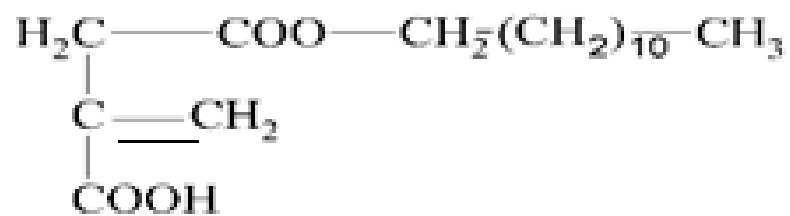


Polymerisable bond

Itaconic acid is used to generate the surfmer .
Lauryl itaconate was synthesized and used as a surfmer



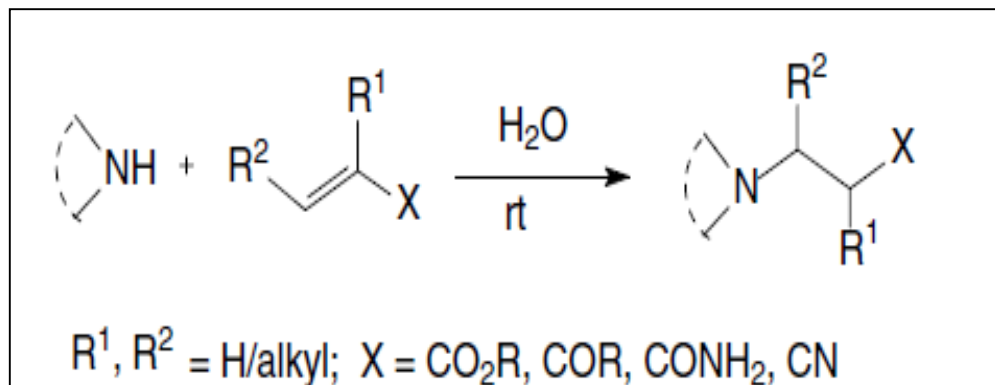
Our commercial products, Balmol SWG ,
PG1 , UP101 are formulated with modified
surfmers .



Lauryl Itaconate
(LI)

or PEG Itaconates

can undergo Michael Addition

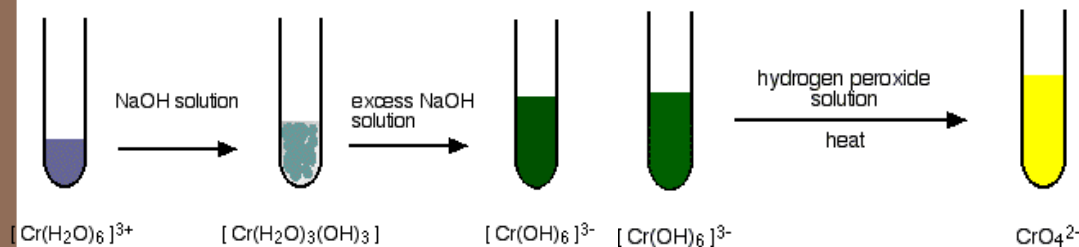
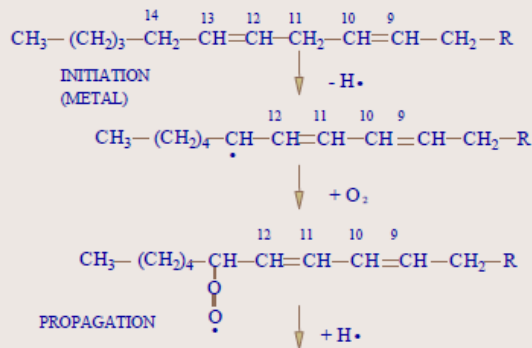


* Ref: Prof. Sherrington papers , Dept. of Chemistry University of Strathclyde ,UK, & Prof. S Ramakrishnan papers , IPC , IISC , Bangalore on Hyperbranched & polymerizable surfactant.

Fatliquor- some new Ideas

- The unsaturated vegetable fat if not properly guarded with antioxidants lead to oxidation of Cr(III) to Cr (VI)

Lipid Oxidation



Oxidation Rates: Types of Fatty Acids

- As # of double bonds increases
– # and reactivity of radicals increases

Type of Fatty Acid	Rate of Reaction Relative to Stearic Acid
18:0	1
18:1Δ9	100
18:2Δ9,12	1200
18:3Δ9,12,15	2500

The oxidation of lipids could accelerate the oxidation of chromium (III) to chromium (VI). Likewise, the presence of chromium (VI) ions could accelerate the oxidation of lipids



Syntheisized fat based fatliquor – Another application of surfmer **Indian Patent No. 282682**

- ❖ This work describes the method for treating leather with excellent light fastness with a retan fatliquor containing a dispersion of a selected amphiphilic copolymer, substantially free from organic solvents.
- ❖ It is formed from a predominant amount of at least one hydrophobic monomer/ surfmer and another copolymerizable hydrophilic monomer.
- ❖ This type of leather being particularly suitable for use in vehicle upholstery, upper leathers etc.

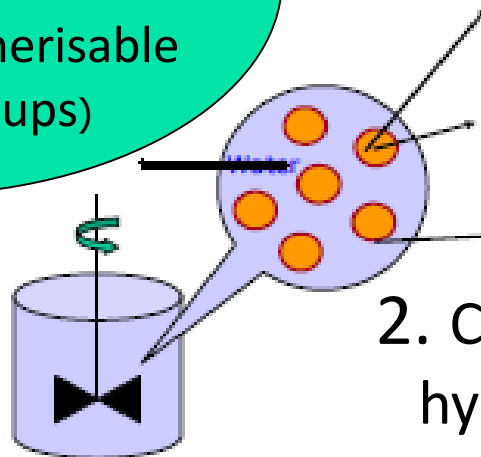
Inverse Emulsion Technique- copolymer with surfmer as co monomer

Sodium salt of surfmer, a polymerisable surfactant (C12-C18 Esters with polymerisable vinyl end groups)

Water soluble monomer

Water soluble initiator

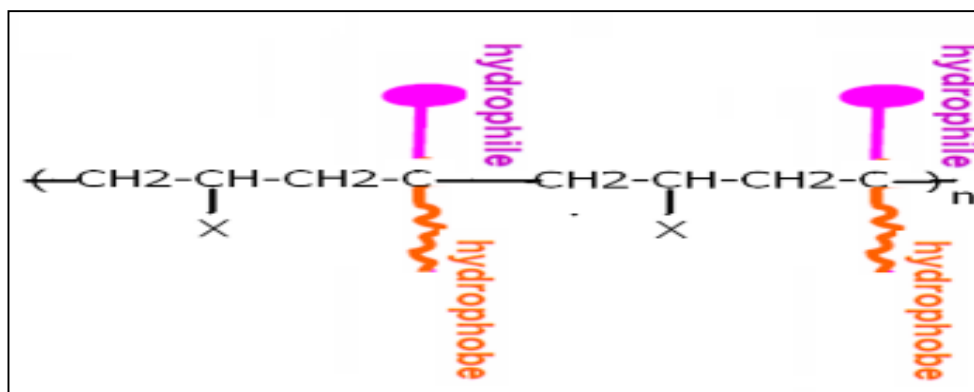
Here surfmer acts as a stabiliser

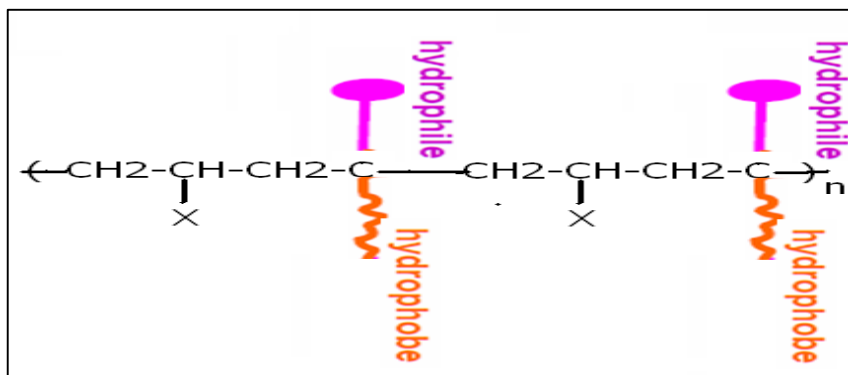


Here surfmer acts as a Continuous phase . A very little amount of water with initiator dissolved in it is added just to form the interface .

