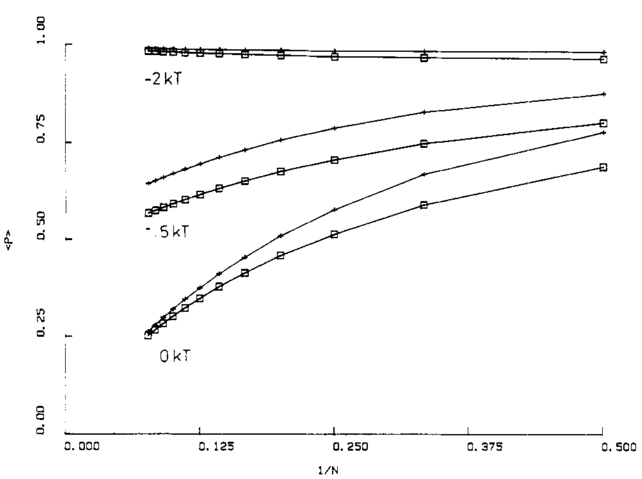

Figure 4. $\langle p \rangle_V$ estimates for the cubic lattice for a terminally anchored chain (+) and a chain with at least one vertex in the adsorption plane (□) as a function of the degree of polymerization at values of the adsorption energy of 0, $-0.5\ kT$ and $-2.0kT$.

In order to evaluate the effect of choosing a terminally anchored chain model, it is possible, using the results of Torrie et al.[20] for the cubic lattice, to calculate $\langle p \rangle$ for an attached walk (i.e., $m > 0$), where the attached segment can be chosen anywhere along the chain. Figure 4 shows the variation in $\langle p \rangle$ as a function of $1/n$ for selected values of ϵ. Clearly, for short walks there is a large difference between the models. As n increases, the extrapolated values become closer, showing that the terminally attached constraint is not a serious limitation.

The model proposed in this paper is for a single polymer molecule with fixed bond angles. The effect of the solvent is only taken account of in the net energy of adsorption; no entropy term has been included for solvent desorption. However, at fixed temperature the qualitative predictions are consistent with experimental evidence. Quantitatively, it is found that the $\langle p \rangle$ values calculated are over estimates, compared to the absolute values obtained by calorimetry,[6] though very few results exist for $\langle p \rangle$ at low coverages in systems where the enthalpy of adsorption is known exactly.

4. Conclusion

Exact enumeration studies of attached self-avoiding walks have been used to calculate $\langle p \rangle$, the fraction of polymer segments in contact with a surface, as a function of the adsorption energy. Reasonable agreement is found with Monte Carlo studies. Below the critical energy of adsorption, $\langle p \rangle$ varies as n^{-1} as the degree of polymerization approaches infinity.

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Calculation of Average Properties of the Pendant Chains in a Network

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ABSTRACT: A recursive approach is used to evaluate number- and weight-average properties of the pendant chains in a network obtained by stepwise polymerization from polyfunctional monomers and comonomers. The results are valid for monodisperse and polydisperse reactive oligomers. The molecular parameters calculated here include the number- and weight-average molecular weight of the pendant chains, the average degree of branching, the average size of the longest chain through a pendant chain, and the extent of reaction at the pendant chains as a function of the overall extent of reaction.

Introduction

A detailed knowledge of the unique structure of rubbery materials is required to be able to relate their rheological properties to different molecular parameters and eventually to synthesis conditions. It is well-known, for example, that elastic properties of amorphous rubbers depend on the number of elastic chains per unit volume as predicted by the kinetic theory of rubber elasticity. This has been

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verified experimentally on different model systems in which it was possible to estimate precisely the concentration of elastic chains. Testing some of these "tailor-made networks" under low-frequency dynamic mechanical deformation, we have found that, while the elastic modulus of the material depends on the number of chains that compose the network, the loss modulus depends mainly on the number of pendant chains that are "hanging" from the network structure.[1] Evidence of the contribution of dangling chains on properties such as swelling,[2] viscoelasticity,[3,4] ultimate properties,[5] and fatigue under alternating stress[6] has been found in the past. As pointed out by Mark and co-workers,[5] the effect of these irregularities on the physical properties of networks is essentially unexplored, mainly because it is very difficult to obtain information on the number of pendant chains in a network and their molecular structure.

It is important then to develop methods to calculate molecular parameters such as the number- and weight-average molecular weights for the pendant chains, the average degree of branching, and the average size of the longest chains through a pendant chain. Doing this, we may be able to gain insight into the influence of each of these structural features on the loss properties of rubbery materials.

In this paper we develop theoretical relations to calculate these parameters in model network polymers made by stepwise polymerization from polyfunctional monomers and comonomers. To do this, we make use of a recursive approach originally developed by Macosko and Miller to evaluate average molecular weights of nonlinear polymers. It will be helpful if the reader is familiar with the recursive method and with the notation used in previous articles.[7-9]

The derivations are performed for two different kinds of chemical systems: homopolymerization of monomer A with functionality f, A_f, and copolymerization of A_f with a bifunctional reactant B_2, where A and B are two kinds of functional groups. We show results valid for initially monodisperse and polydisperse reactants because the second case is frequently found in practice in cross-linking of polydisperse oligomers. The calculations can be easily extended to copolymerization between two polyfunctional reactants A_f and B_g or to chemical systems with more than two reactive monomers.

The derivations assume ideal network polymerization: (1) all functional groups of the same type are equally reactive, (2) all groups react independently, and (3) no intramolecular reaction occurs in finite species and there is no loop formation on the pendant chain.

I. Directional Extent of Reaction on the Pendant Material of the Gel

As will become evident in the following sections, it is necessary to know the extent of reaction in the direction of a finite end in order to evaluate most of the molecular parameters of the pendant material of the gel. The dangling material of the gel has only one end or chain attached to the infinite gel as indicated in Figure 1. Starting at any portion of a pendant chain, it is possible to proceed in two directions: if one proceeds toward the infinite gel, all reactive groups that join the mers when passing from one unit to the next will be reacted. The extent of reaction in the infinite direction, p_{inf}, will then be equal to unity. Proceeding in the opposite direction, it is also conceivable to find reacted groups if initially a nonextreme portion of the pendant chain like the one indicated by a star in Figure 1 has been chosen. But invariably, unreacted groups will be found since one is proceeding in the direction of the chain ends. The average extent of reaction in the finite direction of the pendant chains, p^0, as a function of the overall extent of reaction of the cross-linking reaction, p, will be calculated in this section.

