Progress Report for December, Stewart Lewis

1.

I have explored the use of tri**methoxy**silyl ended PIB in star forming reactions. Preliminary ^{1}H NMR analysis indicates that up to 98% of the polymer chains contained one tri**methoxy**silyl end group. However, preliminary GPC analysis of these uncondensed arms shows that up to 20% have already undergone condensation to give 4 armed stars (figure 1). This unexpected condensation may be due to accidental contamination with protic impurities during purification. Further reaction of this material in the presence of HCl (aq) results in a percent conversion to 5 armed star of only 38% (figure 2). This is very close to the limiting percent conversion to star of 40% seen with tri**ethoxy**silyl ended arms.

Selective ppt via MeOH or H_2O till cloudy → then centrifuge out star. <5% precurs contam.

2.

Another area I have explored is the reduction of tri**chloro**silyl ended PIB to the corresponding silane (figure 3). Preliminary GPC analysis shows that early attempts at this reaction resulted in the conversion of uncondensed arms into stars. However, the percent conversion to star was moderate (30%) as was the star molecular weight (4 to 5 arms). Further attempts resulted in almost similar results, with arms being converted to stars. It is possible that these reactions are again the result of protic impurities, however, steps were taken to ensure the exclusion of water from these reactions.

IR For ?. Use Elemental Analysis to Find weight inorganic then weight organic to then calc # of Arms.

3.

One final area that was explored with tri**chloro**silyl ended PIB was the nonhydrolytic condensation as catalyzed by zinc oxide (figure 4). This resulted in a very moderate conversion of arms to stars (20%) with low molecular weights (mainly 3 arms).

Conclusions and future work

1. Tri**methoxy**silyl groups do not appear to posses the desired reactivity necessary for the exclusive production of stars. These materials are more reactive than the corresponding tri**ethoxy**silyl ended materials. This is demonstrated by unexpected condensation reactions of these groups in the presence of minute impurities. A few follow up studies will be conducted on these materials but the **main focus** of my work will center on tri**chloro**silyl ended arms.

viscosity Imp.

