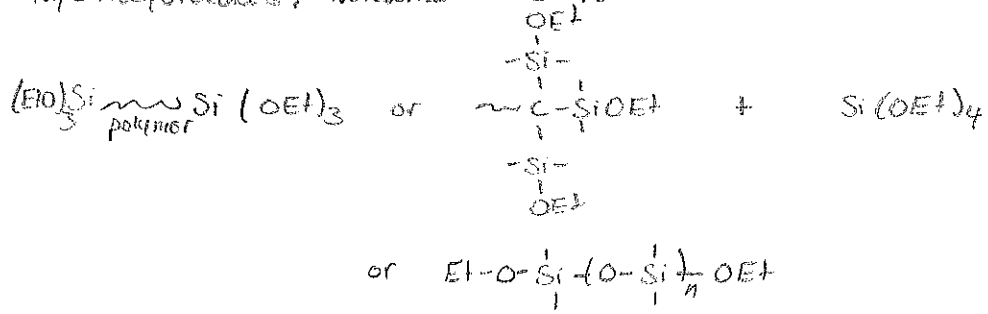
①

Nanocomposites:

End functionalized PEG star + layered silicate

Problem, prove intercalation really occurs

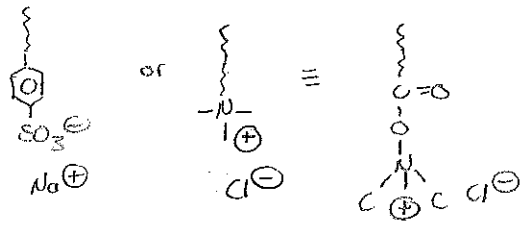
Polysilsesquioxanes: Networks and Stars



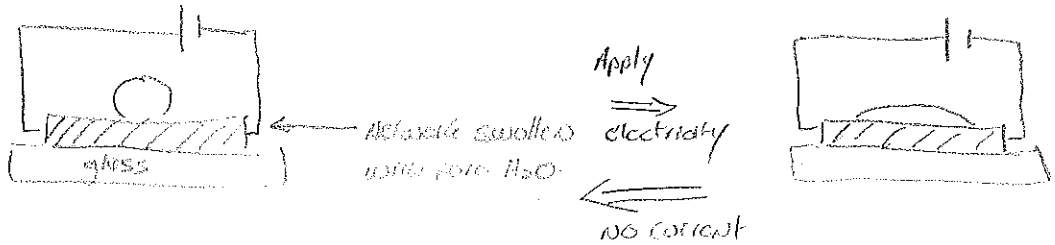
See Wilkes

Ionomeric Ampiphilic Network:

what if the network contained groups such as:

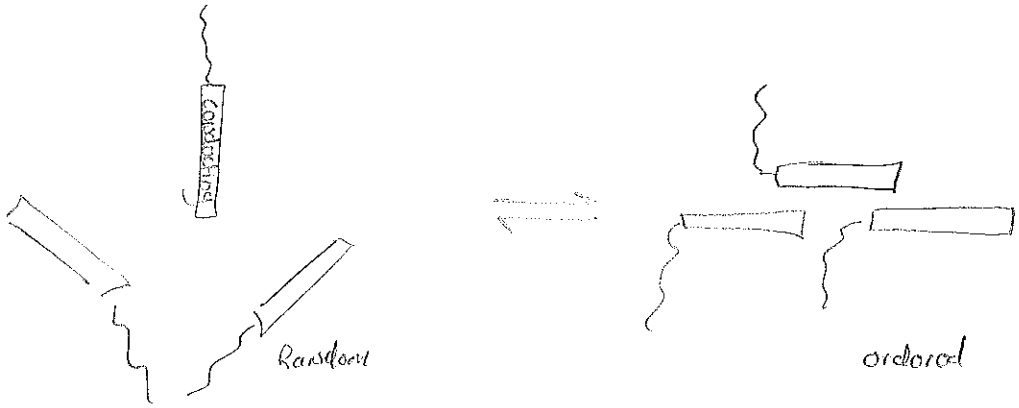


measure changes through contact angle?