2. Copolymerising surfmer with a hydrophilic monomer

Mole ratio of surfmer : Acrylic acid is 1.2:1





“ Surfmr based “ Patent No. 282682 , granted

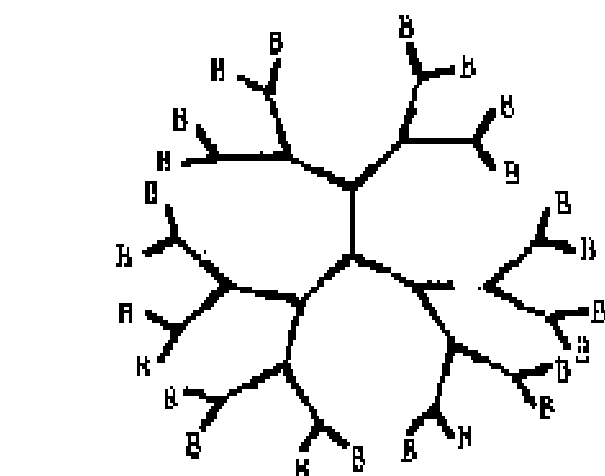


- The Copolymer structural formula prepared above has a maximum loading of 80% by weight ratio of surfactant in its copolymer composition
- The structural elucidation have been done with ^1H NMR
- Such a high molecular weight polymer surfactant is very much useful in emulsifying most of the oils

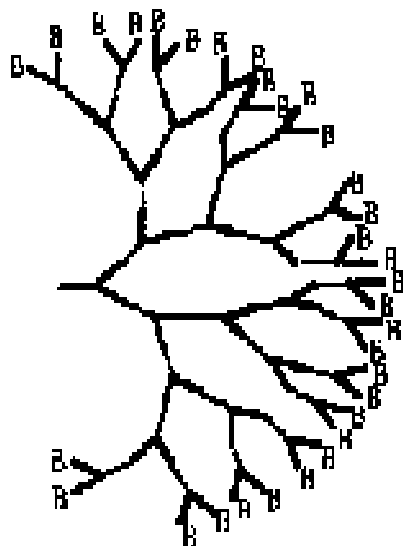
- To Improve Cr-fixation(in Leather and exhaust bath)
- To avoid Cr-VI formation



Structural representation

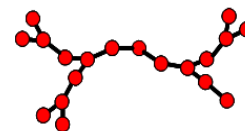


dendrimers

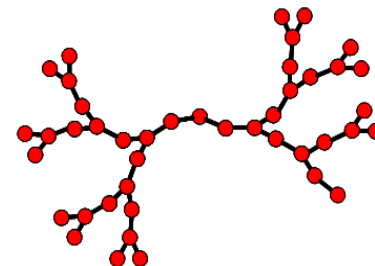


Hyperbranched polymer

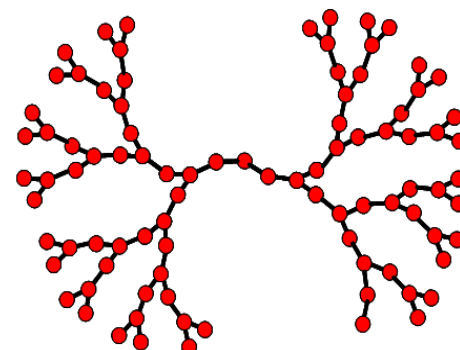
Hyper branched polymers are under the class of Dendritic macromolecules. In contrast to dendrimers, hyperbranched polymers are not perfectly monodisperse.



19 beads



43 beads

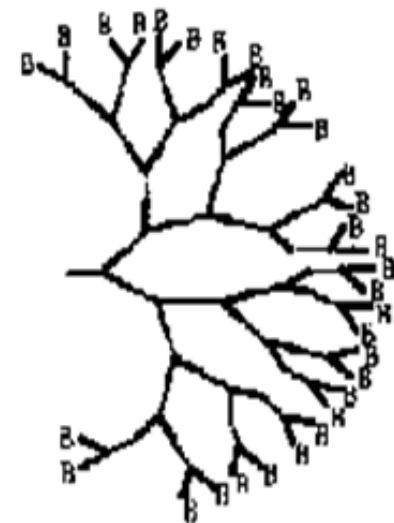
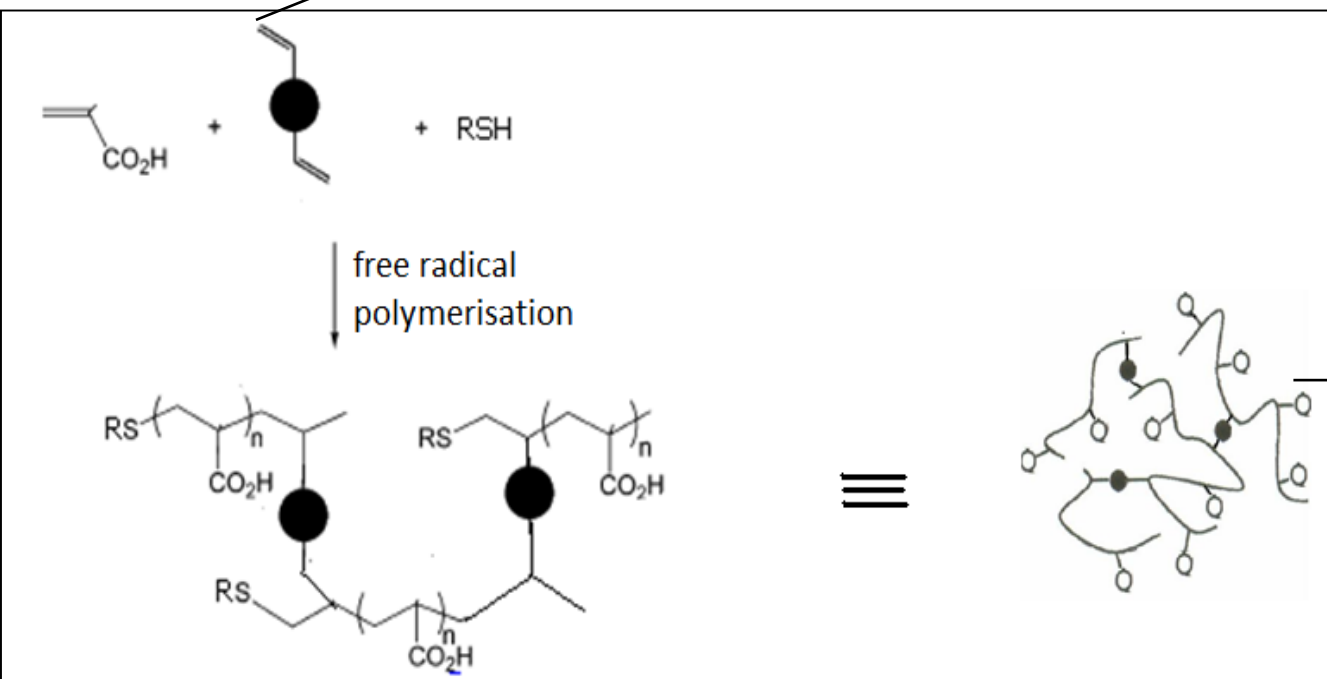


