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CALCULATION OF AVERAGE MOLECULAR PROPERTIES DURING NONLINEAR, LIVING COPOLYMERIZATION

Dedicated to Paul Rempp in honor of his 60th birthday

by

Christopher W. Macosko
Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN 55455

and

Douglas R. Miller
Department of Operations Research and Applied Statistics
George Mason University
Fairfax, VA 22030

Summary

Describing network formation during chainwise polymerization is more complex than for stepwise (condensation) systems. The kinetics of chain growth must be combined with probability laws for random linking between chains. This approach is used to derive molecular weight averages, gel point and sol fraction during living, anionic copolymerization of vinyl with divinyl monomers. Comparison of predicted molecular weight and gel point to experimental values from Worsfold (1970), Lutz, Beinert and Rempp (1982) and others indicate that a significant amount of intramolecular linking or cyclization occurs in this system.

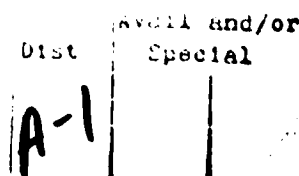
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INTRODUCTION

The development of molecular structure during nonlinear polymerization can be modelled with reasonable accuracy for stepwise (condensation) growth. For the ideal case all functional groups combine randomly, independent of the state of neighboring groups or size of the molecule to which they are attached. Intramolecular reactions do not occur between finite species. With these assumptions nonlinear stepwise polymerization can be modelled by branching theory. The branching probability model can be solved by combinatorial methods¹, probability generating functions² or directly³ to calculate parameters such as molecular weight averages, gel point, soluble fraction and crosslink density.¹⁻⁶ Time only enters the problem through a single equation relating the conversion of functional groups to the reaction rate.

A number of real, bulk condensation systems do polymerize nearly ideally. Experimental measures of weight and number average, gel point and sol fraction agree well with branching model results (e.g. ref. 7-10). When functional groups are not equally reactive, kinetic equations to describe the various linking probabilities for some cases can be solved analytically and incorporated into the branching model.^{4,11,12} Intramolecular cyclization generally is only important in dilute systems. Even for this case introduction of kinetic equations for the smallest size cycles provides useful results.^{13,14}

Nonlinear polymerization by chainwise addition is more difficult to model. In general chains do not grow randomly so kinetic equations must be solved for the length distribution of the primary chains in the network and then a probability model devised to combine these chains randomly into a network. For the special case of slow chain initiation compared to propagation (i.e. free radical polymerization) with chain termination by disproportionation and equal reactivity of the different vinyl groups Flory¹ showed that the random branching model can be applied. However, when there is termination by coupling the direction of propagation along each chain must be considered.¹⁵ Unequal reactivity can be treated with kinetic equations for the various linking probabilities in a manner similar to that used for condensation systems. Cyclization is very important in nonlinear free radical polymerization (e.g. ref 16). Long chains with many pendent functional groups form early in the reaction. Thus the network is typically formed in dilute solution.



In this paper we are interested in "living" anionic chain copolymerization. *Linear* anionic copolymerization has been treated by solving the kinetic equations¹⁷ and by Monte Carlo simulation.¹⁸ The gel point for nonlinear copolymerization with equal reactivity was derived by Eschwey and Burchard.¹⁹ Bokare and Gandhi²⁰ treated combined stepwise and living polymerization. Dusek and Somvarsky²¹ modelled molecular weight up to the gel point for non-linear anionic homopolymerization, but it appears that no one has modelled the general problem of nonlinear copolymerization with unequal reactivity. Nor has there been much comparison to experimental data.

The anionic homopolymerization of diepoxides and diisocyanates have been used to make network polymers.^{20,22} There has also been considerable interest in making star molecules²³ and controlled microgel particles²⁴ via anionic polymerization of divinyl monomers.^{19,23-26} These studies have examined what reactivity ratios and what vinyl to divinyl ratios will *prevent* gelation in anionic polymerization of divinyl monomers: i.e. how can a controlled amount of branching be introduced? Several studies indicate that cyclization is important in these systems.^{19,29}

In this paper we treat "living" anionic copolymerization using the kinetic-Markovian approach described recently.²⁷ A kinetic model describes the growth of the primary chains which are connected randomly via a branching model to give a network polymer. The model includes the possibility of unequal rates of addition of the different types of vinyl groups and we indicate how other complications such as slow initiation can be treated. We derive relations for number and weight average molecular weight up to the gel point and weight fraction solubles beyond the gel point. These relations are compared to experimental results from the literature.

We consider a system consisting of two types of reactants, A_2 and A_4 , and an initiator I . We use the notation A_2 to denote a monomer with one reactive site which when activated acts as a 2-functional unit. In this paper we compare data for anionic polymerization of vinyl monomers. Therefore the reactive site is $C = C$ but it could also be an isocyanate, epoxide or other ring. The notation A_4 denotes a monomer with two reactive sites so that when both are activated the monomer acts as a 4-functional unit. Divinyl benzene is an example of an A_4 monomer. The different units have masses denoted:

M_{A_2} , M_{A_4} , and M_I

Their initial concentrations are

$[A_2]_0$, $[A_4]_0$, and $[I]_0$

respectively.

THE IDEAL CASE

Before we construct the general model it is useful to consider the simplified, ideal case. If we assume

1. equal reactivity between all reactants: initiator, A_2 and both vinyls on the A_4
2. no substitution effect, all groups react independently throughout the polymerization and
3. no cycles form in finite species.

These are the same assumptions as for the ideal stepwise case mentioned above. In addition, we will make three additional assumptions:

4. The rate of activation of the initiator is very fast compared to the growth rate and is assumed to be instantaneous.
5. The initiation rate is the same as the growth rate.
6. The mass of the initiator is negligible and is assumed to be zero.

Recently Gupta and Macosko³⁰ have solved the case of A_f polymerization with initiators I_g . The general case of any ratio of initiation to growth has been solved.

With these assumptions we can separate the living, anionic chain growth from crosslinking and treat crosslinking as a completely random process. Initially we will ignore the connection between the two vinyl groups on the A_4 's and solve the kinetic equations for the linear chain length distribution. Since all species are equally reactive and have the same mass, we do not need to distinguish between A_2 and A_4 until the crosslinking step. Let $[A_2]_0 + 2[A_4]_0 = [M]_0$, the initial concentration of monomers. The initiation and growth reactions can be written as





where P_n is a living, linear chain, n monomer units long. The rate equations become

$$\frac{d[I]}{dt} = -k[M][I] \quad (3)$$

$$\frac{d[P_1]}{dt} = k[M][I] - k[M][P_1]$$

$$\frac{d[P_n]}{dt} = k[M][P_{n-1}] - k[M][P_n] \quad \text{for } n = 2, 3, \dots \quad (4)$$

Time and the rate constant, k , can be eliminated from these equations by considering the overall decrease of monomer

$$\frac{d[M]}{dt} = -k[M][I]_0 \quad (5)$$

which when divided into the above gives

$$\frac{d[I]}{d[M]} = \frac{[I]}{[I]_0}$$

$$\frac{dP_1}{dM} = \frac{[I]}{[I]_0} + \frac{[P_1]}{[I]_0}$$

$$\frac{d[P_n]}{d[M]} = \frac{[P_{n-1}]}{[I]_0} + \frac{[P_n]}{[I]_0} \quad \text{for } n = 2, 3, \dots$$

whose solution is

$$[I] = [I]_0 e^{-\mu} \quad (6)$$

$$[P_1] = [I]_0 \mu e^{-\mu}$$

$$[P_n] = [I]_0 \mu^n e^{-\mu} / n! \quad \text{for } n = 2, 3, \dots \quad (7)$$

where

$$\mu = \frac{[M]_0 - [M]_t}{[I]_0} = \frac{\text{reacted vinyl groups}}{\text{initiator}}$$

or in terms of the conversion, α :

$$\mu = \alpha[M]_0/[I]_0 \quad (8)$$

This number-distribution (Equations 6 and 7) is the well-known Poisson distribution, just the result that we expect for anionic living polymerization.²⁸ The mean of the distribution is μ , the number average chain length. The actual chains may consists of 0, 1, 2, ... monomer units. (A chain of 0 length corresponds to an unreacted, activated initiator.) Furthermore, because A_2 's and A_4 's join living chains independently and at equal rates, the fraction of crosslinkable monomers (A_4 's) in the chain is

$$p = 2([A_4]_0)/([A_2]_0 + 2[A_4]_0) = 2[A_4]_0/[M]_0 \quad (9)$$

and the number of A_4 's in a random chain has a Poisson number-distribution with mean $p\mu$. Similarly the number of A_2 's in a chain has a Poisson number-distribution with mean $(1-p)\mu$, independent of the number of A_4 's.

Now let us put back in the links (between the vinyls) on the A_4 monomers. These will become crosslinks between chains. Under our idealizing assumptions it is possible to derive formulae for $\bar{M}_w$ and α_c at gel using the recursive method.^{3,6} We first randomly pick a root by mass; it will be an A_4 or A_2 with probabilities

$$w_{A_4} = \frac{[A_4]_0 (1 - (1 - \alpha)^2) M_{A_4}}{[A_4]_0 (1 - (1 - \alpha)^2) M_{A_4} + [A_2]_0 \alpha M_{A_2}} \quad (10)$$

$$w_{A_2} = \frac{[A_2]_0 \alpha M_{A_2}}{[A_4]_0 (1 - (1 - \alpha)^2) M_{A_4} + [A_2]_0 \alpha M_{A_2}}$$

respectively. Note that $[A_2]_0 \alpha$ is the concentration of reacted A_2 's and $[A_4]_0 (1 - (1 - \alpha)^2)$ is the concentration of A_4 's with at least one reacted vinyl group. The denominator above is the usual polymer "yield," the mass after unreacted monomers have been removed.

