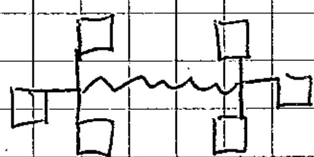
Name: Stewart P Lewis
Date: 4/20/00
Experiment: Project ideas - PIB-POSS

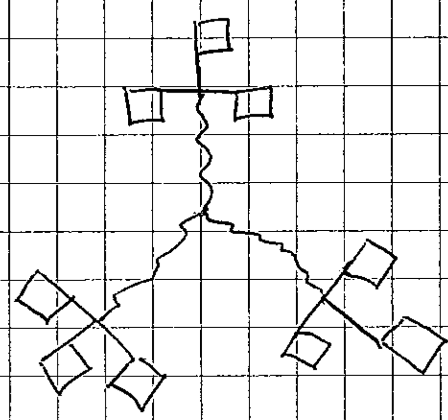
A, B, C with n3 C=C bonds at the functionalized ends can yield materials as follows using similar reaction conditions as those described on PG 14.

For "A" with n3 C=C bonds (n=1) as formed from either "1" or "2",

For "B" with 3 C=C bonds as formed from either "1" or "2" (3 on each func. end)



For "C" with 3 C=C bonds (on each funct. end) as formed from either "1" or "2"

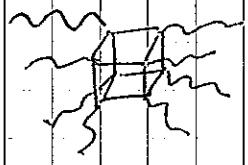


Similar chemistry using the hydrosilylation technique can be used to make PIB stars with a POSS core or crosslinked PIB networks where the crosslinking junction is a POSS cage. This can be accomplished using the following POSS material in conjunction with A, B, or C.

04.20.2000

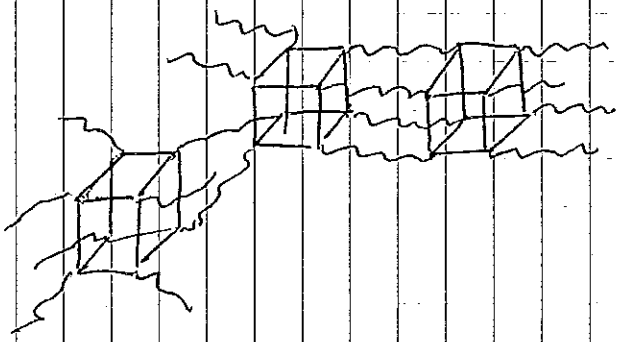
For example, an eight armed PIB star with a POSS core could be formed under conditions similar to those described on PG 14 with the use of the POSS material shown on PG 17 in place of that shown on pg 14.

For "A" with R = $CH_2-CH=CH_2$

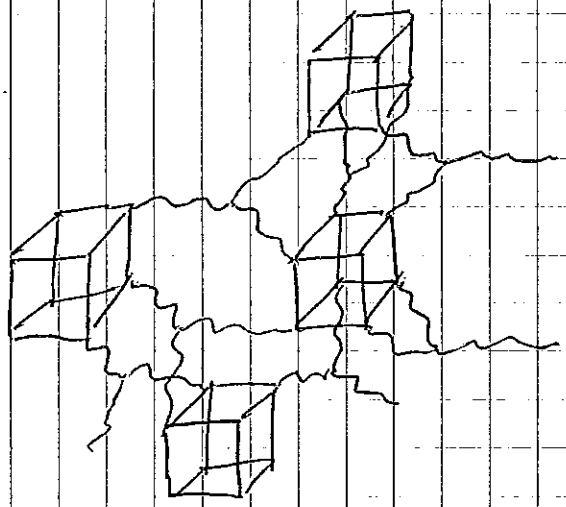


If "B" or "C" with R = $CH_2-CH=CH_2$ are used with the POSS described on PG 17 the following networks can be obtained

