Influence of Pendant Chains on Mechanical Properties of Model Poly(dimethylsiloxane) Networks. 1. Analysis of the Molecular Structure of the Network

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ABSTRACT: A recursive approach is used to evaluate the resulting molecular structure of a network-forming system composed of a mixture of bifunctional and monofunctional prepolymer chains reacting with a polyfunctional cross-linker ($A_f + B_2 + B_1$). This system can be used to find formulations for model networks with pendant chains composed of linear molecules of known and uniform molecular weight. Several important molecular parameters, such as the weight fraction of pendant chains, number- and weight-average molecular weights, and polydispersity of the pendant chains in the network, are calculated as a function of the weight fraction of monofunctional chains (B_1) added to the reaction mixture. In a naive analysis of the system $A_f + B_2 + B_1$, it may be wrongly assumed that networks obtained from the reaction of these components are formed by elastically active chains comprising B_2 molecules and pendant chains comprising B_1 molecules. A careful analysis shows that this hypothetical situation would take place only under certain formulation conditions. Either a defect or an excess of cross-linker leads to networks with branched pendant structures. Calculations also show that, even for stoichiometrically balanced, completely reacted networks, there exists a limiting amount of monofunctional chains that can be added to the reaction mixture to obtain model networks with linear pendant chains.

I. Introduction

Well-characterized model networks are very important for the study of structure−property relations. This has focused attention on synthetic procedures that link telechelic long chains of a given linear polymer by their ends.[1−5] In this kind of reaction, the end functional groups are reacted with cross-linking agents having a functionality *f*, where *f* is an integer greater than 2. If every prepolymer chain has two terminal reactive groups (B_2), and each group effectively reacts with different cross-linker molecules (A_f), then an ideal or model network is obtained. The average chain length between cross-linking points is, in this case, equal to the length of the bifunctional B_2 molecules used to prepare the model network. Thanks to modern anionic polymerization procedures, today it is possible to build model networks with chains of a narrow molecular weight distribution. This has been of great importance in the evaluation of molecular theories.[6−9] In particular, a great amount of effort has been made to elucidate the influence of the elastic chains and trapped entanglements on the equilibrium properties. However, there are very few studies of the influence of network defects on the nonequilibrium properties of networks.[10]

Pendant chains are among the more important sources of network defects. They are commonly formed in any of the usual cross-linking procedures, like vulcanization and irradiation or by addition of polyfunctional cross-linkers in nonlinear stepwise polymerization.[6] It is well known that the presence of long pendant chains in a network significantly increases relaxation times.[11] Recent theoretical models of the dynamics of networks with pendant chains suggested that their relaxation times should depend exponentially on the lengths of these chains.[12−14] To study the influence of pendant chains on the mechanical properties of networks, we are interested in synthesizing model networks with controlled amounts of monodisperse linear chains dangling from the infinite gel structure. These networks are prepared by reacting a mixture of a bifunctional prepolymer with reactive functional groups at the chain ends (B_2), linear monodisperse chains of the same polymer with only one functional end group (B_1), and a polyfunctional cross-linker (A_f). The final structure of the network obtained by this procedure depends on the relative amounts in which these components are mixed in the initial formulation of the cross-linking reaction. We present here a parametric analysis of formulation variables in order to identify the necessary conditions to obtain networks with pendant chains of known and uniform molecular weight. The recursive method developed by Miller and Macosko,[15−17] particularly the derivation made by Bibbó and Vallés[18] with some extensions, is used to estimate the molecular structure of the network.

II. Preliminary Considerations

When the gel point is reached in a network-forming reaction, the molecular chains of the reacting mixture are divided into three different categories: the so-called "elastic chains", which are those joined by both ends to the infinite gel structure; the "pendant chains", which are attached by only one end to the gel; and the "soluble chains", which are those with no connection to the gel structure. An illustration for the system $A_3 + B_2 + B_1$ at this stage of the reaction is shown in Figure 1, where the arrows indicate the connection of the B_2 and B_1 prepolymer chains to the infinite gel structure.

