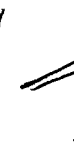
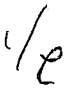
one half (less initiator → bigger $\bar{x}_n$)

$$\bar{x}_n \propto [M]$$

$$\bar{x}_n \propto [I]^{-\frac{1}{2}}$$

Monomer Reactivity

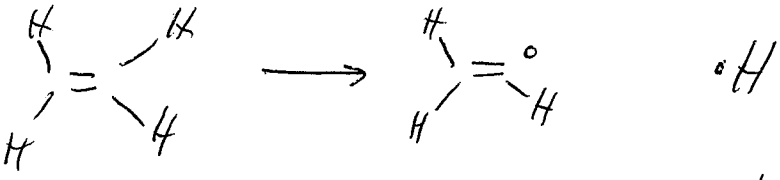
In General  will react to form polymers while  will not.

This is specifically true for radical polymerizations with some exceptions.

For example when side reactions occur due to the presence of an abstractable hydrogen atom in the monomer.

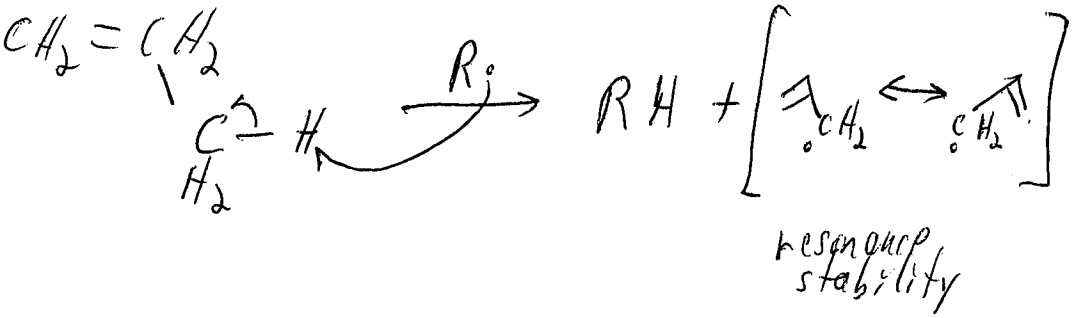
$$CH_2=CH_2 \xrightarrow{R\cdot} R\cdot CH_2-CH_2\cdot$$

Ethylene will polymerize radically.

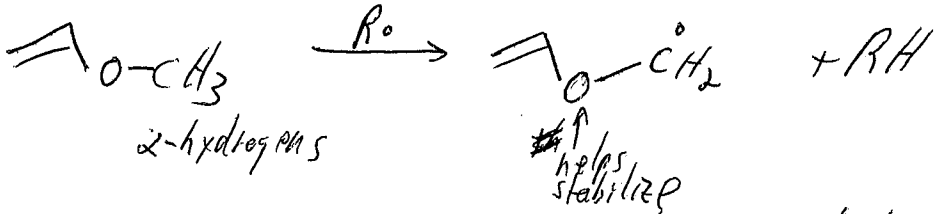


The dissociation energy for one hydrogen is 104 kcal/mole. This is about the same as methane (the methyl radical is the least stable of those discussed.)

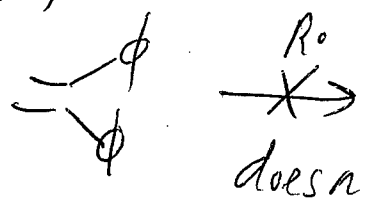
The radical polymerization of propylene is impossible due to the presence of allylic hydrogens,



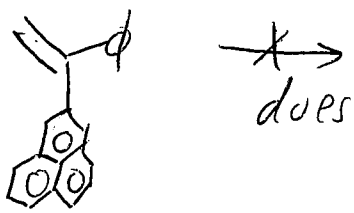
Vinyl ethers (with α-hydrogens) have similar problems,



The oxygen in the radical helps to stabilize the electron desficient group. Molecules with steric hindrance do not polymerize radically,