Let the additional average weight of the branched chain through a reacted A-unit be denoted as $E(W_{out}^A)$. Using the recursive method and the fact that the average number of additional A_2 's and A_4 's on a chain are $(1-p)\mu$ and $p\mu$, respectively, we have

$$E(W_{out}^A) = (1-p)\mu M_{A_2} + p\mu[M_{A_4} + \alpha E(W_{out}^A)]$$

which becomes

$$E(W_{out}^A) = \frac{(1-p)\mu M_{A_2} + p\mu M_{A_4}}{1 - \alpha p\mu} \quad (11)$$

If chosen root is an A_2 , the average molecular weight is

$$E(W_{A_2}) = M_{A_2} + E(W_{out}^A) \quad (12)$$

If the chosen root is an A_4 , we know that there is at least one chain through the unit and possibly two. For a randomly chosen A_4 we get 0, 1, or 2 chains with probabilities $(1 - \alpha)^2$, $2\alpha(1 - \alpha)$, or α^2 , respectively; thus conditioning on the A_4 being part of the yield we have 1 or 2 chains with probabilities $2\alpha(1 - \alpha)/(1 - (1 - \alpha)^2)$ or $\alpha^2/(1 - (1 - \alpha)^2)$, respectively, so the expected number of chains equals $[2\alpha(1 - \alpha) + 2\alpha^2]/[1 - (1 - \alpha)^2] = 2\alpha/(2\alpha - \alpha^2) = 2/(2 - \alpha)$. Thus

$$E(W_{A_4}) = M_{A_4} + [2/(2 - \alpha)] E(W_{out}^A) \quad (13)$$

Combining equation 10 through 13 gives

$$\bar{M}_w = w_{A_2} E(W_{A_2}) + w_{A_4} E(W_{A_4}) \quad (14)$$

Note that this is the weight average molecular weight of the yield.

In order to compute the weight average molecular weight of the entire species the above analysis must be modified, using the following equations

$$w_{A_4} = \frac{[A_4]_0 M_{A_4}}{[A_4]_0 M_{A_4} + [A_2]_0 M_{A_2}} \quad (10')$$

$$w_{A_2} = \frac{[A_2]_0 M_{A_2}}{[A_4]_0 M_{A_4} + [A_2]_0 M_{A_2}}$$

$$E(W_{A_2}) = M_{A_2} + \alpha E(W_{out}^A) \quad (12')$$

$$E(W_{A_4}) = M_{A_4} + 2\alpha E(W_{out}^A) \quad (13')$$

The resulting weight average molecular weight using equations 10', 11, 12', 13', and 14 will be for the entire species rather than for the yield.

From equation 11, we see that the average weight diverges and we have gelation at conversion

$$\alpha_c = 1/p\mu \quad (15)$$

Combining equations 8, 9 and 15 gives

$$\alpha_c = \sqrt{[I]_0 / 2[A_4]_0} \quad (16)$$

Note that $2[A_4]_0/[I]_0$ equals the ratio of the number of potentially crosslinkable chain segments to the number of chains; this number must be greater than 1 in order for gelation to occur.

Now we restrict our attention to systems consisting of only A_4 units. The weight average molecular weight of such an anionic polymerization from equations 10 through 14 becomes

$$\bar{M}_w = E(W_{A_4}) = M_{A_4} + \left(\frac{2}{2 - \alpha} \right) E(W_{out}^A) = M_{A_4} + \left(\frac{2}{2 - \alpha} \right) \frac{\mu M_{A_4}}{1 - \alpha \mu}$$

$$\bar{M}_w = M_{A_4} \left(1 + \frac{2\mu}{(2 - \alpha)(1 - \alpha\mu)} \right) \quad (17)$$

This is the weight average molecular weight of the yield. If we consider the entire species, including unreacted A_4 's we get

$$\begin{aligned} M_w = E(W_{A_4}) &= M_{A_4} + 2\alpha E(W_{out}^A) \\ &= M_{A_4} + 2\alpha \frac{\mu M_{A_4}}{1 - \alpha\mu} \\ &= M_{A_4} \left(1 + \frac{2\alpha\mu}{1 - \alpha\mu} \right) \\ &= M_{A_4} \left(\frac{1 + \alpha\mu}{1 - \alpha\mu} \right) \end{aligned} \quad (18)$$

the weight average molecular weight of the entire species.

Comparison to Step and Chain Addition

It is of interest to compare these weight averages (equations 17 and 18) to the averages for free-radical chain addition homopolymerization and stepwise homopolymerization, respectively.

For stepwise homopolymerization¹⁻³

$$M_w = \frac{M_{Af}(1 + \alpha)}{1 - \alpha(f - 1)} \quad (19)$$

which simplifies to

$$= \frac{M_{A_4} (1 + \alpha)}{1 - 3\alpha} \quad \text{for tetrafunctional monomers}$$

and the gel point is

$$\alpha_c = \frac{1}{f-1} \quad (20)$$

Ideal free radical homopolymerization of multivinyl monomers leads to (eqs. 77, 79 pg. 204, ref. 3 with $M_{A_2} = 0$ and $a_f = 1$)

$$M_w = \frac{M_{A_f} (1 + q)}{1 - q [1 + (f - 2)\alpha]} \quad (21)$$

where q is the probability that a growing chain will add one more monomer unit rather than terminate by disproportionation. The gel conversion is

$$\alpha_c = \frac{1 - q}{(f - 2)q} \quad (22)$$

Figure 1 compares M_w for the three polymerization mechanisms. For typical conditions we see that living polymerization shows characteristics of both the step and chain mechanisms for molecular weight growth. Like the stepwise case, the initial molecular weight of the living chains is that of the monomer (since we ignore initiator weight). But as the A_4 monomers add to the living end the functionality of these chains increases rapidly and they begin to branch. At the gel point the weight average functionality of each living chain is 10.

The ideal chainwise mechanism produces long chains of A_4 in the first instant of polymerization. Their high weight average length, $L_w = 100$, means that they have, on average, 100 functional groups per chain. It takes very little further reaction for these groups to connect the few chains around into a network.

For all three mechanisms the gel point is determined by the weight average functionality at that point. This can be shown by comparing the three gel point equations.

$$\text{living} \quad \alpha_c = 1/\mu \quad \text{eq. (15)}$$

$$\text{step} \quad \alpha_c = 1/(f - 1) \quad \text{eq. (20)}$$

$$\text{chain} \quad \alpha_c = 1/[(f-2) q/(1-q)] \quad \text{eq. (22)}$$

If we consider the effective functionality of all three systems, we see that it is exactly the weight average chain length, $\bar{L}_w$ (because every segment is a potential crosslink). The weight average length for the living anionic is (from eq. 7)

$$\bar{L}_w = \mu + 1 \quad (23)$$

The result, with eq. 15, gives

$$\alpha_c = 1/(\bar{L}_w - 1) \quad (24)$$

which is the same form as α_c for the stepwise case.

In the chain addition case, assuming a most-probable distribution, we have⁶ $\bar{L}_n = 1/(1-q)$ and $\bar{L}_w = 2\bar{L}_n - 1$. This gives

$$\bar{L}_w = (1 + q)/(1 - q) \quad (25)$$

which when substituted into eq. 22 with $f = 4$ gives eq. 24. So all the gel point equations are of the same form. This is illustrated in Figure 1 where $\bar{L}_w$ is set at 4 for the living ($2[A_4]_0/[I]_0 = 9$), and for the chain systems ($q = 0.6$). Although gel points are matched we still see differences in the shape of the molecular weight rise due to each mechanism.

Instantaneous Initiation

In deriving the Poisson distribution above we assumed initiation and growth reactions proceeded at the same rate. However, this is not generally the case. Typically initiation is faster than propagation and often chains are preinitiated. A small amount of monomer is added to the initiator ($[M]_i \sim 2[I]_0$) and then after the chains have all started growing the rest of the monomer is put in. Thus it is important to determine the role of initiation rate. Let us assume initiation is instantaneous. Then at time $= 0^+$, $[I]_0 = 0$ and $[P_1] = [I]_0$. Applying these initial conditions to the above derivation gives a slightly different distribution

$$P_n = [I]_0 v^{n-1} e^{-v}/(n-1)! \quad n = 1, 2, 3, \dots \quad (26)$$

where

$$v = \frac{[M]_{0^+} - [M]_t}{[I]_0} = \frac{[M]_0 - [I]_0 - [M]_t}{[I]_0} \quad (27)$$

$$= \mu - 1$$

This can be called a shifted or alternate Poisson distribution.²⁸

The weight average chain length for this distribution is ²⁸

$$\overline{L}_w = (1 + 3v + v^2)/(1 + v) \quad (28)$$

$$\overline{L}_w = \mu + 1 - 1/\mu \quad (29)$$

This result can be substituted into equation 25.

The gel point becomes

$$\alpha_c = \left\{ [I]_0/2[A_4]_0 + ([I]_0/2[A_4]_0)^2 \right\}^{1/2} \quad (30)$$

This result converges to eq. 16 for long chains. This is illustrated in Table 1. We see from the table that for chains with 10 or more divinyl units incorporated at complete conversion there is essentially no difference between equal and fast initiation. Dusek and Somvarsky²¹ have solved homopolymerization with arbitrary initiation rate. Some of their results are included in Table 1. We see that when the initiation rate becomes 10 times the propagation rate it is essentially instantaneous. We will assume fast initiation in the remainder of this paper.

UNEQUAL REACTIVITY

In anionic copolymerization the monomers are generally not equally reactive. The A_2 , the first vinyl group on an A_4 and pendent vinyl groups add to the growing chain at unequal rates. To model this problem we make the following assumptions:

1. initiation reaction is very fast compared to the chain-growth reaction, so that the initiation can be assumed to occur instantaneously at time $t = 0$.
2. second order kinetics during chain growth.
3. rate of a unit joining one of the living chains depends solely on the type of unit and not the type of unit on the living end. This assumption appears valid for a number of anionic copolymerizations.^{22,29}
4. units join chains independently of one another.
5. no intramolecular reactions, i.e. no cycles in the finite species.

We shall explicitly treat the case where the initiator creates a chain with *one* live end. The case where a chain has *two* live ends is virtually identical; the chains grow twice as fast because there are double the number of chain ends. Each chain also has two initiated units instead of just one.

We take a hybrid modelling approach similar to those described by Miller and Macosko²⁸. The kinetic aspects are modelled separately, yielding superspecies; these superspecies are then combined randomly into molecules and networks using a probability model. This system is an especially interesting modelling exercise because it breaks into four conceptual stages: the initiation stage, the chain growth

kinetic stage, the chain growth random combination stage, and the chain crosslinking stage. At the end of the paper we show some calculations and compare to some experimental results in the literature.