The evolution of the weight fractions of the elastic, pendant, and soluble chains as a function of the extent of reaction (*p*) in stoichiometrically balanced reactions, for the systems $A_3 + B_2$ and $A_4 + B_2$ where no B_1's were included, has been shown in previous work.[17] The results are shown in Figure 2. The onset of gelation is

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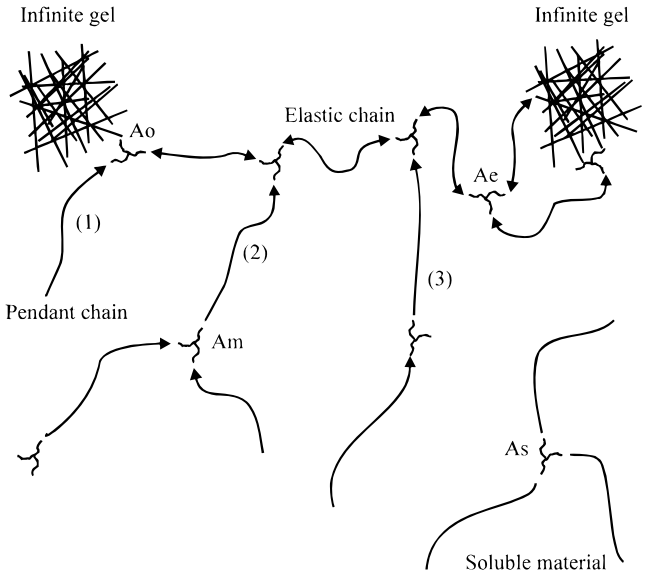

Figure 1. Schematic representation of the state of a network after the gel point for the system $A_3 + B_2 + B_1$. Arrows indicate reacted chain ends in the infinite direction, i.e., in the direction in which they are connected to the gel.

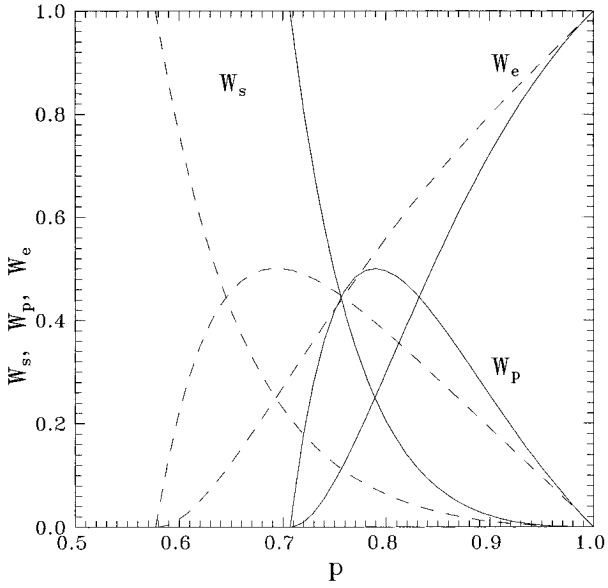

Figure 2. Weight fractions of solubles (W_s), pendant chains (W_p), and elastic material (W_e) for stoichiometrically balanced networks ($r = 1$) as a function of extent of reaction: — system $A_3 + B_2$; - - - system $A_4 + B_2$.

obtained at $p_g = 1/2^{1/2}$ for $A_3 + B_2$ and at $p_g = 1/3^{1/2}$ for $A_4 + B_2$. At the gel point, all the material is soluble ($W_s = 1$, $W_p = 0$, and $W_e = 0$). When the reaction is complete, a perfect network results with no solubles or pendant chains ($W_e = 1$, $W_p = 0$, and $W_s = 0$). Between these extreme points, the fraction of pendant chains goes from zero to a maximum of 0.5 at an intermediate point and then decays again to zero when the reaction is completed.

For $A_f + B_2$ systems, the only way to obtain dangling ends at complete reaction is to prepare formulations with an initial stoichiometric imbalance. In this case, the amount of pendant material that remains in the network at the end of the reaction depends on r. The principal disadvantage of these systems is that the resultant pendant chains have complex branched structures that are not suitable for structural studies.[18,19]

Networks with simple linear pendant chains may be obtained by adding to the original reaction mixture ($A_f + B_2$) monofunctional prepolymer molecules with a terminal reactive group at one end (B_1). In these systems, the amount of pendant material is a function not only of the stoichiometric imbalance but also of the proportion of B_1 groups added to the system. The advantage of this procedure is that it allows the synthesis of model networks with pendant chains of any desired length and structure. We feel that the study of these kinds of systems is extremely valuable for analyzing the influence of pendant chains on network physical properties. In the following sections, we show how to calculate several molecular parameters that are important in the evaluation of the final structure of networks with controlled amounts of pendant chains. These calculations are used in the interpretation of the results in the following paper.[20]