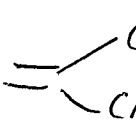


does not polymerize

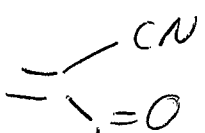


does not polymerize

When the monomer has two strong resonance electron withdrawing groups,

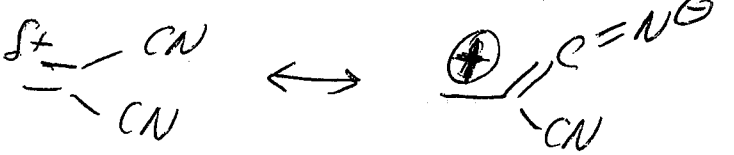


1,1 diethylcyanolene

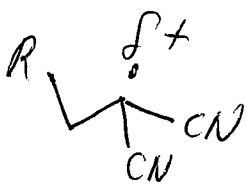


Crazy Glue
Cyanoacrylic

radical polymerization cannot occur. (Kinetic inhibition)
These monomers can be anionically polymerized. 1,1-diethyl cyanolene has two resonance structures which give the monomer added stability

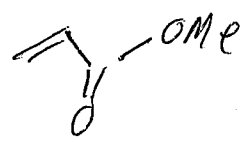
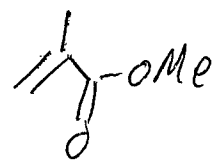
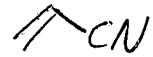
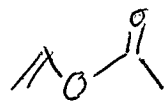
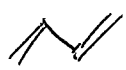


It can, however, be copolymerized through the use of an ethylene monomer. The positively charged growing polymer repells the positively charged monomer,



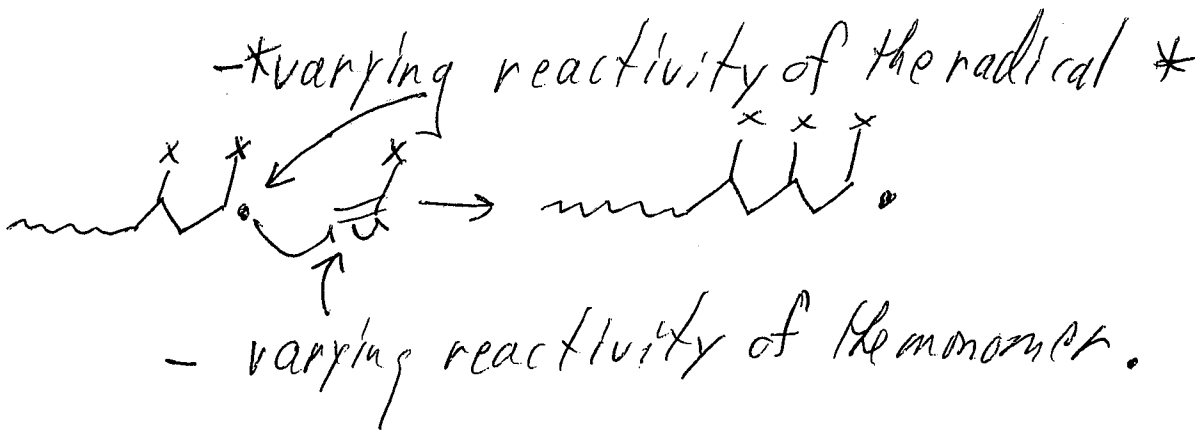
In general most monomers polymerize radically.

Relative Reaction Rates

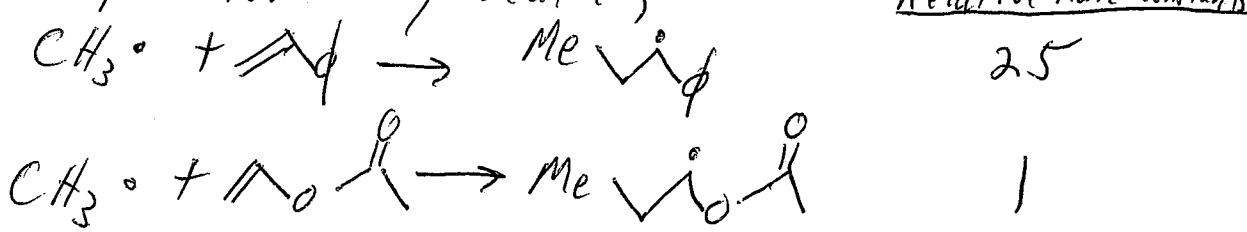
Monomer		K_p l/mole sec	
Methyl acrylate		2090	due to -Steric effects -Tertiary radical is more stable than the di substituted
Methyl methacrylate		705	
Acrylonitrile		1960	
Methyl Acrylonitrile		184	
Styrene		145	
Vinyl Acetate		2300	
Vinyl chloride		12300	More reactive chlorine radical than in butadiene
Butadiene		100	