Initiation Stage

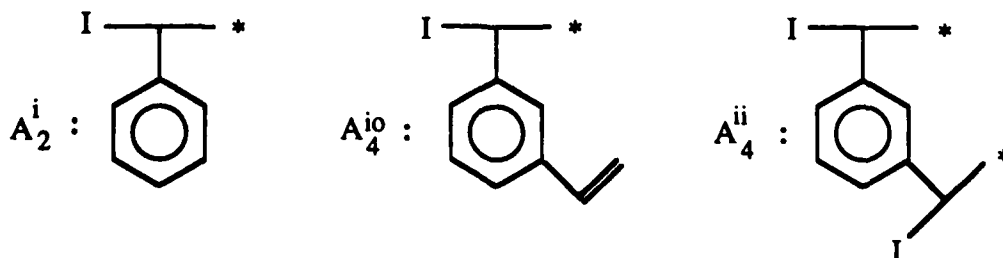
During the initiation stage the initiator activates sites on the A_2 and A_4 monomers. The unreacted monomers can be denoted as



Here styrene and m-divinyl benzene have been used to illustrate our notation. A short-hand notation will also prove useful for illustrating the growing chain structure

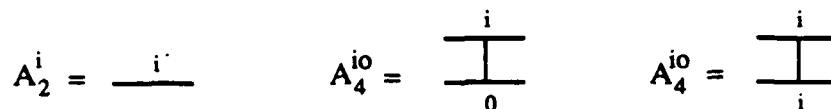


These unreacted monomers greatly outnumber the initiator so after the initiation stage most of them will remain but some of them will be activated into the following species



where "*" denotes the live end of a chain.

We can use the following short-hand notation for these species



We assume that the initiator attacks all of the double bond sites with equal probability and independently. We also assume a virtually instantaneous initiation stage, so that initiation is complete by time $t=0^+$. This can be forced by preinitiating a small amount of monomer slightly in excess of $[I]$ then adding the remainder.

When initiation is complete, the proportion of initiated double bonds equals

$$q_i = \frac{[I]_0}{[A_2]_0 + 2[A_4]_0}$$

Since the initiator attacks all double bonds with equal probability and independently, the concentration of the various species $t = 0^+$, are

$$\begin{aligned} [A_2^0]_{0^+} &= (1-q_i)[A_2]_0 \\ [A_2^i]_{0^+} &= q_i[A_2]_0 \\ [A_4^{oo}]_{0^+} &= (1-q_i)^2[A_4]_0 \\ [A_4^{io}]_{0^+} &= 2q_i(1-q_i)[A_4]_0 \\ [A_4^{ii}]_{0^+} &= q_i^2[A_4]_0 \end{aligned} \tag{32}$$

It is possible that the initiator attacks sites (i.e. double bonds) with different rates depending on whether they are on A_2 's or A_4 's and whether the other site on an A_4 has already been initiated. For such a case the concentrations of initiated species will differ from the above; they can be computed if a complete description of the kinetics is available.

Chain-Growth-Kinetics Stage

During the chain growth stage unreacted sites seek out live ends of chains and attach themselves to the chain. A given site is equally likely to join any of the live chains, subject to the restriction of no intra-molecular reactions. Different vinyl groups (on A_2 , on unreacted A_4 , and on A_4 with one previously activated double bond) react at different kinetic rates: r_1 , r_2 , and r_3 respectively. We assume second order kinetics. Since we assume fast initiation and no termination, the number of living chains is constant, $[I]_0$.

During the growth stage of the reaction, previously unactivated double bonds (which we have denoted as "o") are broken and the site attaches to the living chain and becomes the new live end. We shall denote this site with a "g", to signify the "growth" stage. During the growth stage we get some new species, which we shall denote as follows:



The kinetic equations governing the concentrations of these and the initial species over time are:

$$\frac{d}{dt} [A_2^o]_t = -r_1 [I]_0 [A_2^o]_t$$

$$\frac{d}{dt} [A_2^g]_t = +r_1 [I]_0 [A_2^o]_t$$

$$\frac{d}{dt} [A_4^{oo}]_t = -2r_2 [I]_0 [A_4^{oo}]_t \quad (33)$$

$$\frac{d}{dt} [A_4^{go}]_t = +2r_2 [I]_0 [A_4^{oo}]_t - r_3 [I]_0 [A_4^{go}]_t$$

$$\frac{d}{dt} [A_4^{gg}]_t = +r_3[I]_0[A_4^{go}]_t$$

$$\frac{d}{dt} [A_4^{io}]_t = -r_3[I]_0[A_4^{io}]_t$$

$$\frac{d}{dt} [A_4^{ig}]_t = +r_3[I]_0[A_4^{io}]_t$$

These kinetic equations can be solved by integration. The solution, for $t > 0$, is:

$$[A_2]_t = [A_2]_{0+} \exp(-r_1[I]_0 t)$$

$$[A_2^g]_t = [A_2]_{0+} - [A_2]_t$$

$$[A_2^i]_t = [A_2]_{0+}$$

$$[A_4^{oo}]_t = [A_4^{oo}]_{0+} \exp(-2r_2[I]_0 t) \quad (34)$$

$$[A_4^{go}]_t = \begin{cases} [A_4^{oo}]_{0+} + \frac{2r_2}{r_3 - 2r_2} [\exp(-2r_2[I]_0 t) - \exp(-r_3[I]_0 t)] \\ \text{or } [A_4^{oo}]_{0+} + 2r_2[I]_0 \exp(-r_3[I]_0 t), \text{ if } r_3 - 2r_2 = 0 \end{cases}$$

$$[A_4^{gg}]_t = [A_4^{oo}]_{0+} - [A_4^{oo}]_t - [A_4^{go}]_t$$

$$[A_4^{io}]_t = [A_4^{io}]_{0+} \exp(-r_3[I]_0 t)$$

$$[A_4^{ig}]_t = [A_4^{io}]_{0+} - [A_4^{io}]_t$$

$$[A_4^{ii}]_t = [A_4^{ii}]_{0+}$$

Returning to our assumption of fast initiation, if we define conversion to be the proportion of activated double bonds at time t , we get

$$\alpha(t) = \frac{[A_2^g]_t + [A_2^i]_t + [A_4^{go}]_t + [A_4^{io}]_t + 2[A_4^{ii}]_t + 2[A_4^{ig}]_t + 2[A_4^{gg}]_t}{[A_2]_0 + 2[A_4]_0} \quad (35)$$

If we define yield as the percentage mass of the reacted species, we get

$$\text{Yield} = \frac{W}{M_{A_2}[A_2]_0 + M_{A_4}[A_4]_0 + M_I[I]_0} \quad (36)$$

where W is the total mass of polymer (We no longer neglect the mass of the initiator, M_I):

$$W = M_{A_2} ([A_2^g]_t + [A_2^i]_t) + M_{A_4} ([A_4^{go}]_t + [A_4^{io}]_t + [A_4^{ii}]_t + [A_4^{ig}]_t + [A_4^{gg}]_t) + M_I[I]_0 \quad (37)$$

The number average molecular weight can be calculated from its definition, the weight per polymer molecule:

$$M_n = W/[N] \quad (38)$$

The total number of chains is $[I]_0$ less the number of crosslinks:

$$[N] = [I]_0 - [X] \quad (39)$$

$[X]$ is just the concentration of doubly reacted A_4 monomers:

$$[X] = [A_4^{gg}] + [A_4^{ig}] + [A_4^{ii}] \quad (39)$$

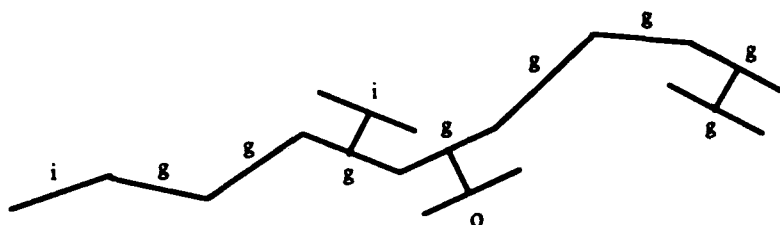
Thus eq. 38 becomes

$$M_n = \frac{W}{[I]_0 - [A_4^{gg}] - [A_4^{ig}] - [A_4^{ii}]} \quad (38)$$

Chain-Growth-Random-Combination Stage

At this point we have all the concentrations of species from our kinetic analysis. We now make up our linear chains by randomly combining our two monomers. In the next section we allow these chains to crosslink by making the connections between them through the reacted A_4 groups.

Each chain consists of *one* initiated segment, denoted by "i", and a random number of segments which attached themselves during the growth phase, denoted by "g":



The initial segment, "i", may belong to one of four different species

$$A_2^i, A_4^{io}, A_4^{ii}, A_4^{ig}$$

The growth segments, "g's", may be part of

$$A_2^g, A_4^{go}, A_4^{ig}, A_4^{gg}$$

At time t , the mean number of each "g" segment per chain are, respectively,

$$\begin{aligned}\mu_2^g &= [A_2^g]_t / [\Pi]_0 \\ \mu_4^{go} &= [A_4^{go}]_t / [\Pi]_0 \\ \mu_4^{ig} &= [A_4^{ig}]_t / [\Pi]_0 \\ \mu_4^{gg} &= 2[A_4^{gg}]_t / [\Pi]_0\end{aligned}\tag{40}$$

where $[\Pi]_0$ equals the concentration of chains. Thus the number average length of the chains is

$$E_n(L) = 1 + \mu_2^g + \mu_4^{go} + \mu_4^{ig} + \mu_4^{gg}\tag{41}$$

For any randomly (by number) chosen chain the distribution of the number of a particular type of "g" segment is Poisson. For example, if L_2^g equals the number of A_2^g units in the chain, for $\ell = 0, 1, 2, \dots$,

$$P_n(L_2^g = \ell) = \exp(-\mu_2^g)(\mu_2^g)^\ell / \ell! \quad (42)$$

The Poisson distribution follows from the well-known Poisson approximation to the Binomial distribution: suppose we pick a chain randomly (by number) by randomly choosing an "i"-segment. There are $[A_2^g]_t$ g-segments of type A_2 in one unit of volume. In this unit of volume there are $[I]_0$ chains to which the A_2^g may belong, all being equally likely. Thus a given "g"-segment chooses our chain with probability $1/[I]_0$. This random choice is repeated independently by each of the $[A_2^g]_t$ segments. The total number that join our chain will have a Binomial distribution with number of trials equal to $[A_2^g]_t$ and probability of success equal to $1/[I]_0$, yielding a mean of $[A_2^g]_t / [I]_0$. It is well known that, when the number of trials is large and the probability of success is small, the Poisson distribution is an excellent approximation²⁹. So, the length of a random chain is

$$L = 1 + L_2^g + L_4^{go} + L_4^{gi} + L_4^{gg} \quad (43)$$

where the number distribution corresponds to the sum of independent Poisson random variables with means μ_2^g , μ_4^{go} , μ_4^{gi} and μ_4^{gg} , respectively.