Prior to the computation of the average molecular structures for $A_f + B_2 + B_1$ systems, we must define some parameters that will be employed in the calculations. To account properly for the amount of B_1 chains that are incorporated into the reactive systems, we define ν as the initial fraction of B reactive groups belonging to difunctional molecules:

$$\nu = \frac{2[B_2]}{2[B_2] + [B_1]} \tag{1}$$

For simplicity, ν will be called the fraction of B groups on bifunctional molecules. The stoichiometric imbalance, r, is computed as

$$r = \frac{f[A_f]_0}{2[B_2]_0 + [B_1]_0} \tag{2}$$

III. Molecular Parameters for the $A_f + B_2 + B_1$ System

In this section, we present an analysis to describe how the initial formulation employed in the synthesis of the $A_f + B_2 + B_1$ system affects some of the more interesting postgel molecular parameters, such as the weight fraction of the elastic, pendant, and soluble material and the number- and weight-average molecular weights and the polydispersity of the pendant chains. We show the dependence of these structural parameters as a function of the stoichiometric imbalance, the weight fraction of B_1 in the initial formulation, and the molecular weights of the prepolymers to be used (M_{B_1} and M_{B_2}). All calculations are computed at complete reaction. The usual simplyfing assumptions about the reactivity of the different end groups are adopted. They imply that (1) all functional groups of the same type are equally reactive, (2) all groups react independently of one another (no substitution effects), and (3) no intramolecular reactions occur in finite species. For generality, the ensuing results were obtained for systems composed of a monodisperse polyfunctional cross-linker, A_f, and polydisperse prepolymer chains of type B_2 and B_1. For this reason, M_{nB_2}, M_{nB_1}, M_{wB_2}, and M_{wB_1}, appear in the equations given in the following sections.

III.1. Weight Fractions of Elastic, Pendant, and Soluble Materials. Consider the copolymerization of A_f with B_2 and B_1 where some degree of initial stoichiometric imbalance ($r \neq 1$) has been allowed. If we selected an A_f molecule at random from this reacted mixture, there are four possible roles for the A_f group

in the resulting structure, as shown in Figure 1. The A_f may be a cross-linking point (A_e), the root of a pendant chains (A_o), a chain extender in the pendant structure (A_m), or a chain extender in the soluble material (A_s).

The fraction of each of these molecules in the network is obtained from the following expressions:[18]

$$f_{A_e} = (1 - P(F_A{}^{out}))^f$$

$$f_{A_o} = \sum_{i=2}^{f-1} \binom{f}{i} P(F_A{}^{out})^{f-i}(1 - P(F_A{}^{out}))^i \qquad (3)$$

$$f_{A_m} = fP(F_A{}^{out})^{f-1}(1 - P(F_A{}^{out}))$$

$$f_{A_s} = P(F_A{}^{out})^f$$

where $P(F_A{}^{out})$ represents the probability that, looking out from an A group, the reaction leads to a finite or dangling chain rather than to the infinite network. These probabilities for randomly reacted chemical systems with trifunctional or tetrafunctional cross-linkers are given by

$$P(F_A{}^{out}) = \frac{1 - rvp^2}{rvp^2} \qquad \text{for } f = 3 \qquad (4)$$

$$P(F_A{}^{out}) = \left(\frac{1}{rvp^2} - \frac{3}{4}\right)^{1/2} - \frac{1}{2} \qquad \text{for } f = 4 \qquad (5)$$