91 beads

Synthesis approach

Here the diacrylate is a surfmer

Hyper branched polymer - HBP



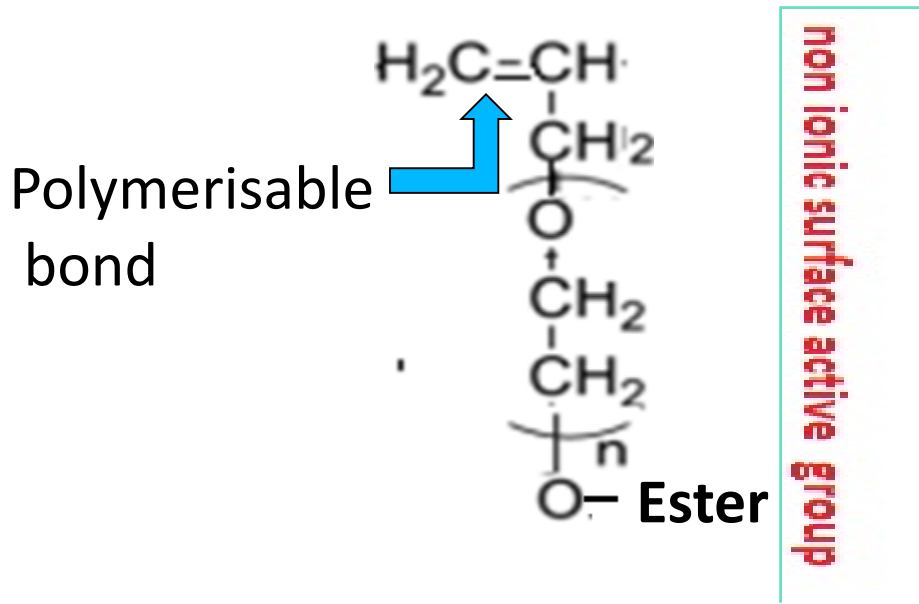
Leather trial results

This is a patented process from Balmer Lawrie . This process is based on recently developed a facile and generic synthetic methodology the "Strathclyde methodology" . **The Hyper branched polymer is crosslinked with surfmer**

	Trial with 3% HBP	Coventional process
Chromium in the bath	3238.5 mg/L	4409.0 mg/L

Polycarboxylates – Free Chrome Binding agent in Leather

Example for surfmer application - **Polycarboxylate ether**- For avoiding Chromium (VI)



Allylether of PEG (**APEG**) ester copolymerized with other monomers to make **Polycarboxylate ether**

Other acrylic monomers used for copolymerizing are Acrylamido 2- methyl propane sulphonic acid-



The vinyl ends in the APEG can form Michael Adduct with Collagen

Application of the
Chrome fixing agent
Polycarboxyate

"Hyperbranched Acrylic
Copolymers " **Patent No.
286195**

Polycarboxyate is
used after adding
the chrome tanning
agent;

The perfect
dosage is 2%;

The basifying
pH is 4.0~4.2.

**Our product
in this range is
Balfix PAC 20**

In leather, Cr (VI) after ageing not detected and free
chrome oxide is reduced to less than 50 ppm

BL process for wet white tanning



Wet-White process flow



Wet-White crust process flow



* **WW-** Wet white special combination of Balsyn DRW and Balsyn DDS - products to improve tanning in combination with Gluteraldehyde

Properties Wet white and Crust leather

Leather Properties

Wet White

- Excellent grain flatness
- Whitish appearance
- Very tight grain
- Shrinkage temperature $\sim 94^{\circ}\text{C}$
- Suitable for shoe upper and fancy leathers, Lining and softer articles

Physical Properties

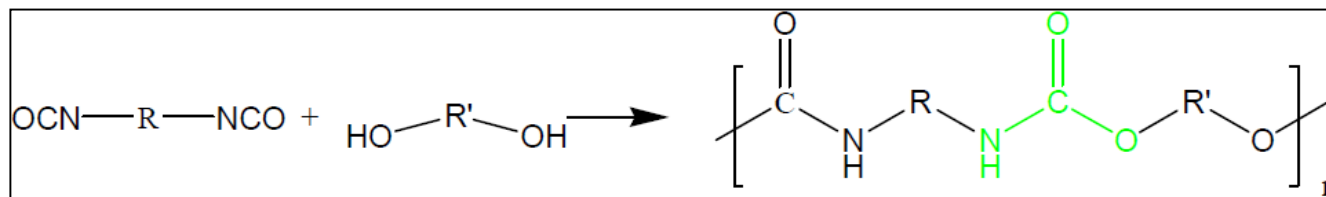
Strength properties are comparable with conventional system. This process commercially running in some Tanneries in Ambur and other parts of India.

Finishing- new chemistries related to sustainability

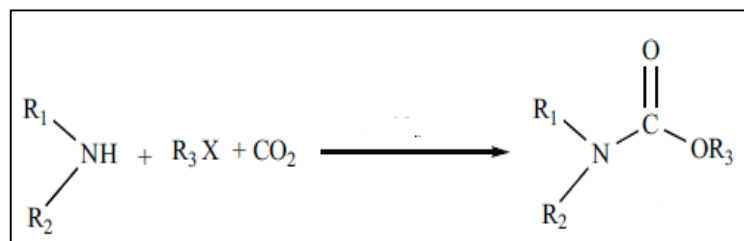


New chemistries in finishing chemicals towards sustainability

Urethanes are made by using different blocked isocyanates and diols.

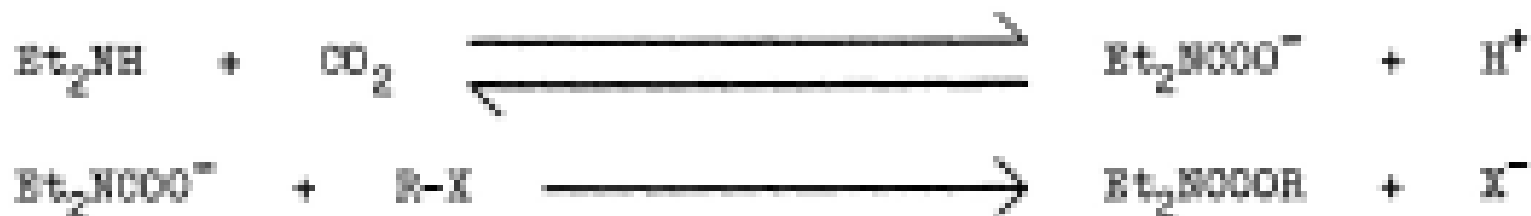


Yoshida *et al* have also reported synthesis of carbamates through the one-pot reaction of amines with alkyl halides using gaseous CO_2 .

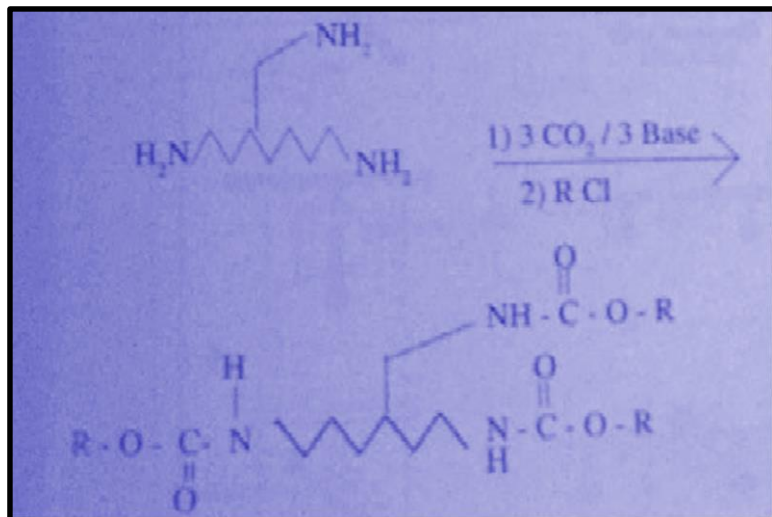


Ref : Yoshida, Y.; Ishii, S.; Yamashita, T. *Chem. Lett.*, 1984, 13, 1571-1572

A mixture of amine and alkyl halide was placed in a 100 cm³-autoclave under pressure of carbon dioxide (40 atm;) at 70⁰ C for 48 h.