②

would in one state (whether electricity is applied or not) will there be ordering and in the other disorder?

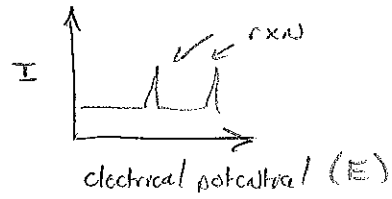


comments:

Dr Tayesic:

look at changes in γ_{gel} (interfacial tension of the gel), make sure these are due to application of current.

look to see whether electron transfer reactions occur. these might be avoided by using low voltages $\leq 1.0V$.



Pore size may change due to — E, pH, IS (ionic strength

uses - ① motor in which bolt is immersed in two separate solutions of different ionic strength. ② Drug release controlled by current.

(3)

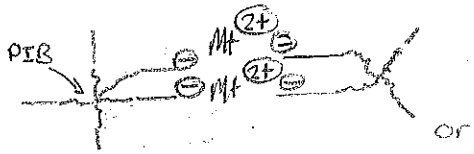
Dr Rendler:

Measure of contact angle may not work, it is possible that the droplet might fly apart before any changes in contact angle are detected.

Make the material non-centro symmetric, this could result in an electrostrictive material.

Reversible Networks — (Similar to endless ionomers)

An amphiphilic network with ionomeric crosslinking sites.



or

Amphiphilic stars with ionomeric end groups

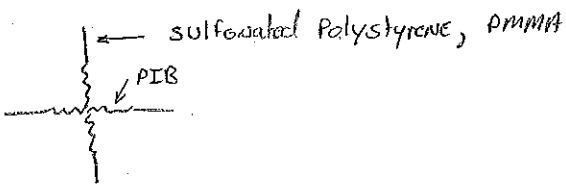
Amphiphilic triblock with ionomeric endgroups

Dr. Teyssie — may be effected by solvent, pH, Heat, etc.

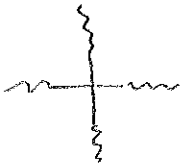
Differs only by the fact that all crosslinks are of the ionomer type.

Possible use — Rheology control by current.

Amphiphilic Stars:

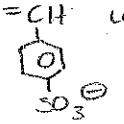


I

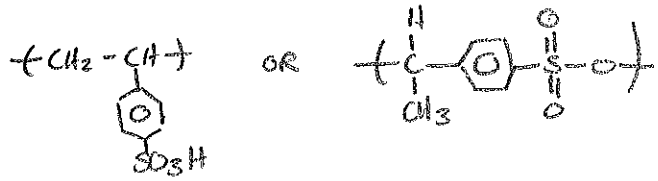


II

Dr. Harwood — monomer is usually $CH_2=CH$ with KI stabilizer that must be



removal before polymerization. Polymerization might be affected by lowering the pH to give:



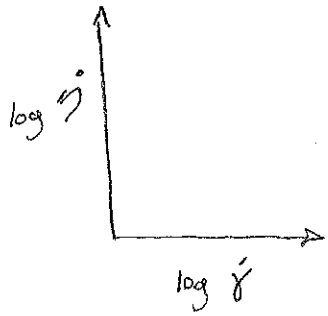
OR

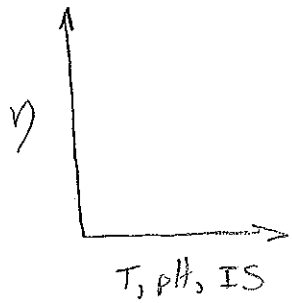
linking of opposite charged species

Might be able to cross over from PIB to polystyrene by ATRP.

Possible uses – surfactants (I – aqueous II – hydrocarbon). They might also be useful in solvent purifications if they can be easily removed. They may also show interesting rheological properties under various conditions (temperature, pH, ionic strength). May be of use in emulsions. Viscosity improvers with chelating groups – traps metals and water. Gas hydrates.

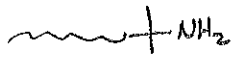
Dr. Teyssie – look at dynamic viscosity vs. shear rate, or static viscosity.