where

$$p = p_A = \frac{[A]_0 - [A]_t}{[A]_0} = \frac{p_B}{r} \qquad (6)$$

For stoichiometrically balanced networks at complete reaction, the fractions of cross-linker molecules in different positions of the network as a function of the parameter v, which accounts for the fraction of B groups on bifunctional molecules in the initial formulation, are shown in Figure 3. Values of v close to 1 correspond to networks obtained from formulations with low concentrations of B_1's. On the other extreme of the plot, calculations show that no gel can be obtained at complete reaction if the concentration of B_1's in the initial formulation doubles the concentration of the B_2 groups ($v < 0.5$). Looking at the relative fraction of the different trifunctional molecules at different values of v, it is possible to get a good picture of the type of network that is obtained in each case. The fraction of A_3 groups that are roots of pendant chains (A_o) increases with v until a critical value of v is reached (v_c). It then decreases steadily to zero at $v = 1$. This point corresponds to a perfect network, obtained from an $A_3 + B_2$ system with no B_1's, where no pendant chains are present. For v values between v_c and unity, A_s remains very low, implying that, in this region, B_1 molecules form mainly pendant chains. For values of v close to unity, where A_m is close to zero, most of the chains are single B_1 chains with linear structure, becoming more branched as v approaches v_c. For values of v lower than v_c but not far from it, monofunctional B_1 molecules belong mostly to a combination of branched and linear pendant chains. When v gets closer to the limiting value compatible with the existence of the gel structure ($v = 1/(f - 1)$), most of the B_1's belong to the soluble fraction. At this point, the network has a few elastic chains, a few highly branched pendant chains, and a considerable amount of soluble material.

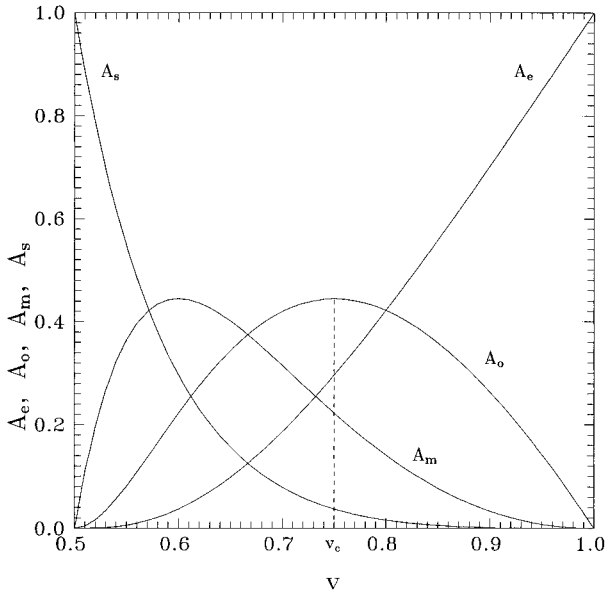

Figure 3. Weight fractions of cross-linker molecules (A_3) belonging to soluble fraction (A_s), elastic material (A_e), roots of pendant chains (A_o), and cross-linker molecules belonging to the interior of those chains (A_m). Calculations are for completely reacted ($p = 1$), stoichiometrically balanced ($r = 1$), trifunctional networks as a function of v.

In the same way that we choose A_f groups, we may now randomly select B_2 or B_1 units from the reacted mixture. If we picked B_2 groups at random, there are three possible positions for this group. First, B_2 may belong to the soluble material. This happens if, looking out in both directions from the center of the selected chain, the two extremes are finite (event with probability $P(F_B{}^{out})^2$). Second, B_2 may belong to the pendant material if, looking out in the same way, one end is finite and the other is infinite (event with probability $[2P(F_B{}^{out})(1 - P(F_B{}^{out}))]$. Third, B_2 may belong to the elastic material if, when looking out in both directions, infinite ends are found (event with probability $[1 - P(F_B{}^{out})]^2$).

Here, $P(F_B{}^{out})$ is, as defined previously for the A groups, the probability that, looking out from a B group, the reaction leads to a finite or dangling chain rather than to the infinite network. This probability is also a function of p, r, and v in analogy with the definitions given in eqs 4 and 5:

$$P(F_B{}^{out}) = 1 + rp(P(F_A{}^{out})^{f-1} - 1) \qquad (7)$$

When B_1 molecules are selected at random from the reacting mixture, the following events are possible. B_1 may belong to the soluble material. This happens if, when looking out toward the end that holds the reactive end group, the chain is a finite one (event with probability $P(F_B{}^{out})$). B_1 also may belong to the pendant material if, when looking out from the same end, the chain is connected to the infinite structure of the gel (event with probability $[1 - P(F_B{}^{out})]$).

