9/11/00

Today I did the workup (finished it) for my grignard rxn — this simply consisted to adding H_2SO_4 to the ether/THF/water mixture. This caused all salts to dissolve. I separated the organic layer and washed the aqueous layer (to which I added salt (NaCl) until no more dissolved) with both ether and ethyl acetate.

9/12/00

Today I started recrystallizing my fricaryl alcohol. This was done by dissolving the material into hot ethyl acetate.

9/13/00

I learned that acetone is also a relatively good recrystallization solvent and isn't quite as stinky as ethyl acetate.

9/20/00

I haven't been doing much lab work recently - mainly I have been reading about POSS. I did run GPC of the separated PIB stars (separated from solid silica) today. I have to pick up half this monday the 25th and figure out why this POSS stuff isn't working. It seems to be a question of solubility to me — the alkyl substituents on the POSS probably make it too much like PIB such that there is no phase separation to form physical crosslinks.

10/2/00 I have been thinking about this POSS problem for some time — my solution to the solubility problem is as follows:

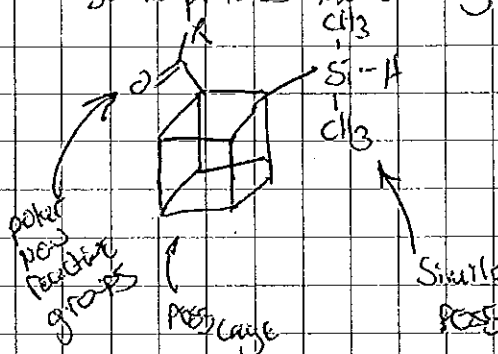
(1) hydrosilylate a POSS cage bearing polar nonreactive groups to allyl telechelics of PIB. Such groups could be carbonyl, etc. By nonreactive - I mean groups which (that) will not interfere with the hydrosilylation rxn.

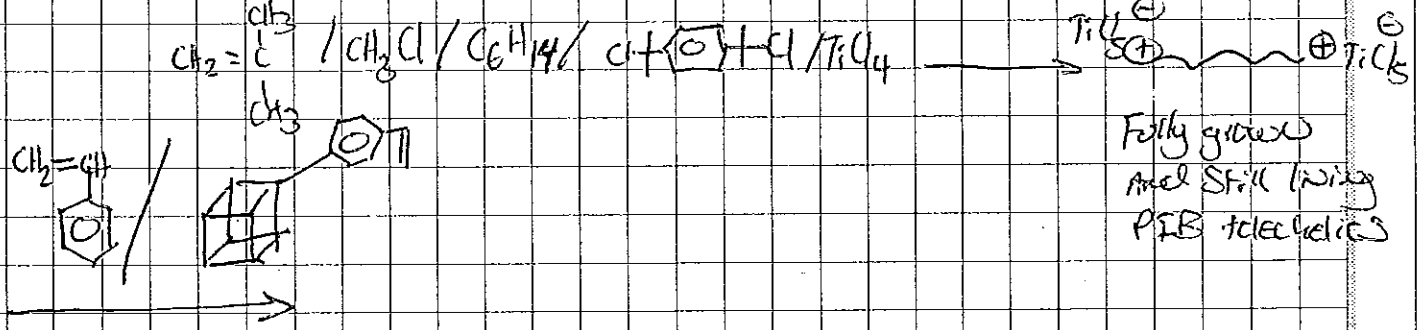
(2) Copolymerize a suitable POSS monomer with another monomer known (this is) to phase segregate from PIB. This sequential copolymerization is the following manner (living carbocationic pol of IB vice multifunction initiators such as dicumyl-Cl after the IB is consumed styrene and styryl-POSS are added and there is formed a styrene-styrene/POSS copolymer containing block attached chemically to a PIB block.