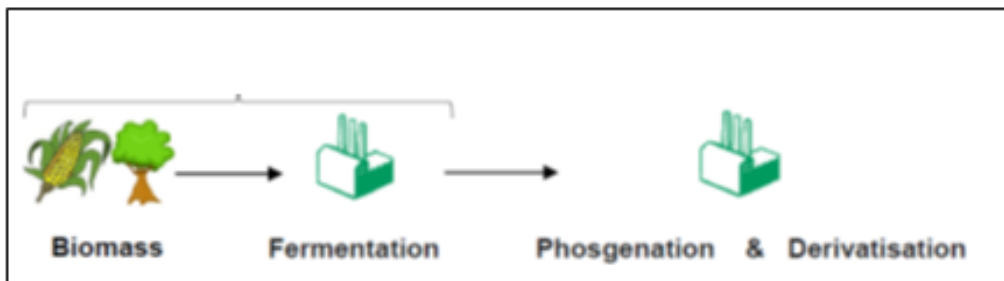
Formation of tri urethanes by this reactions with gaseous CO₂



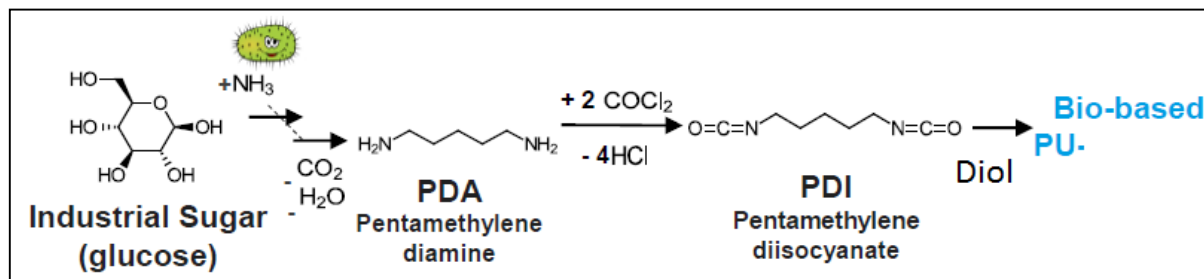
Ref: Manoj R. Nair and V.C.Malshe , Paint India , November 1999

Bio based urethanes

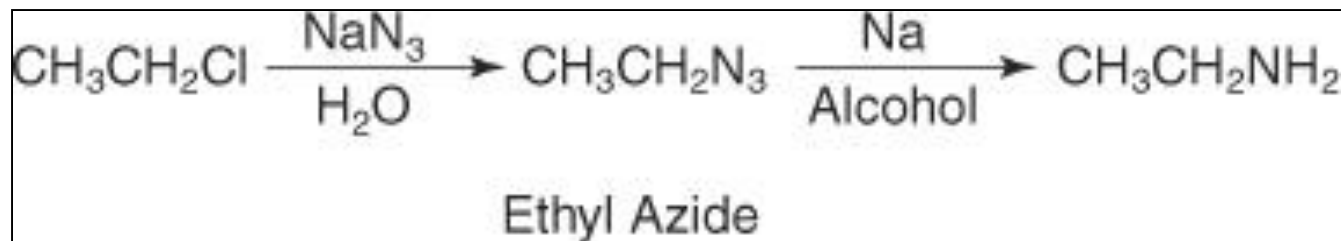
Urethanes can be made from sugars which will reduce carbon foot print



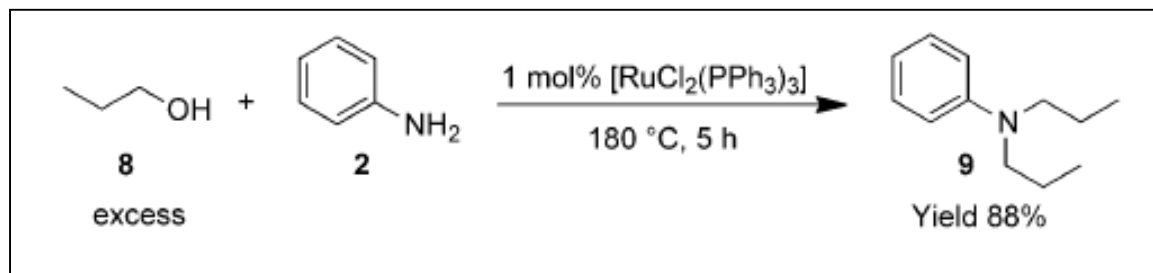
Ref: Dr. Berta Vega et.al from Covestro , NVVT Symposia 2016



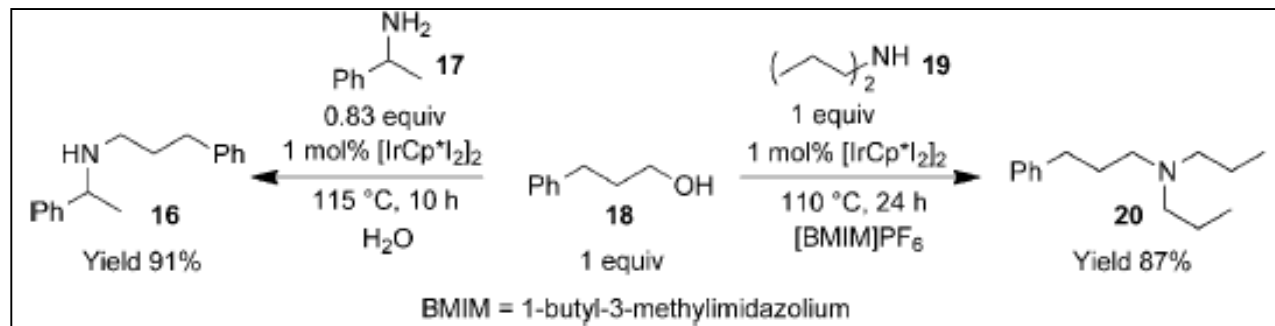
Gabriel Synthesis for Amination



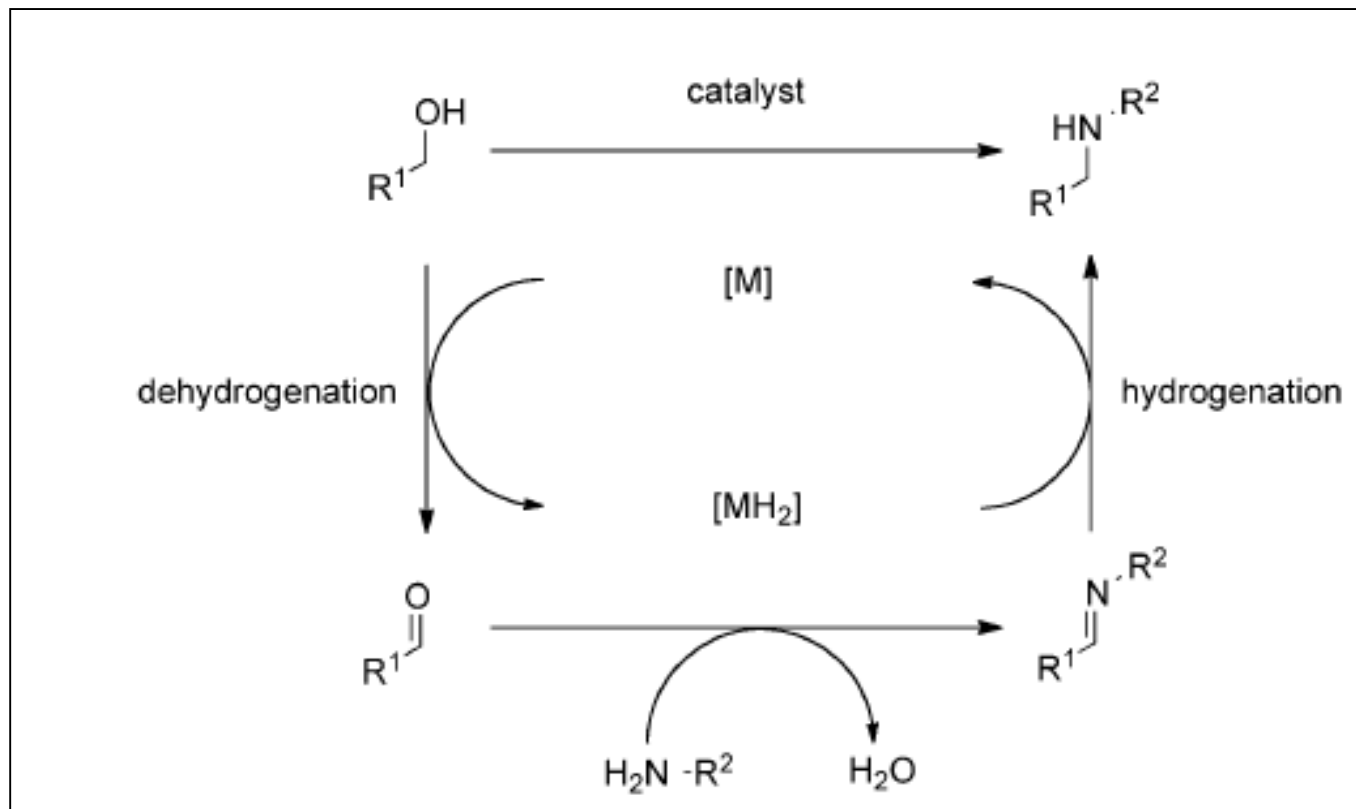
Catalytic amination of alcohols involves the synthesis of amines by means of the so-called borrowing hydrogen methodology,



