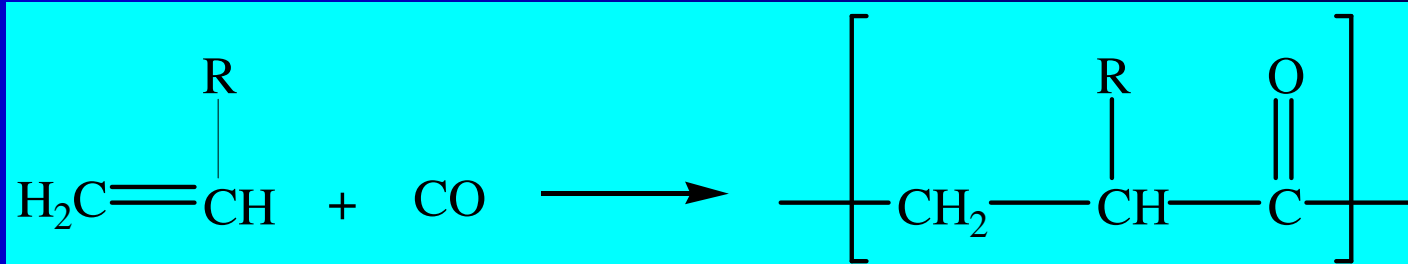


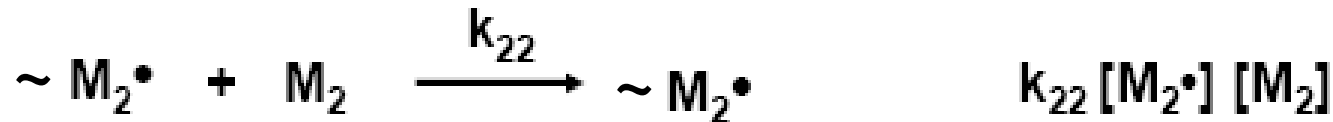
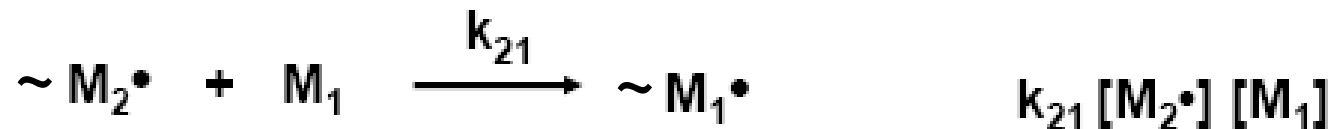
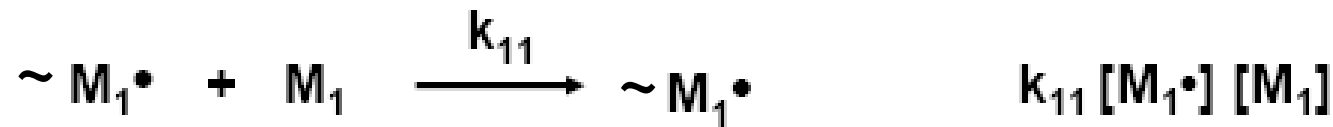
Macromolecular Chemistry



Free Radical Co-polymerization

Reaction

Rate



where k_{11} and k_{22} : **self-propagation** rate constant

k_{12} and k_{21} : **cross-propagation** rate constant

Assume chain end concentrations are constant at “steady state”

o Monomer reactivity ratio

$$\frac{k_{11}}{k_{12}} = r_1 \quad \frac{k_{22}}{k_{21}} = r_2$$

If $r_1 > 1$ this means that $\sim M_1 \cdot$ adds M_1 more readily than M_2 . If r_1 is zero then M_1 does not undergo homopolymerization!!

o Copolymer (composition) equation

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right)$$

This important relationship can be expressed in terms of mole fractions rather than concentrations

o **Instantaneous composition** of feed and polymer

- f_1 = mole fraction of M_1 in the **feed**
- f_2 = mole fraction of M_2 in the **feed**
- F_1 = mole fraction of M_1 in the **copolymer**
- F_2 = mole fraction of M_2 in the **copolymer**

Copolymerization Equation

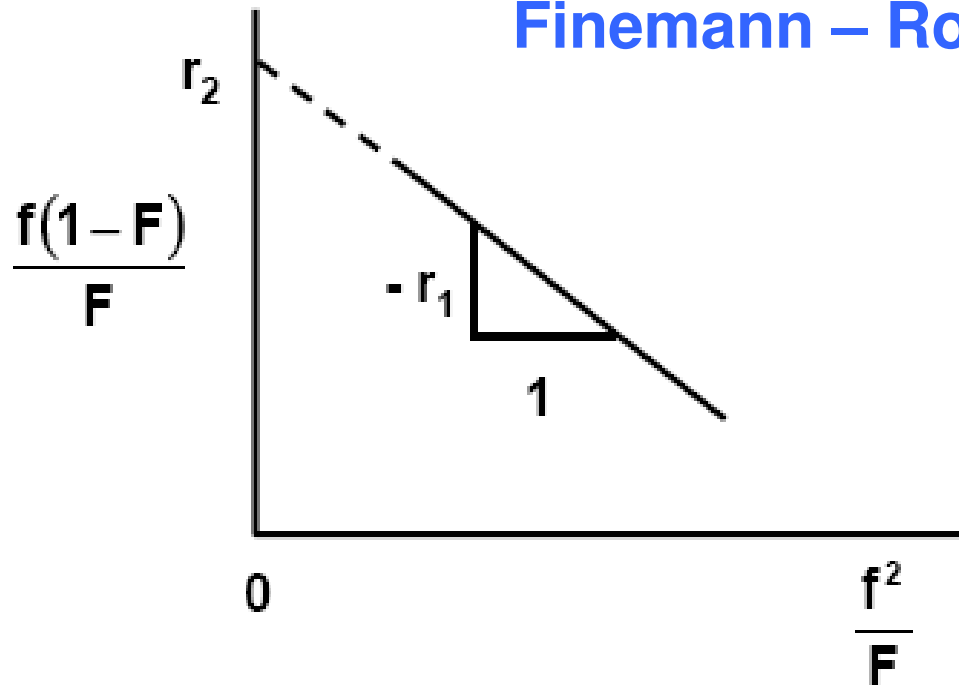
$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2}$$

This gives the Instantaneous mole fraction of M_1 in the copolymer

Finemann-Ross Equation

$$\frac{f(1-F)}{F} = r_2 - \left(\frac{f^2}{F}\right)r_1$$

Finemann – Ross Equation



Reactivity Ratios

M_1	M_2	r_1	r_2	Temperature($^{\circ}C$)
Styrene	Methyl methacrylate	0.52	0.46	60
Styrene	Acrylonitrile	0.40	0.04	60
Styrene	Vinyl acetate	55	0.01	60
Styrene	Maleic anhydride	0.041	0.01	60
Styrene	Vinyl chloride	17	0.02	60
Styrene	1,3-Butadiene	0.58	1.35	50
Styrene	Isoprene	0.54	1.92	80
Methyl methacrylate	Vinyl chloride	10	0.1	68
Methyl methacrylate	Vinyl acetate	20	0.015	60
Methyl methacrylate	Acrylonitrile	1.20	0.15	60
Methyl methacrylate	1,3-Butadiene	0.25	0.75	90
Ethylene	Tetrafluoroethylene	0.38	0.1	25
Ethylene	Acrylonitrile	0	7	20
Ethylene	Vinyl acetate	0.97	1.02	130

Let's actually calculate r_1 and r_2 from some data

We run the copolymerization for a very short time starting with different weight ratios of 2 monomers. The assumption is that f does not change in this experiment

We isolate the small amount of polymer generated and determine the ratio of monomers incorporated....by nmr, for example

We apply the Fineman-Ross analysis and extract the reactivity ratios.



