Chapter 9

Copolymerization

Step copolym'n

- polym'n of (ARB + AR'B) or (RA_2 + $R'B_2$ + $R''B_2$)
  - gives copolymers
  - with composition similar to monomer composition ← polym'n to p ≈ 1
- sequence distribution?
  - with functional groups of the same reactivity
    - eg, $HOOC\text{-}R\text{-}NH_2$ + $HOOC\text{-}R'\text{-}NH_2$
    - random copolymer formed
  - with functional groups of different reactivity
    - eg, A = -COOH, B = $-NH_2$, C = -OH
    - eg, B = $-CH_2OH$ vs B = -CHROH
    - 'blocky' structure

Chain copolym’n

- 4 types of copolym’n reaction

$$\sim A^* + A \xrightarrow{k_{AA}} \sim AA^*$$ homopropagation

$$\sim A^* + B \xrightarrow{k_{AB}} \sim AB^*$$ cross-propagation

$$\sim B^* + B \xrightarrow{k_{BB}} \sim BB^*$$

$$\sim B^* + A \xrightarrow{k_{BA}} \sim BA^*$$

  - assumption: Reactivity of active center depends only on terminal monomer unit (--A* and --B*).

- rate of copolym’n

$$-\frac{d[A]}{dt} = k_{AA}[A^*][A] + k_{BA}[B^*][A]$$

$$-\frac{d[B]}{dt} = k_{BB}[B^*][B] + k_{AB}[A^*][B]$$

Copolymer composition equation

- copolymer composition = d[A]/d[B]

$$\frac{d[A]}{d[B]} = \frac{[A]}{[B]}\left\{\frac{k_{AA}[A^*]/[B^*]+k_{BA}}{k_{BB}+k_{AB}[A^*]/[B^*]}\right\}$$

  - steady-state approx $\frac{d[A^*]}{dt}=0$ and $\frac{d[B^*]}{dt}=0$

$$\frac{d[A^*]}{dt} = k_{BA}[B^*][A]-k_{AB}[A^*][B] \qquad \frac{d[B^*]}{dt} = k_{AB}[A^*][B]-k_{BA}[B^*][A]$$

    - Rates of cross-propagation are the same. $\frac{[A^*]}{[B^*]} = \frac{k_{BA}[A]}{k_{AB}[B]}$

$$\boxed{\frac{d[A]}{d[B]} = \frac{[A]}{[B]}\left(\frac{r_A[A]+[B]}{[A]+r_B[B]}\right)}$$

copolymer composition eqn
[Mayo(-Lewis) eqn]

$$\boxed{r_A = \frac{k_{AA}}{k_{AB}} \quad \text{and} \quad r_B = \frac{k_{BB}}{k_{BA}}}$$

monomer reactivity ratio (homo/cross)

- Copolymer composition depends on r and conc'n of monomers ([A] & [B]) at an instant.
  - r depends
    - on type of active center (•, –, or +)
    - on temperature (a little in radical, much in ionic)
    - not on initiator, solvent in radical
    - on initiator [counter-ion], solvent in ionic

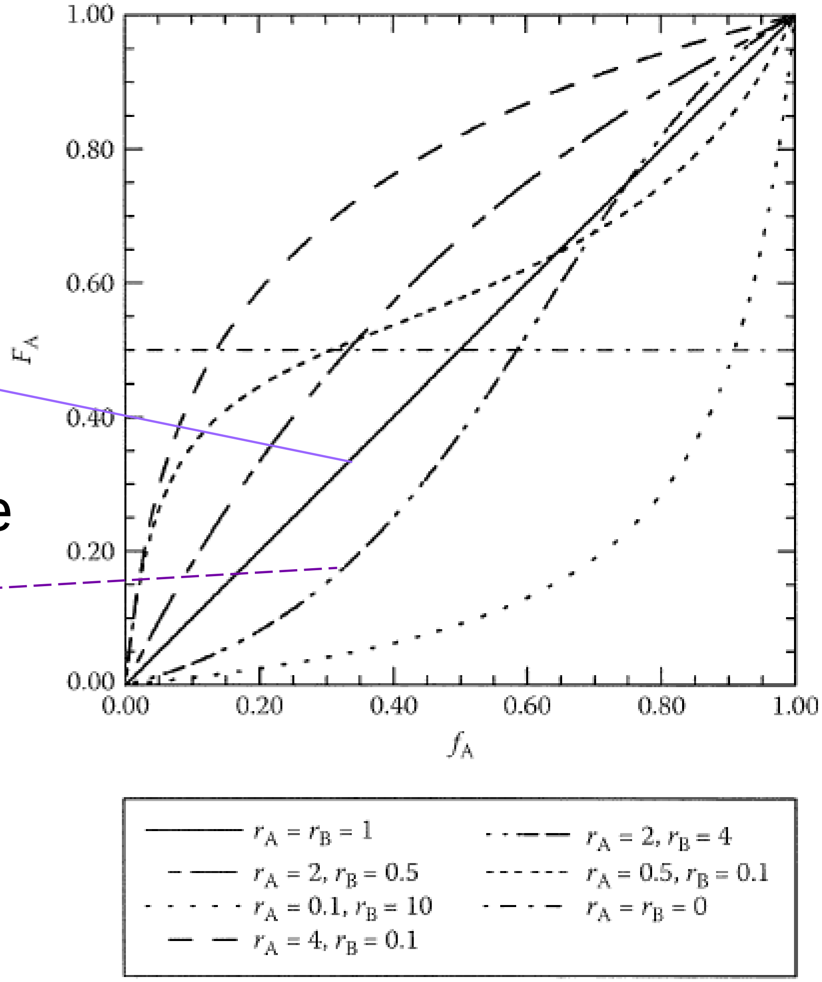
- mole fractions
  - f_A, f_B in the feed: $f_A = [A]/([A]+[B])$
  - F_A, F_B in the copolymer: $F_A = d[A]/(d[A]+d[B])$
  - (another form of) copolymer composition eqn

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2} \qquad F_B = \frac{r_B f_B^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2}$$

(Chain) copolym'n behavior

$$r_A = \frac{k_{AA}}{k_{AB}} \quad \text{and} \quad r_B = \frac{k_{BB}}{k_{BA}}$$

- r determines composition and sequence distribution
  - r > 1 ~ prefer to homopolymerize
    r < 1 ~ prefer to copolymerize
- $r_A = r_B = 1$
  - $F_A = f_A$ (diagonal line)
  - random copolymer
  - rare; A & B of very similar structure
- $r_A >> 1$, $r_B >> 1$
  - block(y) copolymer
  - blockiness up as r_A, r_B up
  - for coordination, <u>not</u> for radical

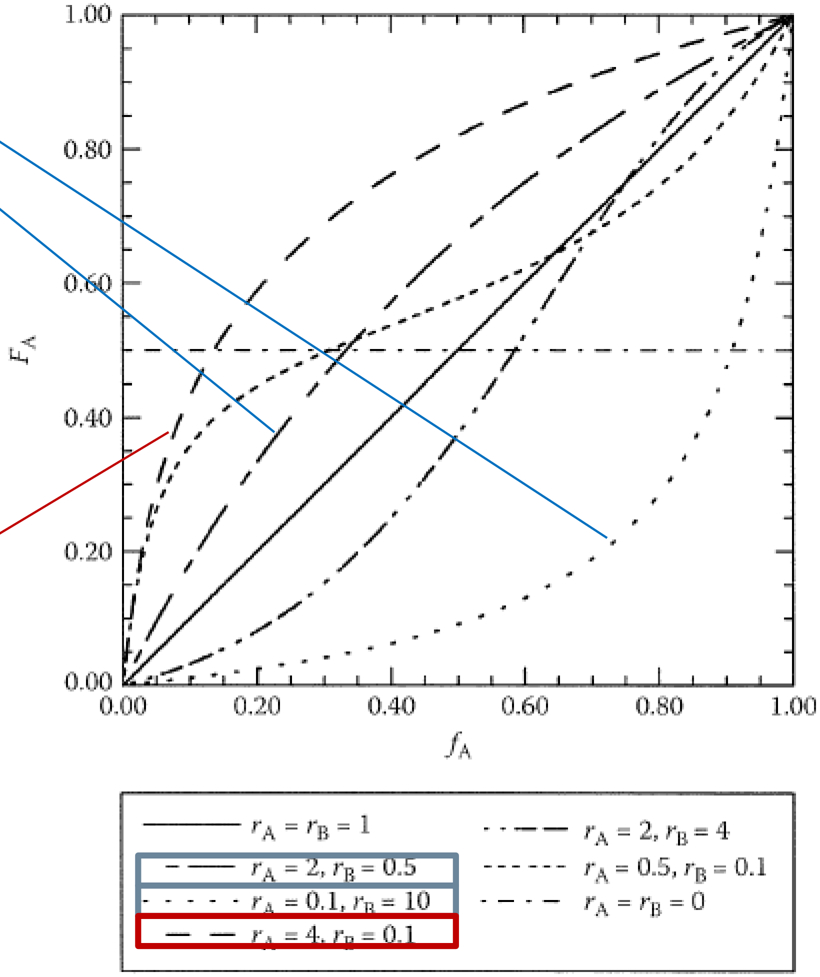


- ❑ $r_A > 1$, $r_B < 1$
  - ❑ special case: $r_A r_B = 1$

    $$r_A = \frac{1}{r_B} \quad \text{i.e.,} \quad \frac{k_{AA}}{k_{AB}} = \frac{k_{BA}}{k_{BB}}$$

    - ‘ideal copolym’n’
    - monomer reactivity depends not on * but on monomer
    - as Δr up, one far more selective
    - Most ionic copolym’n is ideal copolym’n ~ not popular
  - ❑ $r_A r_B \neq 1$ (usually $r_A r_B < 1$)
    - skewed to more reactive M
    - as Δr up, blockiness up
    - conversion dependent ~ A to B