Ref: Matthias Beller et.al
ChemCatChem 2011, 3, 1853 – 1864



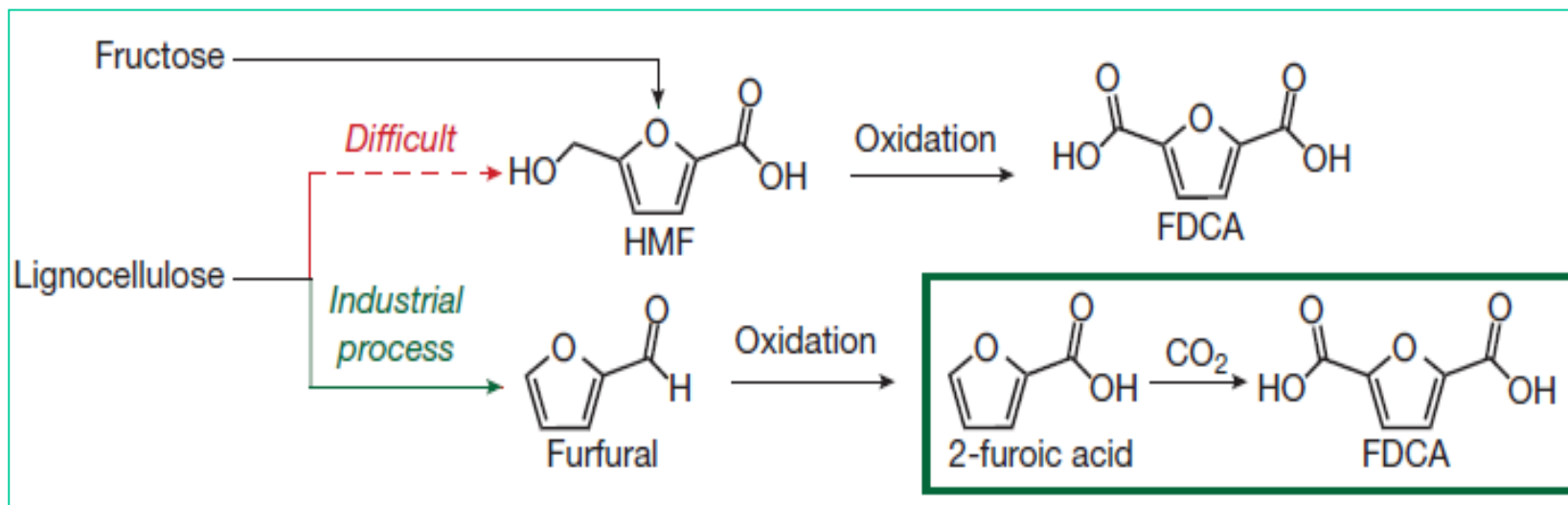
The possible pathway for amination would be borrowing hydrogen methodology



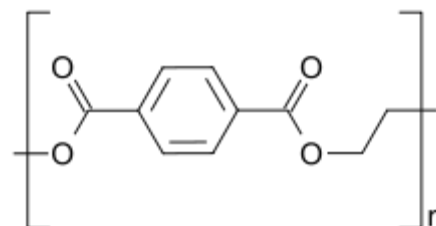
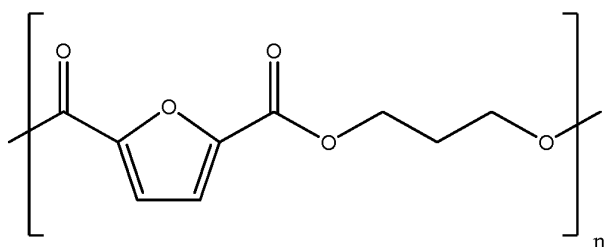
Ref: Matthias Beller et.al ChemCatChem 2011, 3, 1853 – 1864

Preparation of polyester diols from CO₂.

CO₃²⁻ - promoted C-H carboxylation



2-furoic acid, from furfural, PEF, substitute of PET

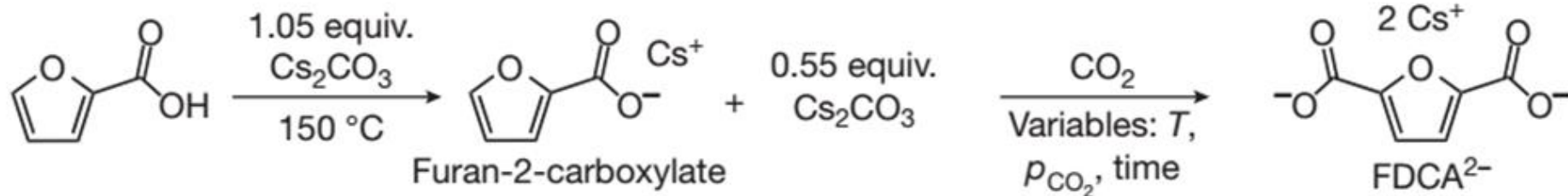


Researchers have shown that Cs_2CO_3 can deprotonate alkynyl, allylic, and activated heteroaryl C–H bonds with pK_a values of up to 27. In this synthesis it is possible to deprotonate C–H bonds of pK_a value- 35 with carbonates

Ref: Aanindeeta Banerjee¹, Graham R. Dick¹, Tatsuhiko Yoshino¹ & Matthew W. Kanan Vol 531, Nature, 215, 2016



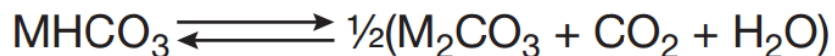
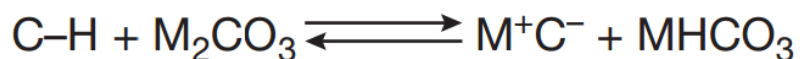
RMgX – Grignard reagent –
Carbon centred nucleophile



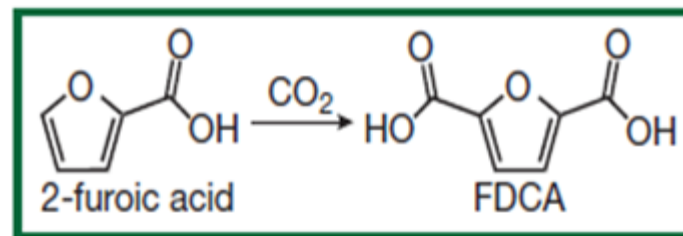
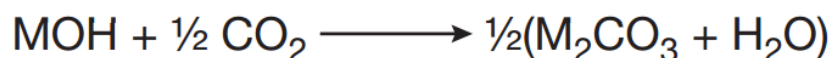
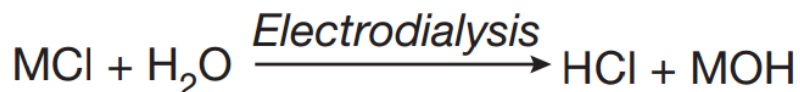
Caesium salts do typically have lower melting points

CO₂ utilization cycle

CO₃²⁻ - promoted C-H carboxylation



Protonation and CO₃²⁻ regeneration



It is similar to an un-substituted furan, the pKa of the C-H at the 5 position of furan-2-carboxylate is ~35.