Chris



1) $r_1 = r_2 = 1$

No preference for homopolymerization or copolymerization

→ Random copolymer

$$F_1 = f_1$$

e.g. $M_1 = \text{ethylene}$ $M_2 = \text{vinyl acetate}$
 $r_1 = 0.97$ $r_2 = 1.02$

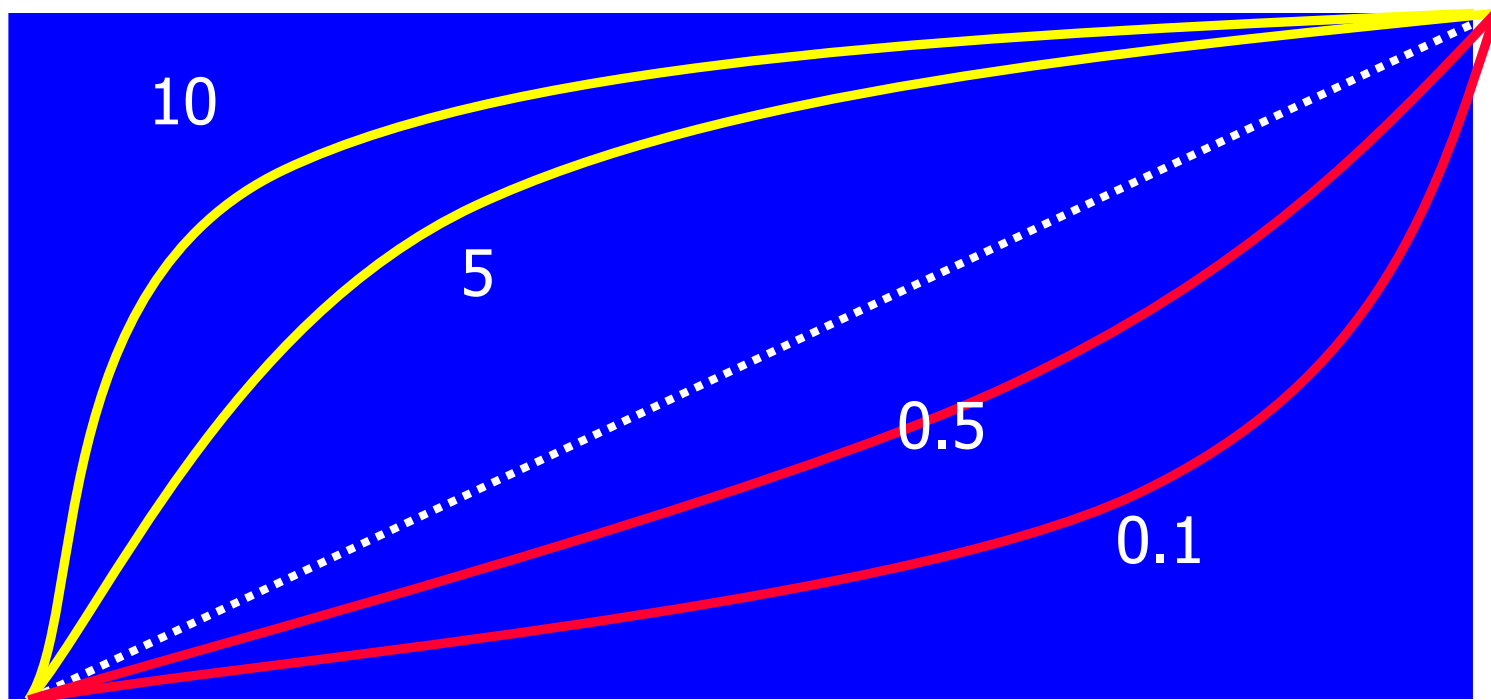
2) $r_1 = r_2 = 0$

Alternating copolymer

$$F_1 = 0.5$$

e.g. $M_1 = \text{styrene}$ $M_2 = \text{maleic anhydride}$
 $r_1 = 0.041$ $r_2 = 0.01$

$r_1 > 1, r_2 < 1$ or $r_1 < 1, r_2 > 1$



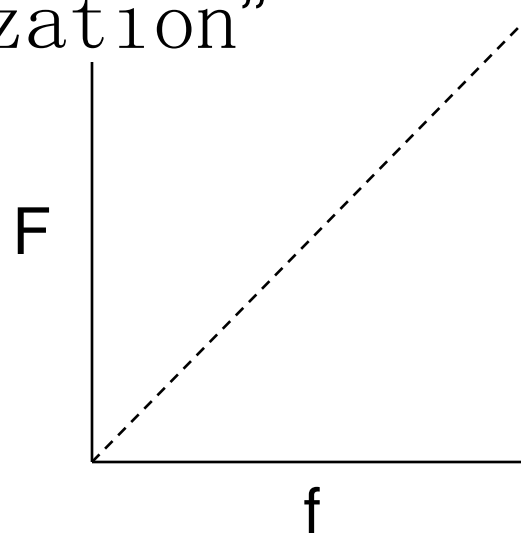
If $r_1 > 1$ ($k_{11} > k_{12}$) and $r_2 < 1$ ($k_{22} < k_{21}$) then M_1 is more active than M_2 whether either \tilde{M}_1 and \tilde{M}_2 . F_1 is always larger than f_1 and the curve is always above the diagonal.

The situation is similar for $r_1 < 1, r_2 > 1$ but the curve is below the diagonal.

Ideal copolymerization

as $r_1 \times r_2 = 1$ ($r_2 = 1/r_1$), it becomes an “ideal copolymerization”

$$\frac{d[M_1]}{d[M_2]} = r_1 \frac{[M_1]}{[M_2]}$$



In this case $\sim M_1 \cdot$ and $\sim M_2 \cdot$ have the same preference for adding either of the two monomers.