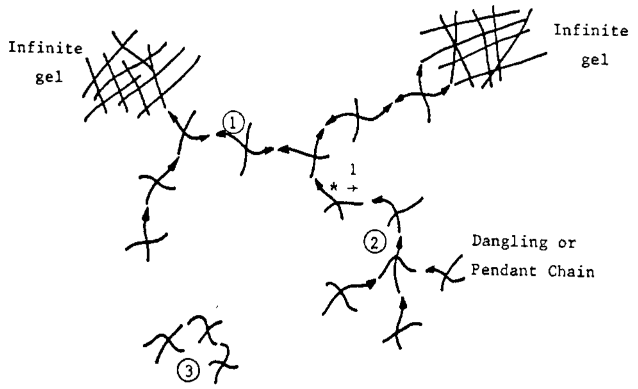
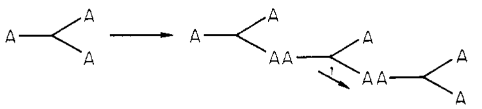


Figure 1. State of a network after the gel point for tetrafunctional polymerization. Arrows indicate chain ends in the infinite direction: (1) elastic chain; (2) pendant chain; (3) soluble material.

Initially, we consider the simplest case of homopolymerization of A_f moles of an oligomeric monodisperse monomer bearing f reactive groups. During the cross-linking reaction the mers react as shown in (I-1). The



(I-1)

polymer increases in size with the extent of reaction, p_A:

$$p_{\mathrm{A}} = (A - A_t)/A$$

where A represents the initial moles of reactive groups and A_t is the amount of moles after some time t.

After the gel point an infinite network is formed. Selecting mers at random, it is possible to identify three different types of units: mers that belong to elastic chains like the one labeled (1) in Figure 1, units that belong to the pendant material (2), and individual molecules that belong to the sol (3). To calculate p_{A}^0 one has to look for the probability that, picking a unit of a pendant chain at random and looking out in the finite direction for an A group, this group has reacted. This can be written as

$$p_{\mathrm{A}}^0 = P(\mathrm{A\ reacts}/F_{\mathrm{A}}^{\mathrm{out}}) \tag{I-2}$$

that is, the conditional probability that the A group is reacted, given that it is also part of a finite chain. $F_{\mathrm{A}}^{\mathrm{out}}$ is the event that a single mer selected at random leads to a finite end rather than to an infinite network when the molecule is viewed in a particular direction such as $\overset{1}{\rightarrow}$ in Figure 1. By definition of conditional probability[10]

$$p_{\mathrm{A}}^0 = \frac{P(\mathrm{A\ reacts} \cap F_{\mathrm{A}}^{\mathrm{out}})}{P(F_{\mathrm{A}}^{\mathrm{out}})} = \frac{P(F_{\mathrm{A}}^{\mathrm{out}}/\mathrm{A\ reacts})P(\mathrm{A\ reacts})}{P(F_{\mathrm{A}}^{\mathrm{out}})}$$

The probability $P(F_{\mathrm{A}}^{\mathrm{out}}/\mathrm{A\ reacts})$ of finding a finite end looking out of a reacted A is equal to the probability of finding a finite end looking into the next mer in the chain, $P(F_{\mathrm{A}}^{\mathrm{in}})$. Therefore

$$p_{\mathrm{A}}^0 = \frac{P(F_{\mathrm{A}}^{\mathrm{in}})P(\mathrm{A\ reacts})}{P(F_{\mathrm{A}}^{\mathrm{out}})} = \frac{P(F_{\mathrm{A}}^{\mathrm{in}})p_{\mathrm{A}}}{P(F_{\mathrm{A}}^{\mathrm{out}})} \tag{I-3}$$

where $P(\mathrm{A\ reacts})$ is just p_{A}. As $P(F_{\mathrm{A}}^{\mathrm{in}}) = P(F_{\mathrm{A}}^{\mathrm{out}})^{f-1}$

$$p_{\mathrm{A}}^0 = P(F_{\mathrm{A}}^{\mathrm{out}})^{f-2}p_{\mathrm{A}} \tag{I-4}$$

This is, of course, valid for the postgel region, where $p_A > p_A^{\text{gel}}$.

For a monomer of functionality 3, A_3, it has been shown[8] that $P(F_A^{\text{out}}) = (1 - p_A)/p_A$; p_A^0 then becomes

$$p_A^0 = 1 - p_A \quad \text{for } p_A \geq p_{\text{gel}} = \tfrac{1}{2}$$

For a tetrafunctional monomer, A_4, where $P(F_A^{\text{out}}) = (1/p_A - {}^3/_4)^{1/2} - {}^1/_2$, we obtain

$$p_A^0 = \{(1/p_A - \tfrac{3}{4})^{1/2} - \tfrac{1}{2}\}^2 p_A$$

$$\text{for } p_A \geq p_A^{\text{gel}} = \tfrac{1}{3}$$

Copolymerization Relations. For a stepwise copolymerization of a mixture of A_f and B_2, eq I-2 becomes

$$p_A^0 = P(\text{A reacts}/F_A^{\text{out}})$$

$$p_B^0 = P(\text{B reacts}/F_B^{\text{out}}) \qquad \text{(I-5)}$$

and

$$p_A^0 = \frac{P(F_A^{\text{out}}/\text{A reacts})P(\text{A reacts})}{P(F_A^{\text{out}})}$$

$$p_B^0 = \frac{P(F_B^{\text{out}}/\text{B reacts})P(\text{B reacts})}{P(F_B^{\text{out}})}$$

As the A groups can only react with the B groups,

$$P(F_A^{\text{out}}/\text{A reacts}) = P(F_B^{\text{in}})$$

$$P(F_B^{\text{out}}/\text{B reacts}) = P(F_A^{\text{in}})$$

Equation I-5 becomes

$$p_A^0 = \frac{P(F_B^{\text{in}})p_A}{P(F_A^{\text{out}})}$$

$$p_B^0 = \frac{P(F_A^{\text{in}})p_B}{P(F_B^{\text{out}})} \qquad \text{(I-6)}$$

One can also consider here an initial stoichiometric imbalance of the reactants, $r = p_B/p_A$, and make use of the expressions for the probabilities of a finite chain looking into and out of an A or B group,[8] which for functionality 3 are

$$P(F_A^{\text{out}}) = (1 - rp_A^2)/rp_A^2$$

$$P(F_A^{\text{in}}) = P(F_A^{\text{out}})^2$$

$$P(F_B^{\text{out}}) = P(F_B^{\text{in}}) = \frac{1 - 2rp_A^2 + rp_A^3}{rp_A^3}$$

Thus eq I-6 becomes

$$p_A^0 = \frac{1 - 2rp_A^2 + rp_A^3}{1 - rp_A^2}$$

$$p_B^0 = \frac{(1 - rp_A^2)^2}{1 - 2p_A^2 r + rp_A^3} \qquad \text{(I-7)}$$

where p_A^0 and p_B^0 are now given as a function of p_A and the initial stoichiometric imbalance of the reactants.