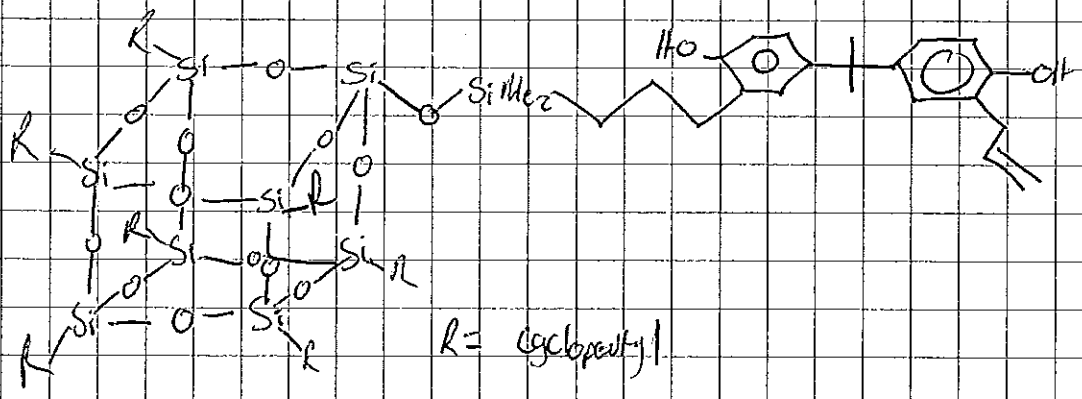
(for "B")



(for "C")

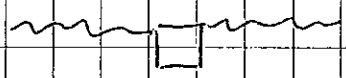


A POSS cage bearing two reactive Si-H groups might be formed by the reaction of two equivalents of $H\text{-}Si(CH_3)_2Cl$ with one of the following poss nucleophiles

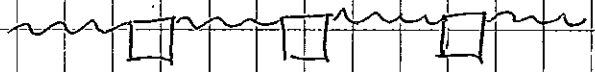


R = Cyclopentyl

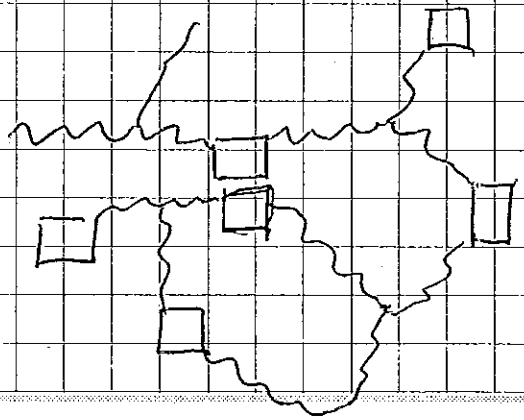
Reaction of such a POSS cage with "A" having $R = CH_2-CH=CH_2$ would lead to linear PEB with a POSS cage in the center of the polymer chain



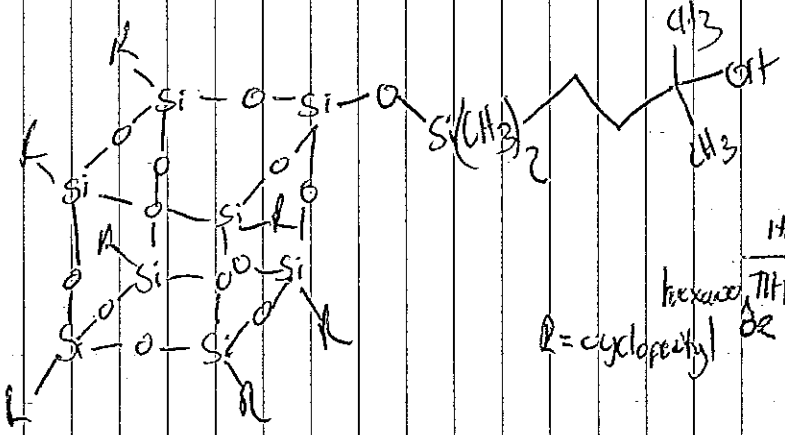
Reaction of this same POSS cage with "B" having $R = CH_2-CH=CH_2$ would lead to linear PEB having several POSS cages in the polymer backbone at regular intervals



Reaction of this same POSS cage with "C" having $R = CH_2-CH=CH_2$ would lead to a network where each crosslink junction being a POSS cage



A poss cage bearing a 3° (tertiary) alcohol could be converted to a 3° chloride and then be used as an initiator for PIB polymerization under living conditions. This might be accomplished in the following manner.

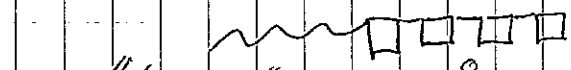


Finally, A, B, and C could bear other functional groups such as NH_2 that could undergo reaction with POSS cages bearing single or multiple epoxide groups to form nanocages similar to those previously described in hydrosilylation reactions. There are many other possible living reactions including PIB - trialkoxysilyl / POSS - trialkoxysilyl, PIB - carboxylic acid / POSS - OH, PIB - OH / POSS - epoxide.