If we allocate one half the mass of A_4^{ii} , A_4^{ig} , and A_4^{gg} units to each chain to which they belong then we can compute the average chain weights. Let

IA $\equiv$ initiated A unit

then

$$P(\text{IA} = A_2^i) = [A_2^i]_t / [I]_0$$

$$P(\text{IA} = A_4^{io}) = [A_4^{io}]_t / [I]_0$$

$$P (IA = A_4^{ig}) = [A_4^{ig}]_t / [I]_0 \quad (44)$$

$$P (IA = A_4^{ii}) = 2[A_4^{ii}]_t / [I]_0$$

if M_{IA} = mass of initiator segment on chain, then

$$E_n(M_{IA}) = M_I + P(IA = A_2^i)M_{A_2} + P(IA = A_4^{io})M_{A_4} + P(IA = A_4^{ig} \text{ or } A_4^{ii})M_{A_4} / 2 \quad (45)$$

Let

GS = totality of growth segments on chain

and

M_{GS} = mass of all growth segments on chain

then

$$E_n(M_{GS}) = \mu_2^g M_{A_2} + \mu_4^{go} + M_{A_4} + (\mu_4^{ig} + \mu_4^{gg}) M_{A_4} / 2 \quad (46)$$

and since the chain consists of initiator and growth segments

$$E_n(CW) = E_n(M_{IA}) + E_n(M_{GS}) \quad (47)$$

is the number-average chain weight, which should also equal "Yield" divided by $[I]_0$.

Now consider the weight average chain weight: a unit of mass is chosen randomly and designated as a root, R. The probabilities of getting various species as a root are

$$P(R = A_2^o) = M_{A_2} [A_2^o]_t / TM$$

$$P(R = A_2^i) = (M_{A_2} + M_I) [A_2^i]_t / TM$$

$$P(R = A_2^g) = M_{A_2} [A_2^g]_t / TM$$

$$P(R = A_4^{oo}) = M_{A_4} [A_4^{oo}]_t / TM$$

$$P(R = A_4^{io}) = (M_{A_4} + M_I) [A_4^{io}]_t / TM \quad (48)$$

$$P(R = A_4^{go}) = M_{A_4} [A_4^{go}]_t / TM$$

$$P(R = A_4^{ig}) = (M_{A_4} + M_I) [A_4^{ig}]_t / TM$$

$$P(R = A_4^{ii}) = (M_{A_4} + 2M_I) [A_4^{ii}]_t / TM$$

$$P(R = A_4^{gg}) = M_{A_4} [A_4^{gg}]_t / TM$$

where

$$TM = M_{A_2} [A_2]_0 + M_{A_4} [A_4]_0 + M_I [I]_0 \quad (49)$$

is the concentration of total mass. If the randomly chosen root is an A_2^o or an A_4^{oo} , we don't get a chain.

Because of this we renormalize these probabilities to just include the yield of the reaction:

$$P'(R = A_2^i) = P(R = A_2^i) / \text{Yield}$$

$$P'(R = A_2^g) = P(R = A_2^g) / \text{Yield}$$

$$P'(R = A_4^{io}) = P(R = A_4^{io}) / \text{Yield}$$

$$P'(R = A_4^{go}) = P(R = A_4^{go}) / \text{Yield} \quad (50)$$

$$P'(R = A_4^{ig}) = P(R = A_4^{ig}) / \text{Yield}$$

$$P'(R = A_4^{ii}) = P(R = A_4^{ii}) / \text{Yield}$$

$$P'(R = A_4^{gg}) = P(R = A_4^{gg}) / \text{Yield}$$

For each root chosen we get the root plus either 1 or 2 chains; each chain will consist of a random additional number of "g"-segments, and an "i"-segment if the root does not include the initial segment.

Let

XGS = Extra growth segments of chain

XIS = Extra initiator segment of chain

and

MXGS = mass of XGS

MXIS = mass of XIS

MRC = mass of root part of chain

it follows that the total mass of the chain is

$$CW = MRC + MXIS + MXGS \quad (51)$$

and the weight average mass is

$$E_w(CW) = E_w(MRC) + E_w(MXIS) + E_w(MXGS) \quad (52)$$

These terms can be evaluated as follows by conditioning over the seven different roots:

$$\begin{aligned} E_w(MRC) &= \sum E_w(MRC | R) P'(R) \\ &= P'(R = A_2^i) (M_{A_2} + M_I) + P'(R = A_2^g) M_{A_2} \\ &+ P'(R = A_4^{io}) (M_{A_4} + M_I) + P'(R = A_4^{go}) M_{A_4} \\ &+ P'(R = A_4^{ig}) (M_{A_4} + M_I) / 2 + P'(R = A_4^{gg}) M_{A_4} / 2 \\ &+ P'(R = A_4^{ii}) (M_{A_4} + 2M_I) / 2. \end{aligned} \quad (53)$$

$$\begin{aligned} E_w(MXIS) &= \sum E_w(MXIS | R) P'(R) \\ &= P'(R = A_2^g) E(M_{IA}) + P'(R = A_4^{go}) E(M_{IA}) \\ &+ P'(R = A_4^{ig}) E(M_{IA}) / 2 + P'(R = A_4^{gg}) E(M_{IA}) \end{aligned} \quad (54)$$

The extra growth portion of the chain is the same regardless of whether the chain is chosen by number or weight, thus

$$E_w(MXGS) = E_n(M_{GS}) \quad (55)$$

completing the formula for $E_w(CW)$.

Crosslinking-of-Chains Stage

Finally we consider the chains of the previous section crosslinked to form large molecules and possibly even a network. The "crosslink" units are the species A_4^{ii} , A_4^{ig} , and A_4^{gg} .

It is tempting to aggregate the three types of crosslinks into one general crosslink thereby forcing the system into the framework of homopolymerization of length- and functionality-distributed chains analyzed by Miller and Macosko⁶ using standard branching process models. However, that approach assumes that the characteristics of two chains with a common crosslink are statistically independent. Our system of living chains does not satisfy that assumption. For example, pick a random crosslink and look at the two chains joined at the crosslink; let their lengths be L_1 and L_2 . We know that the number distribution of L_1 (and L_2) is

$$L = 1 + N_2^g + N_4^{go} + N_4^{ig} + N_4^{gg} \quad (56)$$

where N_2^g , N_4^{go} , N_4^{ig} , and N_4^{gg} are independent Poisson random variables with means μ_2^g , μ_4^{go} , μ_4^{ig} , and μ_4^{gg} respectively. Consider the event $\{L = 1\}$: in order to see a chain of length 1 with a crosslink it is necessary that we have chosen a crosslink with an "i" unit and no growth has occurred:

$$\begin{aligned} P(L = 1) &= P(\text{site} = "i") P(N_2^g + N_4^{go} + N_4^{ig} + N_4^{gg} = 0) \\ &= \frac{2[A_4^{ii}]_t + [A_4^{ig}]_t}{2[A_4^{ii}]_t + 2[A_4^{ig}]_t + 2[A_4^{gg}]_t} \exp(-\mu) \end{aligned} \quad (57)$$

where $\mu = \mu_2^g + \mu_4^{go} + \mu_4^{ig} + \mu_4^{gg}$

$$\begin{aligned} P(L_1 = 1, L_2 = 1) &= P(\text{both sites} = "i") P(\text{no growth on either}) \\ &= \frac{2[A_4^{ii}]_t}{2[A_4^{ii}]_t + 2[A_4^{ig}]_t + 2[A_4^{gg}]_t} [\exp(-\mu)]^2 \end{aligned} \quad (58)$$

For L_1 and L_2 to be independent it is necessary that

$$P(L_1 = 1, L_2 = 1) = P(L_1 = 1) p(L_2 = 1) \quad (59)$$

which is equivalent to

$$\frac{[A_4^{ii}]_t}{[A_4^{ii}]_t + [A_4^{ig}]_t + [A_4^{gg}]_t} = \left(\frac{2[A_4^{ii}]_t + [A_4^{ig}]_t}{[A_4^{ii}]_t + [A_4^{ig}]_t + [A_4^{gg}]_t} \right)^2 \quad (60)$$

which is generally not true. So the crosslinked chains are not statistically independent. Assuming independence is probably not a bad approximation, especially when the mean chain length is not too short. However, in this paper we want to present an exact model, subject to our assumption of no intramolecular reactions. Thus our crosslinking model has three types of crosslinks.

Our crosslink model consists of chains with labelled chain segments, "i" and "g". Crosslinks may be "ii", "ig", or "gg". Conditional on the type of crosslink, the statistical properties of the crosslinked chains are independent. This seems to be an accurate description of our situation. We can analyze it combining ideas from our work on crosslinking chains⁶ and our work on nonideal systems^{11,12}. We shall compute weight average molecular weight in the pre-gel region and weight fraction soluble in the post-gel region. The number average molecular weight was computed in eq. 38.

Weight Average Molecular Weight

To compute the weight average molecular weight, we must first compute the weight seen looking from a crosslink into a chain. There are two possibilities: we may be looking into an "i" segment or into a "g" segment. We denote total weights as $E(W_i^{in})$ and $E(W_g^{in})$, respectively.

First consider an "i" segment. The weight seen looking into this segment includes: mass of root segment, mass of the rest of the chain which consists solely of "g" segments, mass looking out from A_4^{gg} units and A_4^{ig} units on the chain. The mass of the root segment equals $M_I + M_{A4}/2$. The expected mass of the rest of the chain equals E_n (MXGS) by previous reasoning. The expected mass looking out

from A_4^{gg} units equals the expected number of such units times the expected weight looking into random "g" segments. The expected mass looking out from A_4^{ig} units is determined analogously. Combining all this gives

$$E(W_i^{in}) = M_I + M_{A_4} / 2 + E_n(MXGS) + \mu_4^{gg} E(W_g^{in}) + \mu_4^{ig} E(W_i^{in}) \quad (61)$$

Now consider a "g" segment. The weight seen looking in is the same as looking into an "i" segment, expect that the root segment is different and therefore the initiated chain segment must be treated separately. We shall see the mass of the initiating segment as well as the weight attached to it if it is an A_4^{ig} or A_4^{ii} . This gives

$$\begin{aligned} E(W_g^{in}) &= M_{A_4} / 2 + E_n(MXGS) + \mu_4^{gg} E(W_g^{in}) + \mu_4^{ig} E(W_i^{in}) \\ &+ E(M_{IA}) + P(LA = A_4^{ig}) E(W_g^{in}) + P(LA = A_4^{ii}) E(W_i^{in}) \end{aligned} \quad (62)$$

Solving the above two equations we get

$$E(W_i^{in}) = \frac{M_I + M_{A_4} / 2 + E_n(MXGS) + \mu_4^{gg} E(W_g^{in})}{1 - \mu_4^{ig}} \quad (63)$$

$$E(W_g^{in}) = \frac{[1 + P(LA = A_4^{ii})][M_{A_4} / 2 + E_n(MXGS)] + (1 - \mu_4^{ig}) E(M_{IA}) + (\mu_4^{ig} + P(LA = A_4^{ii})) M_I}{(1 - \mu_4^{ig})(1 - P(LA = A_4^{ig})) - \mu_4^{gg}(1 + P(LA = A_4^{ii}))} \quad (64)$$

The equation for $E(W_g^{in})$ can be computed and the value plugged into the equation for $E(W_i^{in})$. Gelation occurs when the above denominator goes non positive, i.e. condition for gelation:

$$(1 - \mu_4^{ig})(1 - P(LA = A_4^{ig})) - \mu_4^{gg}(1 + P(LA = A_4^{ii})) \leq 0 \quad (65)$$

In order to compute the weight average molecular weight we randomly select a unit of mass, designate the monomer obtained as the root, R, and look at the mass of the root plus all attached mass.