Azeotropic copolymerization

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]}$$

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

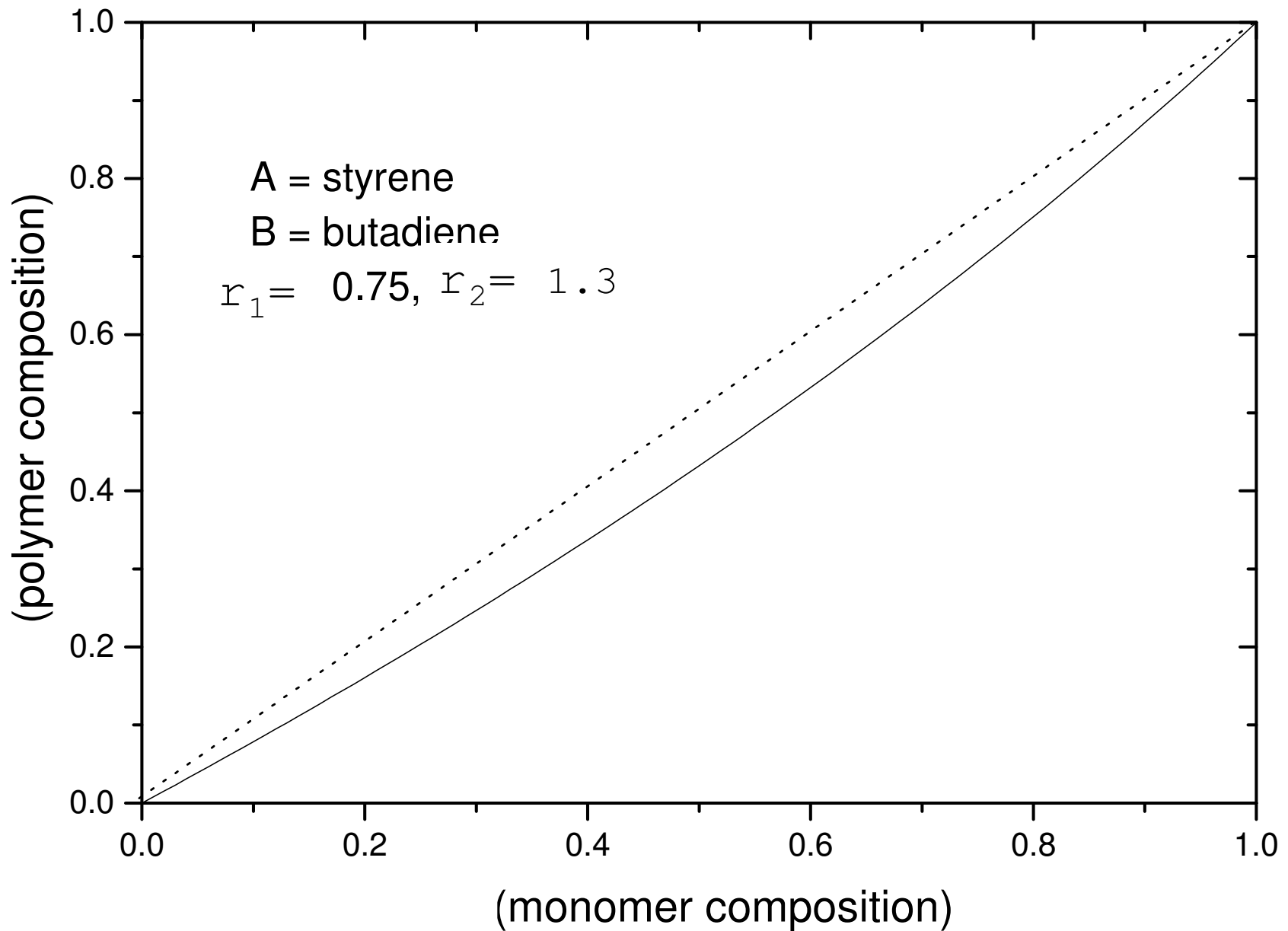
$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left(\frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right)$$

$$\frac{[M_1]}{[M_2]} = \frac{1 - r_2}{1 - r_1}$$

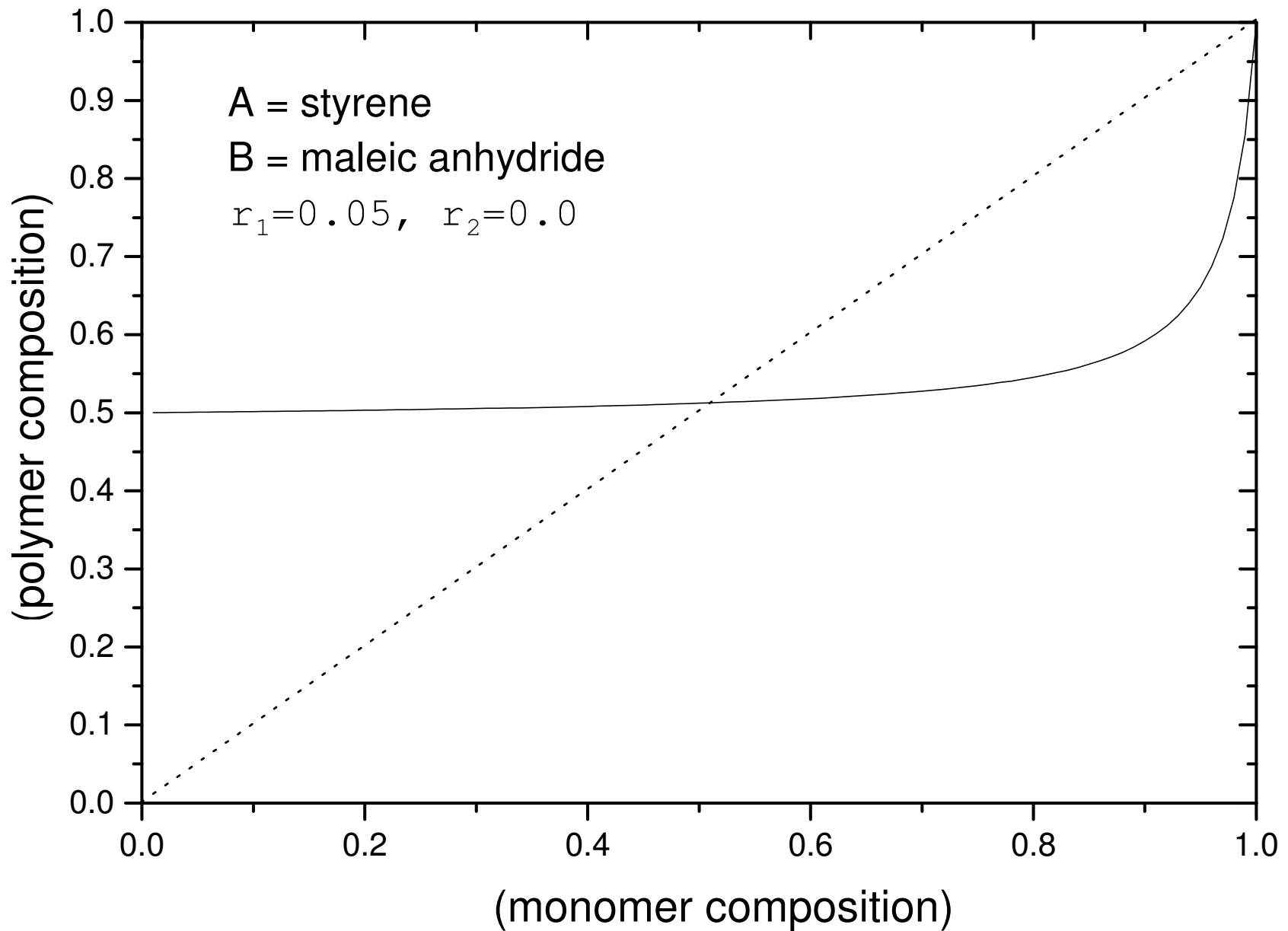
$$f_1 = \frac{1 - r_2}{2 - r_1 - r_2}$$

Condition under which F , the mole fraction of monomer in the polymer and f , the mole fraction in the feed remain constant through the whole polymerization....that is, these ratios are not a function conversion