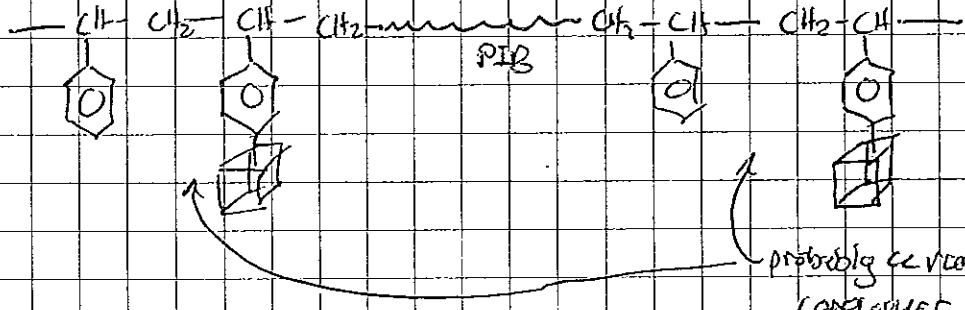
10/02/00

10-2-00

So to picture the following







Anyway— These block sequences will phase segregate from PIB and their Tg's will be much higher than pure PS blocks

And don't forget to sixty nines her

Thomas 10/00/00

10/12/00 I showed Dr. Kennedy these ideas, however, he was not very interested. He wants some sort of interpenetrating network in which you crosslink PIB with POSS. The POSS supposedly will contain other reactive groups that will then crosslink another monomer. He did not give me any specifics as to how this would be done.

10/13/00

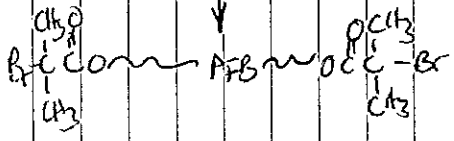
I found toluene to be a good recrystallization solvent for trimethyl alcohol. Here is some solubility stuff.

	trimethyl alcohol	1,3,5-trimethyl benzenetricarboxylate
tol	soluble only on heating	soluble
CH_2Cl_2	soluble	very soluble
MeOH	very soluble	?
Acetone	very soluble	very soluble
THF	very soluble	soluble
ethyl acetate	very soluble	very soluble

10/14/00

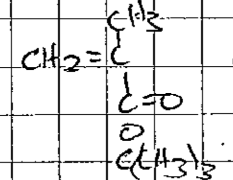
Today I had the following ideas for the project, Hopefully they will interest Dr. Kennedy. Essentially I want to make amphiphilic triblock thermoplastic elastomers by first forming an allyl telechelic of PIB following by polymerization (co-polymerization) of a water soluble monomer and an appropriate POSS. In some cases A radical free radical polymerization method instead of ATRP might have to be used. And this would result in multi-block copolymers of PIB and water sol monomer/POSS.

$CH_2=CH-CH_2\sim PIB\sim CH_2-CH=CH_2$ this can be functionalized for use as an ATRP initiating site for methacrylates and acrylates that are known to undergo ATRP

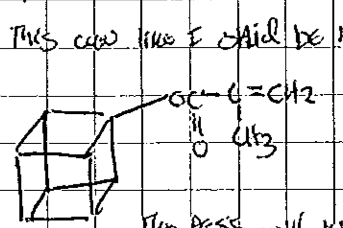


10/4/00

This can also I think be reacted with monomers such as

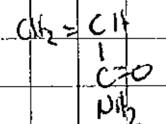


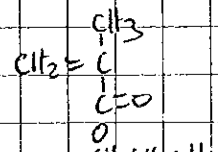
and

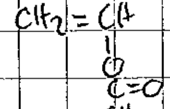


to produce an amphiphilic triblock thermoplastic elastomer. The POSS will increase oxygen permeability and should help increase the Tg and hopefully strength of the physical crosslinks between the hydrophilic blocks by increasing or encouraging their phase separation, etc.