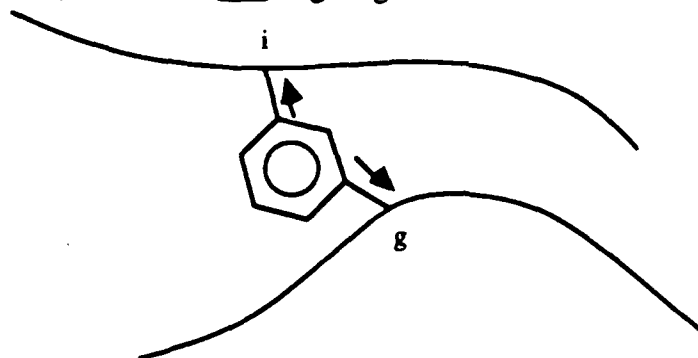
$$\bar{M}_w = \sum E(W | R) P(R)$$

$$\begin{aligned}
&= P(R = A_2^o) M_{A_2} + P(R = A_2^i) (M_{A_2} + EW_i^{in} - M_{A_4}/2) \\
&+ P(R = A_2^g) (M_{A_2} + EW_g^{in} - M_{A_4}/2) \\
&+ P(R = A_4^{oo}) M_{A_4} + P(R = A_4^{io}) (M_{A_4}/2 + EW_i^{in}) \\
&+ P(R = A_4^{go}) (M_{A_4}/2 + EW_g^{in}) + P(R = A_4^{ig}) (EW_i^{in} + EW_g^{in}) \\
&+ P(R = A_4^{ii}) (2EW_i^{in}) + P(R = A_4^{gg}) (2EW_g^{in})
\end{aligned} \tag{66}$$

The weight average of the reacted species can be computed using the probabilities $P'(R = *)$ defined above.

Weight Fraction Soluble

To compute weight fraction soluble we pick a root by mass and look out from it and ask if only a finite amount of mass is seen. Looking out, there are three possibilities: we see nothing, we look into an "i" segment, or we look into a "g" segment:



Define the events

$F_i^{in} \equiv$ finite mass is seen looking into "i" segment

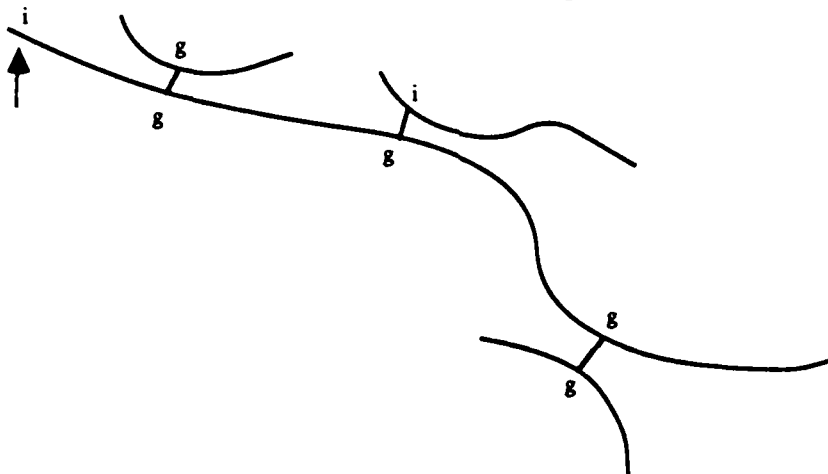
$F_g^{in} \equiv$ finite mass is seen looking into "g" segment

and let $P(F_i^{in})$ and $P(F_g^{in})$ be the probabilities of these events occurring. Then

$$\begin{aligned}
& \text{weight fraction soluble (wfs)} = \\
& P(R = A_2^o) \cdot 1 + P(R = A_2^i) P(F_i^{\text{in}}) + P(R = A_2^g) P(F_g^{\text{in}}) \\
& + P(R = A_4^{oo}) \cdot 1 + P(R = A_4^{io}) P(F_i^{\text{in}}) + P(R = A_4^{ii}) P(F_i^{\text{in}})^2 \\
& + P(R = A_4^{go}) P(F_g^{\text{in}}) + P(R = A_4^{ig}) P(F_i^{\text{in}}) P(F_g^{\text{in}}) + P(R = A_4^{gg}) P(F_g^{\text{in}})^2
\end{aligned} \tag{67}$$

If one desires to compute the weight fraction soluble of the yield, then he should use the above formula with the probabilities, $P'(R = *)$.

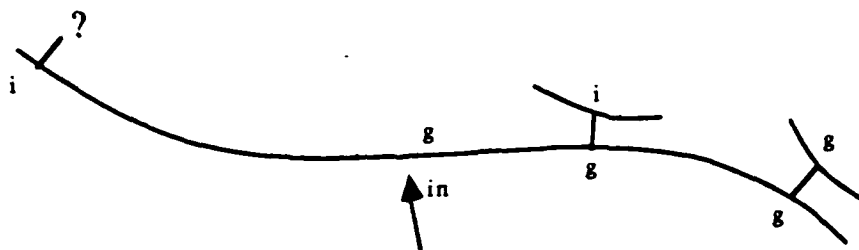
Thus it suffices to compute $P(F_i^{\text{in}})$ and $P(F_g^{\text{in}})$. First consider looking into an "i" segment:



We are interested in the number of "g" segments on the chain which belong to A_4^{ig} and A_4^{gg} species. Recall that the number of these species are L_4^{ig} and L_4^{gg} respectively, independent Poisson random variables with means μ_4^{ig} and μ_4^{gg} , respectively. Thus the event F_i^{in} is identical to the event that all A_4^{ig} species on the chain lead to finite mass and all A_4^{gg} species on the chain lead to finite mass. But the event that an A_4^{ig} species leads to finite mass is simply F_i^{in} , and the event that an A_4^{gg} species leads to finite mass is F_g^{in} . Putting this together we get

$$\begin{aligned}
P(F_i^{\text{in}}) &= \left(\sum_{x=0}^{\infty} P(F_i^{\text{in}})^x P(L_4^{ig} = x) \right) \left(\sum_{x=0}^{\infty} P(F_g^{\text{in}})^x P(L_4^{gg} = x) \right) \\
&= \exp \left(\mu_4^{ig} (1 - P(F_i^{\text{in}})) \right) \exp \left(-\mu_4^{gg} (1 - P(F_g^{\text{in}})) \right) \\
&= \phi \left(P(F_i^{\text{in}}), P(F_g^{\text{in}}) \right)
\end{aligned} \tag{68}$$

Now consider $P(F_g^{in})$. This is more complicated because of the initiated unit:



The event F_g^{in} is equivalent to the event that all additional growth units on the chain lead to finite mass and the initiator unit of the chain leads to finite mass, F_i^{out} .

$$P(F_i^{out}) = P(IA = A_2^0) \cdot 1 + P(IA = A_4^{00}) \cdot 1 \\ + P(IA = A_4^{ii}) \cdot P(F_i^{in}) + P(IA = A_4^{ig}) \cdot P(F_g^{in}) \quad (69)$$

Since growth segments of the chain additional to the randomly chosen root segment of the chain have the same statistical properties regardless of whether the root is an "i" or "g" segment, the event of these leading to finite mass is statistically the same as F_i^{in} . Therefore

$$P(F_g^{in}) = P(F_i^{in}) \cdot P(F_i^{out}) \quad (70)$$

Solving we get

$$P(F_g^{in}) = \frac{P(F_i^{in}) \left[P(IA = A_4^{ii}) P(F_i^{in}) + P(IA = A_2^0) + P(IA = A_4^{io}) \right]}{1 - P(F_i^{in}) P(IA = A_4^{ig})} \quad (71) \\ = \psi(P(F_i^{in}))$$

The equation (68) becomes

$$P(F_i^{in}) = \phi(P(F_i^{in}), \psi(P(F_i^{in}))) \quad (72)$$

and can be solved numerically for the value of $P(F_i^{in})$ by the method of binary search. The value can then be substituted into the equation

$$P(F_g^{in}) = \psi \left(P(F_i^{in}) \right) \quad (73)$$

to obtain the value of $P(F_g^{in})$. These values are then used to compute wfs by equation 67. This approach could also be extended to calculation of crosslink density following ref. 3.

Some Calculations and Comparison to Experiment

The equations derived above were solved using a Fortran program to give M_n (eq. 38); M_w (eq. 66) and w_{sol} (eq. 67) for the living copolymerization of A_2 with A_4 with unequal reactivity. Since the rate equations can be integrated analytically (eq. 34), the program is really just a sequence of algebraic substitutions.

The required inputs are the molecular weights of the monomers and initiator, M_{A_2} , M_{A_4} , and M_I , the ratios of their concentrations $[A_4]_0/[A_2]_0$ and $[I]_0/[A_2]_0$ and of their rates of propagation r_2/r_1 and r_3/r_1 (see eq. 33). Initiation is assumed to be much faster than these propagation rates and independent of monomer type.