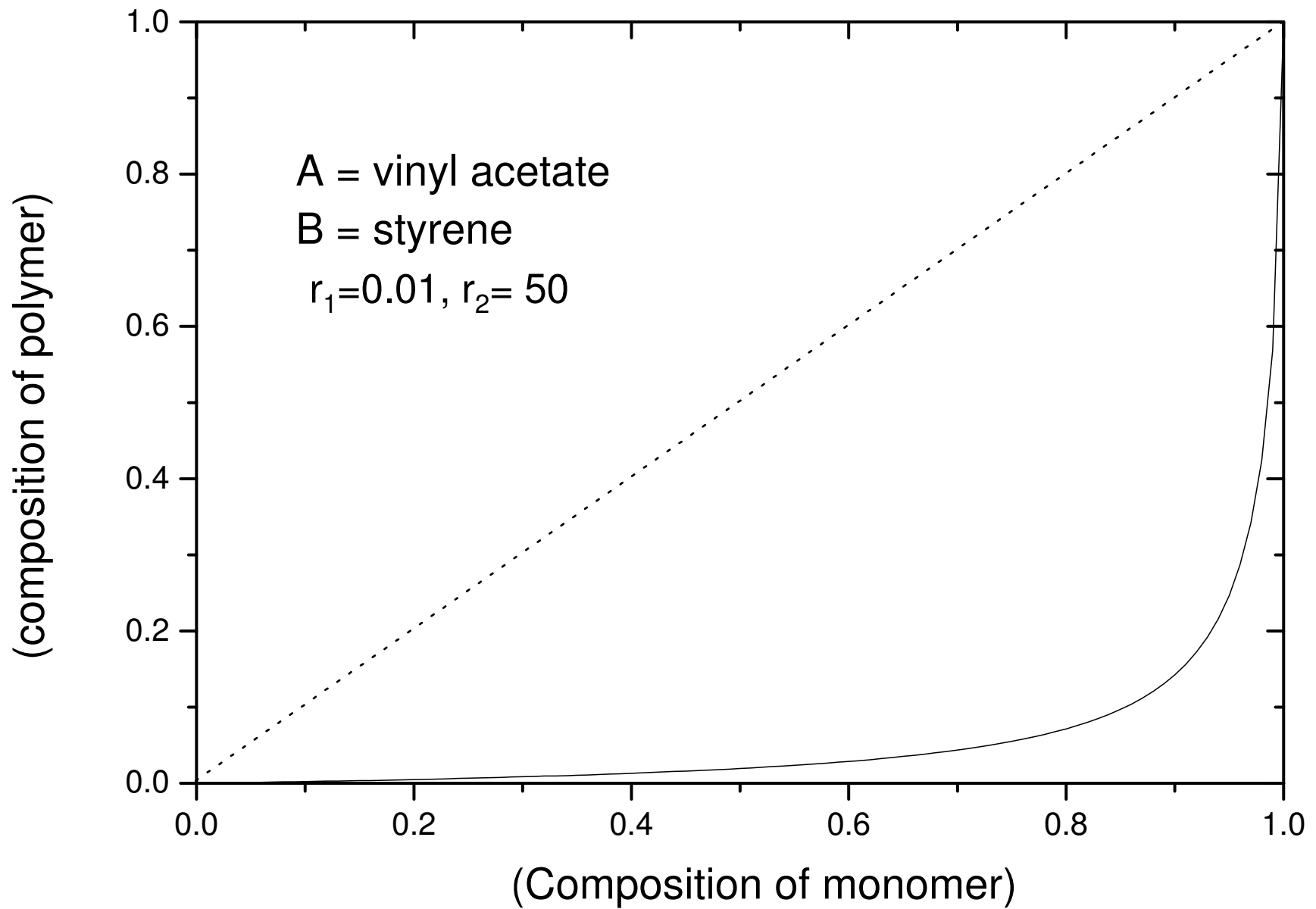
Ideal copolymer



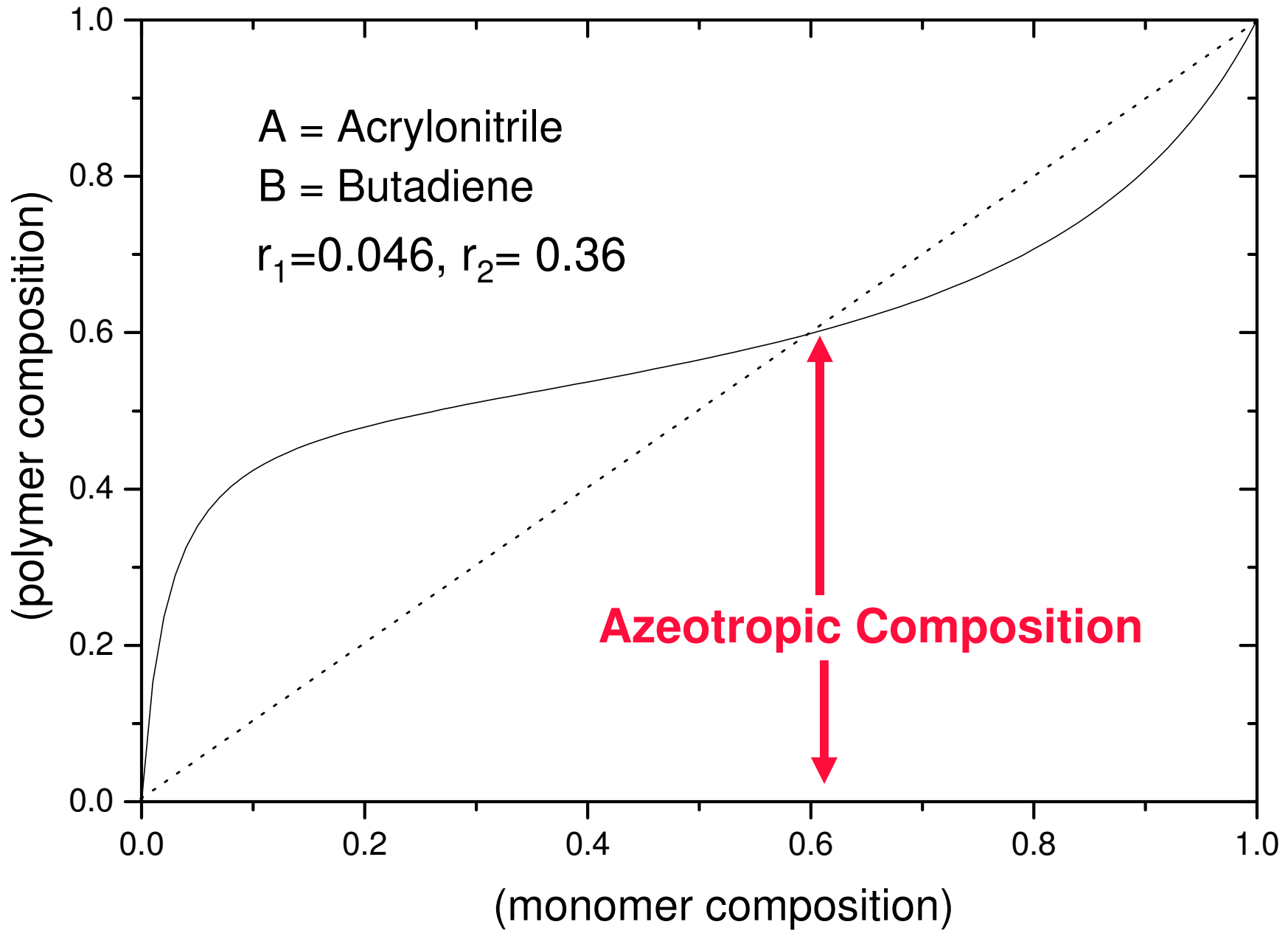
Alternating Copolymer