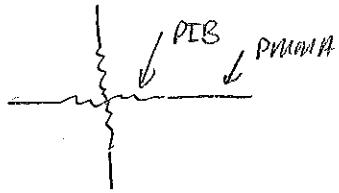


Do both experiments in different solvent types.

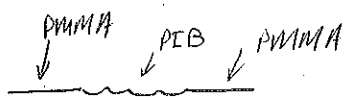
Hydrophobized peptides:



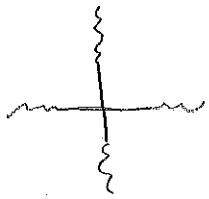
Glassy / Rubbery stars / blocks



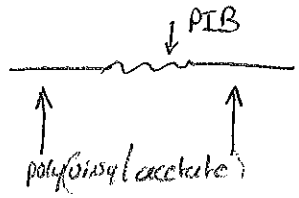
Kraton type materials – compatabilizers for blends.



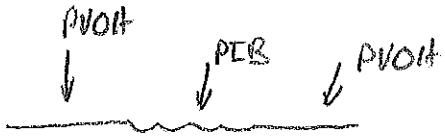
Kraton type materials. Blend compatabilizers. Interesting sealants if α, ω functionalized.



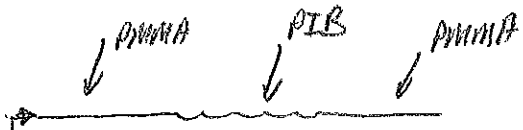
Blocks OR Stars



Interesting adhesives, use in paints? Coatings?

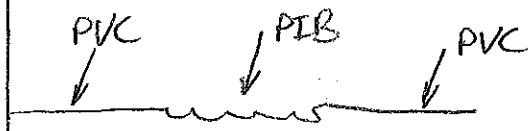


Adhesives, Surfactants, Plasticized poly (vinyl butyral)



Kraton type materials — see Dr JPK's text.

Rubber for electrical tubing, hoses. Lubricant.



PVC with internal plasticizer

only one which will work!

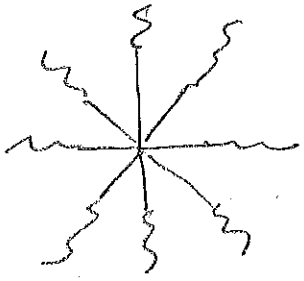
We know – Calix [8] arene $\xrightarrow{PIB}$ PIB Star $\xrightarrow[ATRP]{vinyl}$

This can be done

How to get PIB on the outside?

(1)

divinyl methacrylates $\xrightarrow[ATRP]{}$  PMMA star ?

$\xrightarrow{quench}$ $CH_2=C\phi_2$ $\longrightarrow CH_2C(\phi)_2-Cl$ $\xrightarrow{PIB}$ 

(2)