Figure 2 shows typical results for the simplest nonideal case, homopolymerization of divinyl monomer, A_4 . The conditions were taken from Strachle and Funke²⁴ for the polymerization of ethylene glycol dimethacrylate (EGDMA 5% in toluene) with *n*-butyl lithium. Both vinyl groups on the EGDMA should have the same reactivity but after one becomes incorporated into the chain we might expect the pendent vinyl to be less reactive due to topological hindrance of the chain. This has been noted in free-radical polymerization of the same monomer.¹⁶ Figure 2 shows that the yield of polymer at gel is increased from 0.29 to 0.73 when the pendent vinyl reactivity is reduced by a factor of 12. The shapes of the M_w , M_n and w_{sol} curves remain similar. Polymer yield is plotted in these figures because it is easy to measure experimentally and it is the commonly reported measure of reaction conversion (rather than conversion of vinyl groups).

Strachle and Funke report a gel point at about 40% polymer which corresponds to about a 50% reduction in reactivity. One would expect a greater reduction. It may be that their actual initiator concentration was lower than reported due to deactivation. The value of $[I]_0$ given is rather high and would only lead to a 4000 molecular weight polymer if there were no branching.

A more complete set of data on nonlinear anionic homopolymerization is given by Lutz, Beinert and Rempp²⁶ for 1,3 diisopropenyl benzene 10% in THF at - 30°C initiated with 1 phenylethylpotassium. At the low initiator level used in their experiment the gel point would be at 8.6% polymer if all vinyls were equally reactive. We see that experimentally the gel point occurs much later in the reaction.

A reduction of pendent vinyl reactivity by nearly 500 times fits the experimental M_w and M_n values fairly well. The data was taken by GPC which is surely too low for these branched molecules at high molecular weight. Although the delay in gelation can be explained by reduced pendent vinyl reactivity it could also be due to cyclization.

In the general case of $A_2 + A_4$ copolymerization we can have at least three different propagation rates, r_1 for the rate of addition of the monovinyl, A_2 , r_2 for either of the divinyl groups and r_3 for the pendent. Figure 4 shows the effect of changing r_2/r_1 and r_3/r_1 on the gel point. Initial conditions are from Lutz et al²⁶ and are given in the Figure caption. About 10% of the monomer is divinyl and the initiator concentration is typical (it would produce a linear polymer with $M_w \approx 40,000$).

Since the ideal gel point is rather low, 10.7%, decreasing the relative reactivity of the divinyl or its pendent groups has a much greater effect on gelation than increasing it. When the product $(r_2/r_1) \cdot (r_3/r_1) < 10^{-3}$, the gel point appears to reach a limiting value ~ 0.9 .

We can use Figure 4 to determine the best parameters to fit the data of Lutz et al²⁶ on the small copolymerization of α methyl styrene with 1,3 diisopropenyl benzene (1,3 DIB), see Table 2. By titration and NMR they found that 1,3 DIB goes into the chain about twice as fast as the α methyl styrene. Thus $r_2/r_1 \sim 2$. The gel point was $\sim 80\%$ polymer. From Figure 4 this would indicate $r_3/r_1 \leq 0.01$. For the calculations in Table 2 we used $r_3/r_1 = 0.008$ (or $r_3/r_2 = 0.004$) and get a reasonable match to the molecular weight data.

It is interesting to note that when 1,3 DIB was homopolymerized (Fig. 3) a value of $r_3/r_2 = 0.0022$ fit the data. This is about half the value for copolymerization. It is quite reasonable that the pendent vinyls on the copolymer will be more reactive since they will be much less crowded, spaced

apart by about five α methyl styrene units. Again this discussion assumes that there are no intramolecular cycles.

A complete set of reactivity ratios was reported by Worsfold for the copolymerization of styrene with *p*-divinyl benzene.²⁹ He used UV spectroscopy to measure six of the nine possible propagation rates and estimated the remaining three. He found, as we assumed in our derivation, that rates did not depend on the nature of the chain end but do depend on the adding monomer. The rate constant for *p*-DVB adding to a styrene anion is 12.3 mol/l•s, quite close to that for adding to a DVB anion, which is 11.2. However, the rate constant for adding styrene to the chain end is 1.16 or 1.12 mol/l•s respectively. Thus *p*-DVB adds 10 times faster to a living chain than styrene monomer. The pendent vinyl group has nearly the same reactivity as the styrene 0.9 mol/l•s.

We can use these data to determine r_1 , r_2 and r_3 and with Worsfold's reactant concentrations we have all the information needed to calculate the gel point. From eq. 65 we obtain 8.7% polymer at gel while Worsfold reports 47%! This value was for an initial monomer concentration of only 8.2% in benzene. When he reduced the concentration to 4.3% the gel point increased to 77% polymer. This effect of dilution on gel point is a clear indication of intramolecular cycles. Such large changes in molecular weight and gel point at high dilution are also observed in stepwise polymerizations.^{14,32}

If we plot Worsfold's gel points versus reciprocal monomer concentration in the manner first done by Jacobson and Stockmayer³² we get an intercept at infinite concentration in reasonable agreement with the value we calculate (see Figure 5). Although there is insufficient data to draw strong conclusions, this result indicates that the rate constants are correct and the main deviation is due to intramolecular reaction. Lutz et al's polymerizations were run at about 10% monomer in THF so their polymers must also contain quite significant intramolecular cycles. The r_3 values used to fit the data in Figure 3 and Table 2 are probably much lower than the true values, perhaps ten times, to compensate for the additional effect of cyclization.

Eschwey and Burchard¹⁹ have measured gel points for styrene-divinyl benzene systems at 2.5% monomer in toluene. They found great suppression of the gel point and speculate that over 90% of the reacted pendent double bonds are involved in cyclics.

Both Eschwey and Burchard and Straehle and Funke,²⁴ unlike Lutz et al, report very high molecular weights near the gel point, a decade higher in some cases, than would be predicted by eq. 66 with r_3 adjusted to give their experimental gel point (see Figure 2). This may also be due to extensive cyclization or perhaps microgel and microheterogeneities in the polymerization.

CONCLUSIONS

Following our general paper²⁷ on treatment of combined kinetic and Markovian polymerization problems we have shown how the kinetic process of living, anionic polymerization can be combined with the random process of connecting these living chains into a network. We treated the simplest copolymerization case: a difunctional plus a tetrafunctional, $A_2 + A_4$, but the methodology can readily be extended to several monomers and other functionalities. We have modelled unequal rates of monomer addition but considered these to be independent of chain end type. Rates could be made dependent on chain end but this doesn't seem to be necessary for most anionic polymerizations,^{22,29} unlike the free-radical case.

Initiation rate was assumed fast. This is nearly always the case in anionic polymerization of vinyl monomers but may not be true for other ionic cases such as epoxy ring opening. In Table 1 we show that including initiation rate is only critical for short chains. Variable initiation rate can be treated by introducing another set of differential equations for the A_2^i , A_4^{oi} , etc. species similar to eq. 33.

Our calculations compare well to the living homopolymerization and copolymerization data of Lutz, Beinert and Rempp.²⁶ However, we had no value for their pendent vinyl reactivity and thus adjusted this parameter to fit the data. Reductions in pendent reactivity of 450 for the homopolymerization and 250 for the copolymerization were necessary for a reasonable fit to Lutz et al's molecular weight results. Worsfold's measurement of pendent reactivity by UV spectroscopy on a similar monomer showed only a reduction of ten. We conclude that the apparent additional reduction in reactivity must be due to pendent groups being wasted in intramolecular cycles. Worsfold's gel points at different dilution support this conclusion.

Anionic polymerizations of vinyl monomers are typically run dilute, 5-20% monomer, so cyclization will be a major factor in nonlinear polymerizations. Further experimental work like Figure 5 is needed to quantify the effect. Extension of the theoretical approach given here to include cycles is a formidable challenge.

Acknowledgement

Paul Rempp and Pierre Lutz suggested this problem to us during the sabbatical visit of CWM to Université Louis Pasteur in Strasbourg. A grant from the Office of Naval Research allowed us to complete this work.

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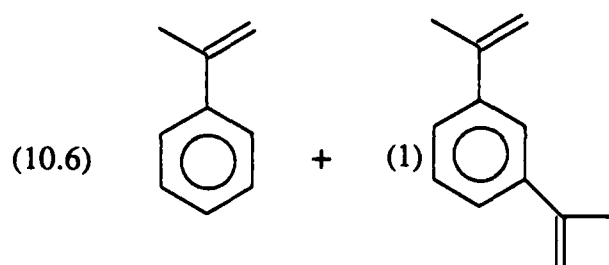
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Table 1. Comparison of gel conversion of equal initiation and propagation rates and for very rapid initiation.

$\frac{2[A_4]_0}{[I]_0}$	α_c		
	$r_1/r_2 = 1$ (eq. 16)	$= \infty$ (eq. 30)	$= 10$ (ref 21)
2	.7071	.8860	.864
10	.3162	.3317	.332
100	.1000	.1005	.100*
1000	.0316	.0316	.032

* The actual value of 0.105 given in ref. 21 was presumed to be in error.

Table 2. Copolymerization of α methyl styrene with 1,3 diisopropenyl benzene.

<u>yield</u>	$\frac{[A_4]}{[A_2]}$ in polymer		M_n		M_w	
	<u>exp.</u>	<u>eq. 40</u>	<u>GPC</u>	<u>eq. 36</u>	<u>GPC</u>	<u>eq. 66</u>
.057	.36	.35	5300	4200	5750	4300
.31	.26	.25	20,600	24,200	24,500	25,800
.62	.17	.16	47,900	62,000	91,500	95,700

*from Lutz et al²⁶ $M_{A_2} = 118$, $M_{A_4} = 158$, $M_I = 106$, $[A_4]_0/[A_2]_0 = 0.0947$, $[A_2]_0/[I]_0 = 556$ (the effective initiator concentration was reduced to 2/3 the reported value to match the low molecular weight data); calculations assume $r_2/r_1 = 2$, $r_3/r_1 = .008$. Reactant concentration was 14% in THF.