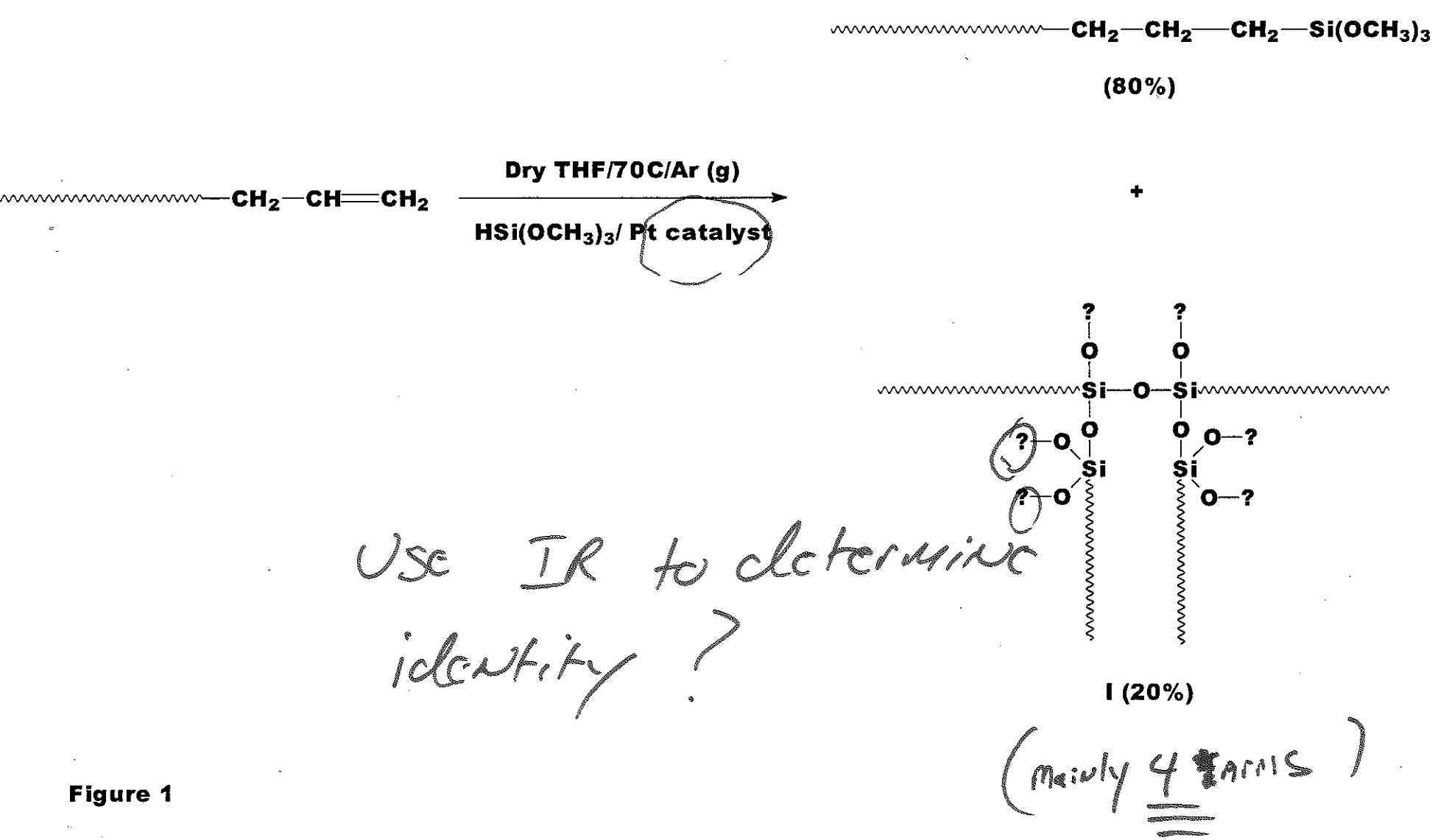
2. Reduction of the Cl-Si bond should be, and appears to be, relatively facile. These reactions may have to be conducted at reduced temperatures to avoid side reactions such as the coupling of arms. Further precautions must also be taken to avoid the inclusion of protic impurities that may be the cause of such side reactions.

3. The yields thus far from nonhydrolytic condensation of tri**chloro**silyl groups do not appear to warrant extensive investigation. However, I will peruse the literature concerning such reactions further in hopes of finding a nonhydrolytic reaction that results in high yields of condensed materials.

4. I am also gearing up to explore the use of sodium tetraorthosilicate and chlorodiphenylsilane for the exclusive production of 4 arms stars.