Grow PIB arms

only ones which will work

 + PIB $\longrightarrow$  $\longrightarrow$ end functionalize

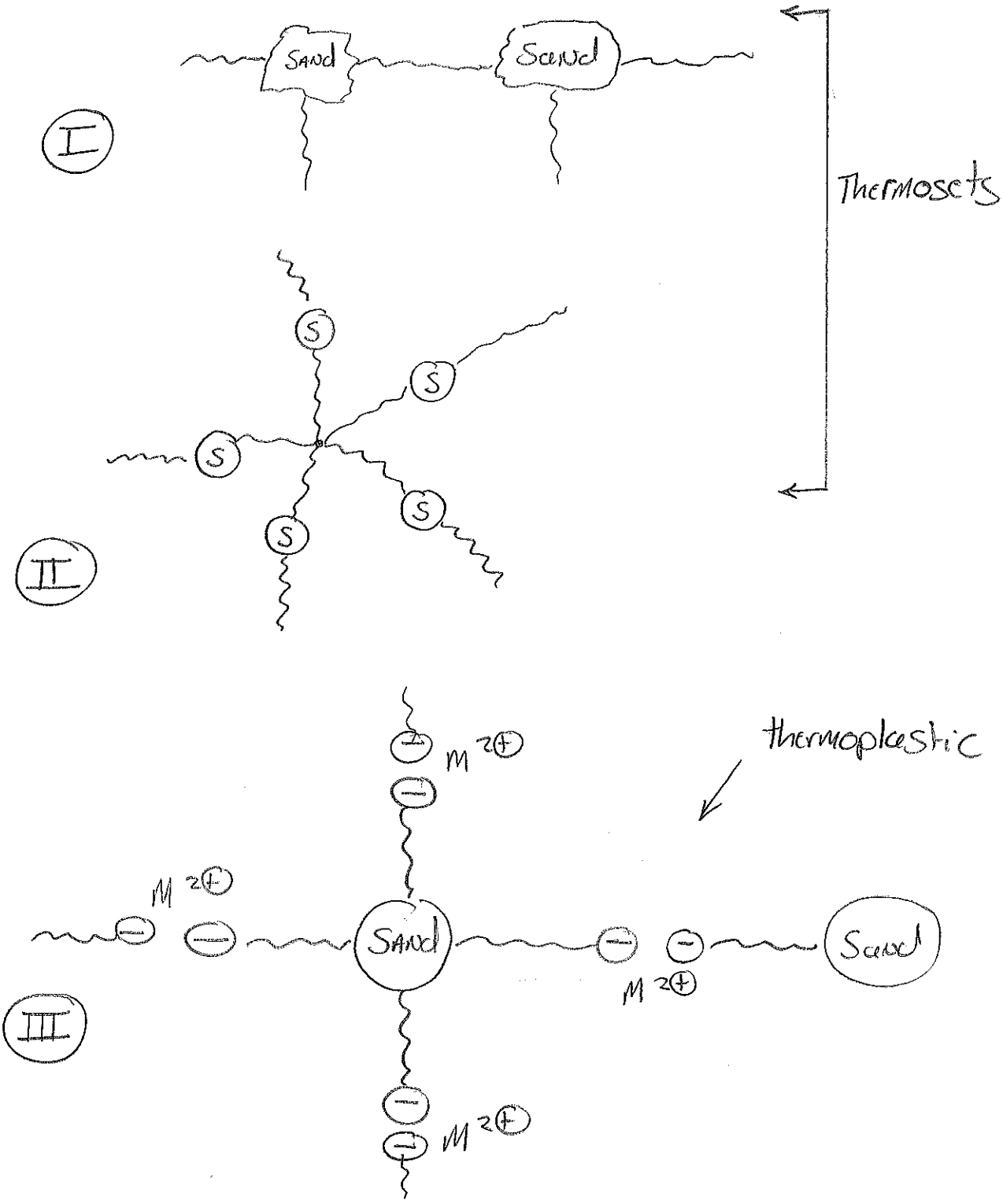
$\xrightarrow[\text{phenol substitute for calix[8]arene}]{\text{use as}}$ $\xrightarrow[\text{using ATRP}]{\text{PZN MMA}}$

(3) calix [8] arene $\xrightarrow[ATRP]{MMA}$ $\xrightarrow[CH_2=C\phi_2]{quench}$ $\xrightarrow{PIB}$

This will not grow PIB

Polysilsesquioxanes:

Networks (three types)



uses:

The thermosetting networks (I and II) could have many potential uses:

1. gaskets / seals which show improved solvent resistance and possibly some barrier properties to gases due to the incorporation of inorganic material. These materials should also find use at high temperatures - engine components, maybe aerospace applications.

2. belts - again, should show strength at high temperatures. May not require addition reinforcing materials such as fibers.

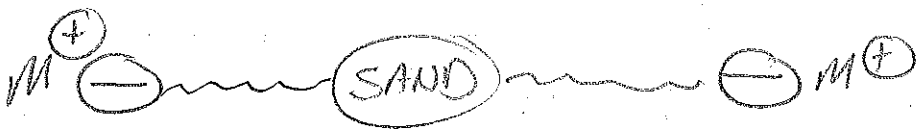
3. hose / tubing - depending on overall stability may find many uses.

4. Strength / brittleness will probably depend on the wt % silica. It might be possible to form objects which are tough, almost hard like a ceramic, and yet the material would be impact resistant due to PIB. Anything which is ceramic could be replaced dishes, cookware, mugs, pottery, floor tiles, table tops, sinks, toilets, etc. Conversely, these materials could also be used in place of many traditional rubbers.

