

Lecture 23: End Group Functionalization. Telechelic Oligomers and Novel Architectures using Coupling Techniques

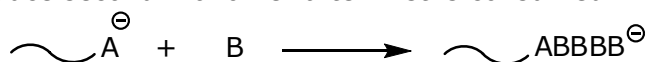
From Last Lecture

Diene polymerization:

1,2 addition:		1,4 addition:	
	(vs)		
		cis:	trans: linkage
			(vs)
		primarily cis:	primarily trans:
		crystallinity suppressed	semicrystalline mat
		low crystallinity	w/T _m ↑ than 25°C
		v. low T _g	
		⇒ used for synthetic rubbers	

Living Polymerization

- allow intentional introduction of terminating group
 → ω end-functionalization
 α - ω functionalization with dianionic initiator
- introduce second monomer after first is consumed

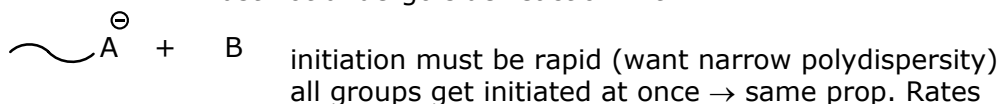
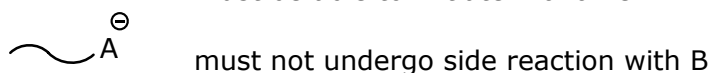


to yield a AnBm block copolymer

- can also have triblock copolymers:
 - ABA triblocks
 - ABC triblocks
 - ⋮
 - ⋮
 - ⋮
 - heptablocks (in literature)

But what limits it?

- we must consider the relative reactivities of the blocks:

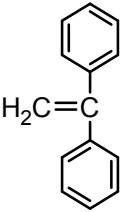



→ uniform blocks

“Food Chain”

short list of monomers, in increasing electrophilicity

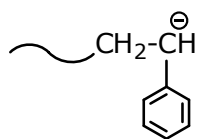
most aggressive:

• dimethyl amino styrene, p-methoxy styrene, p-methyl styrene, α-methyl styrene		} almost the same		Ease of initiation
• styrene				A monomer in the list can initiate anything equal or below it
• butadiene				
• isoprene				
• vinyl naphthalene				
• p-chlorostyrene				
• vinyl pyridine				
* • diphenyl ethylene (DPE)				
• alkyl methacrylates (MMA)				
• propiolactones				
• ethylene oxide			Ex: ethylene oxide cannot initiate vinyl pyridine but can initiate vinylidene cyanides	
	DPE cannot self-propagate (too bulky)			
propylene sulfide				
• vinylidene cyanide			More reactive monomers → faster polymerization	
• α-cyanoacrylates				

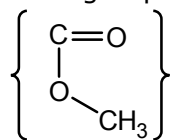
Example: Synthesis of a Diblock Copolymer

want to make polystyrene-b-poly(methyl methacrylate)
PS-b-PMMA

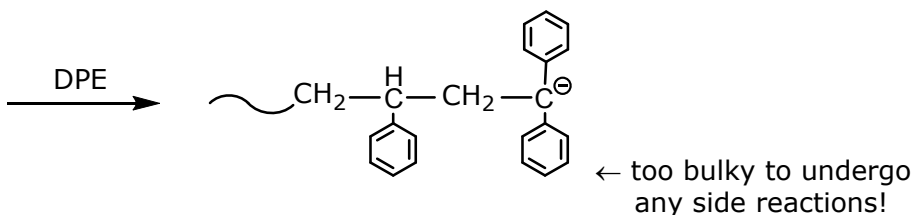
(A) Must start with styrene



But this can react with the carboxylic Ester groups of MMA:

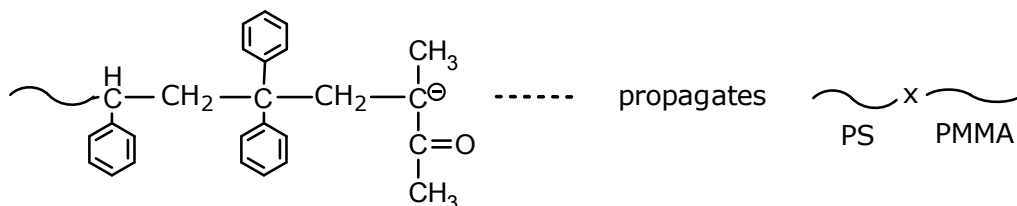


(B) Add DPE



Because only one group of DPE, there is no effect on the properties of copolymer

(C) Add MMA



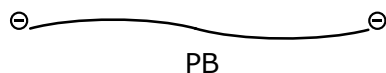
Another Example: Synthesis of a Triblock Copolymer