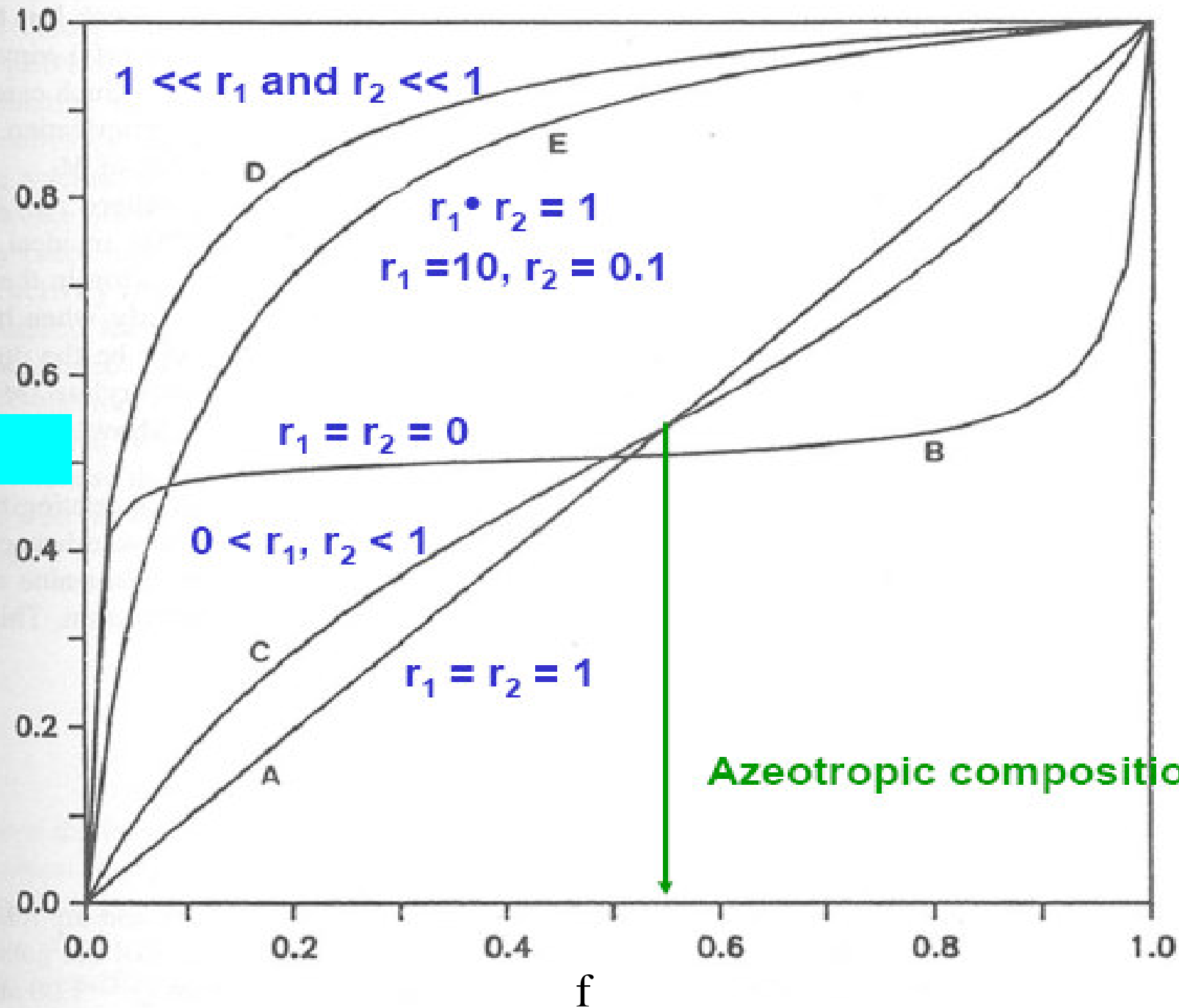
Rich in one monomer



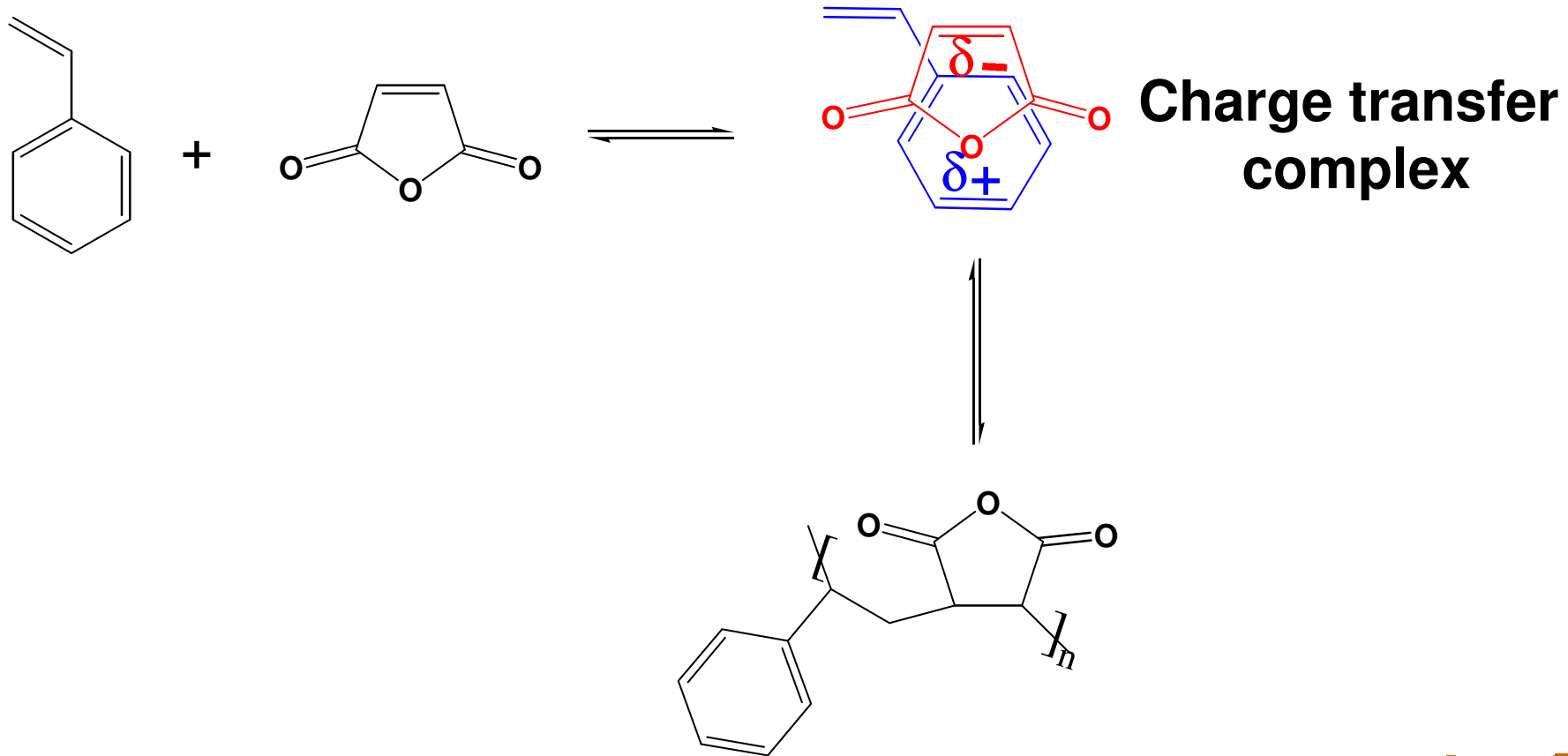
Quite typical copolymerisation



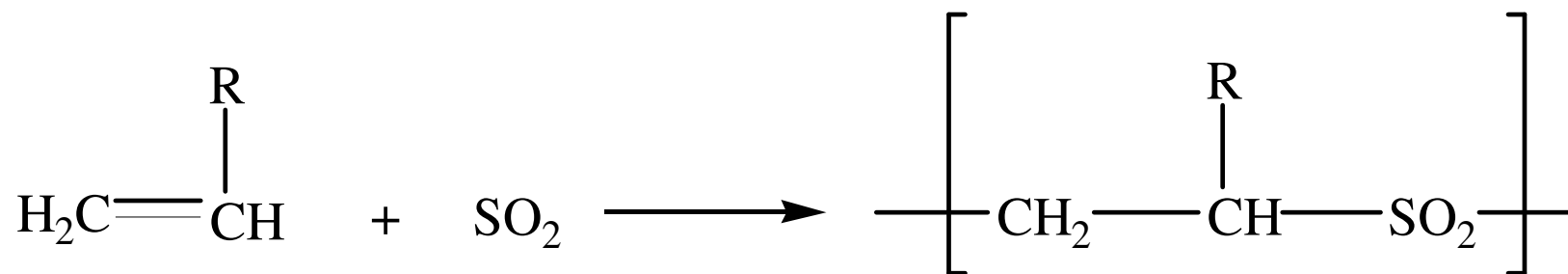