From these definitions, taking into account the weight fraction of each kind of molecule in the network structure and the probability of each species concerned, the weight fraction of elastic (W_e), pendant (W_p), and

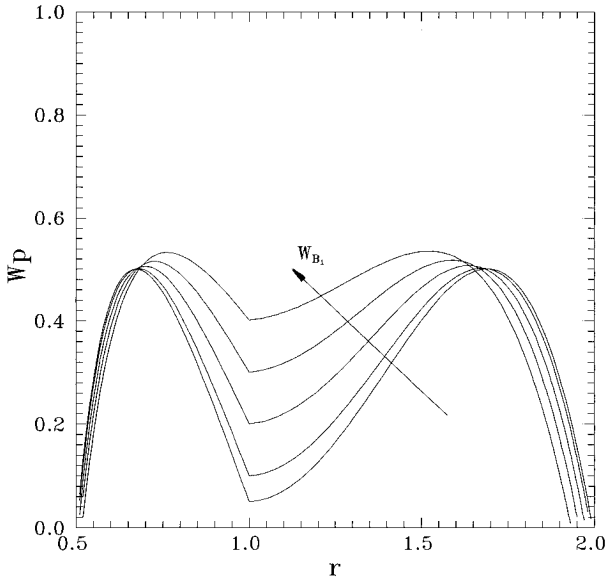

Figure 4. Weight fraction of pendant chains (W_p) as a function of stoichiometric imbalance (r) at complete reaction. Networks are formed from a trifunctional cross-linker of molecular weight $M_A = 330.7$ and linear chains with weights $M_{B_2} = 10\,000$ and $M_{B_1} = 100\,000$. Different curves correspond to various weight fractions of B_1: $W_{B_1} = 0.05$, 0.1, 0.2, 0.3, and 0.4.

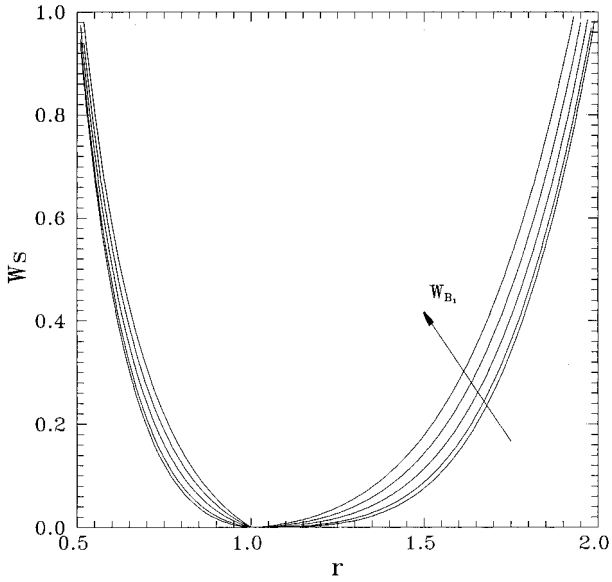

Figure 5. Weight fraction of solubles (W_s) as a function of stoichiometric imbalance (r) at complete reaction. Same conditions as in Figure 4.

soluble materials (W_s) in the network are now calculated:

$$W_e = W_{A_f}\left[(1 - P(F_A{}^{out}))^f + \sum_{i=2}^{f-1}\binom{f}{i}\binom{i}{f}P(F_A{}^{out})^{f-i} \times (1 - P(F_A{}^{out}))^i\right] + W_{B_2}(1 - P(F_B{}^{out}))^2 \quad (8)$$

$$W_p = W_{A_f}\left[fP(F_A{}^{out})^{f-1}(1 - P(F_A{}^{out})) + \sum_{i=2}^{f-1}\binom{f}{i}\left(\frac{f-1}{f}\right)P(F_A{}^{out})^{f-i}(1 - P(F_A{}^{out}))^i\right] + W_{B_2}2P(F_B{}^{out})(1 - P(F_B{}^{out})) + W_{B_1}(1 - P(F_B{}^{out})) \quad (9)$$

$$W_s = W_{A_f}P(F_A{}^{out})^f + W_{B_2}P(F_B{}^{out})^2 + W_{B_1}P(F_B{}^{out}) \quad (10)$$

where W_{B_2}, W_{B_1}, and W_{A_f} are the initial weight fractions of B_2, B_1, and A_f molecules in the reaction mixture, respectively, calculated as

$$W_{B_2} = \frac{M_{nB_2}}{M_{nB_2} + \frac{2}{\nu}\left((1-\nu)M_{nB_1} + \frac{r}{f}M_{A_f}\right)} \quad (11)$$

$$W_{B_1} = \frac{M_{nB_1}}{M_{nB_1} + \left(\frac{1}{1-\nu}\right)\left(\frac{\nu}{2}M_{nB_2} + \frac{r}{f}M_{A_f}\right)} \quad (12)$$

$$W_{A_f} = \frac{M_{A_f}}{M_{A_f} + \frac{f}{r}\left(\frac{\nu}{2}M_{nB_2} + (1-\nu)M_{nB_1}\right)} \quad (13)$$