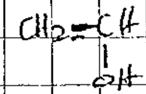
other monomers that might be explored are as follows.







which can be reacted to



for all essential considerations

10/5/00

Well today I recrystallized the tricumyl alcohol again from toluene. The material is slowly getting clearer each time. It will probably take 2-3 more recrystallizations to get a good pure sample of the alcohol. I also ran 3 TGA's on A80, BE80, and BM80. Basically A and BE80 show losses due to ethanol that was still present (you could smell it). BM80 showed a possible 10% wt loss due to polymer. I will have to grind the glasses ~~if I can~~ and boil in hexane to make sure that I can get rid of any ~~gl~~ unbound PIB (chemically extracted).

10/6/00

Today I came up with several ideas for a final project. One idea was to crosslink an allyl telechelic of PIB with ~~and~~ allyl telechelic of a water soluble polymer with hydrido POSS (8 Si-H's). Also I have had another and much better idea – amphiphilic TPE's. Here are some examples.

Polystyrene — PIB — water soluble polymer (PEG) — PIB — Polystyrene

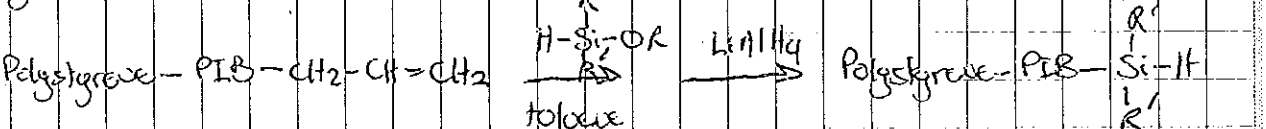
or slightly different

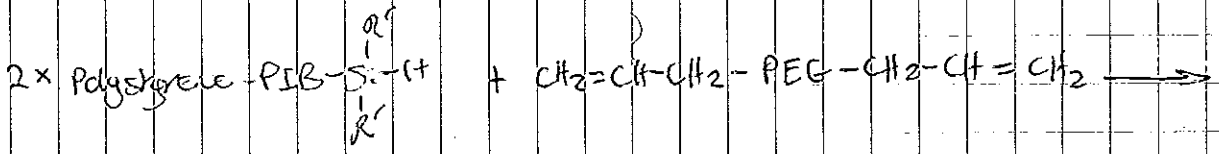
Polystyrene — water soluble polymer (PEG) — PIB — water soluble polymer (PEG) — Polystyrene

10-6-00

The idea is based on having a glassy block on the ends of the block copolymers that is known to result in phase segregation to form physical crosslinks that possess significant strength. Polystyrene is such a material and forms the physical crosslinks of the well known Kratons. A synthesis procedure might be

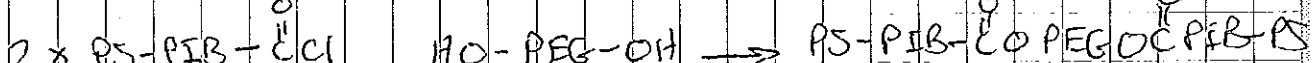
cationic polymerization of styrene followed by polymerization of IB followed by functionalization resulting in either an allyl group or other reactive group that can react with a complimentary group that resides on the water soluble polymer.



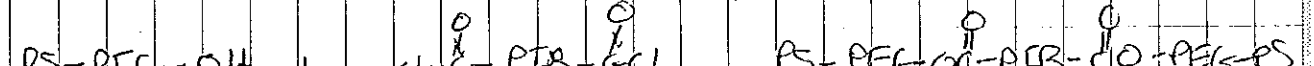


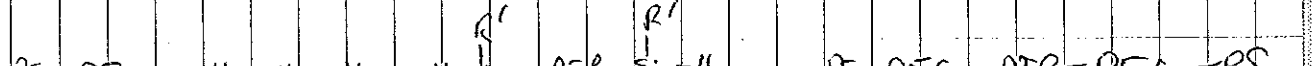
PS – PIB – PEG – PIB – PS

Another, or other linking reactions might include



you might also start with the following polymer made via cationic pzn





many linking reactions are possible – only limited by the imagination however. The idea is that the outermost blocks are glassy such as PS; you have a rubbery block(s) made of PIB and you have water soluble block(s). Other water soluble polymers might include polyoxazoline and various water soluble methacrylates and acrylates.