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2}$$

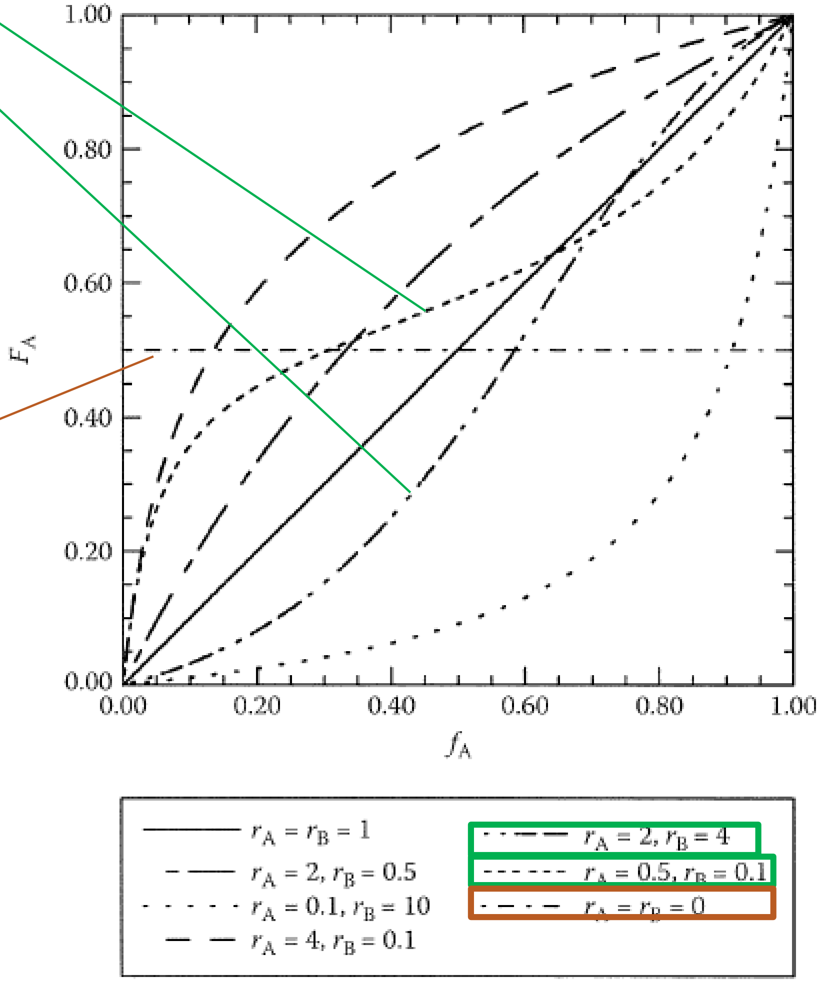


- r_A & $r_B < 1$ or r_A & $r_B > 1$
  - curve intersects diagonal line
  - $F_A = f_A$ at that point
    - azeotropic copolym'n

$$(f_A)_{azeo} = \frac{1 - r_B}{2 - r_A - r_B}$$

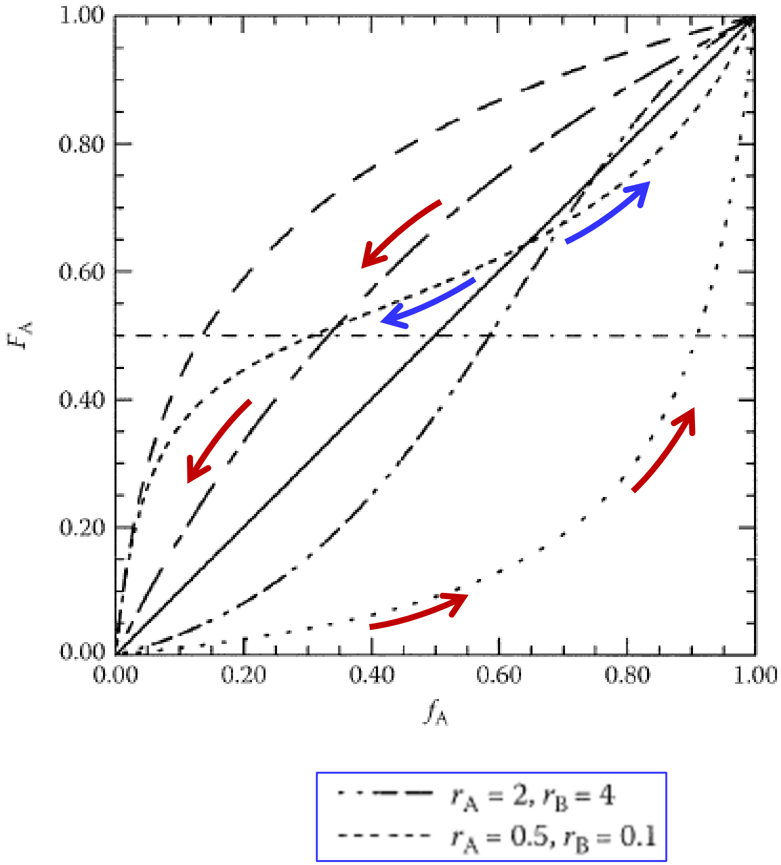
    - not easy to get when Δr is large
  - extreme case: $r_A \approx r_B \approx 0$
    - alternating copolymer
    - $F_A = 0.5$
  - r_A & $r_B > 1$ is rare
  - many r_A & $r_B < 1$ systems
  - alternating tendency up as r down

$$F_A = \frac{r_A f_A^2 + f_A f_B}{r_A f_A^2 + 2 f_A f_B + r_B f_B^2}$$



(Copolymer) composition drift

- Copolymer compos’n changes [drifts] with conversion.
  - copolymer composition eqn is for instantaneous f
  - $F_A \neq f_A$
  - one monomer preferentially consumed
- to minimize drift [for constant F]
  - stop at low conversion
    - monomer recycled
  - continuous feeding monomer of larger r
  - ‘starve-feeding’

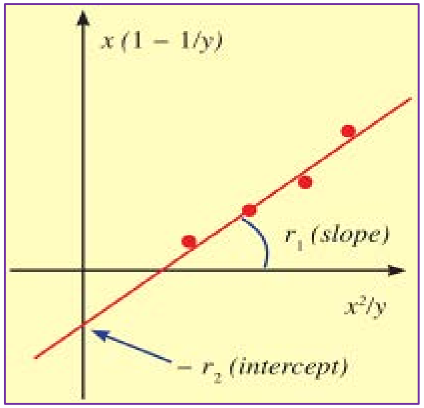


Evaluation of r

❑ Fineman-Ross method

$$\frac{x}{y}(y-1)=\left(\frac{x^2}{y}\right)r_A-r_B \quad \xleftarrow[x=f_A/f_B \text{ and } y=F_A/F_B]{} \quad \frac{d[A]}{d[B]}=\frac{[A]}{[B]}\left(\frac{r_A[A]+[B]}{[A]+r_B[B]}\right)$$

- x from feed; y from analysis of copolymer at low conversion
- one set of data gives a point
- least square fitting to a line

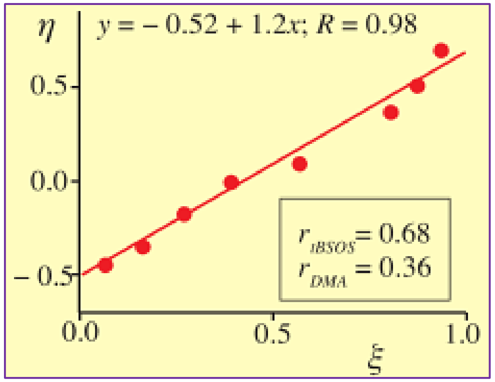


❑ Kelen-Tudos method

$$\frac{(x/y)(y-1)}{\alpha+(x^2/y)}=\left\{\frac{(x^2/y)}{\alpha+(x^2/y)}\right\}\left\{r_A+\frac{r_B}{\alpha}\right\}-\frac{r_B}{\alpha} \qquad \alpha=\sqrt{F_A^{\min}F_A^{\max}}$$

$$\eta=\left\{r_A+\frac{r_B}{\alpha}\right\}\xi-\frac{r_B}{\alpha}$$

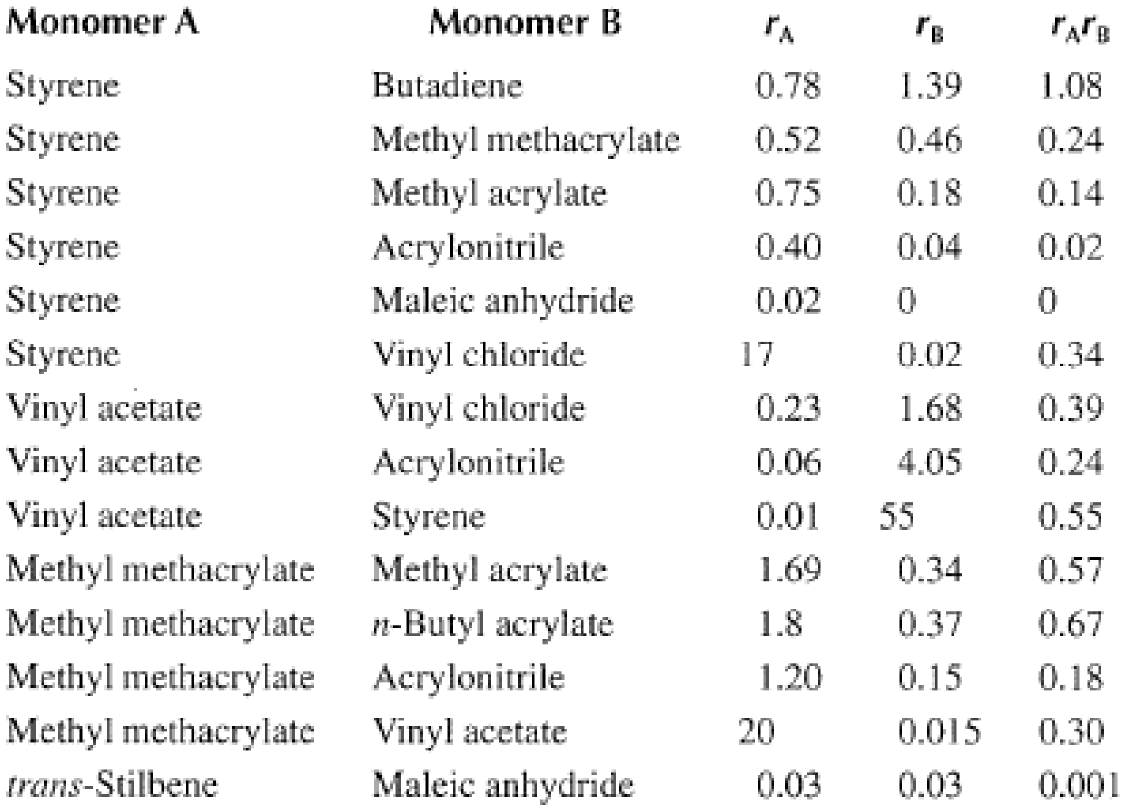
extrapolated to both $\xi=0$ and $\xi=1$



Radical copolym’n

- many commercial copolymers
  - SBR, SAN, (ABS (graft)), EVA, ---
- Most belong to either
  - $r_A > 1$, $r_B < 1$
  - r_A & $r_B < 1$