The stoichiometric imbalance affects considerably all molecular parameters of the networks. Particularly, the weight fraction of pendant chains (W_p) increases with either an excess or a defect of cross-linker, as shown in Figure 4. In this case, the calculations have been made for a system composed of monodisperse B_2 molecules of molecular weight 10 000, B_1 molecules of molecular weight 100 000, and A_f molecules of molecular weight ~300 at complete reaction. The different curves in the plot correspond to various weight fractions of B_1's in the initial formulation ranging from 5 to 40%. When $r = 1$, all the B_1's added to the formulation form single linear pendant chains (like those labeled 1 in Figure 1) and all the B_2's are elastically active chains. In this case, the final fraction of pendant chains, W_p, is exactly equal to the fraction of B_1's incorporated into the system.

For values of r different from unity, there is always a sharp rise in the weight fraction of pendant chains. The increment in W_p grows more rapidly in formulations containing a defect of cross-linker ($r < 1$). Since the molecular weights of all the components of the mixture were kept constant ($M_{B_2} = 10\,000$, $M_{B_1} = 100\,000$, and $M_{A_f} \approx 300$) in the calculations used to build this plot, the rise in W_p can be associated with an increase in the amount of imperfections in the networks. The departure of W_p from the value that corresponds to the weight fraction of monofunctional chains initially added to the mixture (W_{B_1}) indicates that pendant chains are composed not only of B_1 molecules but also of more complex structures, like those labeled 2 and 3 in Figure 1.

The equivalent plot for the weight fraction of solubles (W_s) also exhibits a minimum at $r = 1$, as shown in Figure 5. At this point, there is no soluble fraction in the network. W_s increases when the stoichiometric imbalance moves away from unity. In analogy with W_p, the increase in W_s is more pronounced for a defect of cross-linker ($r < 1$) and becomes more important for higher values of W_{B_1}.

The preceding calculations have been carried out for a system composed of two monodisperse prepolymer molecules, where the molecular weight of the B_1 groups was considerably higher than that of the B_2. The system that we have used as an example shows that stoichiometrically balanced reactions result in networks with higher degrees of perfection. This result is quite general and valid for any other system of the $A_f + B_2 + B_1$ type. Stoichiometric imbalance favors the formation of star-type and more complex branched pendant chains that are not desirable for structural studies like the one