For the thermoplastic network (III)

The uses could be similar. Use temperatures would have to be less than the thermosetting material. Also the material may not hold up under various conditions (how about resistance to water?). It's strong point would be that you could recycle the material.

Another material related to (III) could be

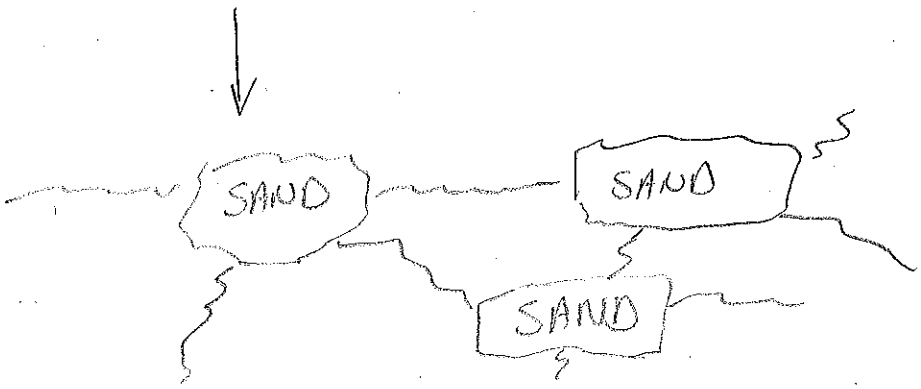


(IV)

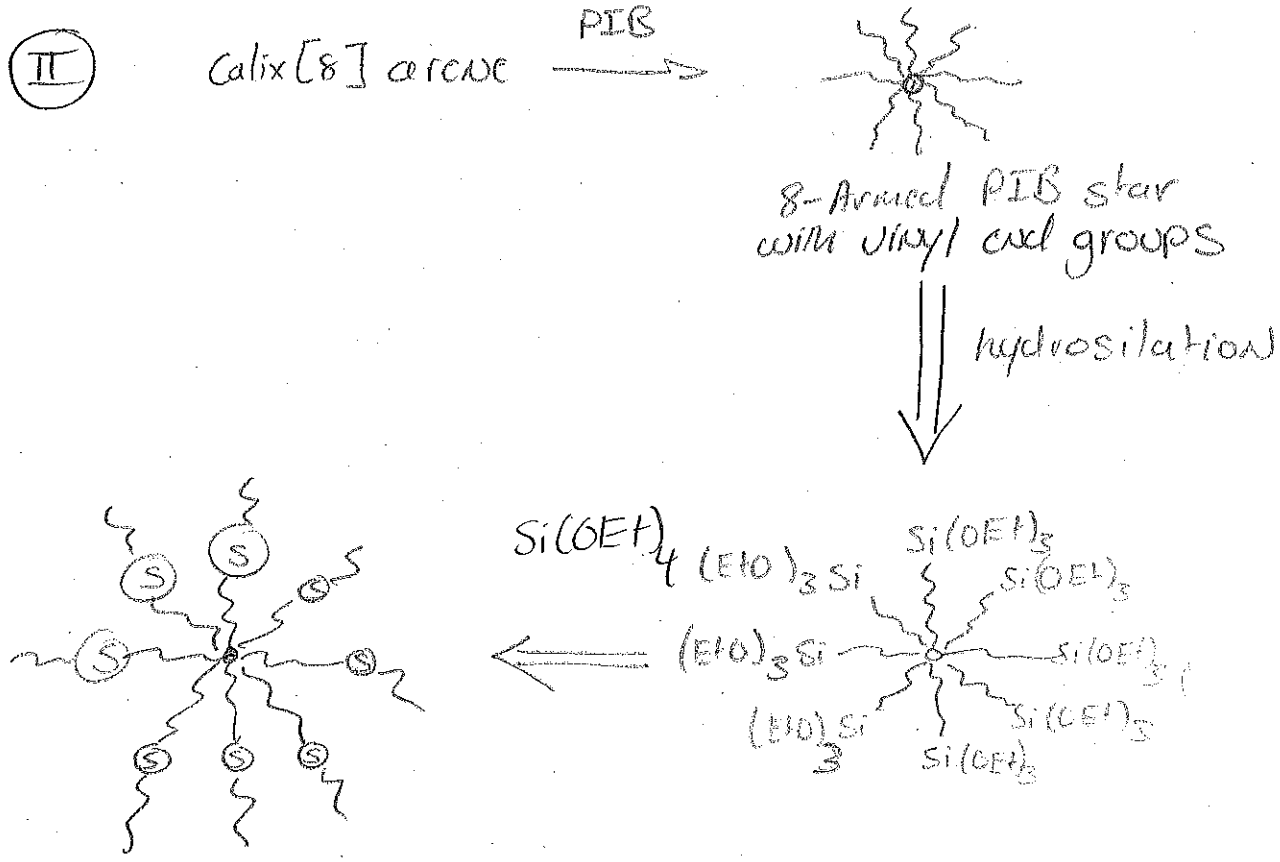
it may have similar uses as material (III)