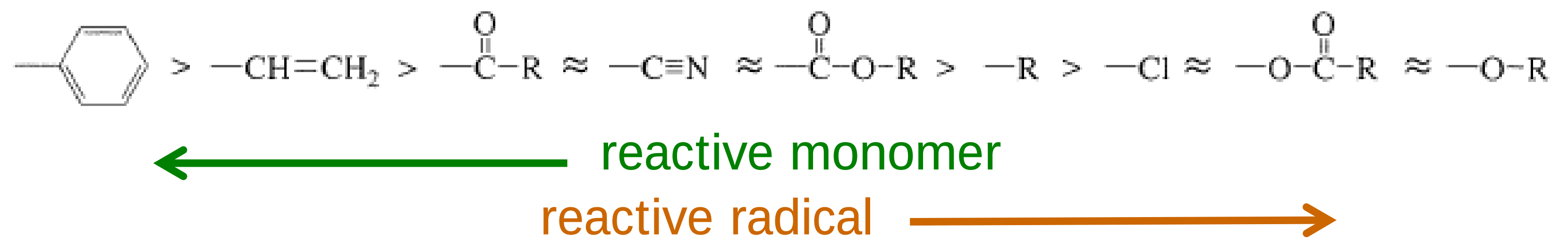
Table 9.1 p212



Monomer A	Monomer B	r_A	r_B	$r_A r_B$
Styrene	Butadiene	0.78	1.39	1.08
Styrene	Methyl methacrylate	0.52	0.46	0.24
Styrene	Methyl acrylate	0.75	0.18	0.14
Styrene	Acrylonitrile	0.40	0.04	0.02
Styrene	Maleic anhydride	0.02	0	0
Styrene	Vinyl chloride	17	0.02	0.34
Vinyl acetate	Vinyl chloride	0.23	1.68	0.39
Vinyl acetate	Acrylonitrile	0.06	4.05	0.24
Vinyl acetate	Styrene	0.01	55	0.55
Methyl methacrylate	Methyl acrylate	1.69	0.34	0.57
Methyl methacrylate	*n*-Butyl acrylate	1.8	0.37	0.67
Methyl methacrylate	Acrylonitrile	1.20	0.15	0.18
Methyl methacrylate	Vinyl acetate	20	0.015	0.30
trans-Stilbene	Maleic anhydride	0.03	0.03	0.001

r in radical copolym’n

- Reactivity of monomer and radical depends on substituent.
  - resonance, polar, (and steric) effects
- resonance effect



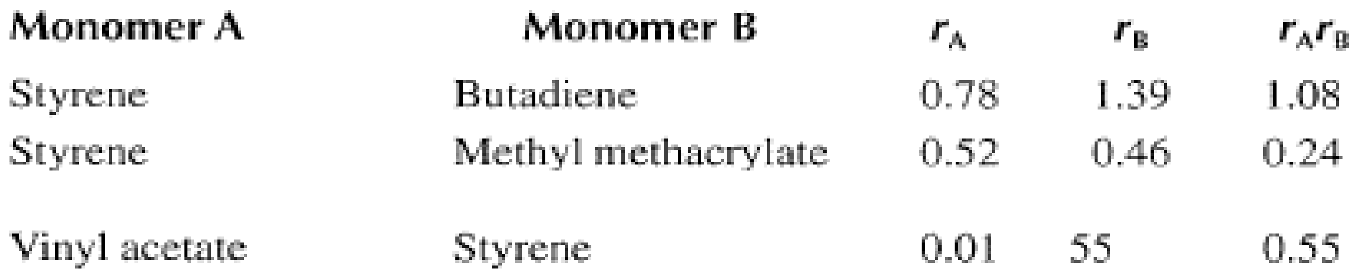
$$-C_6H_5 > -CH{=}CH_2 > -\overset{O}{\overset{\|}{C}}-R \approx -C{\equiv}N \approx -\overset{O}{\overset{\|}{C}}-O-R > -R > -Cl \approx -O-\overset{O}{\overset{\|}{C}}-R \approx -O-R$$

reactive monomer

reactive radical

  - A with stabilizing subs, B with less stabilizing subs
    - eg, A = ST and B = VAc
    - $k_{BA} > k_{BB} > k_{AA} > k_{AB}$
    - $k_{BB} > k_{AA}$ ~ resonance effect larger for radical than for monomer
      - k_p of VAc larger than k_p of ST (in homopolym’ns)!
    - $r_A > 1$, $r_B < 1$ if resonance only

- resonance effect (cont'd)
  - Copolym'n is facile for pairs with small Δr.
    - both with stabilizing subs or both with less stabilizing subs
  - As Δr increases
    - more blocky structure
    - hard to get copolymer with both components
    - If too large, no copolym'n
      - ST is an inhibitor for homopolym'n of VAc!



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Styrene	Butadiene	0.78	1.39	1.08
Styrene	Methyl methacrylate	0.52	0.46	0.24
Vinyl acetate	Styrene	0.01	55	0.55

❑ steric effect

VAc more reactive •

k_{AB}

Odian p496

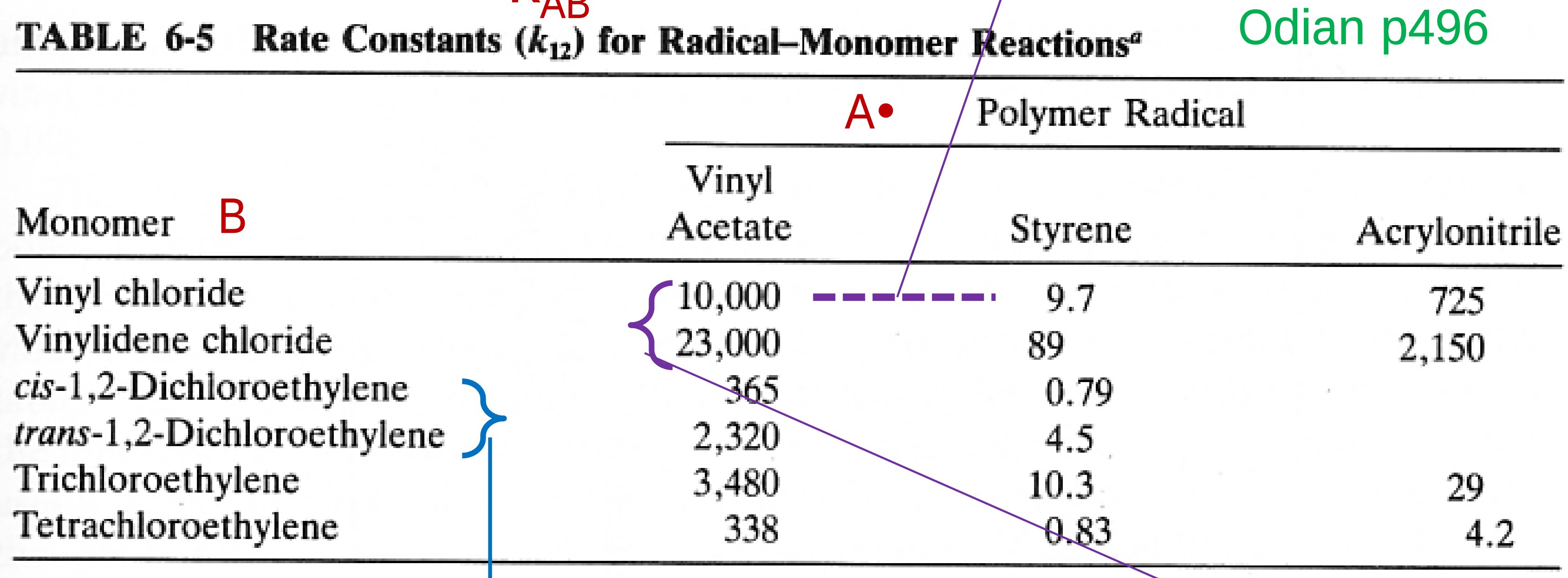


TABLE 6-5 Rate Constants (k_{12}) for Radical–Monomer Reactions[a]

Monomer	Polymer Radical		
	Vinyl Acetate	Styrene	Acrylonitrile
Vinyl chloride	10,000	9.7	725
Vinylidene chloride	23,000	89	2,150
cis-1,2-Dichloroethylene	365	0.79	
trans-1,2-Dichloroethylene	2,320	4.5	
Trichloroethylene	3,480	10.3	29
Tetrachloroethylene	338	0.83	4.2

A•

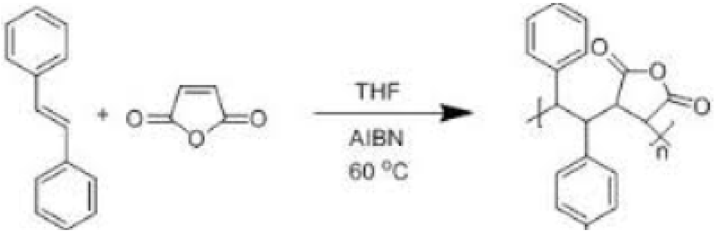
B

- do not homopolymerize, but do copolymerize
- low reactivity due to steric effect
- trans radical more stable (transition state)

VDC more reactive M

competition betw resonance and steric effect

- polar effect
  - $\text{--CH}_2\text{C•H(W)} + \text{CH}_2\text{=CH(W)} \rightarrow k_{AA}$
    $\text{--CH}_2\text{C•H(W)} + \text{CH}_2\text{=CH(D)} \rightarrow k_{AB}$
  - $r_A = k_{AA}/k_{AB} < 1$ and $r_B < 1 \rightarrow r_A r_B << 1$
  - determines alternating tendency
  - alternating tendency up, as $r_A r_B$ down to 0
  - stilbene and MA
    - do not homopolymerize;
      large steric hindrance in copolym’n



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trans-Stilbene	Maleic anhydride	0.03	0.03	0.001

Q-e scheme

- rate constant for p• and m monomer

$$k_{\mathrm{pm}} = P_{\mathrm{p}} Q_{\mathrm{m}} \exp(-e_{\mathrm{p}} e_{\mathrm{m}})$$