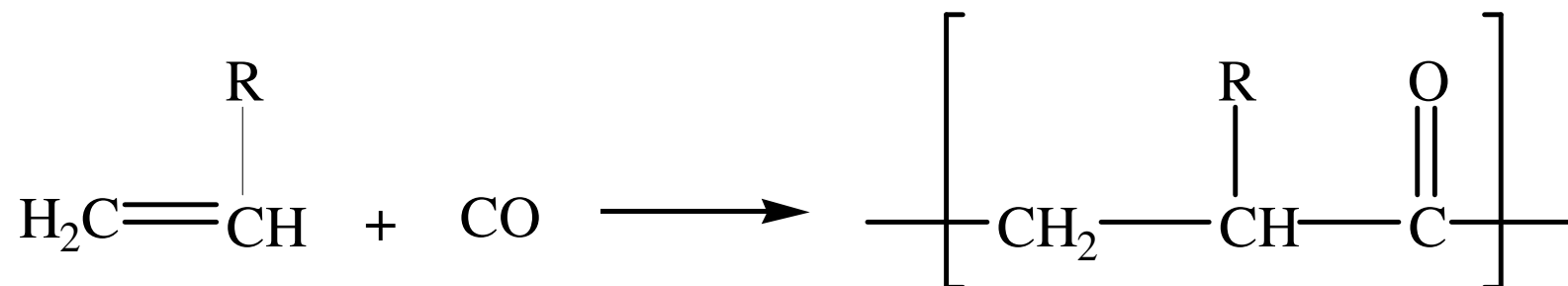
F



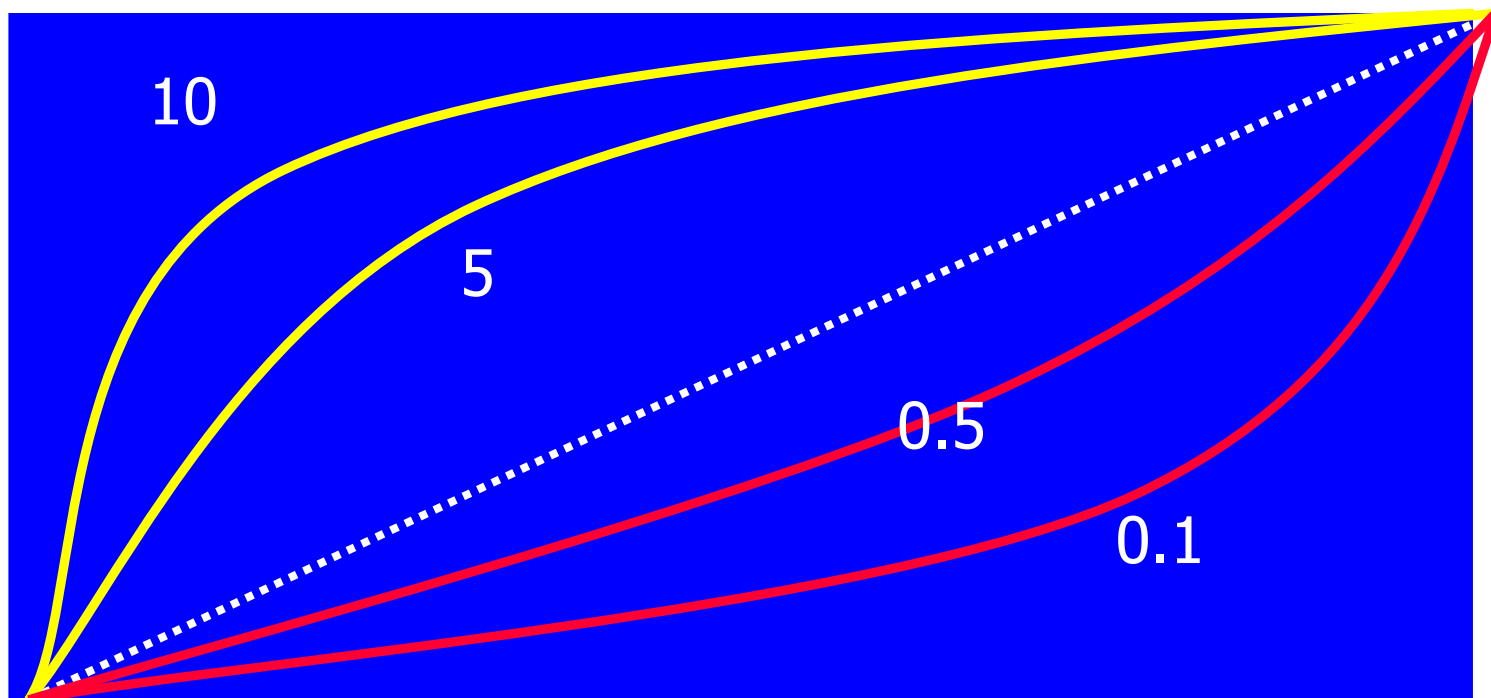
Poly(styrene-alt-maleic anhydride)