Styrene-Butadiene-Styrene triblock
PS-b-PB-b-PS
SBS

Can make this polymer at least 3 different ways:

- consideration: styrene and butadiene are very close in reactivity
So, butadiene can initiate styrene

1. Difunctional initiator: ex: Na naphthalene
+ butadiene



Consume B completely and then add styrene (S)



Symmetric triblock b/c same prop. rate and time

2. Add S+B+S in sequence (w/monomer fully consumed by each step)

3. First initiate PS

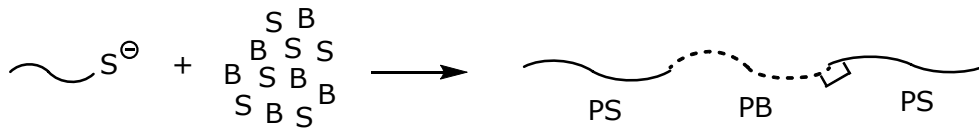
a)



b) add butadiene + styrene together in big aliquot
(in anionic polym, do not get alternating copolymers, get blocky behavior)

- reactivity rates (anionic)

$k_{sb} \gg k_{bs}$
 $r_b = 14$
 $r_s = 0.03$
growing B is preferred



- create block with PB (B preferred over S)
 - then transition (both B and S)
 - then completely PS (all that is left)

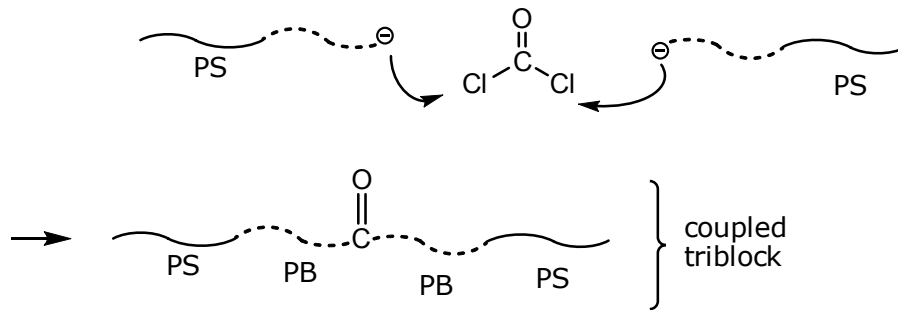
- this is done in industry
 - relatively simple
 - transitional regime enhances surface properties
 - more diffuse interface
 - Better properties

4. Use a coupling agent
(used for systems with no other options)

i) grow diblock of PS-PB

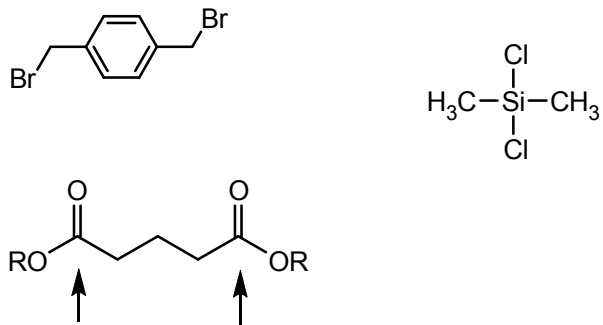


ii) then add reactive coupling agents
e.g. phosgene (extremely reactive)



everytime you introduce a monomer or coupling agent, you risk the chance of impurities (can't get II-block copolymer or high MW copolymer)

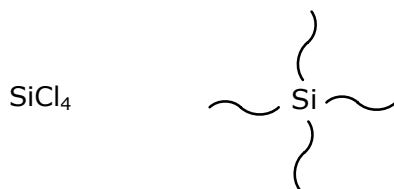
other coupling agents: (Quantitative reactions)



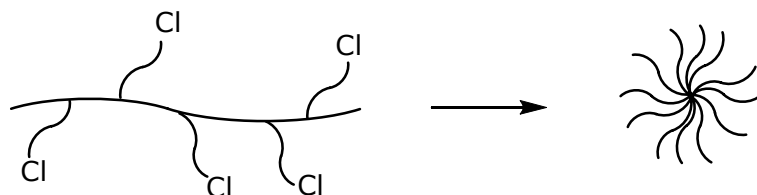
Disadvantages of Coupling

- often get incomplete reaction (diblock + triblock)
- needs perfect stoichiometry (scale is very small)

Despite that, you can be creative:
Can use coupling to make "stars"



Or use short oligomer



Can make graft copolymers: (or comb copolymers)