Similar derivations have been performed for the overall extent of reaction in the pendant material, p_A^p. For example, the final result corresponding to homopolymerization of A_3 is

$$p_A^p = 2(1 - p_A)/(2 - p_A) \qquad \text{(I-8)}$$

Figure 2 shows how p_A^p and p_A^0 change with p_A during the curing reaction. As expected $p_A^p \geq p_A^0$.

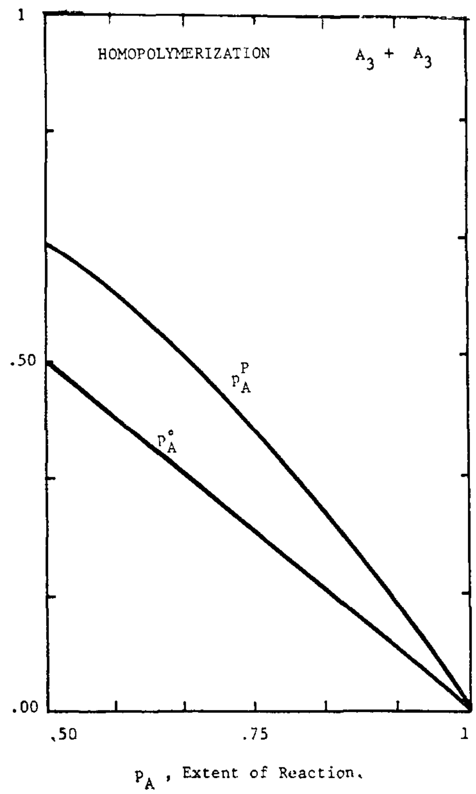


Figure 2. Directional (p_A^0, eq I-4) and overall (p_A^p, eq I-8) extents of reaction in the pendant material as a function of the extent of the cross-linking reaction (p_A) for homopolymerization of a trifunctional monomer A_3.

II. Number-Average Molecular Weight of the Pendant Chains

In this section the number-average molecular weight of the pendant chains is calculated for homopolymerization and copolymerization, beginning with the simplest case of homopolymerization of monodisperse A_f monomers.

Assume that the cross-linking reaction is at some stage after the gel point and focus on the pendant chains of the system. We first want to calculate the expected weight looking out in the finite direction of an A group picked at random from the pendant material, $E(W_A^{\text{out}}{}_{\text{fin}})$. We then ask what is the weight ($W_A^{\text{out}}{}_{\text{fin}}$) attached to this A looking out in the finite direction from its parent molecule in the direction $\xrightarrow{1}$ (Figure 1). The weight will be zero if the A group has not reacted, an event with probability $1 - p_A^0$. If the group has reacted with another A attached to an A_f molecule, then $W_A^{\text{out}}{}_{\text{fin}}$ equals $W_A^{\text{in}}{}_{\text{fin}}$, the weight attached to the second A looking into its parent molecule. We use p_A^0 instead of p_A^p because we are always looking in the finite direction of the pendant chains.

Now we compute the expected weight, making use of the law of total probability for expectation.[10]

$$\begin{aligned} E(W_A^{\text{out}}{}_{\text{fin}}) = {} & E(W_A^{\text{out}}{}_{\text{fin}}/\text{no reaction})P(\text{no reaction}) + \\ & E(W_A^{\text{out}}{}_{\text{fin}}/\text{reaction})P(\text{reaction}) = \\ & 0(1 - p_A^0) + E(W_A^{\text{in}}{}_{\text{fin}})p_A^0 \qquad \text{(II-1)} \end{aligned}$$

The expected weight looking into the next molecule, $E(W_A^{\text{in}}{}_{\text{fin}})$, will be the molecular weight of the A_f group plus the sum of the expected weights on each of the remaining $f - 1$ arms. This will be just $E(W_A^{\text{out}}{}_{\text{fin}})$ for each arm since all the A's are equally reactive.

$$E(W_A^{\text{in}}{}_{\text{fin}}) = M_{A_f} + (f - 1)E(W_A^{\text{out}}{}_{\text{fin}}) \qquad \text{(II-2)}$$

The recursive nature of the polymerization process leads us back to eq II-1. Solving eq II-1 and II-2 for $E(W_A{}^{out}{}_{fin})$, we obtain

$$E(W_A{}^{out}{}_{fin}) = p_A{}^0 M_{A_f}/[1 - p_A{}^0(f-1)] \qquad \text{(II-3)}$$

To calculate the number-average molecular weight, we have to choose chains at random, ensuring that each chain has the same chance of being selected, and then look for the expected weight of the randomly selected chains. This is done by picking the root of the chain at the point at which it is attached to the elastic chains of the gel (Figure 1) and computing the expected weight looking out in the finite direction. The average weight is given by the weight of the first portion of the chain, M_A, plus $E(W_A{}^{out}{}_{fin})$

$$\bar{M}_{n,p} = M_A + E(W_A{}^{out}{}_{fin}) \qquad \text{(II-4)}$$

where $M_A = M_{A_f}/f$ if we assume that all the arms of the monomer have the same length.

Combining eq II-3, II-4, and I-4, we obtain

$$\bar{M}_{n,p} = M_A + \frac{P(F_A{}^{out})^{f-2} M_{A_f} p_A}{1 - p_A P(F_A{}^{out})^{f-2}(f-1)} \qquad \text{(II-5)}$$

which is the final expression for the number-average molecular weight. In the particular case of trifunctional A_3

$$\bar{M}_{n,p} = M_A(2 - p_A)/(2p_A - 1) \qquad \text{(II-6)}$$

The same approach can be extended to copolymerization. We consider here the copolymerization of an oligomer B_2 with a cross-linker A_f. We now allow both reactants to be polydisperse in weight. Each of the reactants will be a mixture of molecules of different sizes i.

$$A_f = \sum_i A_{f,i}$$
$$B_2 = \sum_i B_{2,i} \qquad \text{(II-7)}$$

We define the fraction of molecules of size i as a_i and b_i, respectively.

$$a_i = A_{f,i}/A_f$$
$$b_i = B_{2,i}/B_2 \qquad \text{(II-8)}$$

Applying the same approach as that for homopolymerization, we obtain the following set of equations:

$$E(W_A{}^{out}{}_{fin}) = p_A{}^0 \sum_i b_i E(W_B{}^{in}{}_{fin})_i$$
$$E(W_B{}^{in}{}_{fin})_i = M_{B_2,i} + E(W_B{}^{out}{}_{fin})$$
$$E(W_B{}^{out}{}_{fin}) = p_B{}^0 \sum_i a_i E(W_A{}^{in}{}_{fin})_i$$
$$E(W_A{}^{in}{}_{fin})_i = M_{A_f,i} + (f-1)E(W_A{}^{out}{}_{fin}) \qquad \text{(II-9)}$$

Solving for $E(W_A{}^{out}{}_{fin})$ and making use of the definition of number-average molecular weight

$$\bar{M}_{A_f,n} = \sum_i a_i M_{A_f,i}$$
$$\bar{M}_{B_2,n} = \sum_i b_i M_{B_2,i}$$

we obtain

$$E(W_A{}^{out}{}_{fin}) = \frac{p_A{}^0(\bar{M}_{B_2,n} + p_B{}^0 \bar{M}_{A_f,n})}{1 - p_A{}^0 p_B{}^0 (f-1)} \qquad \text{(II-10)}$$

The roots of the chains can be only portions of the polyfunctional cross-linker; thus

$$\bar{M}_{n,p} = \frac{\bar{M}_{A_f,n}}{f} + \frac{p_A{}^0(\bar{M}_{B_2,n} + p_B{}^0 \bar{M}_{A_f,n})}{1 - p_A{}^0 p_B{}^0 (f-1)} \qquad \text{(II-11)}$$

It is simple to obtain in a similar way results for more general copolymerizations such as $A_f + B_g$.