The above listed values for K_p vary drastically. There are only two possible factors which would cause such differences

In reactivity,



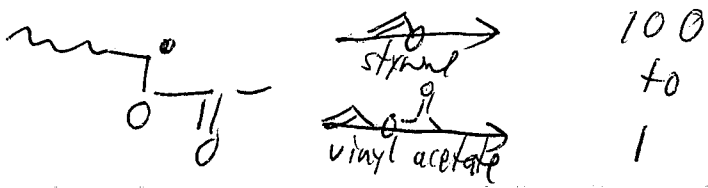
<u>Only the varying reactivity of the radical is important.</u> This is supported by the fact that vinyl acetate reacts sixteen times as fast as styrene, and by the following data,



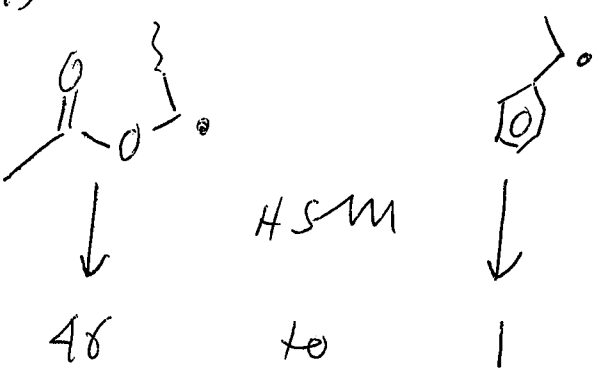
It is seen above that the methyl radical reacts twenty-five times faster with styrene than with vinyl acetate and

yet vinyl acetate reacts sixteen times faster when alone. Thus, the reactivity of the monomer does not control the overall reactivity. (It is important to compare side by side and competative reactions as above in analysizing kinetic data.)

~~The Chain Reactivity of the~~ The following reaction also ~~two monomers can~~ also be compared. supports the above conclusion that the radical reactivity determines the overall reactivity,

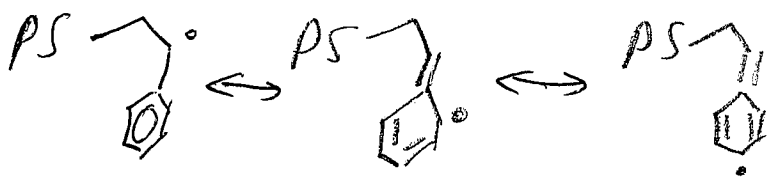


Styrene is preferred in this reaction i.e. styrene monomer is much more reactive. The <u>chain reactivity</u> can be tested with HSM since the S-H bond is weaker than the C-H bond (a carbon radical can abstract the "S-H" hydrogen)



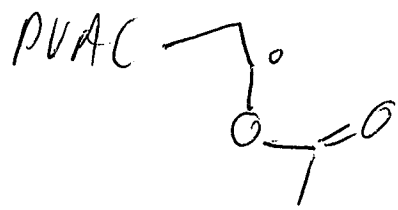
These results conclusively point out that the reactivity of the monomer does not control the rate of polymerization, this is controlled by the reactivity of the

chain end radical. On the end of the polystyrene chain the radical has three resonance structures and is more stable and thus less reactive.