HOW CAN THEY BE FORMED?

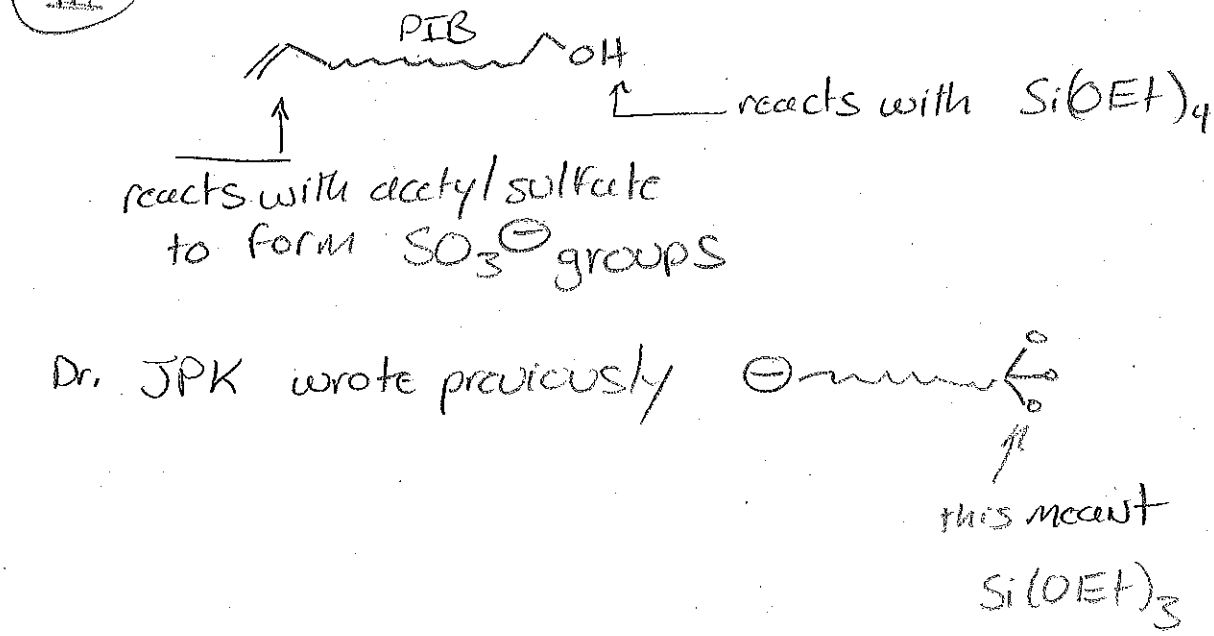
(I)



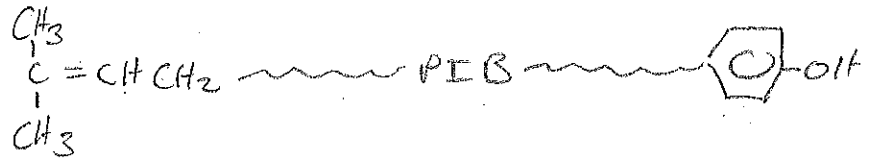
II


Calix[8]arene
PIB
8-Armed PIB star with vinyl end groups
hydrosilation
Si(OEt)4
(EtO)3Si
Si(OEt)3
S