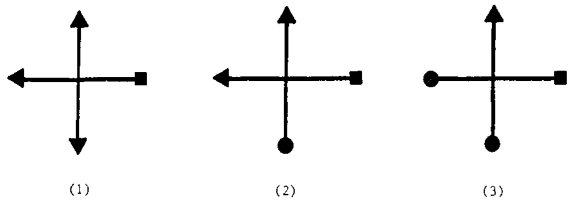


Figure 3. Different states of a tetrafunctional monomer molecule in a pendant chain. Arrows indicate infinite direction, circles finite direction, and squares finite direction from which an observer enters into the molecule. Mers 1 and 2 are roots of pendant chains. Mer 3 is a completely pendant unit.

III. Weight-Average Molecular Weight of the Pendant Chains

To calculate $\bar{M}_w$ of the pendant chains using the recursive approach, we have to pick mass units at random from the pendant material. This is a weight-averaging process for the chains since the larger ones have a better chance of being chosen. As before, we derive in detail the calculation of $\bar{M}_w$ for the simplest case, homopolymerization of monodisperse A_f, and then show the results for copolymerization.

The calculation of $\bar{M}_w$ has an additional complication due to the nonsymmetric structure of the pendant chains. Once we pick a mer at random, we must look for the expected weight looking out of that mer in both directions. We have already calculated in the preceding section the expected weight in the finite direction.

$$E(W_A{}^{out}{}_{fin}) = \frac{p_A{}^0 M_{A_f}}{1 - p_A{}^0(f-1)} \qquad \text{(II-3)}$$

We now proceed to compute the expected weight in the infinite direction, i.e., in the way that goes toward the root of the chain. When one moves toward the root from a randomly chosen mer, continuity of the chain is ensured. All the A's in that direction are reacted, and the extent of reaction $p_{inf} = 1$. The expected weight looking out of an A in the infinite direction is equal to the expected weight going into the next A:

$$E(W_A{}^{out}{}_{inf}) = E(W_A{}^{in}{}_{inf}) \qquad \text{(III-1)}$$

When we move in the infinite direction, we eventually arrive at the root of the pendant chain. We then have to introduce in the computation a new parameter C, which is the probability that a mer that belongs to a pendant chain is a continuation of the chain instead of being the root of the chain. In Figure 3 we show as an example all the possible states in which we may find a mer belonging to a pendant chain for polymerization of a tetrafunctional monomer. The arrows mean infinite direction, the circles indicate finite direction, and the squares are the arms from which we are entering the mer. The entering arms are also finite. The mer unit 3 has only one infinite arm and is therefore a mer that continues the pendant chain toward the root. Mers 2 and 1 have two and three infinite arms and constitute a root of the pendant chain. The two other possibilities for A_4 after the gel point are either four infinite or four finite branches, which correspond to totally elastic or totally soluble material but not to pendant material.

We define then C as (fraction of mers that continue the pendant chain toward the root)/(fraction of mers that belong to the pendant material). In the example that we are considering, this is equivalent to the fraction of mers of type 3 divided by the fraction of mers 1, 2, and 3 together. This is given in general by

$$C = \frac{\binom{f-1}{1} P(F_{\mathrm{A}}{}^{\mathrm{out}})^{f-2}(1 - P(F_{\mathrm{A}}{}^{\mathrm{out}}))}{\sum_{i=1}^{f-1} \binom{f-1}{i} P(F_{\mathrm{A}}{}^{\mathrm{out}})^{f-i-1}(1 - P(F_{\mathrm{A}}{}^{\mathrm{out}}))^{i}} \qquad \text{(III-2)}$$

where $P(F_{\mathrm{A}}{}^{\mathrm{out}})$ is the probability of a finite chain and $\binom{f-1}{i}$ indicates the number of combinations of $f - 1$ elements taken i at a time. The probability that a mer picked at random from the pendant material is a root of a chain is just $1 - C$.

We can now go back to eq III-1 and conclude that the weight into an A unit in the infinite direction is given as follows:

$$(W_{\mathrm{A}}{}^{\mathrm{in}}{}_{\mathrm{inf}}) = \begin{cases} M_{\mathrm{A}} & \text{with probability } 1 - C \\ M_{\mathrm{A}_f} + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) + (f - 2)\, E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}}) \\ \qquad \text{with probability } C \end{cases}$$

Thus

$$E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) = C\{M_{\mathrm{A}_f} + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) + (f - 2)E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})\} + (1 - C)M_{\mathrm{A}} \qquad \text{(III-3)}$$

Solving eq III-1 and III-3 gives

$$E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) = \frac{C\{M_{\mathrm{A}_f} + (f - 2)E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})\} + (1 - C)M_{\mathrm{A}}}{1 - C} \qquad \text{(III-4)}$$

In the homopolymerization system there are two possible choices for picking an A_f. If the unit is a root of the pendant chain, the expected weight becomes

$$E(W_{\mathrm{A}_f,\mathrm{r}}) = M_{\mathrm{A}} + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}}) \qquad \text{(III-5)}$$

If the A_f is not a root of the pendant chain

$$E(W_{\mathrm{A}_f,\mathrm{d}}) = M_{\mathrm{A}_f} + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) + (f - 1)E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}}) \qquad \text{(III-6)}$$

To find the weight-average molecular weight, we pick a unit of mass at random from the pendant material and compute the expected weight of the chain of which it is a part. To do this we have to calculate the weight fractions of the two possible choices: roots like (1) and (2) in Figure 3 or mers along the pendant chains (3).