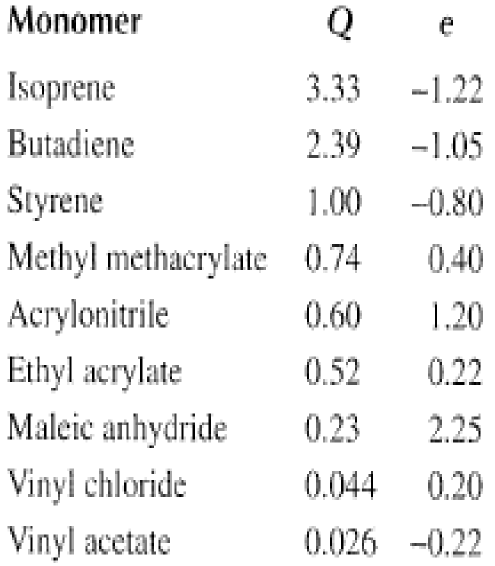
  - P, Q ~ reactivity ~ resonance effect
  - e ~ electrostatic charge ~ polar effect

$$r_{\mathrm{A}} = \left(\frac{Q_{\mathrm{A}}}{Q_{\mathrm{B}}}\right) \exp\left[-e_{\mathrm{A}}(e_{\mathrm{A}} - e_{\mathrm{B}})\right] \quad r_{\mathrm{B}} = \left(\frac{Q_{\mathrm{B}}}{Q_{\mathrm{A}}}\right) \exp\left[-e_{\mathrm{B}}(e_{\mathrm{B}} - e_{\mathrm{A}})\right]$$

$$\boxed{r_{\mathrm{A}} r_{\mathrm{B}} = \exp[-(e_{\mathrm{A}} - e_{\mathrm{B}})^2]}$$

  - setting Q = 1.0 and e= –.8 for ST
    - with experiments with ST and others
- large Q ~ large resonance ~ reactive M
  - large ΔQ → blocky
- large e ~ large e withdrawer
  - large Δe → small $r_A r_B$ → alternating

Table 9.2 p214



Monomer	Q	e
Isoprene	3.33	–1.22
Butadiene	2.39	–1.05
Styrene	1.00	–0.80
Methyl methacrylate	0.74	0.40
Acrylonitrile	0.60	1.20
Ethyl acrylate	0.52	0.22
Maleic anhydride	0.23	2.25
Vinyl chloride	0.044	0.20
Vinyl acetate	0.026	–0.22

Living radical copolym’n

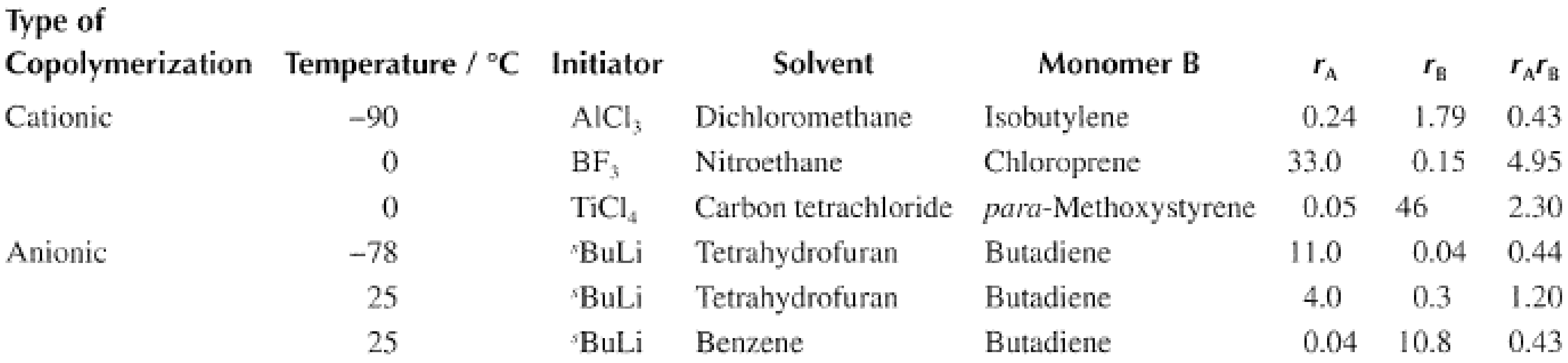
- living → All the chains have the same composition and sequence distribution.
- statistical only when $r_A \approx r_B \approx 1$
- If not, composition drift in a chain
  - no statistical new chain
  - gradient [tapered] copolymer

R-A-A-A-B-A-A-B-A-A-B-A-B-A-B-B-A-B-B-A-B-B-B-A-B-B-B-B—▨

- r the same to normal radical copolym’n?
  - should be, but not really
  - affected by type of end-capping
  - more tapered for ST copolym’n

Ionic copolym’n

- r the same to radical copolym’n? Table 9.3 p215
- hard to get copolymers with both components
  ← large Δr ← larger effect of substituent
- r depends greatly on solvent and counter-ion
- Cationic copolym’n of isobutylene and isoprene is the only commercial practice.



Type of Copolymerization	Temperature / °C	Initiator	Solvent	Monomer B	r_A	r_B	r_Ar_B
Cationic	−90	$AlCl_3$	Dichloromethane	Isobutylene	0.24	1.79	0.43
	0	BF_3	Nitroethane	Chloroprene	33.0	0.15	4.95
	0	$TiCl_4$	Carbon tetrachloride	*para*-Methoxystyrene	0.05	46	2.30
Anionic	−78	^{s}BuLi	Tetrahydrofuran	Butadiene	11.0	0.04	0.44
	25	^{s}BuLi	Tetrahydrofuran	Butadiene	4.0	0.3	1.20
	25	^{s}BuLi	Benzene	Butadiene	0.04	10.8	0.43

ZN copolym’n

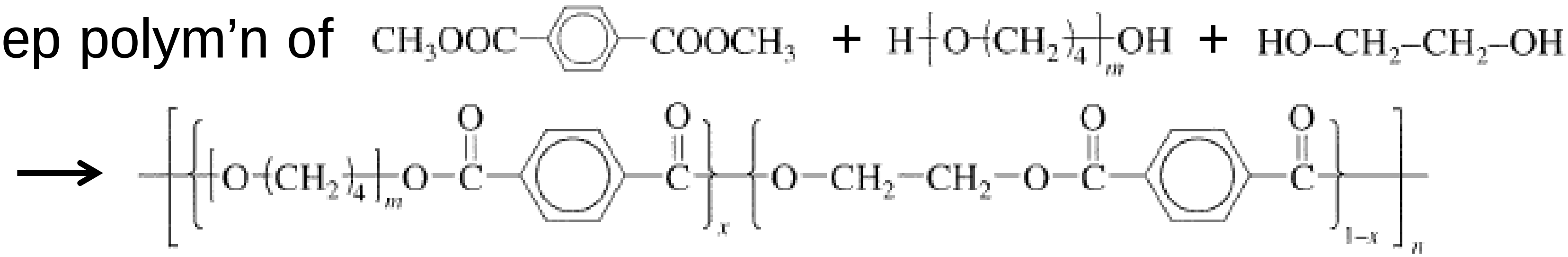
- heterogeneous ‘multi-site’ catalyst
  - r observed is the average
    - each site has different activity and stereoselectivity
- used in EPDM rubber and LLDPE
    - EPDM ~ ethylene propylene (non-conjugated) diene monomer
  - large Δr ~ $r_{ethylene} > 50$ and $r_{1\text{-}butene} < .1$
    - higher $r_{\alpha\text{-}olefin}$ for smaller subs
  - r depends on catalyst
    - higher $r_{ethylene}$ for Ti catalysts

Metallocene copolym’n

- homogeneous ‘single-site’ catalyst
  - one r and CCE applicable
- more comonomer pairs are possible
- in copolym’n of ethylene or propylene with α-olefin
  - higher content (large r), uniform (inter and intra) distribution of α-olefin
    - better mechanical property with less content
  - narrower MMD
    - beneficial to rheology? ~ wrong

Segmented alternating block copolymers

- poly(ester-ether) ~ polyester TPE
  - step polym'n of



- a thermoplastic elastomer (TPE)
  - a segmented (block) copolymer
  - polyether block ~ flexible ~ 'soft segment'
  - polyester block ~ crystallizable ~ 'hard segment'
  - behaves as rubber but thermoplastic
  - physical crosslinking

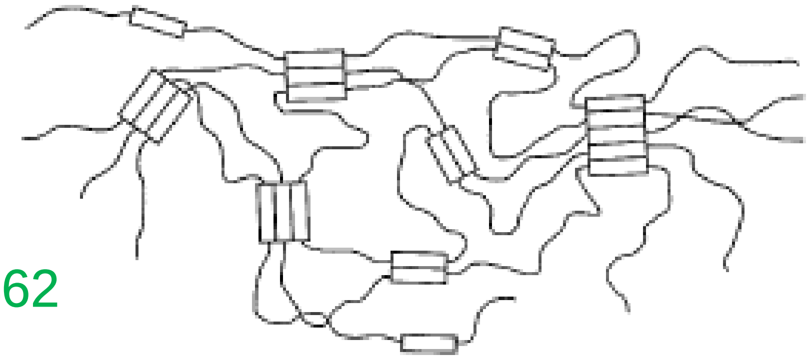
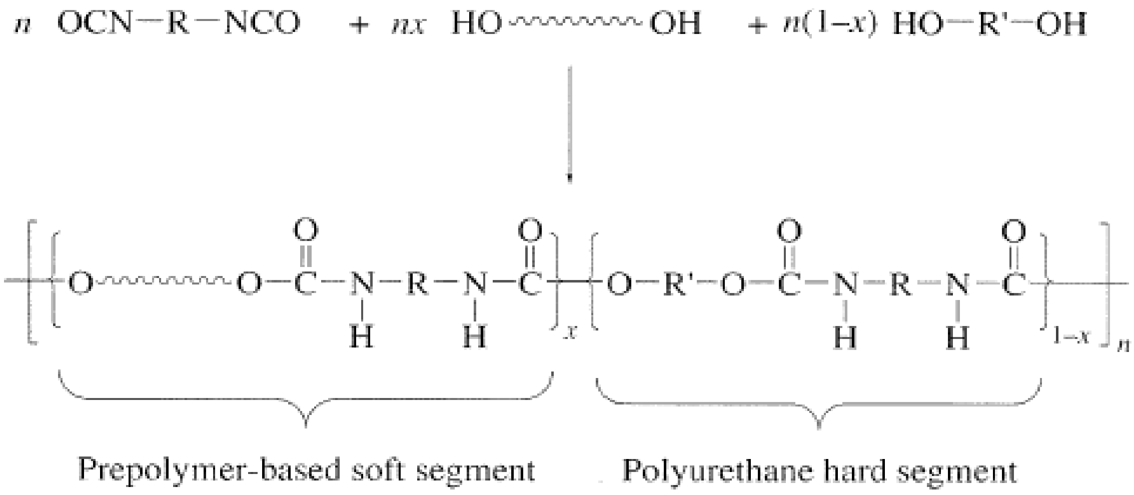