Recent Progress in future work area

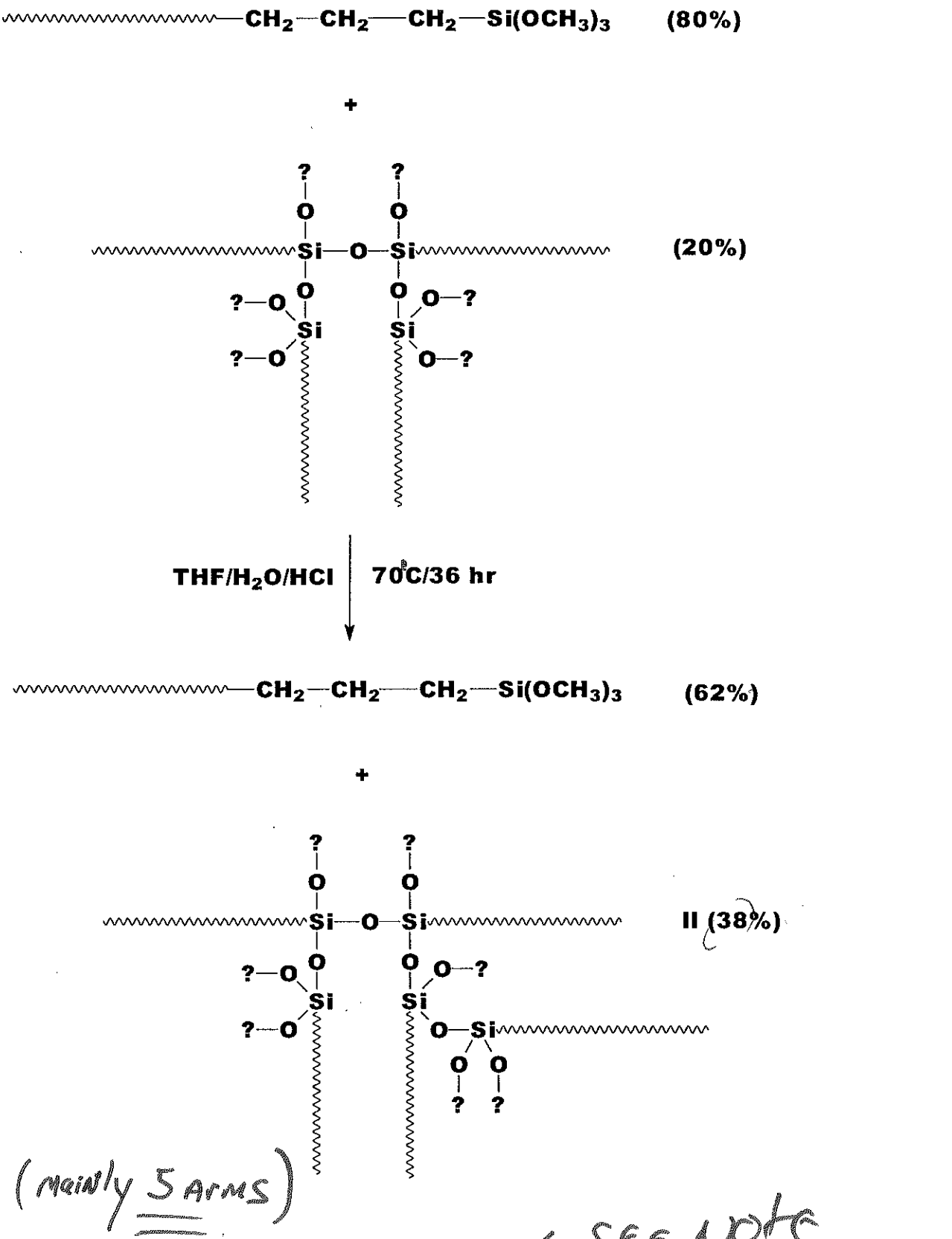
1. I am currently working on generating a large amount of allyl ended PIB for use as starting material in the exploration of these areas of interest.



Use IR to determine identity ?

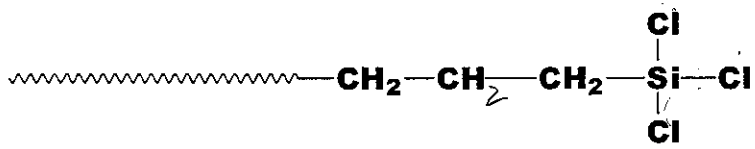
(mainly 4 forms)

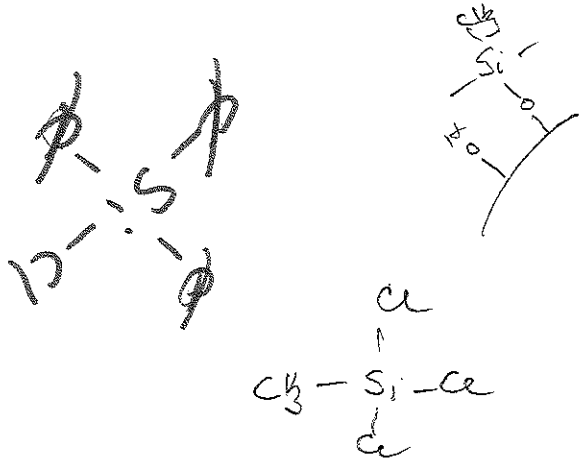
Figure 1



SEE NOTE ABOUT ? → (USE I.R.)