The weight of the roots in the system is given by

$$a_{\mathrm{r}} = (A_0)M_{\mathrm{A}_f} \sum_{i=2}^{f-1} \frac{f-i}{f} \binom{f}{i} P(F_{\mathrm{A}}{}^{\mathrm{out}})^{f-i}(1 - P(F_{\mathrm{A}}{}^{\mathrm{out}}))^{i}$$

where (A_0) is the initial concentration of A_f groups, the weight of the dangling units a_{d} is

$$a_{\mathrm{d}} = (A_0)M_{\mathrm{A}_f} fP(F_{\mathrm{A}}{}^{\mathrm{out}})^{f-1}(1 - P(F_{\mathrm{A}}{}^{\mathrm{out}}))$$

and the corresponding weight fractions a_{r}' and a_{d}' are

$$a_{\mathrm{r}}' = a_{\mathrm{r}}/(a_{\mathrm{r}} + a_{\mathrm{d}})$$

$$a_{\mathrm{d}}' = a_{\mathrm{d}}/(a_{\mathrm{r}} + a_{\mathrm{d}}) \qquad \text{(III-7)}$$

The final result for $\bar{M}_{\mathrm{w,p}}$ is then

$$\bar{M}_{\mathrm{w,p}} = a_{\mathrm{d}}'E(W_{\mathrm{A}_f,\mathrm{d}}) + a_{\mathrm{r}}'E(W_{\mathrm{A}_f,\mathrm{r}}) \qquad \text{(III-8)}$$

For the copolymerization between polydisperse A_f and B_2 the derivation follows a similar approach. The set of recursive equations in the infinite direction is

$$E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) = \sum_{i}^{\infty} b_i E(W_{\mathrm{B}}{}^{\mathrm{in}}{}_{\mathrm{inf}})_i$$

$$E(W_{\mathrm{B}}{}^{\mathrm{in}}{}_{\mathrm{inf}})_i = M_{\mathrm{B}_2,i} + E(W_{\mathrm{B}}{}^{\mathrm{out}}{}_{\mathrm{inf}})$$

$$E(W_{\mathrm{B}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) = \sum_{i}^{\infty} a_i E(W_{\mathrm{A}}{}^{\mathrm{in}}{}_{\mathrm{inf}})_i$$

$$E(W_{\mathrm{A}}{}^{\mathrm{in}}{}_{\mathrm{inf}})_i = C\{M_{\mathrm{A}_f,i} + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) + (f - 2)E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})\} + (M_{\mathrm{A}_f,i}/f)(1 - C)$$

where $E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})$ has been calculated in (II-10). Solving for $E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}})$ and $E(W_{\mathrm{B}}{}^{\mathrm{out}}{}_{\mathrm{inf}})$ and making use again of the definition of number-average molecular weight, we obtain

$$E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) = \{\bar{M}_{\mathrm{B}_2,\mathrm{n}} + C(\bar{M}_{\mathrm{A}_f,\mathrm{n}} + (f - 2)E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})) + (\bar{M}_{\mathrm{A}_f,\mathrm{n}}/f)(1 - C)\}/(1 - C)$$

$$E(W_{\mathrm{B}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) = E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) - \bar{M}_{\mathrm{B}_2,\mathrm{n}}$$

Now we have three different groups in the pendant chains: A_f dangling groups, A_f groups that constitute a root of a pendant chain, and B_2 dangling groups.

The expected weights for each of these groups are

$$E(W_{\mathrm{A}_f,\mathrm{d}})_i = M_{\mathrm{A}_f,i} + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) + (f - 1)E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})$$

$$E(W_{\mathrm{A}_f,\mathrm{r}})_i = M_{\mathrm{A}_f,i}/f + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})$$

$$E(W_{\mathrm{B}_2,\mathrm{d}})_i = M_{\mathrm{B}_2,i} + E(W_{\mathrm{B}}{}^{\mathrm{out}}{}_{\mathrm{fin}}) + E(W_{\mathrm{B}}{}^{\mathrm{out}}{}_{\mathrm{inf}})$$

The probabilities of picking units of each of the groups at random are

$$a_{\mathrm{d},i}' = a_{\mathrm{d},i}/(a_{\mathrm{d}} + a_{\mathrm{r}} + b_{\mathrm{d}})$$

$$a_{\mathrm{r},i}' = a_{\mathrm{r},i}/(a_{\mathrm{d}} + a_{\mathrm{r}} + b_{\mathrm{d}})$$

$$b_{\mathrm{d},i}' = b_{\mathrm{d},i}/(a_{\mathrm{b}} + a_{\mathrm{r}} + b_{\mathrm{d}})$$

with

$$a_{\mathrm{d}} = \sum_i a_{\mathrm{d},i}$$

$$a_{\mathrm{r}} = \sum_i a_{\mathrm{r},i}$$

$$b_{\mathrm{d}} = \sum_i b_{\mathrm{d},i}$$

$$a_{\mathrm{d},i} = (A_{f,i})_0 M_{\mathrm{A}_f,i} fP(F_{\mathrm{A}}{}^{\mathrm{out}})^{f-1}(1 - P(F_{\mathrm{A}}{}^{\mathrm{out}}))$$

$$a_{\mathrm{r},i} = (A_{f,i})_0 M_{\mathrm{A}_f,i} \sum_{i=2}^{f-1} \frac{f-i}{f} \binom{f}{i} P(F_{\mathrm{A}}{}^{\mathrm{out}})^{f-i}(1 - P(F_{\mathrm{A}}{}^{\mathrm{out}}))^{i}$$

$$b_{\mathrm{d},i} = 2(B_{2,i})_0 M_{\mathrm{B}_2,i} P(F_{\mathrm{B}}{}^{\mathrm{out}})(1 - P(F_{\mathrm{B}}{}^{\mathrm{out}}))$$

With the following definitions of weight-average molecular weight

$$\bar{M}_{\mathrm{A}_f,\mathrm{w}} = \sum_i A_{f,i} M_{\mathrm{A}_f,i}{}^2 / \sum_i A_{f,i} M_{\mathrm{A}_f,i}$$

$$\bar{M}_{\mathrm{B}_2,\mathrm{w}} = \sum_i B_{2,i} M_{\mathrm{B}_2,i}{}^2 / \sum_i B_{2,i} M_{\mathrm{B}_2,i}$$

we obtain the total expected weights for each species:

$$E(W_{\mathrm{A}_f,\mathrm{d}}) = \bar{M}_{\mathrm{A}_f,\mathrm{w}} + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{inf}}) + (f - 1)E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})$$

$$E(W_{\mathrm{A}_f,\mathrm{r}}) = \bar{M}_{\mathrm{A}_f,\mathrm{w}}/f + E(W_{\mathrm{A}}{}^{\mathrm{out}}{}_{\mathrm{fin}})$$

$$E(W_{\mathrm{B}_2,\mathrm{d}}) = \bar{M}_{\mathrm{B}_2,\mathrm{w}} + E(W_{\mathrm{B}}{}^{\mathrm{out}}{}_{\mathrm{fin}}) + E(W_{\mathrm{B}}{}^{\mathrm{out}}{}_{\mathrm{inf}})$$

and

$$a_{\mathrm{d}} = (A_f)_0 \bar{M}_{\mathrm{A}_f,\mathrm{n}} fP(F_{\mathrm{A}}{}^{\mathrm{out}})^{f-1}(1 - P(F_{\mathrm{A}}{}^{\mathrm{out}}))$$

$$a_{\mathrm{r}} = (A_f)_0 \bar{M}_{\mathrm{A}_f,\mathrm{n}} \sum_{i=2}^{f-1} \frac{f-i}{f} \binom{f}{i} P(F_{\mathrm{A}}{}^{\mathrm{out}})^{f-i}(1 - P(F_{\mathrm{A}}{}^{\mathrm{out}}))^{i}$$

$$b_{\mathrm{d}} = 2(B_2)_0 \bar{M}_{\mathrm{B}_2,\mathrm{n}} P(F_{\mathrm{B}}{}^{\mathrm{out}})(1 - P(F_{\mathrm{B}}{}^{\mathrm{out}}))$$