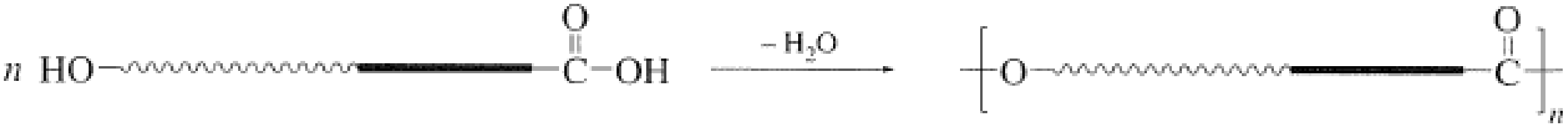
Fig 18.13 p462

- segmented PU ~ thermoplastic PU [TPU]



  - stiff to flexible ~ dep on soft segment ~ diverse applications

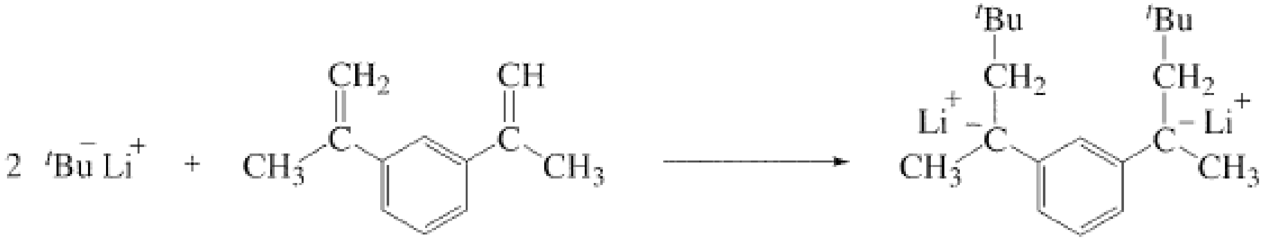
- step polym’n of functionalized diblock copolymer



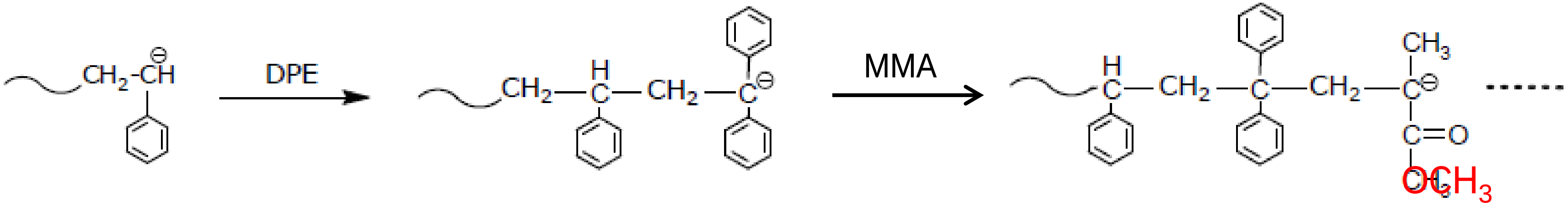
  - from living anionic ~ controllable and uniform block lengths

Block copolymer via anionic living

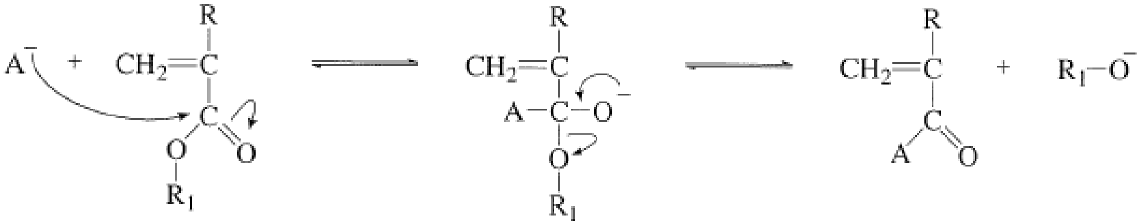
- using one-end living chain
  - Bu-AA---AA$^{(-)}$ Li$^{(+)}$ + n B → Bu-AA---AA-BB---BB$^{(-)}$ Li$^{(+)}$
  - AB (di)block copolymer, ABC triblock copolymer
- using two-end living chain
  - Na$^{(+)}$ $^{(-)}$AA---CH$_2$CH$_2$---AA$^{(-)}$ Na$^{(+)}$ + n B →
    Na$^{(+)}$ $^{(-)}$BB---BB-AA-----AA-BB---BB$^{(-)}$ Na$^{(+)}$
  - Li$^{(+)}$ $^{(-)}$AA---R---AA$^{(-)}$ Li$^{(+)}$ + n B →
    Li$^{(+)}$ $^{(-)}$BB---BB-AA-----AA-BB---BB$^{(-)}$ Li$^{(+)}$
  - ABA triblock copolymer



- B must be of higher reactivity (better e$^-$-withdrawing)
  - A=MMA and B=ST → PMMA only
    - pK_a(toluene) ~ 43; pK_a(ethyl acetate) ~ 30
  - A=ST and B=MMA → poly(ST-*b*-MMA)
    - Usually, small amount of CH_2=CPh_2 added
      - before MMA addition



      - to prevent side reaction



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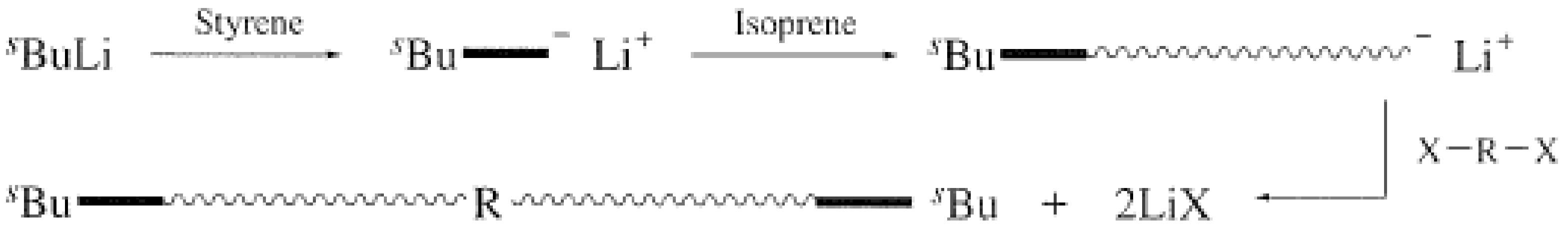
- SIS (or SBS)
  - linking two SI (or SB) living chains in nonpolar solvent



  - using two-end living IP (or BD) chain in polar solvent

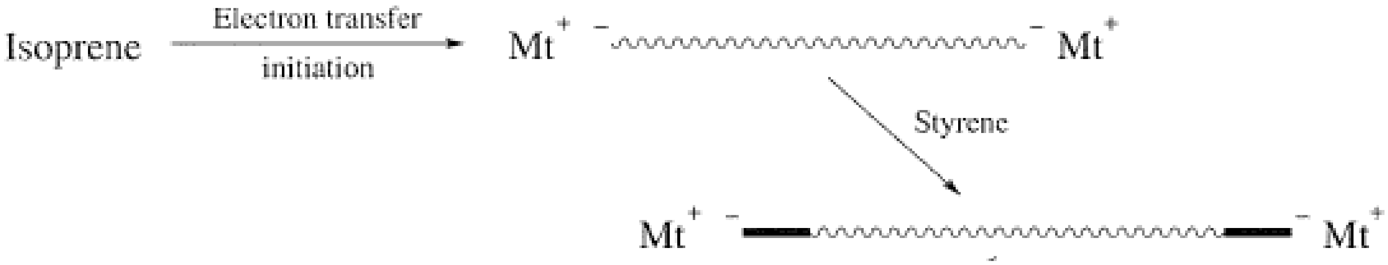


Table 9.3 p215

r_A, r_B
when A = ST

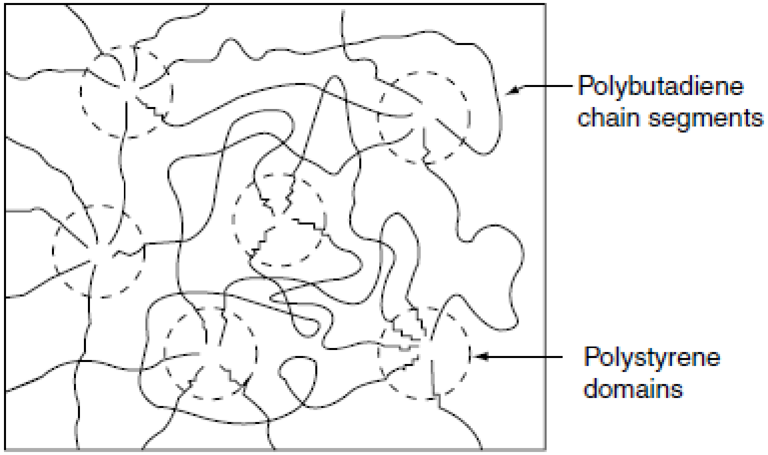
^{s}BuLi	Tetrahydrofuran	Butadiene	4.0	0.3
^{s}BuLi	Benzene	Butadiene	0.04	10.8
^{n}BuLi	Tetrahydrofuran	Isoprene	9.0	0.10
^{n}BuLi	Benzene	Isoprene	0.26	10.6

❑ SIS (or SBS) (cont'd)

- sequential addition of ST, IP (or BD), and ST
  - ST and IP (BD) are of similar reactivity ($pK_a \approx 43$).
- anionic copolym'n of IP (BD) and ST in the presence of living ST chain ~ commercial (Kraton®)

- in nonpolar solvent (with Li)
  - 1,4 > 1,2 See p151
- a TPE (or HIPS*)

* HIPS, actually, is a graft copolymer.