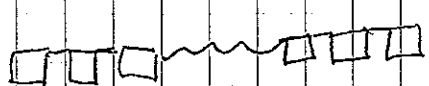
Furthermore if A, B, and C bear methacrylate groups, blocks of POSS can be attached using ATRP.

For example

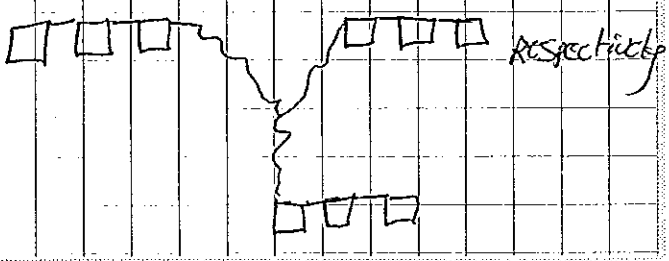
"A" with R = $OC(=O)C(CH_3)_2Br$ could give



or "B" or "C" with R = $OC(=O)C(CH_3)_2Br$ could give



or



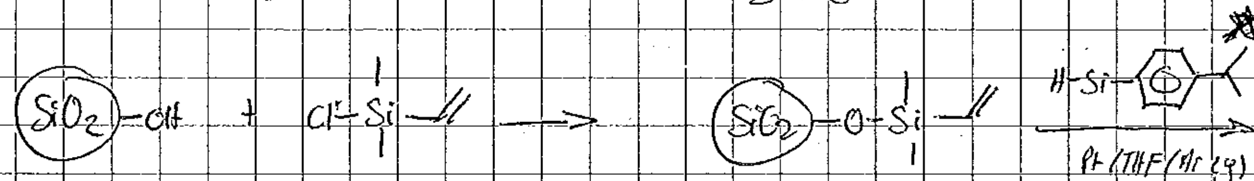
respectively

Important:

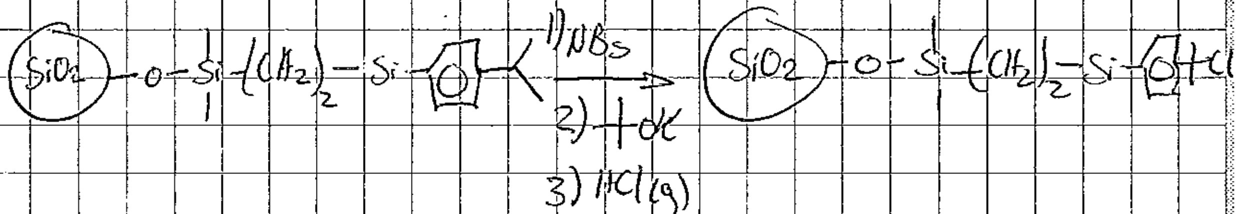
Name: Stewart P Lewis Date: 4/20/00

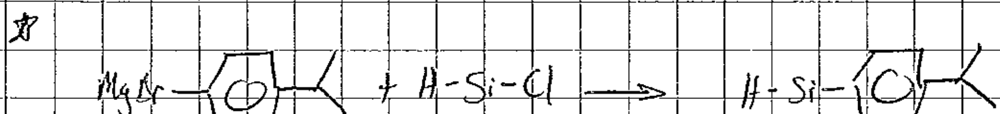
Experiment: Project ideas – Fab- colloidal silica (core) stars / Synthesis dicumyl-chloride

Although the direct functionalization of silica has been done prior in this group another method that I term indirect/passive functionalization could be used to functionalize colloidal silica with groups that can initiate the living polymerization of IB.



colloidal silica with active silanol





Similar chemistry could be used to functionalize colloidal silica with TMP–Cl.

Pias was synthesizing dicumyl chloride from commercially available dicumyl alcohol and HCl. The typical reaction conditions are as follows: CH_2Cl_2 is added to a flask, next the required charge of HCl is added then with vigorous stirring (at room temp) the required amount of dicumyl alcohol is added. The reaction mixture is allowed to stir for several hours before the methylene chloride layer is isolated (via a separatory funnel) and the product is isolated via vac. distillation. However, Pias' product was yellow in color. He found that this color was due to an impurity in the dicumyl alcohol. He attempted to remedy this by several recrystallizations of the dicumyl alcohol from ethanol. He conducted 3 such recrystallizations of the dicumyl alcohol before reacting it to form the chloride. Still, the product was slightly yellow. I decided to study the solubility of the alcohol and his crude dicumyl chloride in various common solvents.

04 · 20 · 00