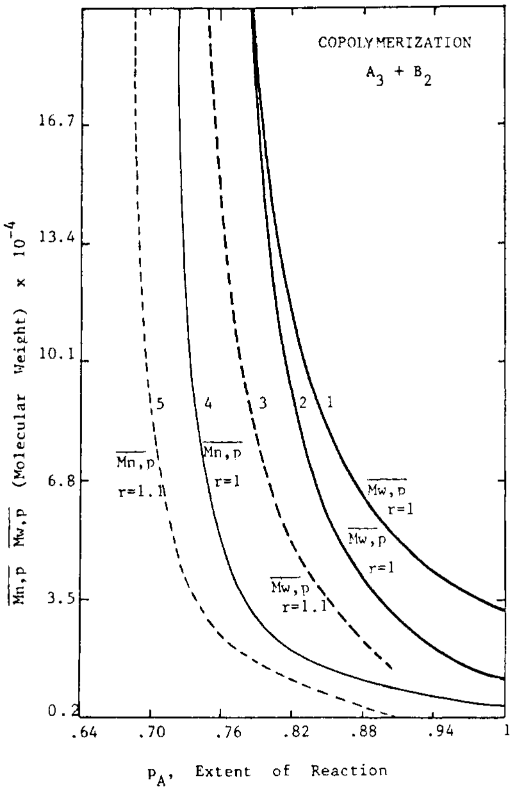


Figure 4. Copolymerization of a B_2 prepolymer of $\bar{M}_n = 10\,800$ with a monodisperse trifunctional cross-linker A_3 (MW = 330). Curves 2 and 4 correspond to $\bar{M}_{n,p}$ and $\bar{M}_{w,p}$ when B_2 is monodisperse, curve 1 shows how $\bar{M}_{w,p}$ changes with polydisperse B_2 with $\bar{M}_w/\bar{M}_n = 3$, and curves 3 and 5 correspond to a stoichiometric imbalance $r = 1.1$ with monodisperse reactants.

We can finally obtain the expression for the weight-average molecular weight of the pendant chains as

$$\bar{M}_{w,p} = a_d'E(W_{A_f,d}) + a_r'E(W_{A_f,r}) + b_d'E(W_{B_2,d}) \qquad \text{(III-9)}$$

with

$$a_d' = a_d/(a_d + a_r + b_d)$$
$$a_r' = a_r/(a_d + a_r + b_d)$$
$$b_d' = b_d/(a_d + a_r + b_d) \qquad \text{(III-10)}$$

Figure 4 shows the results obtained for copolymerization of a B_2 prepolymer of $\bar{M}_n = 10\,800$ with a monodisperse trifunctional cross-linker with MW = 330. Curves 2 and 4 correspond to $\bar{M}_{w,p}$ and $\bar{M}_{n,p}$ when B_2 is also monodisperse. Both curves have an infinite value at the gel point and approach the expected values at complete conversion. Curve 1 shows how $\bar{M}_{w,p}$ changes when B_2 is polydisperse with $\bar{M}_w/\bar{M}_n = 3$. $\bar{M}_{n,p}$ is not affected by polydispersity. Curves 3 and 5 show the effect of an excess of cross-linker on the molecular weight averages of the pendant material. As predicted, an imbalance of A_3 depresses both $\bar{M}_{n,p}$ and $\bar{M}_{w,p}$ since it increases the amount of branches and hence diminishes the average molecular weight per chain. The effect is reinforced here because the molecular weight of the cross-linker used in the calculations is lower than the molecular weight of prepolymer B_2.

IV. Number of Branch Points and Chains per Pendant Chain

We now show how to calculate the number- and weight-average number of branch points and chains of the pendant material. The derivation is performed only for the stepwise copolymerization. Results for the homopolymerization case have been obtained but are not included here. We begin with the number-average number of branch points. To calculate the number-average number of branch points, we must pick a root of a pendant chain at random and look for the expected branch points in the finite direction. Only the polyfunctional A_f can be roots of pendant chains. The expectancy looking out of an A group, $E(B_A{}^{out}{}_{fin})$, is

$$E(B_A{}^{out}{}_{fin}) = p_A{}^0E(B_B{}^{in}{}_{fin}) + (1 - p_A{}^0)0 \qquad \text{(IV-1)}$$

The expectancy of branching is zero if the A group has not reacted.

If we continue through the chain in the finite direction, we obtain

$$E(B_B{}^{in}{}_{fin}) = E(B_B{}^{out}{}_{fin}) \qquad \text{(IV-2)}$$

$$E(B_B{}^{out}{}_{fin}) = p_B{}^0E(B_A{}^{in}{}_{fin}) + (1 - p_B{}^0)0 \qquad \text{(IV-3)}$$

$$E(B_A{}^{in}{}_{fin}) = C_1 + (f - 1)E(B_A{}^{out}{}_{fin}) \qquad \text{(IV-4)}$$

where C_1 is the expected number of branches at the corresponding A_f group. As we have mentioned in a previous publication,[9] there are at least two different ways to count the number of branches at an A_f group: (i) considering that the group is one branch if at least three of the A's are reacted, irrespective of how many of them have indeed joined B_2 groups, or (ii) including a weighting factor of the functionality of the branch, i.e., counting as one branch point if three A's are reacted, two branch points if four A's are reacted, etc. The first approach gives

$$C_1 = \sum_{i=2}^{f-1} \binom{f-1}{i} (p_A{}^0)^i (1 - p_A{}^0)^{f-i-1}$$

and the second approach

$$C_1' = \sum_{i=2}^{f-1} \binom{f-1}{i} (i - 1)(p_A{}^0)^i (1 - p_A{}^0)^{f-i-1}$$

Solving IV-1 to IV-4

$$E(B_A{}^{out}{}_{fin}) = \frac{p_A{}^0 p_B{}^0 C_1}{1 - p_A{}^0 p_B{}^0 (f - 1)} = \bar{B}_n \qquad \text{(IV-5)}$$

which is the desired result for the number-average number of branches. With the second approach

$$\bar{B}_n' = E(B_A{}^{out}{}_{fin}) = \frac{p_A{}^0 p_B{}^0 C_1'}{1 - p_A{}^0 p_B{}^0 (f - 1)} \qquad \text{(IV-6)}$$