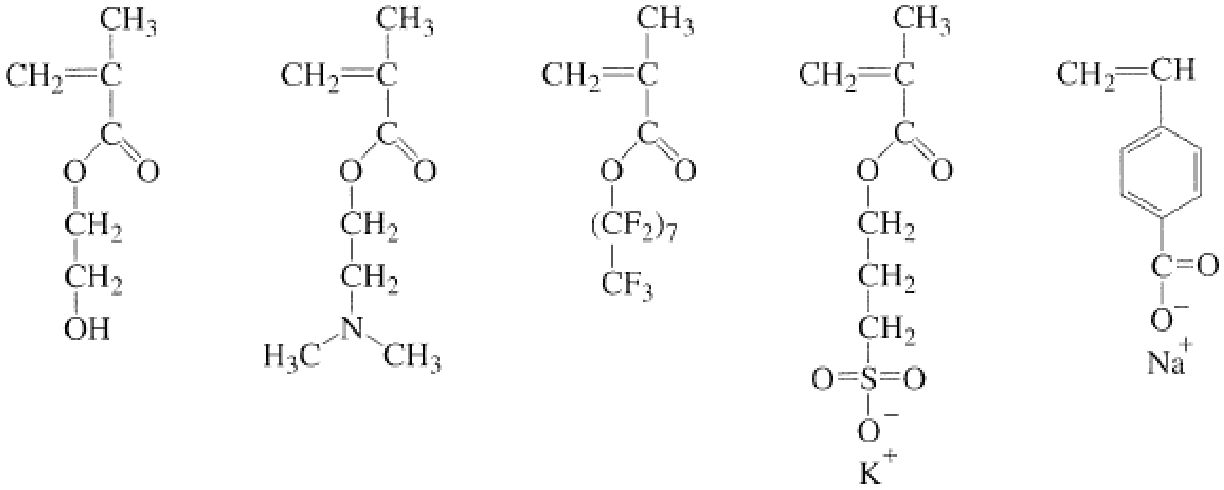


Block copolymer by LRP

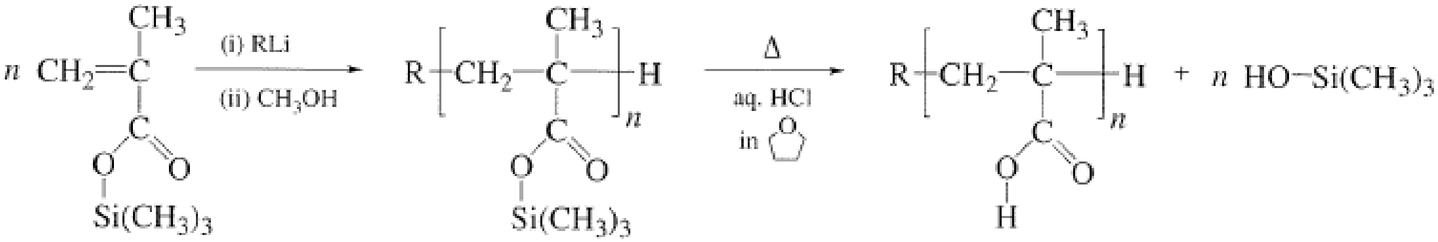
- Compared to anionic;
  - for more diverse monomers
  - with less stringent rxn condition
  - <u>no</u> control of stereochemistry

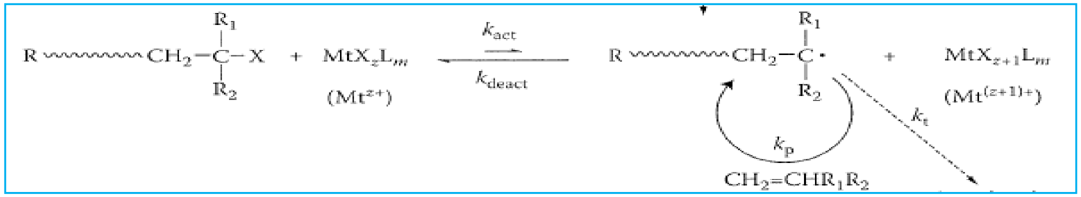
- NMP
  - for ST and some acrylates
  - not for methacrylates
  - order of addition dep on the catalyst
    - more reactive monomer later
    - if using TIPNO, Bu-acrylate first then ST

- ATRP
  - for more monomers than NMP and anionic
    - especially methacrylates
    - acidic H should be ionized or protected



p141

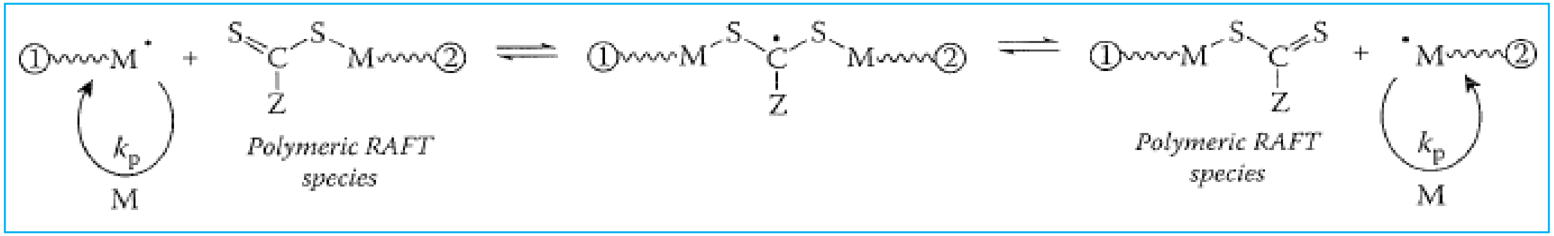




- ATRP (cont'd)
  - order of addition
    - reactivity of M-X ~ AN > methacrylates > ST ≈ acrylates
      - order of K, <u>not</u> of monomer reactivity (p222 wrong)
    - copolym'n in a family preferable; eg, -COOMe and -COOBu
      - sequential addition gives AB, ABA, ABC, ---
    - monomer with higher K first
      - ---MMA-Br + ST → PMMA-*b*-PS
      - ---ST-Br + MMA → PS + PS-*b*-PMMA
        - Initiation of MMA is slower than propagation of MMA.
    - if ST-MMA sequence necessary, use 'halogen exchange'
      - ---ST-Br + MMA with CuCl

        Fig 9.2 p223
        - C–Br > C–Cl
        - Initiation of MMA is faster than propagation of MMA.

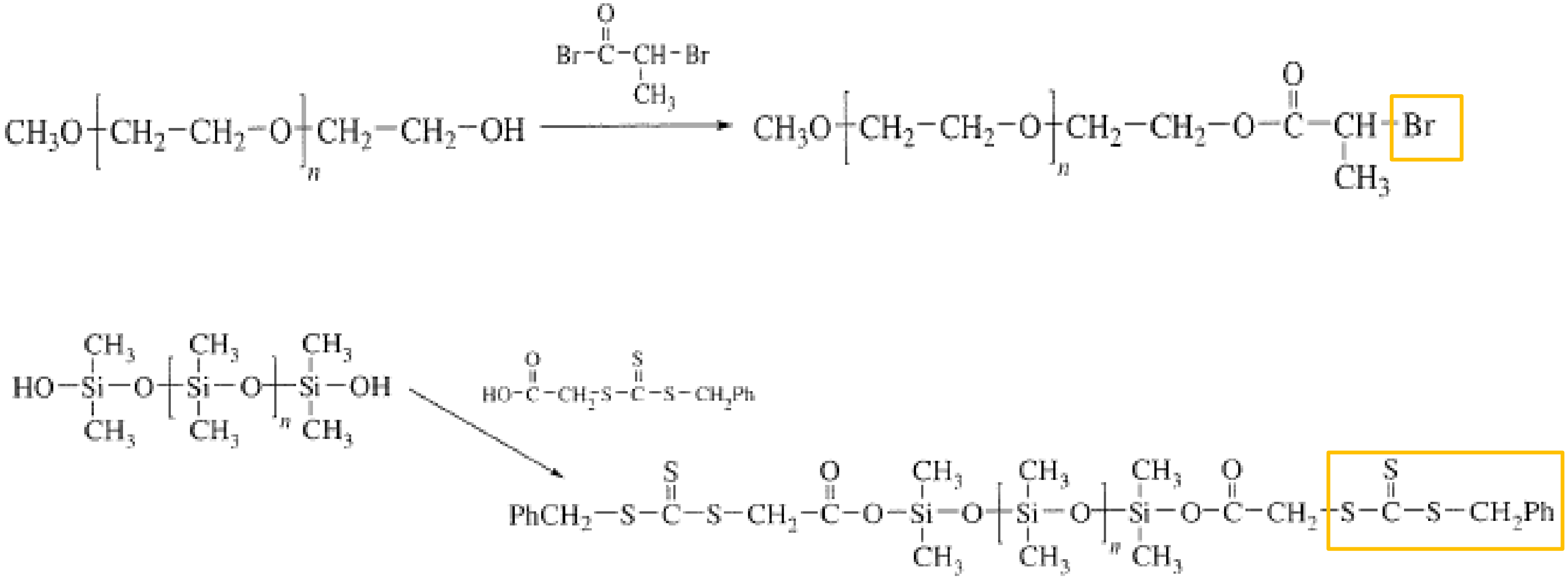
- RAFT
  - for more versatile monomers
  - order of addition
    - 1st monomer must be of better-leaving radical



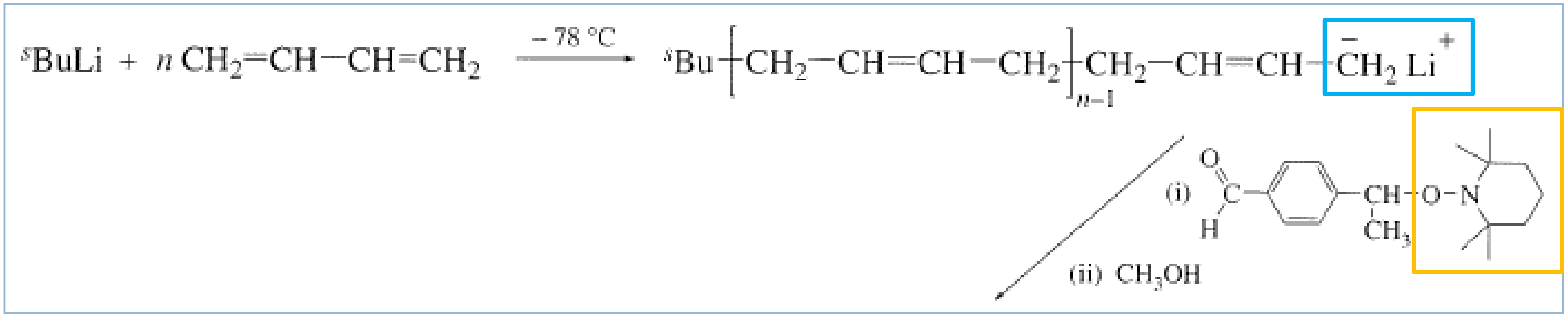
      - same order as in ATRP? not sure
    - seems to be not that critical
    - switchable RAFT agent p223
      - more reactive RAFT agent for more reactive monomer
- Other living polym'ns can also be used.
  - living cationic, GT, ZN, metallocene, RO