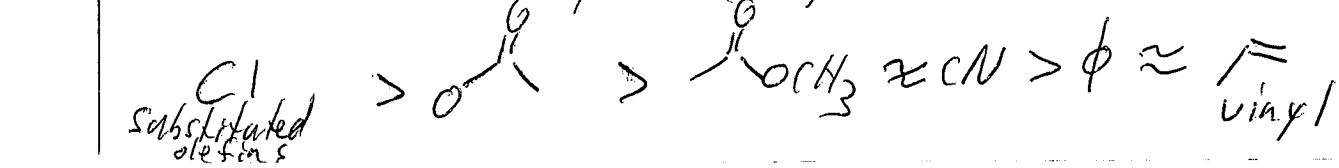
?

The polyvinyl acetate chain end radical has no resonance structures and is therefore less stable and more reactive.



No Resonance

The reactivity of the chain end radicals follows the following order:



COPOLYMERS

There are four classes of copolymers

① statistical — Enter the chain randomly obeying statistical laws

② Alternating

homopolymers linked together { ③ Block, ④ Graft

$$-(M_1)_x-(M_2)_y-(M_3)_z-$$

It is observed that the copolymer composition differs from the feed composition. In 1944 Lewis and Mayo proposed the Terminal Kinetic Model. This model is based on the assumption that only the terminal unit determines the reactivity. (~~~ $M_1^\bullet$)

There are four possible combinations for a copolymer

$$\sim M_1^{\bullet} + M_1 \xrightarrow{K_{11}} \sim M_1 M_1^{\bullet}$$

$$\sim M_1^{\bullet} + M_2 \xrightarrow{K_{12}} \sim M_1 M_2^{\bullet}$$

$$\sim M_2^{\bullet} + M_1 \xrightarrow{K_{21}} \sim M_2 M_1^{\bullet}$$

$$\sim M_2^{\bullet} + M_2 \xrightarrow{K_{22}} \sim M_2 M_2^{\bullet}$$

We have,

$$-\frac{d[M_1]}{dt} = K_{11}[M_1^{\bullet}][M_1] + K_{21}[M_1][M_2^{\bullet}]$$

and

$$-\frac{d[M_2]}{dt} = K_{12}[M_2][M_1^{\bullet}] + K_{22}[M_2^{\bullet}][M_2]$$

The Copolymer Composition Ratio is given by

$$= \frac{\frac{d[M_1]}{dt}}{\frac{d[M_2]}{dt}} = \frac{K_{11}[M_1^{\bullet}][M_1] + K_{21}[M_1][M_2^{\bullet}]}{K_{12}[M_2^{\bullet}][M_1] + K_{22}[M_2^{\bullet}][M_2]}$$

$$= \frac{m_1}{m_2}$$

#moles m_1 & m_2 in the copolymer

At Low Conversions

As the conversion proceeds the seed is depleted. The $[M_\cdot]$'s are unknown. Thus the steady state approximation is used,

$$K_{12}[M_1\cdot][M_2] = K_{21}[M_2\cdot][M_1]$$

The number of $[M_1\cdot]$ terminated chains changing to $[M_2\cdot]$ terminated chains equals the number of $[M_2\cdot]$ terminated chains changing to $[M_1\cdot]$ terminated chains. $\therefore$ the number of $[M_1\cdot]$ and $[M_2\cdot]$ terminated chains remains constant.

Thus,

$$\frac{m_1}{m_2} = \frac{\left[\frac{K_{11}[M_1\cdot][M_1]}{K_{12}[M_1\cdot][M_2]} + 1\right]}{\left[\frac{K_{22}[M_2\cdot][M_2]}{K_{21}[M_2\cdot][M_1]} + 1\right]} = \frac{\left[\frac{K_{11}}{K_{12}}\frac{[M_1]}{[M_2]} + 1\right]}{\left[\frac{K_{22}}{K_{21}}\frac{[M_2]}{[M_1]} + 1\right]}$$

$$r_1 = \frac{K_{11}}{K_{12}} \qquad r_2 = \frac{K_{22}}{K_{21}}$$

$$\frac{m_1}{m_2} = \frac{\left[r_1\frac{[M_1]}{[M_2]} + 1\right]}{\left[r_2\frac{[M_2]}{[M_1]} + 1\right]} = \frac{r_1[M_1]^2 + [M_1][M_2]}{[M_2]\left(r_2[M_2] + [M_1]\right)}$$

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]} \quad \frac{r_1[M_1]+[M_2]}{[M_1]+r_2[M_2]}$$

$$r_1 = \frac{K_{11}}{K_{12}}$$

$$r_2 = \frac{K_{22}}{K_{21}}$$

A number of special cases will be considered.