We have shown that the number-average number of chains per pendant molecule, $\bar{Z}_n$, is

$$\bar{Z}_n = 1 + \bar{B}_n + \bar{B}_n' \qquad \text{(IV-7)}$$

To calculate the weight-average number of branch points, we pick a unit of mass at random and we look for the expected number of branches in both directions, finite and infinite. We then need to calculate the expected number in the infinite direction. As we explained in the molecular weight derivation, in this direction all the functional groups are reacted. The corresponding system of equations is

$$E(B_A{}^{out}{}_{inf}) = E(B_B{}^{in}{}_{inf})$$

$$E(B_B{}^{in}{}_{inf}) = E(B_B{}^{out}{}_{inf})$$

$$E(B_B{}^{out}{}_{inf}) = E(B_A{}^{in}{}_{inf})$$

$$E(B_A{}^{in}{}_{inf}) =$$
$$C\{C_2 + E(B_A{}^{out}{}_{inf}) + (f - 2)E(B_A{}^{out}{}_{fin})\} + (1 - C)0 \qquad \text{(IV-8)}$$

where C is again the probability that a mer that belongs to a pendant chain is a continuation of the chain rather than being a root of the chain and C_2 is the expected number of branches of the A_f group at which we are entering from a finite end. In this case, we know that at least the A group that continues the branch to the gel is reacted. Therefore

$$C_2 = (f-1)\sum_{i=1}^{f-2}\binom{f-2}{i}(p_A{}^0)^i(1-p_A{}^0)^{f-2-i}$$

$$C_2' = (f-1)\sum_{i=1}^{f-2} i\binom{f-2}{i}(p_A{}^0)^i(1-p_A{}^0)^{f-2-i} \qquad \text{(IV-9)}$$

Solving IV-8 for $E(B_A{}^{\text{out}}{}_{\text{inf}})$, we get

$$E(B_A{}^{\text{out}}{}_{\text{inf}}) = \frac{C\{C_2 + (f-2)E(B_A{}^{\text{out}}{}_{\text{fin}})\}}{1-C} \qquad \text{(IV-10)}$$

For weighted functionality, C_2' must replace C_2.

When we pick a unit of mass, we can get three different kinds of groups as explained above: dangling A_f groups, A_f groups that constitute a root, and dangling B_2 groups. The expectancies of branching for these groups are

$$E(B_{A_f,d}) = C_3 + E(B_A{}^{\text{out}}{}_{\text{inf}}) + (f-1)E(B_A{}^{\text{out}}{}_{\text{fin}})$$

$$E(B_{A_f,r}) = E(B_A{}^{\text{out}}{}_{\text{fin}})$$

$$E(B_{B_2,d}) = E(B_B{}^{\text{out}}{}_{\text{inf}}) + E(B_B{}^{\text{out}}{}_{\text{fin}}) \qquad \text{(IV-11)}$$

where C_3 is the expected branching of the A_f unit that was picked from the system. C_3 is replaced by C_3' in the case of weighted functionality.

$$C_3 = f\sum_{i=2}^{f-1}\binom{f-1}{i}(p_A{}^0)^i(1-p_A{}^0)^{f-1-i}$$

$$C_3' = f\sum_{i=2}^{f-1}\binom{f-1}{i}(i-1)(p_A{}^0)^i(1-p_A{}^0)^{f-1-i} \qquad \text{(IV-12)}$$

The probabilities for each of the groups in IV-11 were given in III-10. The weight-average number of branches is finally obtained as

$$\bar{B}_w \text{ or } \bar{B}_w' = a_d'E(B_{A_f,d}) + a_r'E(B_{A_f,r}) + b_d'E(B_{B_2,d}) \qquad \text{(IV-13)}$$

The weight-average number of chains per pendant molecule is

$$\bar{Z}_w = 1 + \bar{B}_w + \bar{B}_w' \qquad \text{(IV-14)}$$

In Figure 5 we plot the number- and weight-average number of branching points per pendant molecule for a copolymerization reaction between a bifunctional prepolymer and a tetrafunctional cross-linker A_4.

The $\bar{B}_n'$ and $\bar{B}_w'$ curves correspond to weighted functionality. $\bar{B}_n$ and $\bar{B}_w$ correspond to the first criterion that counts as one branch of any A_4 group that has at least three reacted A's.

Both approaches give infinite branching at the gel point and approach zero branching for complete reaction.

The number- and weight-average number of chains follow the same pattern except that, as expected, they converge to unity for $p_A = 1$ since the last pendant chains in the network have no branches if the reaction is stoichiometrically balanced.

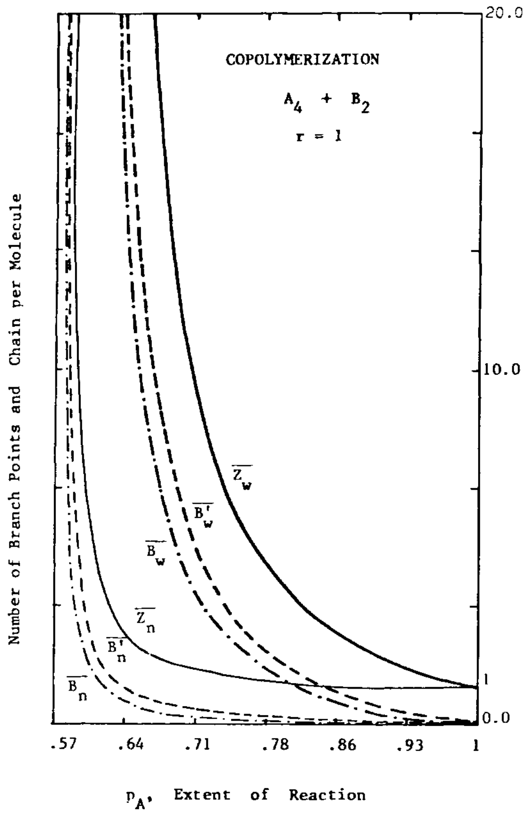


Figure 5. Weight- and number-average number of branch points and chains per pendant chain. The $\bar{B}_n$ and $\bar{B}_w$ curves correspond to the first criterion for counting branches, the $\bar{B}_n'$ and $\bar{B}_w'$ curves correspond to the second criterion with weighted functionality, and the $\bar{Z}_n$ and $\bar{Z}_w$ curves correspond to the number- and weight-average number of chains per pendant chain.

V. Length of the Longest Subchain through a Pendant Chain

It has been shown[9] that the length of the longest linear chain through a randomly branched polymer is an important parameter because it can be correlated with the zero shear rate viscosity of melts. We believe that the contribution of this parameter to the rheological properties of cross-linked systems will also be important.