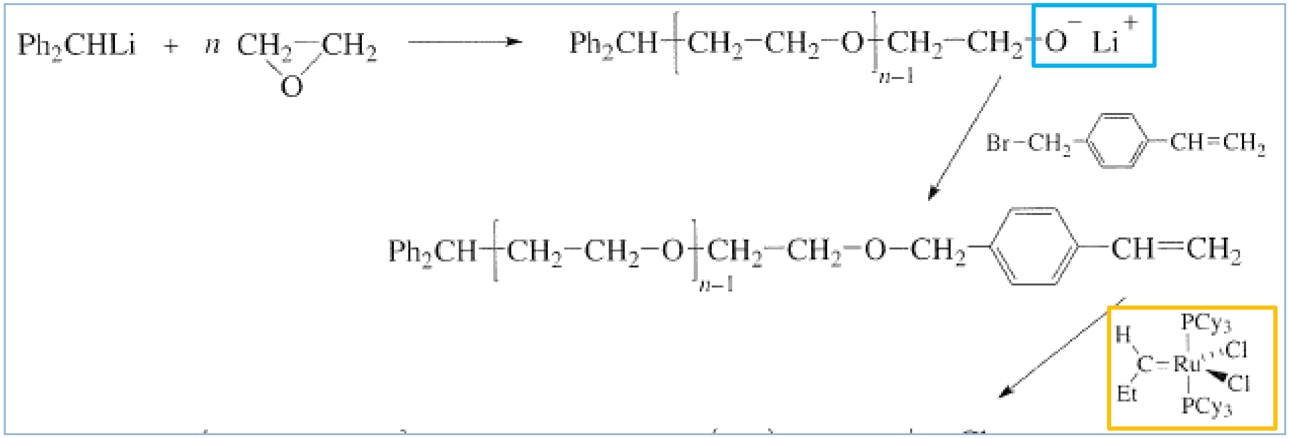
Block copolymer by tandem approach

- convert end-group of a (commercial) polymer to initiating functional group

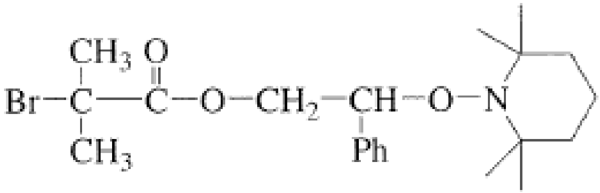


- transform living end to initiating functional group



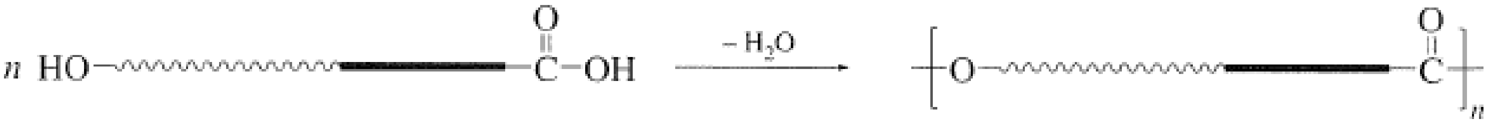


- using dual-function initiator

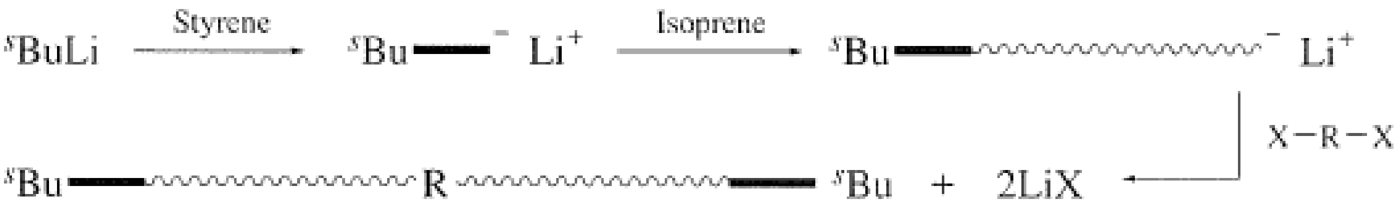


Block copolymer by coupling

- general methods
  - step polym'n of functionalized (co)polymers

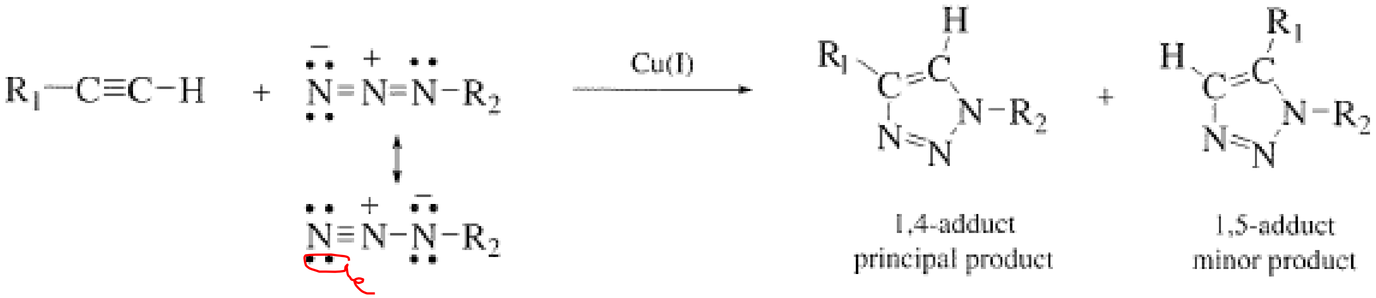


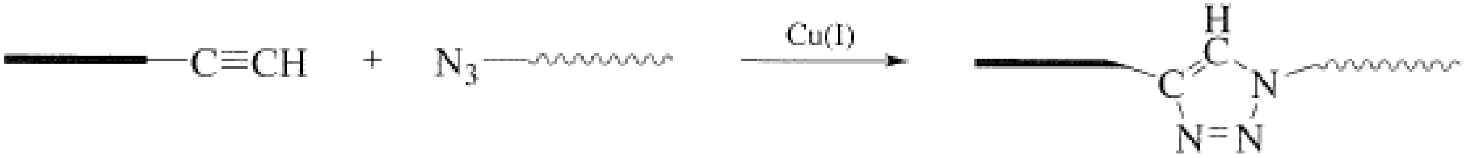
  - linking living chain ends (with X-R-X)



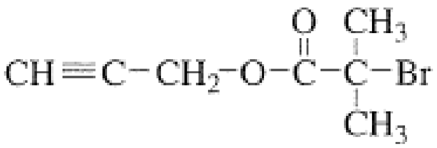
  - hard to be complete and give contamination
    - due to low conc'n of functional groups
    - contamination like homopolymers has to be removed
      - often not possible

- using ‘click chemistry’
  - fast, high selectivity, high yield, no side rxn, ---
- Huisgen cycloaddition

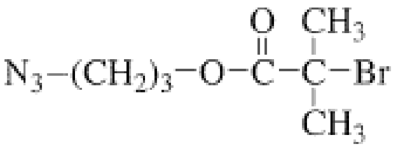




  - converting end-group of polymer, or
  - using initiator or terminator of living polym’n



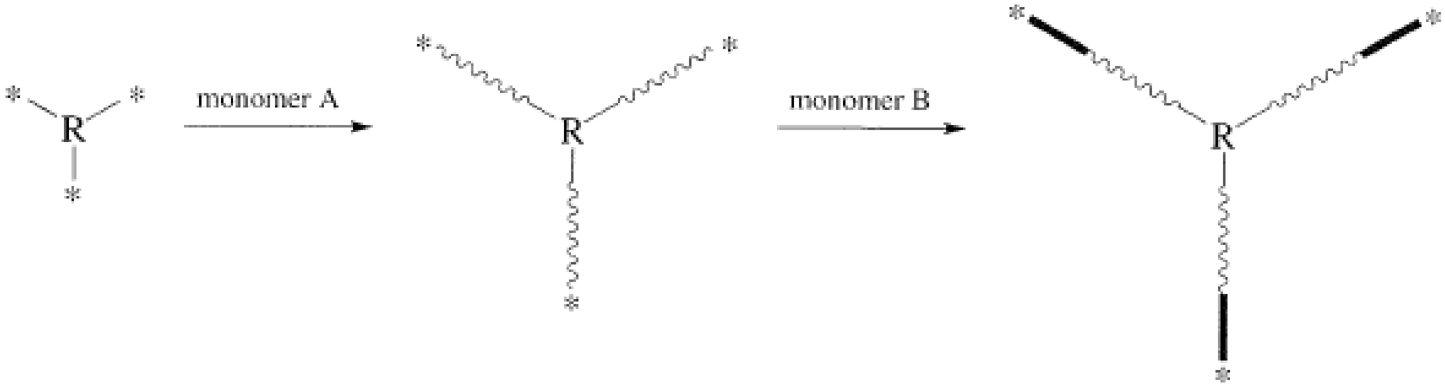
$CH\equiv C-CH_2-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br$



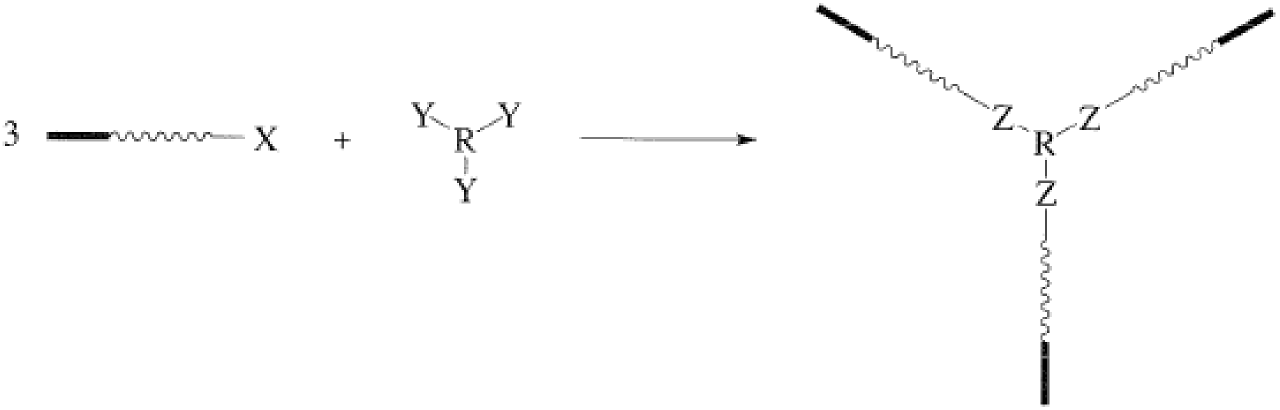
$N_3-(CH_2)_3-O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Br$