Case ①

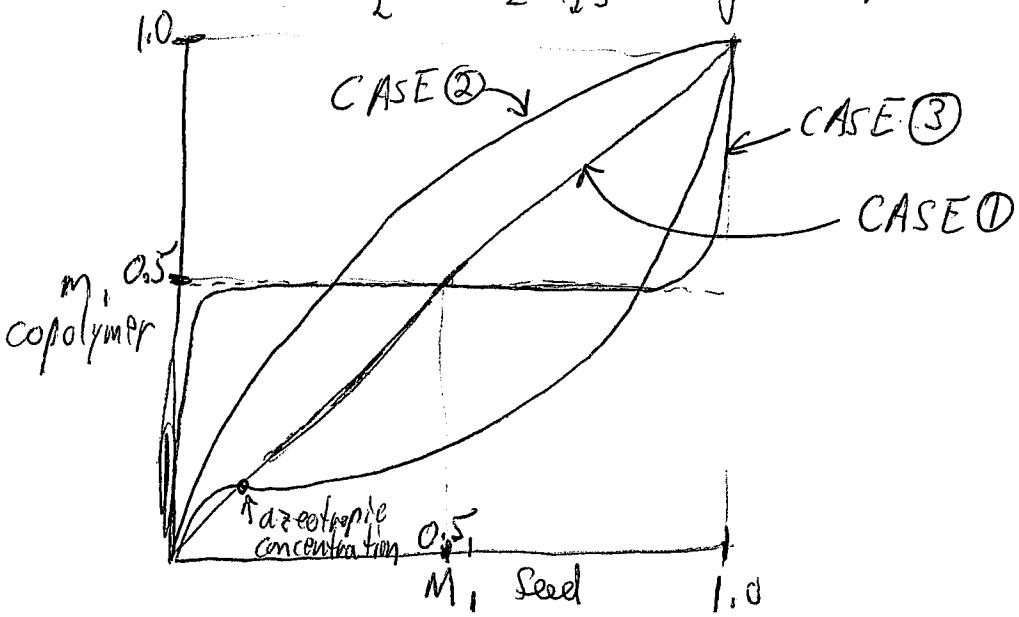
Homopropagation rate = Copropagation Rate

$$r_1 = r_2 = 1$$

This is the Bernullian statistical case

$$\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]}$$

the copolymer composition is given by the feed composition



Case ②

$r_1 = \frac{1}{r_2}$

M_1° adds M_2 at the same rate as M_2° adds M_1

$$\frac{m_1}{m_2} = \frac{r_1 \frac{[M_1]}{[M_2]} + 1}{r_2 \frac{[M_2]}{[M_1]} + 1} = \frac{r_1 [M_1]}{[M_2]}$$

∴ the copolymer is richer in the more reactive monomer

Case ③

$r_1 = r_2 \cong 0$

neither chain end adds its own type of monomer

⇓

an alternating copolymer

$\frac{m_1}{m_2} = 1$

Case ④

$r_1 < 1$
$r_2 < 1$

As $r_1 r_2 \Rightarrow 0$ the tendency to alternate increases

In this case an azeotropic composition forms. For the azeotropic composition

$$\left(\frac{m_1}{m_2} = \frac{[M_1]}{[M_2]}\right)_{\text{Azeotrope}}$$

or

$$r_1[M_1] + [M_2] = [M_1] + r_2[M_2]$$

$$\therefore \quad \boxed{\frac{[M_1]}{[M_2]} = \frac{r_2 - 1}{r_1 - 1}}_{\text{Azeotrope}}$$

$r_1 \frac{m_1}{m_2} = \frac{m_1}{m_2} + r_2$

$-1 + r_2 = \frac{m_1}{m_2}(-1 + r_1)$

Case ⑤ $r_1 > 1$
$r_2 > 1$

This case leads to a mixture of homopolymers or a "blocky" copolymer