We show therefore how to calculate the average length of the longest subchain through a pendant chain in a gel system obtained by cross-linking long B_2 molecules with short A_f molecules. To determine the number-average length of the longest chain through a randomly selected pendant chain, we proceed as follows.

We pick at random one of the long B_2 molecules that are joined to the root of the pendant chain and seek the expected length in the finite direction. The probability that the length of the chain looking out of the B_2 unit in the finite direction is longer than a certain l number of B_2 units is

$$P(L_B{}^{\text{out}} > l) = p_B{}^0 P(L_A{}^{\text{in}} > l) \qquad \text{(V-1)}$$

The probability that looking into a polyfunctional A_f group through one of its arms we will find all of the other arms shorter than a certain length l is

$$P(L_A{}^{\text{in}} \leq l) = \{P(L_A{}^{\text{out}} \leq l)\}^{f-1} \qquad \text{(V-2)}$$

Since the complementary event is the probability that looking into an A_f group at least one of the arms is longer than l, we can write (V-2) as follows:

$$\{1 - P(L_A{}^{\text{in}} > l)\} = \{1 - P(L_A{}^{\text{out}} > l)\}^{f-1} \qquad \text{(V-3)}$$

Moving forward through the pendant chain, we find that

$$P(L_A{}^{\text{out}} > l) = p_A{}^0 P(L_B{}^{\text{in}} > l) \qquad \text{(V-4)}$$

$$P(L_B{}^{\text{in}} > l) = P(L_B{}^{\text{out}} > l - 1) \qquad \text{(V-5)}$$

Solving the set of equations for $P(L_B{}^{\text{out}} > l)$, we find

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$$P(L_B{}^{out} > l) = p_B{}^0\{1 - (1 - p_A{}^0 P(L_B{}^{out} > l - 1))^{f-1}\} \quad \text{(V-6)}$$

The probability that $L_B{}^{out} > 0$ length is just

$$P(L_B{}^{out} > 0) = p_B{}^0\{1 - (1 - p_A{}^0)^{f-1}\} \quad \text{(V-7)}$$

where the term in braces is the probability that at least one of the $f - 1$ arms of the A_f group attached to the B_2 group has reacted.

We can now solve (V-6) and (V-7) recursively, starting with $l = 0$. The expected length looking out of a B_2 unit is

$$E(L_B{}^{out}) = \sum_{l=0}^{\infty} lP(L_B{}^{out} = l) = \sum_{l=0}^{\infty} lP(L_B{}^{out} > l - 1) - \sum_{l=0}^{\infty} lP(L_B{}^{out} > l) = \sum_{l=0}^{\infty} P(L_B{}^{out} > l) \quad \text{(V-8)}$$

The number-average molecular weight of the longest chain for monodisperse B_2 is

$$\bar{M}_{n,L,p} = M_{B_2} + E(L_B{}^{out})M_{B_2} \quad \text{(V-9)}$$

If B_2 is polydisperse, M_{B_2} must be replaced by $\bar{M}_{B_2,n}$.

In order to obtain the weight-average molecular weight, we have to select a portion of a B_2 molecule at random from the pendant material and look for the expected weight in the finite and the infinite directions. As we have already calculated the expectancy in the finite direction, we have to look for the expected weight from the point selected at random up to the root of the pendant chain. This is done with an approach similar to the one we used for $\bar{M}_{w,p}$. Again, all the groups in the infinite direction have reacted, and the expectancy is calculated from the following set of equations:

$$E(W_A{}^{out}{}_{inf}) = E(W_B{}^{in}{}_{inf})$$

$$E(W_B{}^{in}{}_{inf}) = \bar{M}_{B_2,n} + E(W_B{}^{out}{}_{inf})$$

$$E(W_B{}^{out}{}_{inf}) = E(W_A{}^{in}{}_{inf})$$

$$E(W_A{}^{in}{}_{inf}) = CE(W_A{}^{out}{}_{inf}) + (1 - C)0 \quad \text{(V-10)}$$

Solving for $E(W_B{}^{out}{}_{inf})$ yields $\bar{M}_{B_2,n}C/(1 - C)$, and the weight-average molecular weight of the longest chain is given by

$$\bar{M}_{w,L,p} = \bar{M}_{B_2,w} + E(W_B{}^{out}{}_{inf}) + E(L_B{}^{out})\bar{M}_{B_2,n} \quad \text{(V-11)}$$

which is valid for polydisperse B_2.

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Halato-Telechelic Polymers. 5. A Theoretical Approach to Gel Formation in Nonpolar Solvents

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ABSTRACT: Ion aggregation in halato-telechelic polymers (HTP) is treated from a theoretical point of view. When diluted in media of low dielectric constant, HTP would easily form ionic multiplets up to sextets whereas the energy gained in the formation of higher multiplets would decrease rapidly. This expectation is qualitatively confirmed by the very early gelation of HTP in nonpolar solvents. At high concentration, the ionic multiplets can possibly aggregate and form periodic structures, as evidenced in barium α,ω-carboxylato-polybutadiene. A theoretical relationship is proposed between the critical concentration of gelation (C_{gel}) and the molecular weight of the telechelic prepolymer ($\bar{M}_n$) for a given ion pair, solvent, and temperature: $C_{gel} = k\bar{M}_n{}^{-1/2}$. This relation is largely confirmed by experience. The proportionality constant k depends on the lability of the ionic bonds and on the conformational state of the polymeric carrier: $[\langle r^2\rangle/M]^{1/2}$. The longer the distance between the ion pairs, the earlier the gelation.

I. Introduction

In previous papers[1,2] we have studied in detail the dilute-solution behavior of halato-telechelic polymers (HTP).

HTP are obtained by the complete ionization of both ends of telechelic polymers and behave as model ion-containing polymers.[1,2] In nonpolar solvents, a sharp gel formation is noted at concentrations as low as 1–1.5 g·dL^{-1}. The electrostatic origin of this phenomenon is assessed by a large amount experimental evidence as the effect of temperature and nature of solvent or ion pairs.[1,2] For a given HTP, the molecular weight ($\bar{M}_n$) of the prepolymer, i.e., the distance between ion pairs, has a determining effect on the ion aggregation responsible for gelation. In toluene at 25 °C, magnesium α,ω-carboxylato-polyisoprene (PIP), -polybutadiene (PBD), -polystyrene (PS), -poly(*tert*-butylstyrene) (PTBS), and -poly(α-methylstyrene) (PMS) gel at concentrations (C_{gel}) that vary inversely with $\bar{M}_n$, and the apparent general relationship

$$C_{gel} = k\bar{M}_n{}^{-0.5} \quad (1)$$

is experimentally observed, where k is a function of the solvent, temperature, and nature of the prepolymer. This

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