Figure Captions

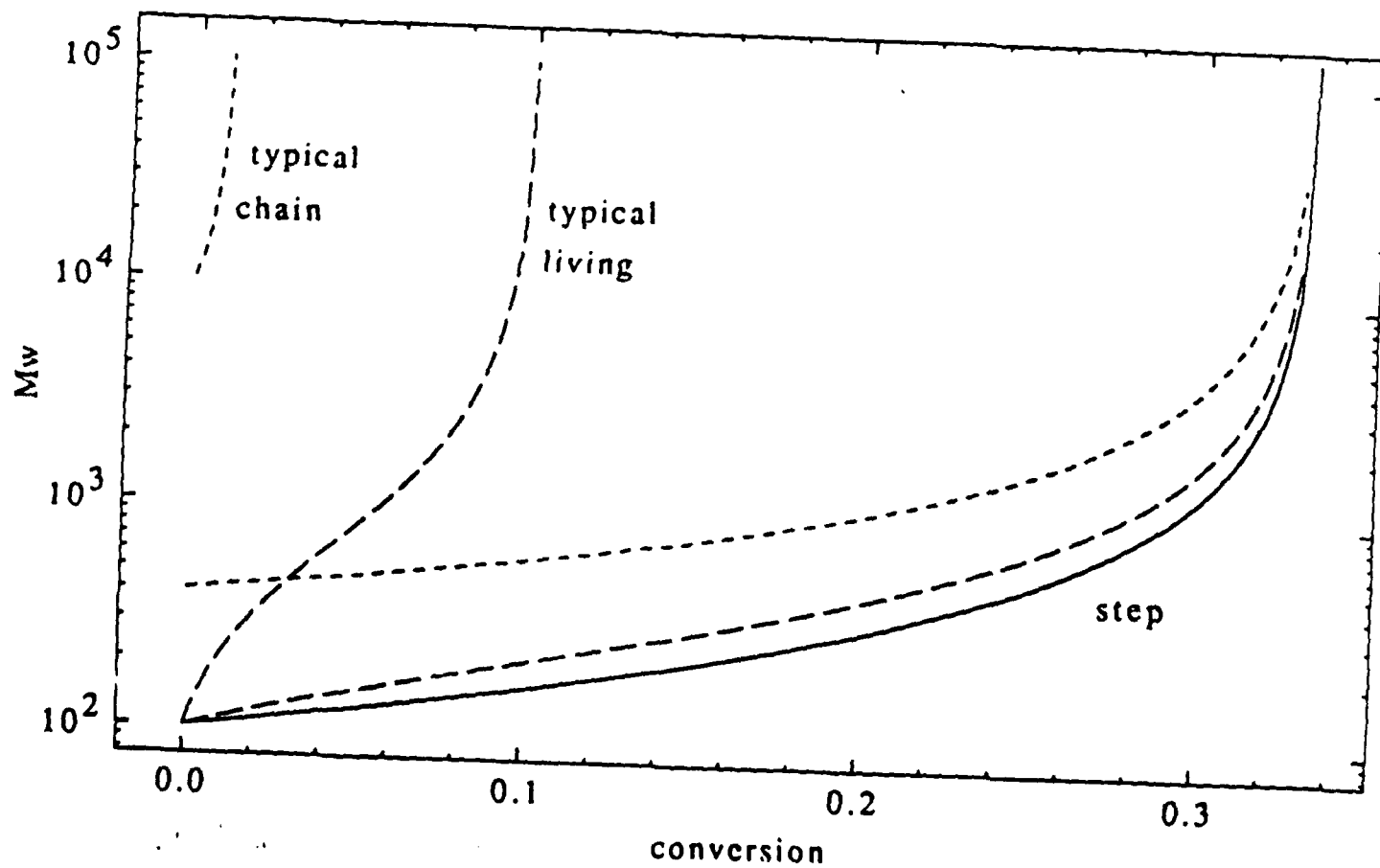
- Figure 1. Molecular weight build up during ideal polymerization of a tetrafunctional monomer by three different mechanisms: chain (—— eq. 21), living (- - - -, eq. 17) and step (—, eq. 19). The "typical" conditions are : kinetic chain length of 50 for the chain addition ($q = 0.98$) and $2[A_4]_0/[I]_0 = 100$ for the living system. For the dashed lines to the right these parameters have been reduced to match the gel point of the stepwise polymerization which will always gel at $\alpha_c = 1/(f - 1)$ or $1/3$.
- Figure 2. Number average and weight average molecular weight and soluble fraction vs. polymer yield (fraction of monomer incorporated into polymer). A_4 homopolymerization: ——— ideal; ——— pendent vinyls are 12 times less reactive. $M_{A_4} = 198$, $M_I = 56$, $2[A_4]_0/[I]_0 = 43.4$, the conditions reported by Straehle and Funke²⁴ to polymerize ethylene glycol dimethacrylate.
- Figure 3. Homopolymerization of 1,3 diisopropenyl benzene. ■ M_w and ▲ M_n data et al.²⁶ Open points are believed to be in error (low) due to the method used, GPC. Solid curves are M_w from eq. 66 at various ratios of pendent vinyl to monomer reactivity r_3/r_2 . Dashed curve is for M_n (eq. 36) for $r_3/r_2 = 0.0022$.
- Figure 4. The effect of unequal reactivity on yield at gel. The ideal gel point occurs at 0.107 polymer fraction. Decreasing the reactivity of the divinyl monomer, r_2 , or the vinyl pendent on the chain, r_3 , with respect to the monovinyl monomer, r_1 , increases dramatically the fraction of polymer at gel. $[A_4]_0/[A_2]_0 = 0.0974$; $[A_2]_0/[I]_0 = 556$.

Figure 5. Gel point vs. reciprocal monomer concentration for copolymerization of styrene with *p*-divinyl benzene.²⁹

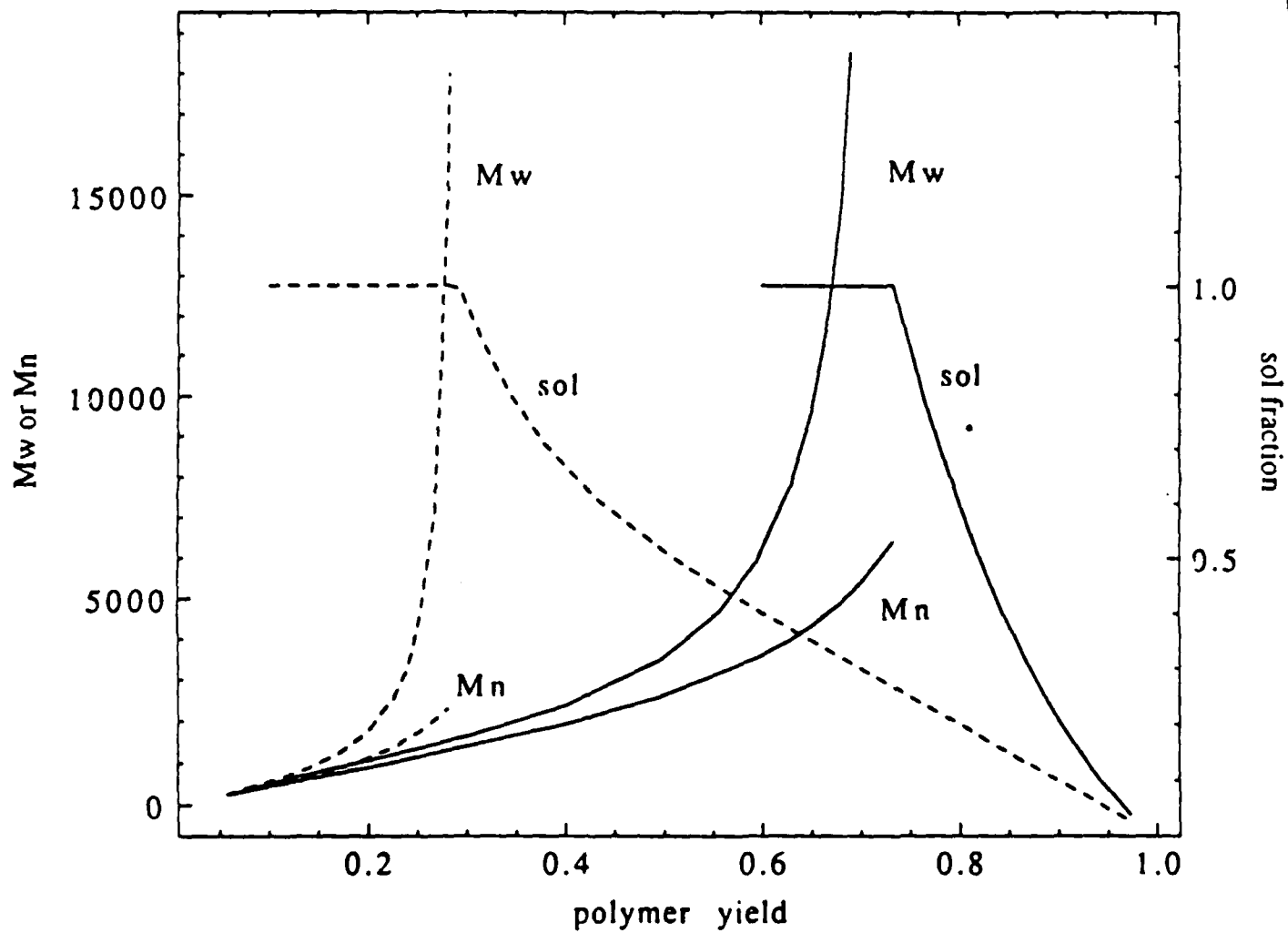
- ◊ $[A_2]_0 = 0.374 \text{ mol/l}$, $[A_4]_0/[A_2]_0 = 4.28 \times 10^{-3}$, $[A_2]_0/[I]_0 = 4560$
- ◻ $[A_2]_0 = 0.714 \text{ mol/l}$, $[A_4]_0/[A_2]_0 = 1.57 \times 10^{-3}$, $[A_2]_0/[I]_0 = 8500$
- ⊙ calculated for same conditions as ◻ with $r_1 = 1.14$, $r_2 = 11.7$, $r_3 = 0.9$, the average values given by Worsfold.²⁹