Charge transfer complex polymerization (alternating copolymer).



$$r_1 > 1, r_2 < 1 \quad \text{or} \quad r_1 < 1, r_2 > 1$$



If $r_1 > 1$ ($k_{11} > k_{12}$) and $r_2 < 1$ ($k_{22} < k_{21}$) then M_1 is more active than M_2 whether either \tilde{M}_1^* and \tilde{M}_2^* . F_1 is always larger than f_1 and the curve is always above the diagonal.

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Reactivity Ratios

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Methyl met				
Methyl met				
Methyl met				
Methyl met				
Ethylene				
Ethylene				
Ethylene	Vinyl acetate	0.97	1.02	130

What is constant here???

This is a bit discouraging!



Estimating Reactivity Ratios

measurement of r_1 and r_2 is possible by applying the Fineman Rose equation but it is a bit tedious!

copolymerization reactivity ratios (r_1 , r_2) depend on:

- temperature
- solvent
- mechanism of polymerization
- **pair** of monomers



development of a more general system

Q-e-scheme of Alfrey and Price

allows estimation of (radical) copolymerization reactivity ratios
of unknown pairs of monomers

Q-e-scheme of Alfrey and Price

- allows estimation of (radical) copolymerization reactivity ratios of unknown comonomers

- two parameters:

Q – value resonance stabilisation of radical

$0 < Q < 0.35$ poor stabilization
 $Q > 0.35$ good stabilization

e – value electro negativity of C=C-double bond

$e < 0$ electron rich
 $e > 0$ electron poor

- reference: styrene $Q = 1$ $e = - 0.8$

- calculation of reactivity ratios:

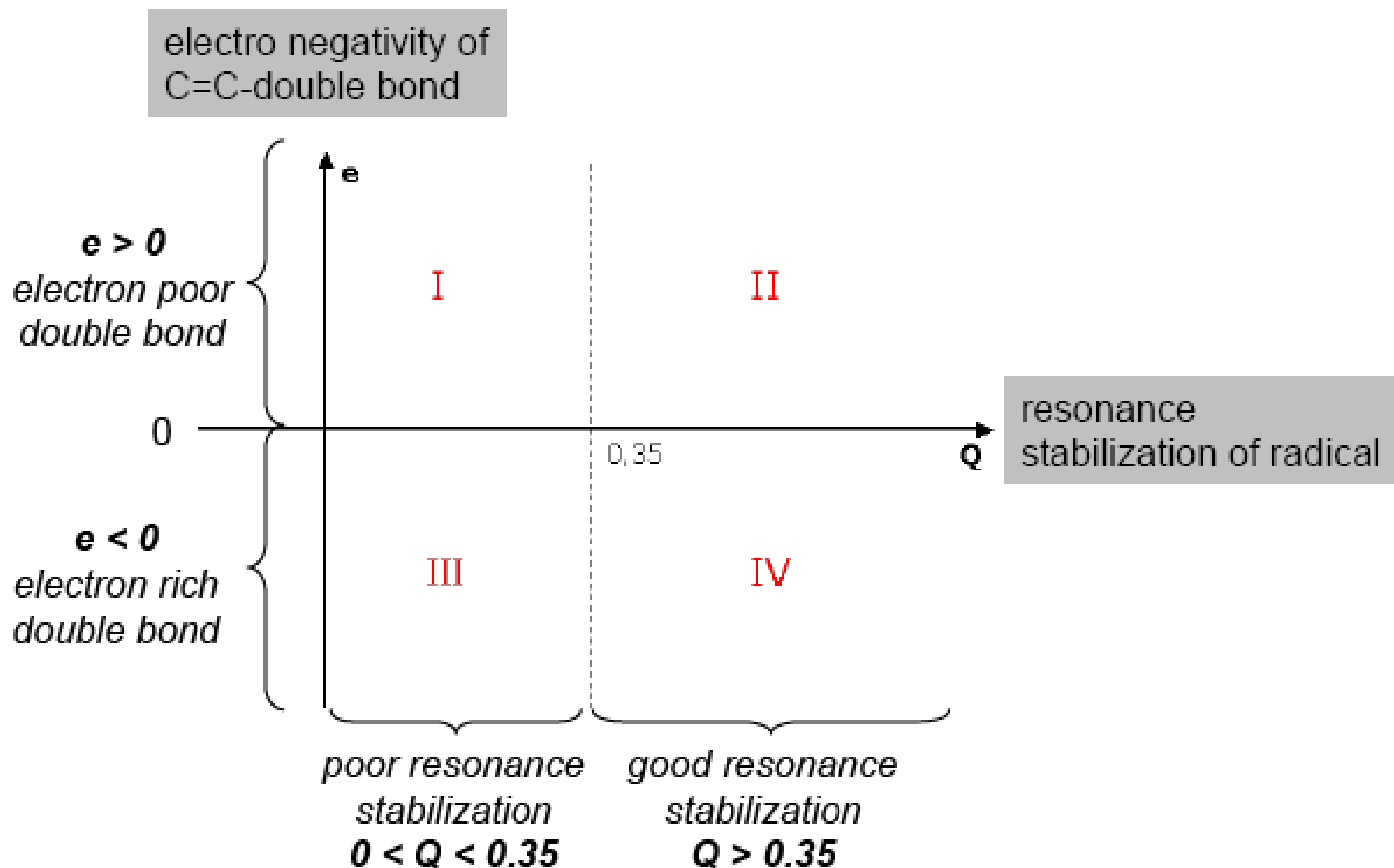
$$r_1 = \frac{Q_1}{Q_2} \cdot e^{(-e_1(e_1 - e_2))} \quad r_2 = \frac{Q_2}{Q_1} \cdot e^{(-e_2(e_2 - e_1))}$$