In this synthesis it is hypothesized that **CO₃²⁻** would deprotonate furan-2-carboxylate if the reaction were performed in a molten salt with a high concentration of alkali cations to stabilize the conjugate base by ion pairing.

When we launched the first indigenous rocket SPV 3, when we successfully sent Agni and tested nuclear weapons in Pokran, I was really very happy. But today when I see children run around and cycle with the artificial limbs we designed, it is sheer bliss

Dr. A.P.J Kalam

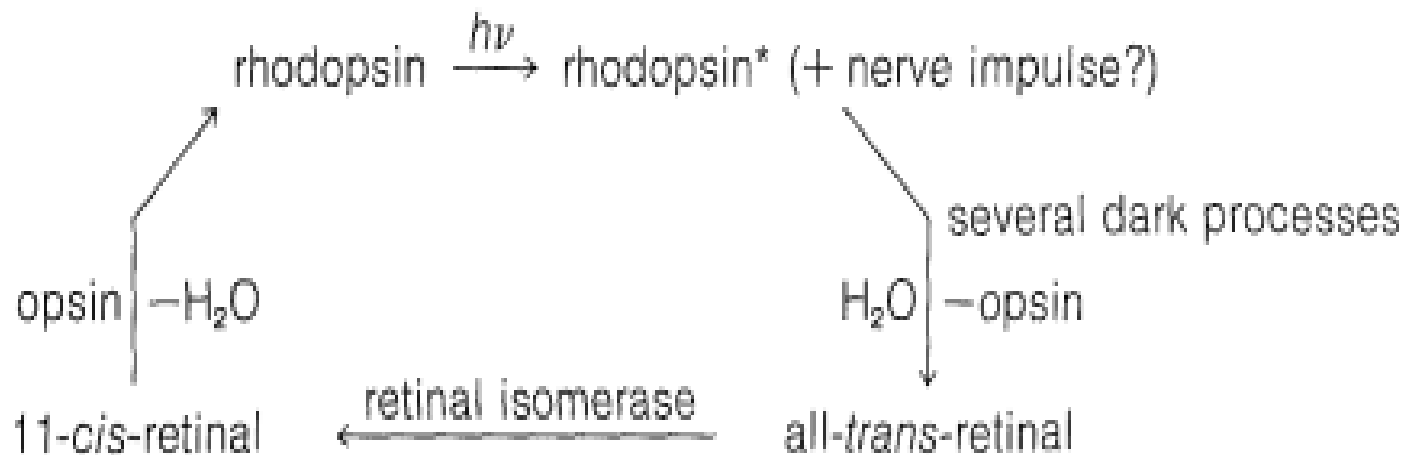
"I had seen these children struggling with the artificial limbs that weighed at least 4 kg. My team made one with composite heat materials used for rockets. This one is 10 times lighter,"

Technological translation from ISRO

Rockets to Polio Crutches

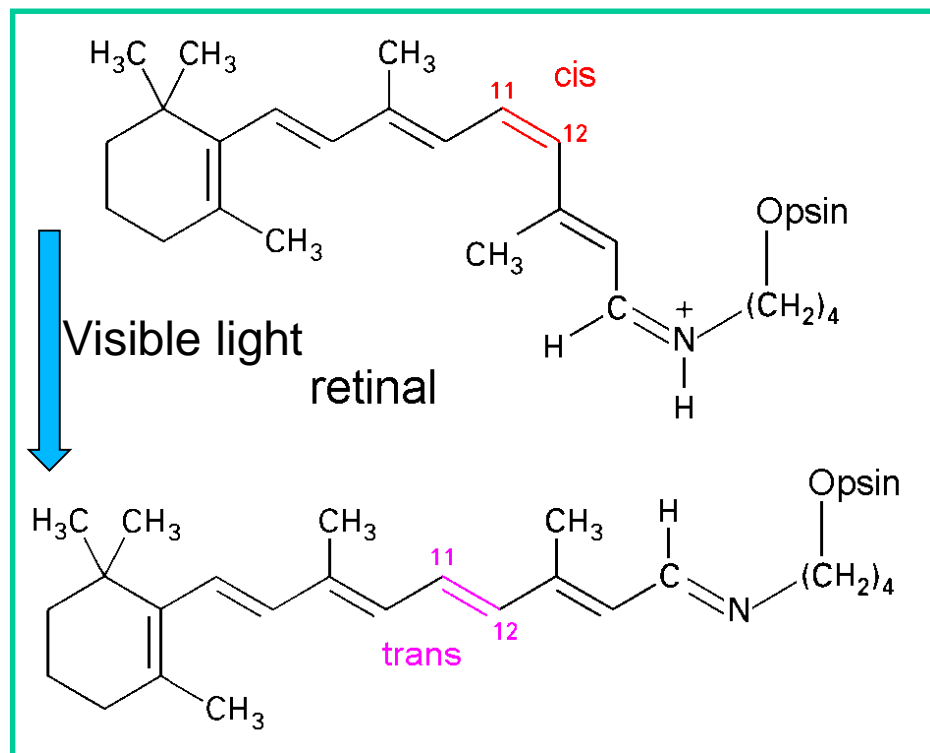
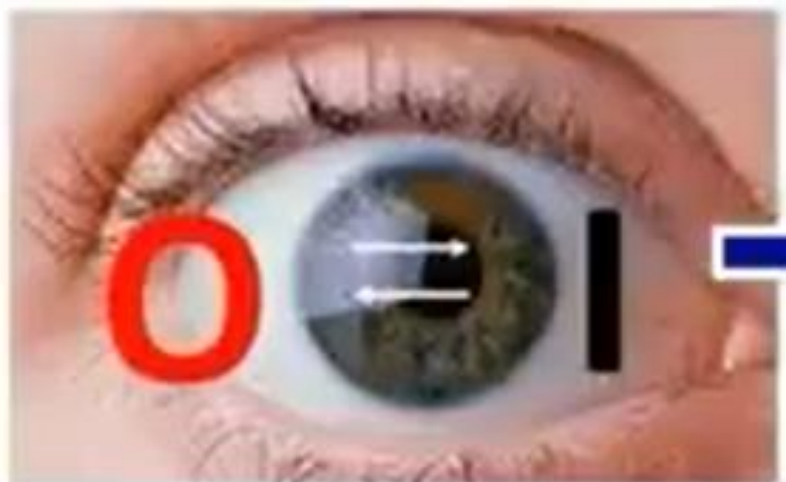


Photochemistry of Vision

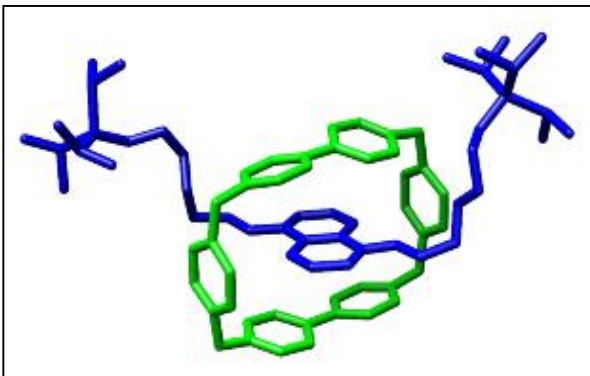


G.Wald (Nobel Laureate in Physiology and Medicine, 1967)