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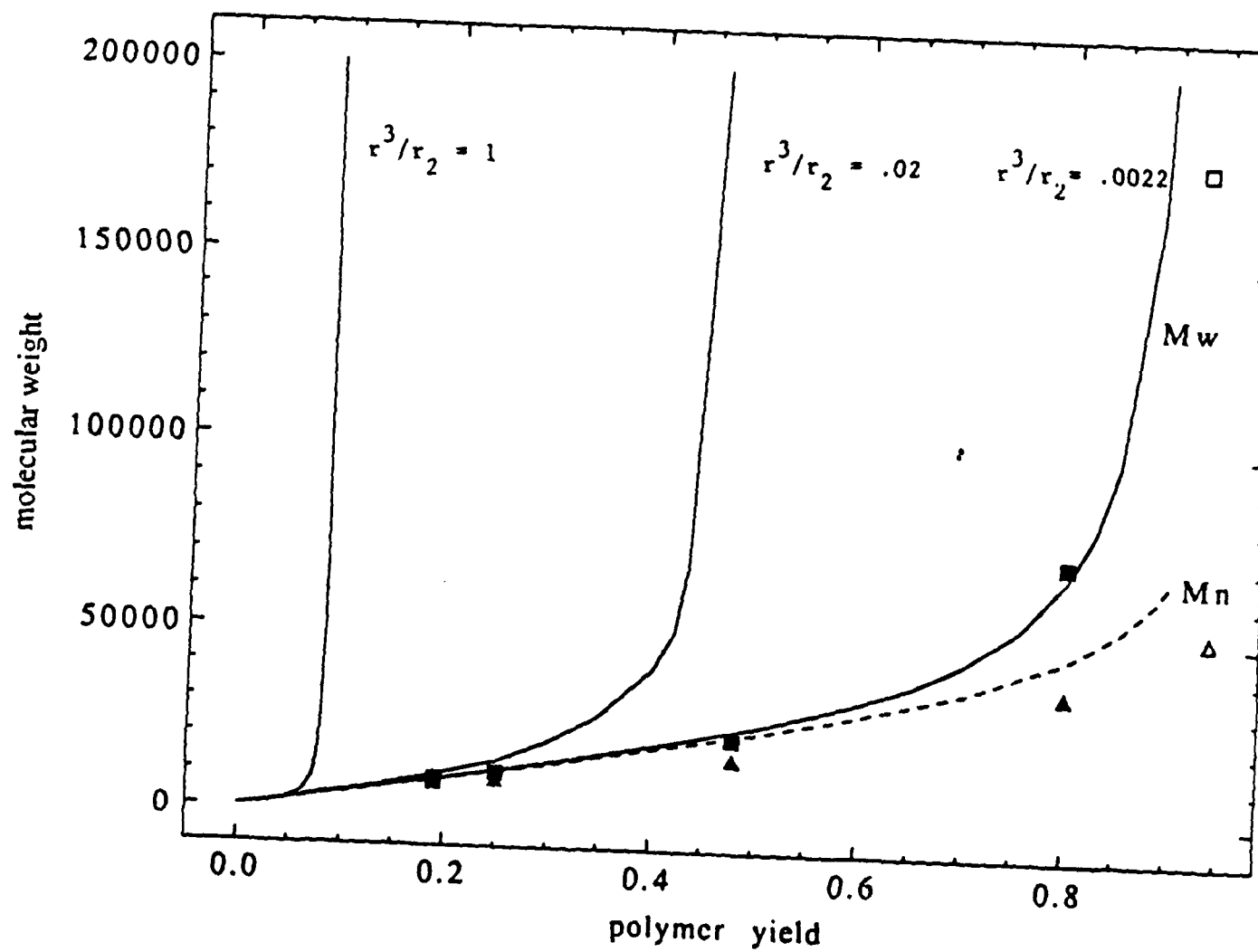
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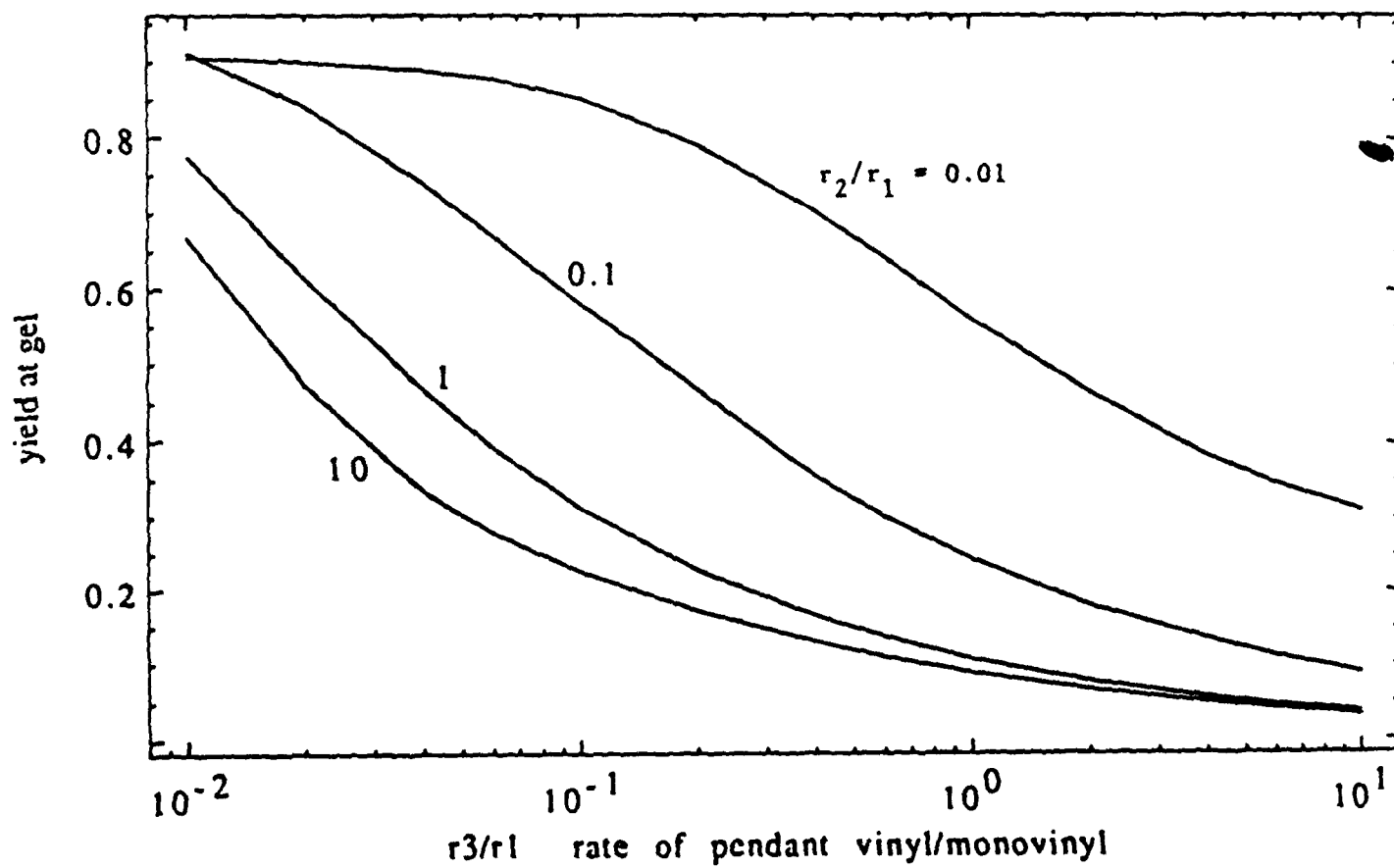
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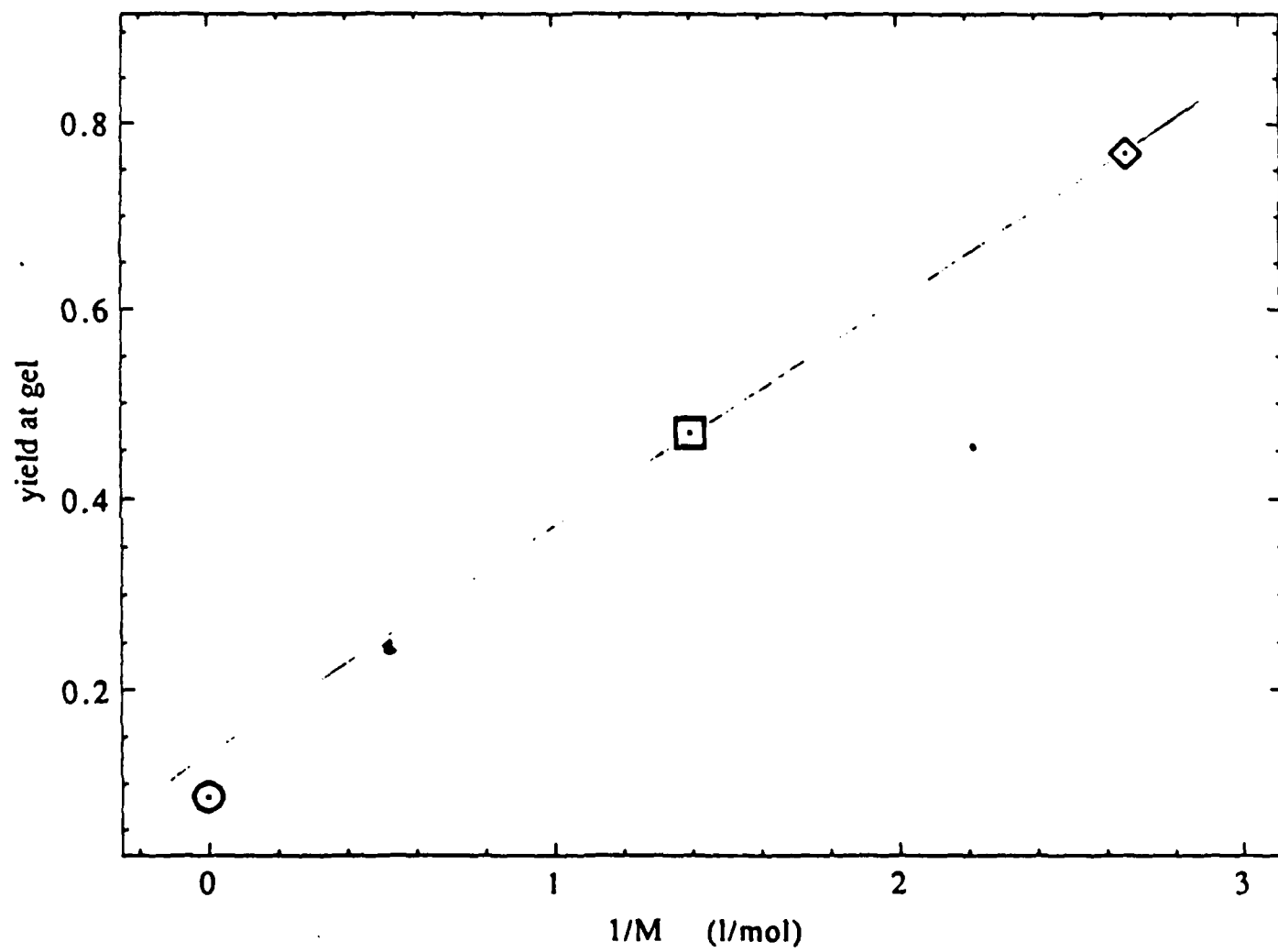
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