Q and e

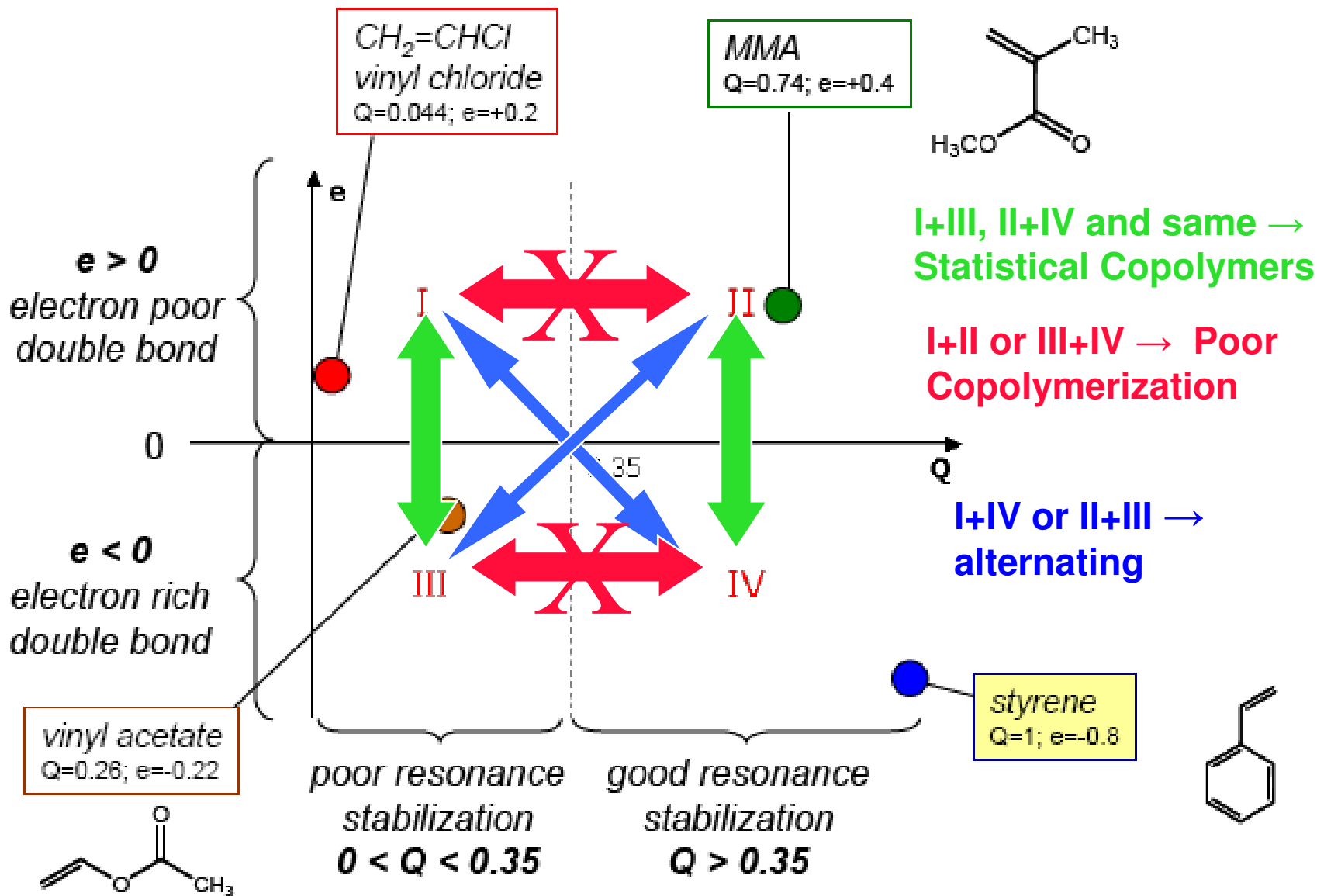
- Generalizations:

- This is a purely empirical relationship
- Q and e come from measurements of r_1 and r_2
- Ideal condition is same Q and e values
- Proceeds poorly if Q_1 and Q_2 are very different
- Tends toward alternating if Q's are the same and e's are large but of opposite sign.

Q-e-scheme of Alfrey and Price



Q-e-scheme of Alfrey and Price



Reactivity (Q) and Polarity (e) of Monomer

<i>Monomer</i>	Q	e
1-vinylnaphthalene	1.94	-1.12
p-Nitrostyrene	1.63	0.39
p-Methoxystyrene	1.36	-1.11
Methyl methacrylate	0.74	0.40
Acrylonitrile	0.60	1.20
Methyl acrylate	0.42	0.60
Vinyl chloride	0.044	0.20
Vinyl acetate	0.026	-0.22



Conclusions-radical copolymers

- **Co-polymers are important**
 - Properties depend on composition
- **In general, these materials are heterogeneous**
- **Mayo equation allows calculation of composition knowing r_1 and r_2**
- **Finemann Ross approach allows determination of r_1 and r_2**
- **Alfrey – Price allows estimate of r_1 and r_2**

What about step growth copolymers??

We discussed A B type step growth polymers -ABABABA-

If N_A^0 is the number of A molecules at the beginning of the polymerization and N_B^0 is the number of B molecules,

We define r , the **stoichiometric imbalance** as

$$r = \frac{N_A^0}{N_B^0}$$

If p is the conversion (as in Carothers equation) then fraction of B at p is $p N_A^0$ or $pr N_B^0$ and the number of unreacted groups N_A and N_B is ...

$$N_A = (1 - p)N_A^0 \quad N_B = (1 - pr)N_B^0 = (1 - pr)\frac{N_A^0}{r}$$

At this point, the number of A and B end groups is $N_A + N_B$, but 2 ends per chains...the number N of chains in the jar is....

$$N = \frac{1}{2}(N_A + N_B)$$

Which is....
$$N = \frac{1}{2} \left[(1-p)N_A^0 + (1-pr) \frac{N_A^0}{r} \right]$$

Or.....
$$N = \frac{N_A^0}{2} \left(1 + \frac{1}{r} - 2p \right)$$

Now..the total number of repeat units, N_r is

$$N_r = \frac{1}{2}(N_A^0 + N_B^0) \quad \text{One repeat unit formed per reaction}$$

Remember.... $r = \frac{N_A^0}{N_B^0}$ So....

$$N_r = \frac{1}{2} \left(N_A^o + \frac{N_A^o}{r} \right) = \frac{N_A^o}{2} \left(\frac{r+1}{r} \right)$$

DP is the number of monomer units divided by number of chains

$$DP = \frac{N_r}{N} = \frac{\frac{N_A^o}{2} \left[\frac{r+1}{r} \right]}{\frac{N_A^o}{2} \left[1 + \frac{1}{r} - 2p \right]}$$

Supplementary
Homework...
Show Algebra

Which luckily reduces to...

$$DP = \frac{1+r}{r+1-2p}$$

To here!



$$DP = \frac{1+r}{r+1-2rp} \quad \text{This is nice!!!}$$

Note that if there is no stoichiometric imbalance, $r = 1$ and we get.....

$$DP = \frac{1}{1-p} \quad \text{The Carothers Equation!!}$$

When A is totally consumed ($p = 1$) then....

$$DP = \frac{1+r}{1-r}$$