Molecular Switches

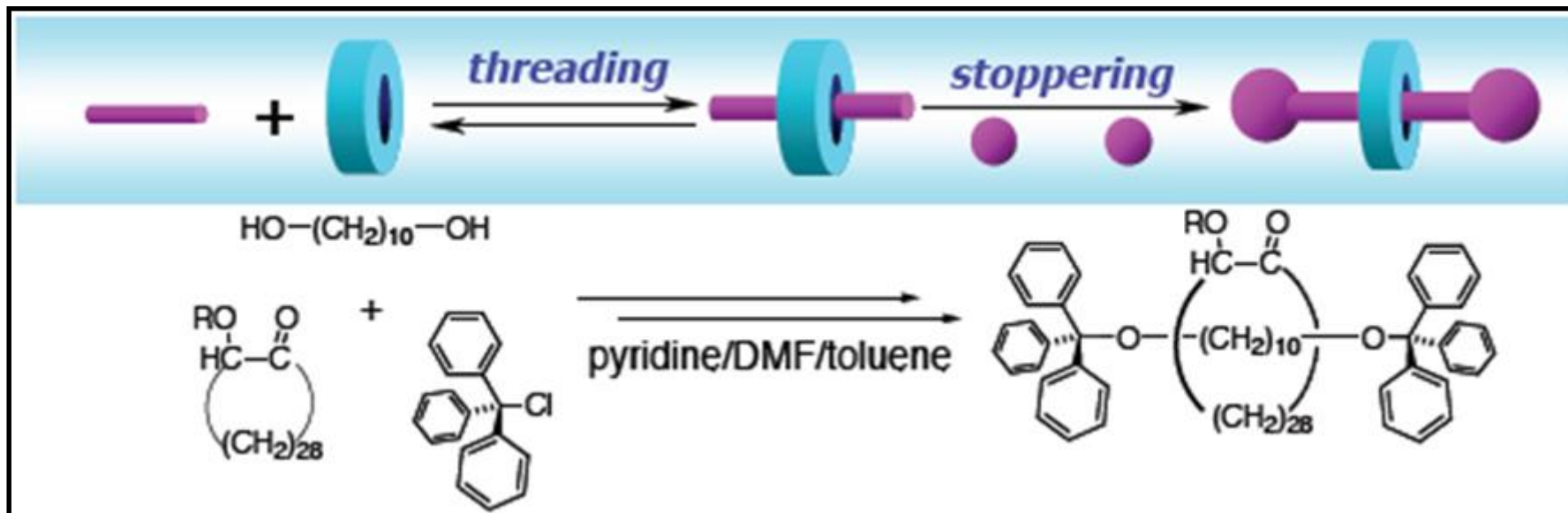


A **rotaxane** consists of a "dumbbell shaped molecule" which is threaded through a "**macrocycle**"



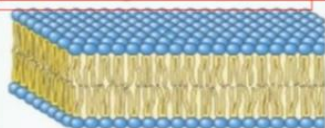
Ref: <https://en.wikipedia.org/wiki/Rotaxane>

These molecules can be considered for film formation. They are formed by different approaches like capping and clipping

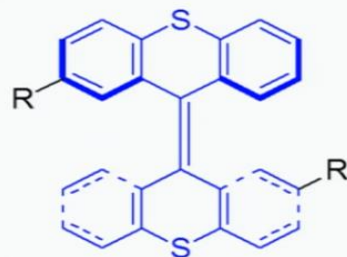
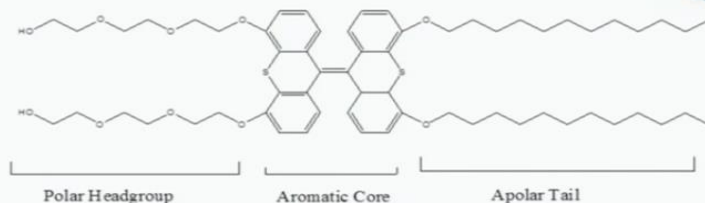