Non-linear block copolymer

- using multi-functional initiator

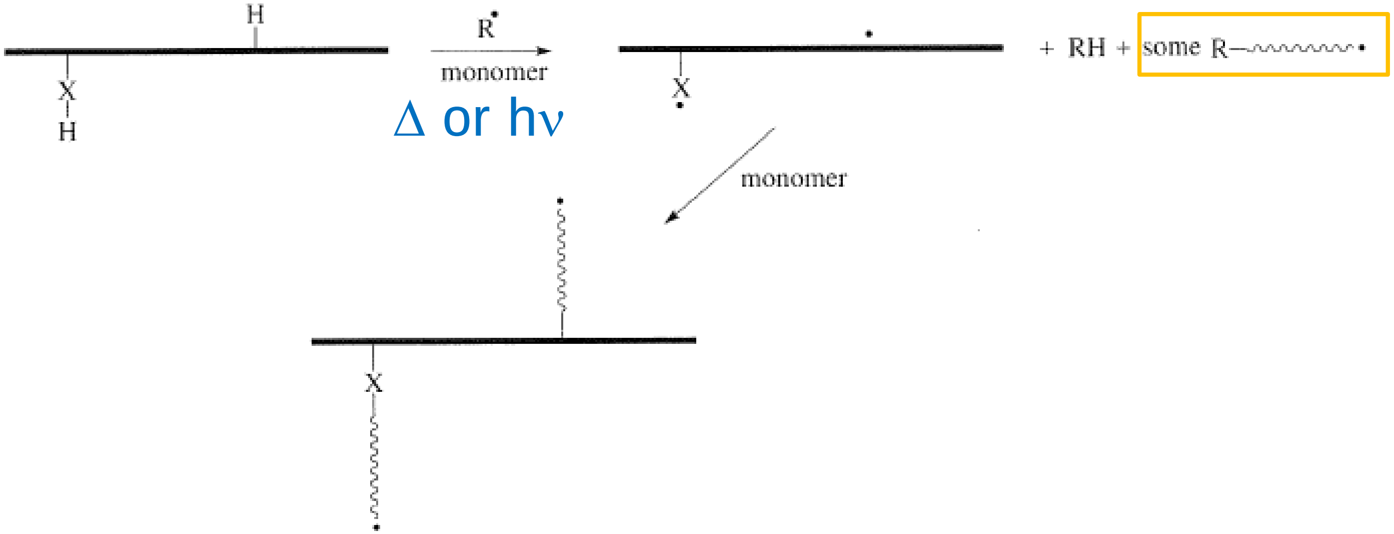


- linking block copolymer with multi-functional reagent



Graft copolymer synthesis

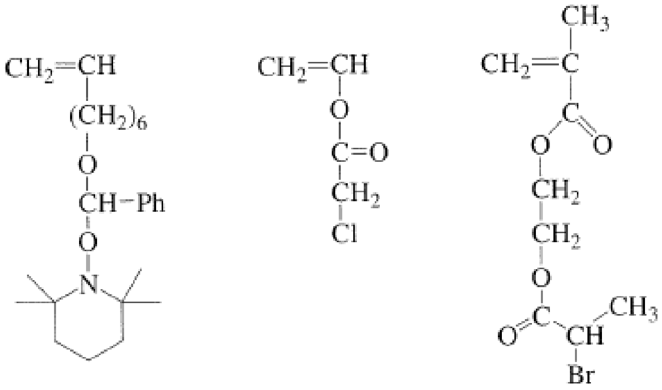
- ‘grafting from’ backbone
  - direct formation of radical on the backbone

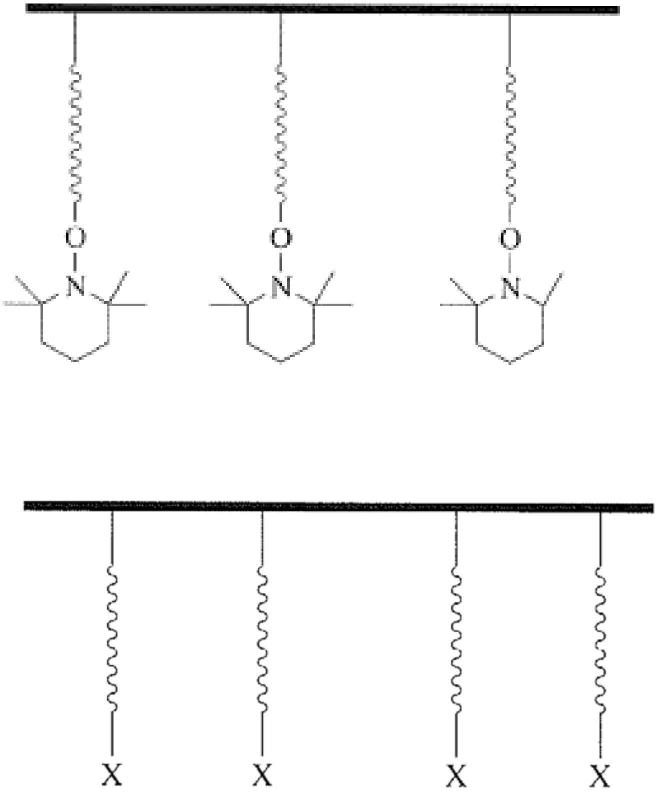


  - enhanced by copolym’n with small portion of reactive group (like $-CH_3$ or = (diene))
  - simple and versatile, but not controlled and contamination

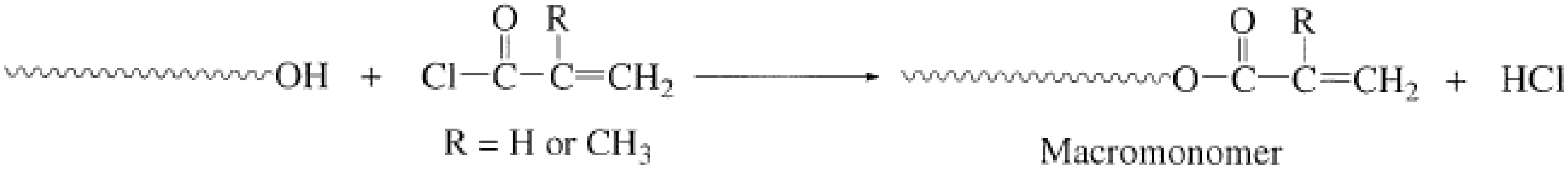
Graft copolymer synthesis

- ‘grafting from’ backbone (cont’d)
  - using LRP





- using macro(mono)mer
  - by converting chain-end to =

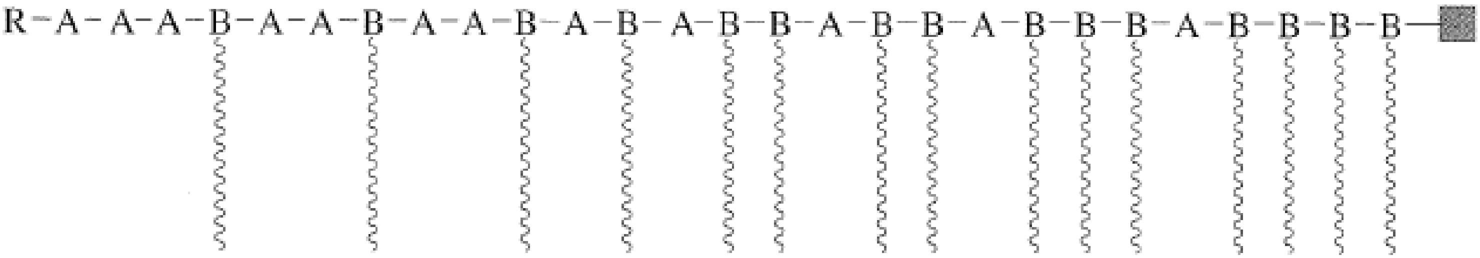


$$\sim\sim OH + Cl-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{C}=CH_2 \longrightarrow \sim\sim O-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{C}=CH_2 + HCl$$

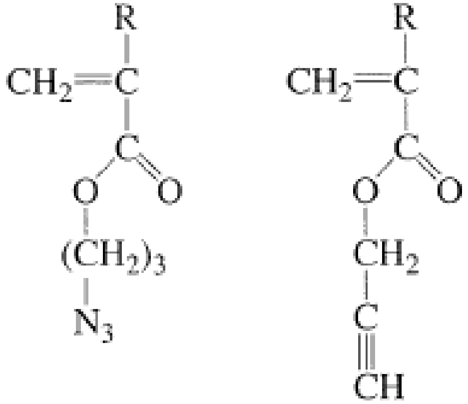
$R = H$ or CH_3

Macromonomer

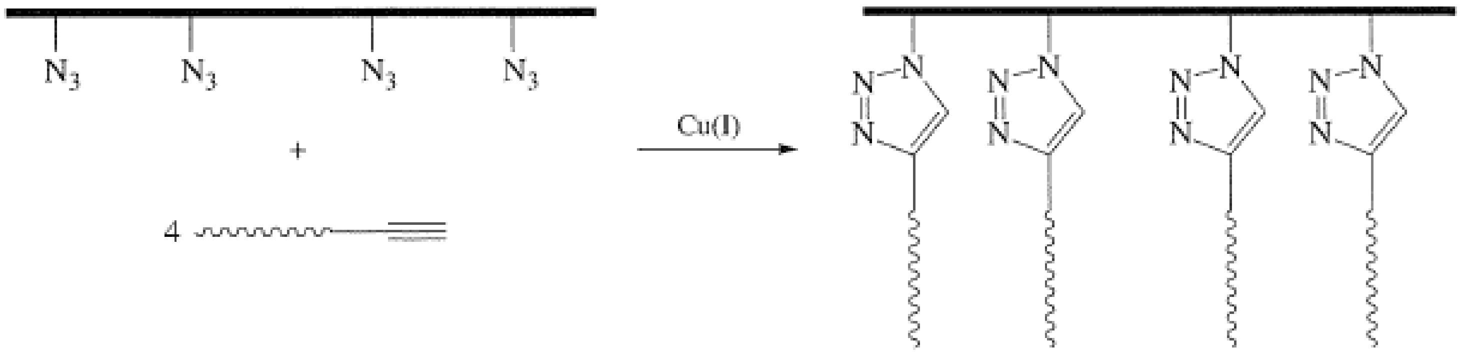
  - by catalytic chain transfer p80
  - random, tapered, or block sequence
    - depending on A and B



- ‘grafting onto’ backbone
  - copolymerization of backbone with



  - and ‘grafting onto’



Why block (and graft) copolymer?

- TPE
  - SBS, polyester TPE, TPU
- template for
  - functional materials
  - nanocomposites
  - lithography
- drug delivery
  - stimuli-sensitive block