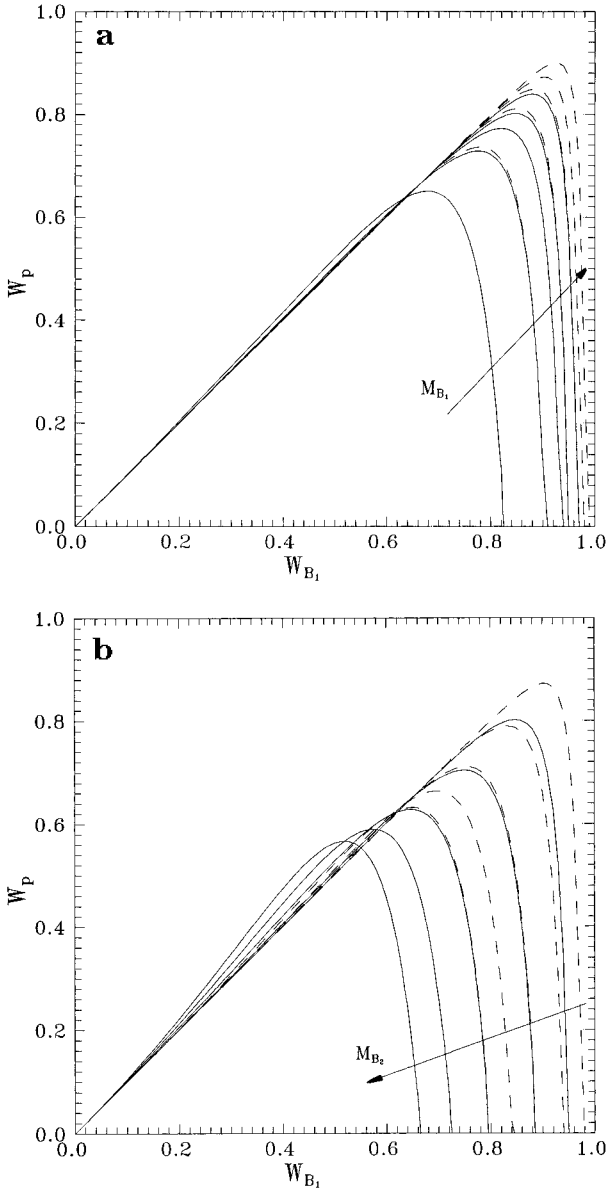

Figure 6. Weight fraction of pendant chains (W_p) as a function of weight fraction of monofunctional chains (W_{B_1}) initially added to the system. Calculations are for stoichiometrically balanced networks ($r = 1$) at complete reaction ($p = 1$). (a) Networks with $M_{B_2} = 10\,000$ and $M_{B_1} = 25\,000$, 50 000, 75 000, 100 000, and 150 000; —, system $A_3 + B_2 + B_1$; - - -, system $A_4 + B_2 + B_1$. (b) Networks with $M_{B_1} = 100\,000$ and $M_{B_2} = 10\,000$, 25 000, 50 000, 75 000, and 100 000; —, system $A_3 + B_2 + B_1$; - - -, system $A_4 + B_2 + B_1$.

that we report in the following paper.[20] For this reason, we are now going to analyze in more detail the influence of the molecular weights of the B_2 and B_1 molecules and their relative fractions on the structure of completely reacted, stoichiometrically balanced networks ($r = 1$).

First, we analyze how the initial weight fraction of monofunctional chains incorporated to the system, W_{B_1}, affects W_p, the weight fraction of pendant chains in the network. This is shown in Figure 6. Figure 6a describes the evolution of the final content of pendant chains in the network, expressed as weight fraction (W_p), with the initial weight fraction of monofunctional chains incorporated to the reactive system (W_{B_1}) when the molecular weight of the bifunctional prepolymer B_2 is kept constant ($M_{B_2} = 10\,000$). Different curves depict results from the calculations when the molecular weight of the B_1 is changed from 25 000 to 150 000. Full lines correspond to the results obtained with a trifunctional cross-linker, and dotted lines correspond to the equivalent results with a tetrafunctional cross-linker. Figure 6b shows the same results for a different system. In this case, M_{B_1}, the molecular weight of the B_1's, is kept constant at 100 000, while M_{B_2} varies from 10 000 to 100 000. In a given range, for low values of W_{B_1}, the weight fraction of monofunctional molecules initially added to the system is equal to the weight fraction of pendant material in the network (45° line), indicating that only B_1 molecules are forming the pendant chains. The range of values of W_{B_1} for which this equality is verified is a function of formulation variables, such as the molecular weights of B_1 and B_2 and the functionality of the cross-linking agent. If we analyze networks with low M_{B_2} molecules and relatively high M_{B_1} molecules, like those illustrated in Figure 6a, it is possible to get a broad range of W_{B_1} values, where W_p is almost equal to W_{B_1}. In this case, all dangling ends will essentially consist of linear monofunctional molecules with molecular weight equal to M_{B_1}. The higher the functionality of the cross-linker, the higher the range where W_p and W_{B_1} are coincident. When the molecular weight of B_2 is comparable to or higher than the molecular weight of the B_1's, W_p departs from the 45° line at lower values of W_{B_1}, as shown in Figure 6b. Here, separation from the $W_p = W_{B_1}$ line begins for the most unfavorable cases at values of W_{B_1} close to 0.1. Networks now contain branched pendant chains with B_2 molecules incorporated into the dangling structures.

Analysis of the calculations for the weight fraction of solubles, for the same numerical values used in Figure 6a, shows that W_s is practically negligible when the weight fraction of monofunctional molecules is less than about 40%. For higher values of W_{B_1}, W_s begins to be significant. This is shown in Figure 7a. In this case, as before, the molecular weight of the B_2's was kept constant at 10 000, and the different full lines show the changes in the evolution of W_s versus W_{B_1} for several values of M_{B_1}. Since M_{B_2} is the same for all the curves, at a fixed value of W_{B_1}, there are more monofunctional prepolymer chains in the initial mixture when the molecular weight of the B_1 molecules is lower. In this case, v decreases and the amount of solubles increases.