Figure 2



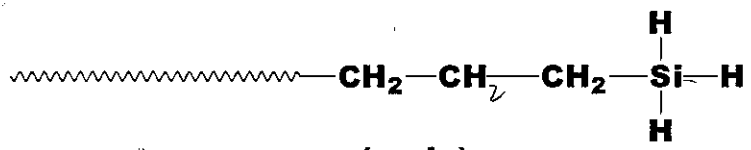


1) $LiAlH_4$/THF

2) centrifuge then rotovap

3) hexane then centrifuge then rotovap

Water contaminant?
OR does LiAlH4 have the
Ability to couple arms



(main)

~70%

+

I + II (30%) → ~Si-O-Si~ OR is it? ~Si-Si~

see prev. note

Figure 3

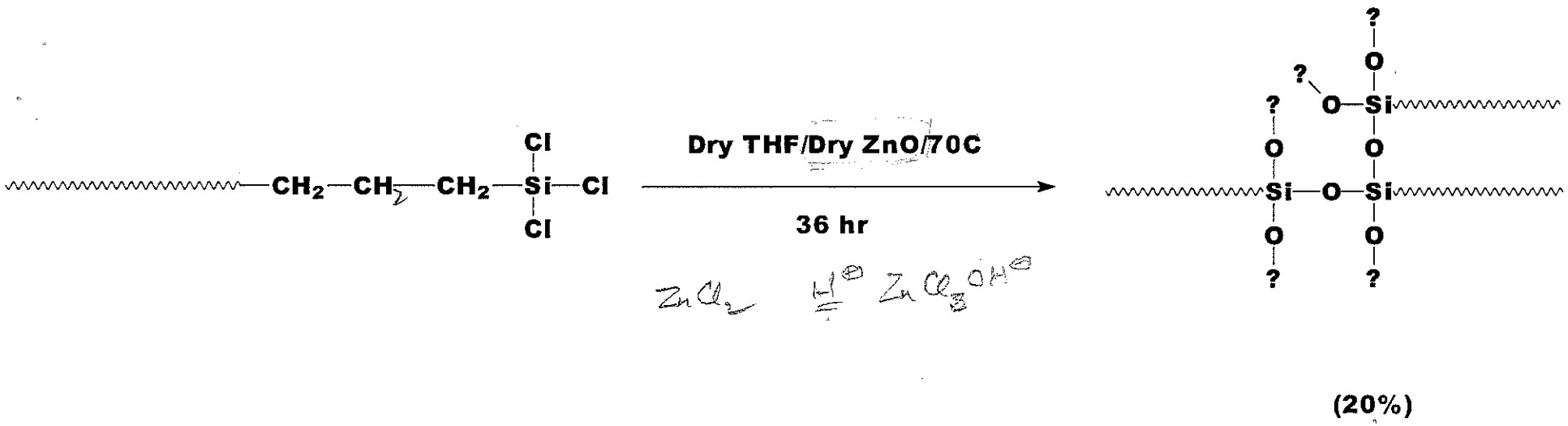


Figure 4

See prev. note
About I.R.

Omura (Macromolecules)

He made stuff like this  and

found these materials were stable to acids and bases because the polymer chain protected the Si-O bond. The stars should be treated with acids and bases to see if they will be chemically resistant viscosity improvers, paints, etc.

Also use Omura's selective ppt to isolate star from arms. Then see if arms will further react. Do this for the trimethoxsilyl-ended PIB. IR can tell you what groups are at the end of arms.

Elemental analysis will eventually be done since we will know the MW of a certain arm - from this analysis we get wt inorganic - then find total wt. organic then divide this by arm wt to get # of arms.

If moisture on the surface of glass is a problem you can hydrophobize the glass with $(CH_3)_3SiCl$.