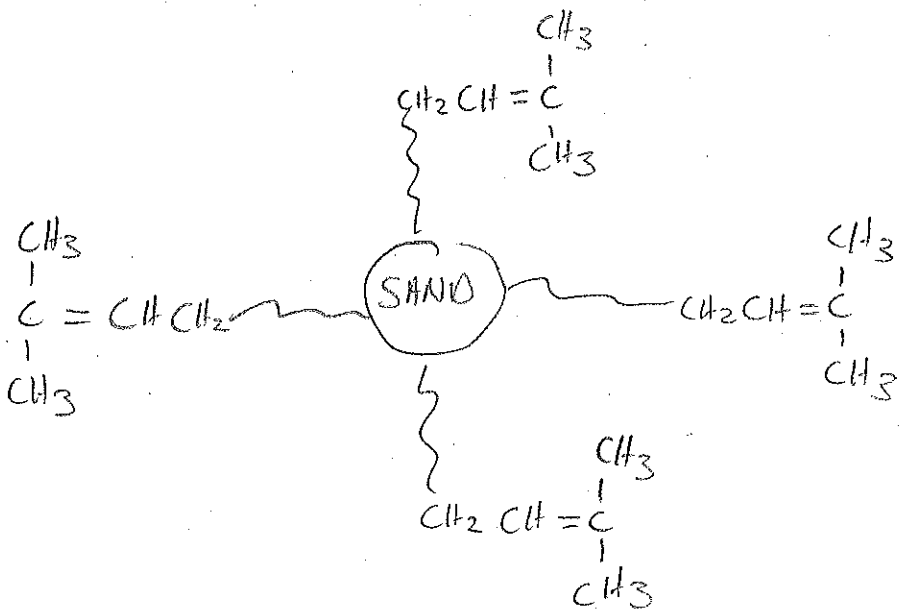
III


PIB
OH
reacts with Si(OEt)4
reacts with acetyl sulfate to form SO3⊖ groups
Dr. JPK wrote previously
this meant
Si(OEt)3

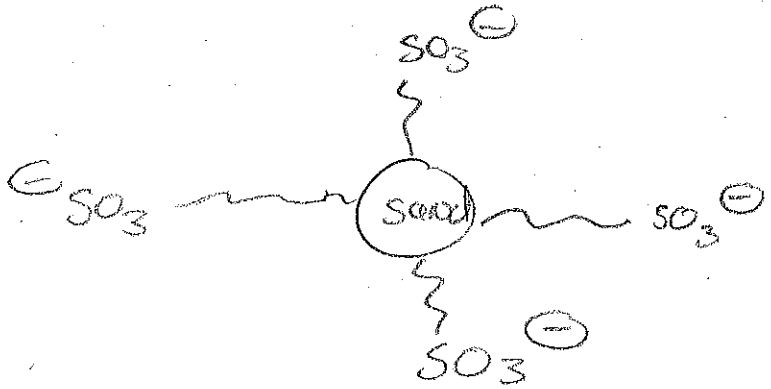
$(CH_3)_2C{=}CH{-}CH_2Cl \,/\, BCl_3 \,/\, iC_4H_8 \xrightarrow{\text{phenol, } BF_3OEt_2}$

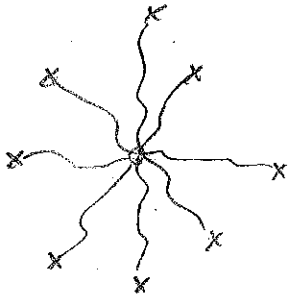


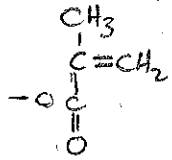
$\downarrow$ $Si(OEt)_4$



$\downarrow$ acetyl sulfate ?





X ≡ 

$-OH$

$-NH_2$

These simple PIB stars could be used in coatings.

Dr JPK – learn from Jack, and functionalization for instance. Then eventually try and make PIB star with sound core.