MEMBRANE

Self-Assembly



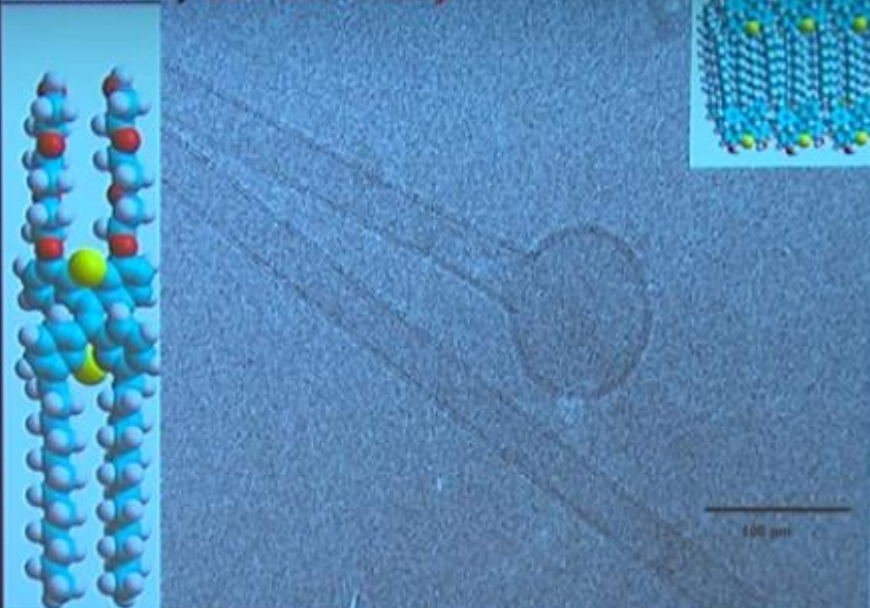
amphiphile



Molecular switch
photo- and electro-chemical switching

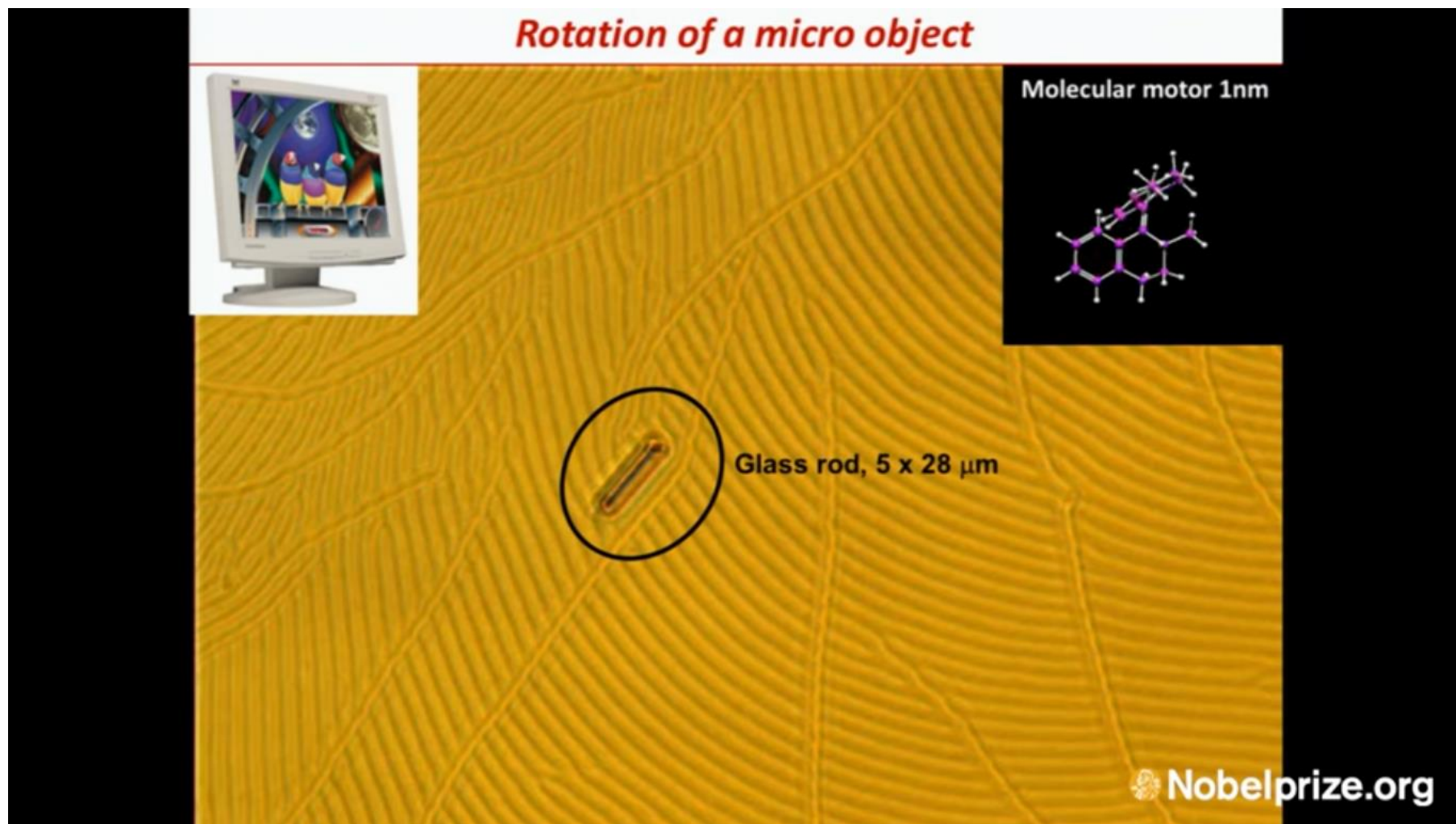
 Nobelprize.org

Nanotube by self-assembly



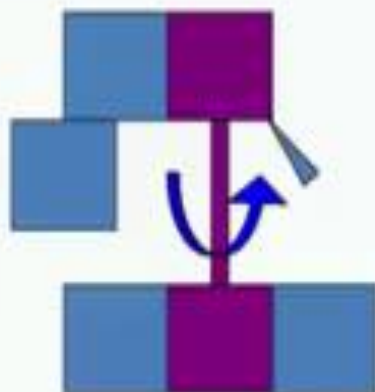
Ref: Nobel lecture: Bernard L. Feringa, Nobel Laureate in Chemistry 2016

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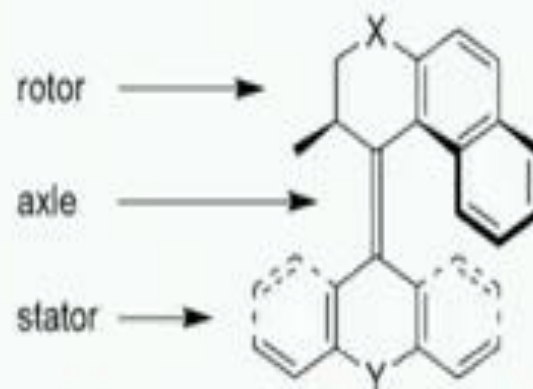


Plausible Applications in Leather for Future

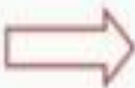
Second Generation Molecular Motor



Molecular Design

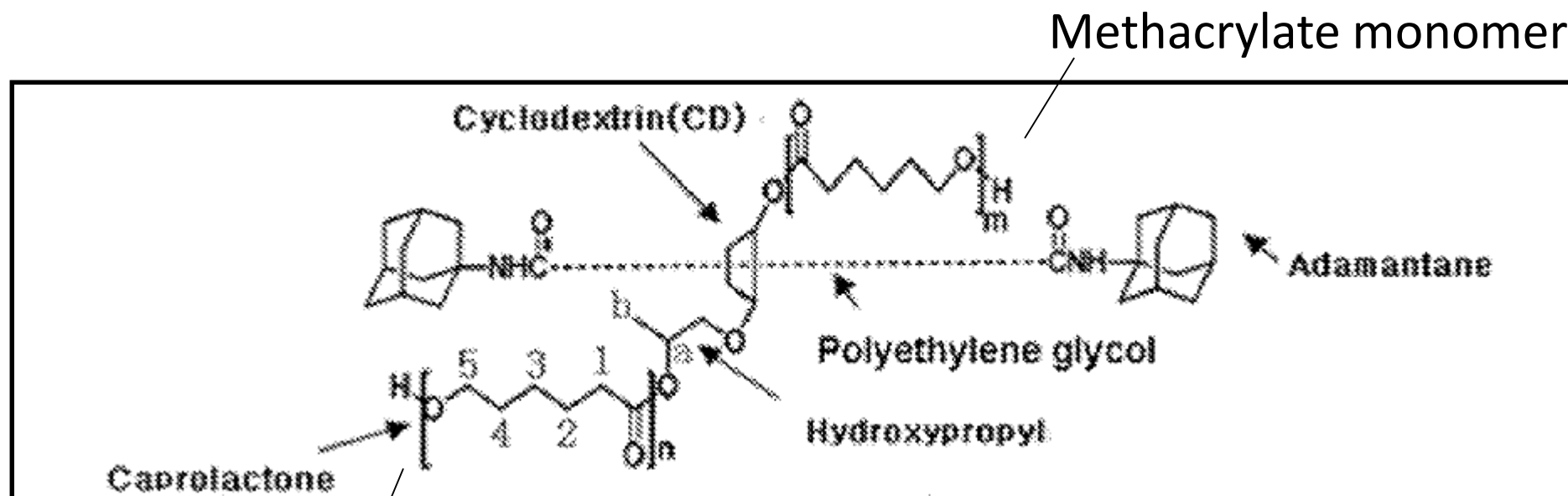


enhancing the speed

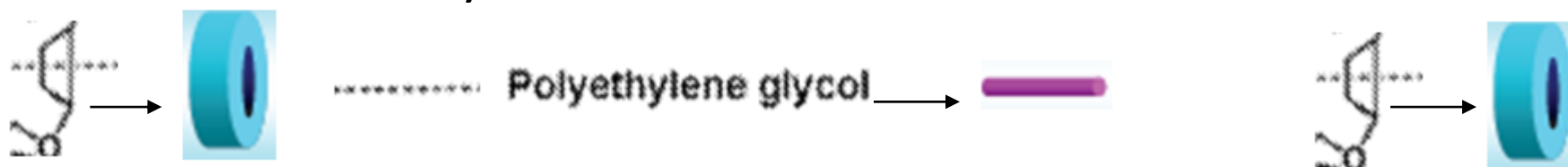
from 1 rotation/hour  to more than 10 million rotations/sec



Application of Rotaxanes in Finishing



Methacrylate monomer



The above is a photocurable Rotaxane with excellent mechanical properties and self healing capabilities. This concept can be applied for exotic and costly leathers

Ref : US patent 20140080936

New chemistries Discussed So Far

- ❖ Polymerisable surfactants – Surfmer in fatliquors
- ❖ Hyper branched polymers as chrome fixing agents & acrylic syntans
- ❖ Utilization of CO₂ in making polyester polyols and isocyanates from Biosources for making PU
- ❖ Rotaxanes in self healing finishing

Surfmer - Reactive surfactants applications from Balmer Lawrie -BL

- ❖ Reconstituted fat was synthesized with better light fastness and less fogging .
- ❖ Hyperbranched polymers based on surfmers helps in penetration of free chrome and helps in binding chromium with collagen . These surfmer based polymer avoids Cr(VI) formation



Thank you all for your patience