For a constant value of $M_{B_1} = 100\,000$ (Figure 7b), W_s increases when M_{B_2} increases. There are more B_1 molecules in the initial mixture for higher values of M_{B_2}. In this case, v also goes down, and networks are more imperfect, with branched pendant chains and a higher amount of soluble material. The weight fraction of elastic chains (W_e) has a slight dependence on M_{B_1}. Changes become more important when W_{B_1} is higher than 0.5.

III.2. Number- and Weight-Average Molecular Weights and Polydispersity in the Pendant Material. Other relevant network parameters are the number- and weight-average molecular weights of the pendant chains (M_{np} and M_{wp}). Those parameters are of great importance because they give information about the structure of the dangling ends. Weight-average molecular weight is particularly useful because it is used in structure−properties relationships. Since one of the main goals in the synthesis of $A_f + B_2 + B_1$ systems is to obtain model networks with single B_1 pendant chains of narrow molecular weight distribution, polydispersity of the pendant chains (M_{wp}/M_{np}) is an important tool to quantify whether the molecules are linear and to identify for which values of W_{B_1} branched or complex pendant chains begin to appear.

Dangling chains have only one end attached to the infinite gel. By picking up any repeat unit of a pendant

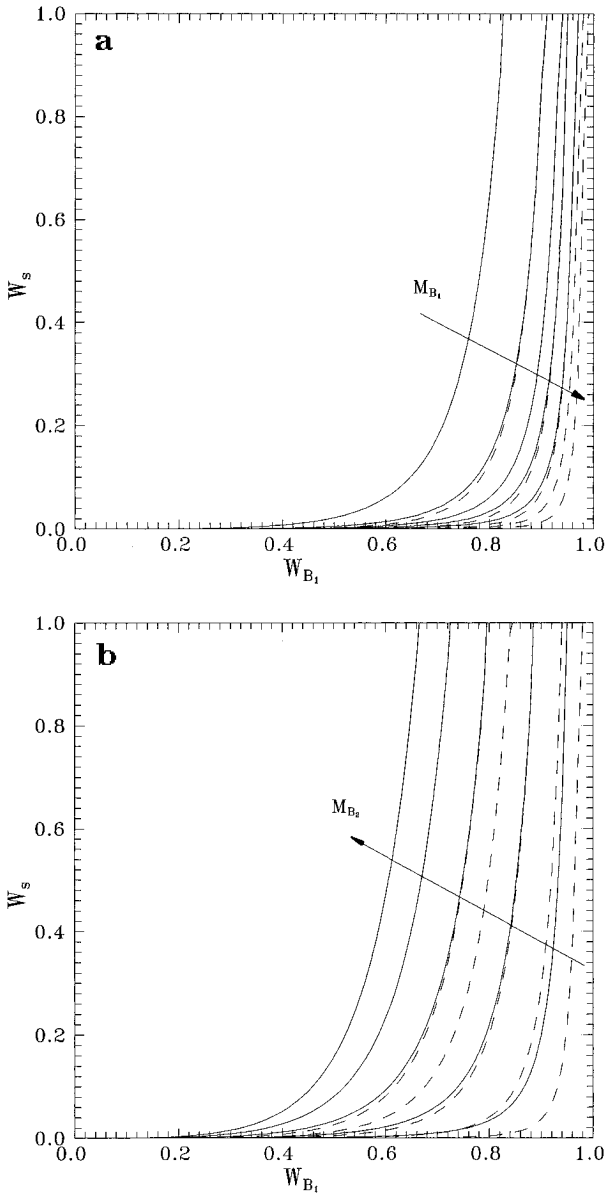

Figure 7. Weight fraction of solubles (W_s) as a function of weight fraction of monofunctional chains (W_{B_1}) for stoichiometrically balanced networks ($r = 1$) at complete reaction ($p = 1$). (a) Same conditions as in Figure 6a. (b) Same conditions as in Figure 6b.

chain at random, it is possible to proceed in two directions: toward the infinite gel or in the direction of the chain ends. As was explained in detail in previous publication,[18] in order to evaluate the molecular properties of the pendant chains, it is necessary to calculate the directional extent of reaction of the reactive end groups in the direction of the finite ends of the dangling chains. If one picks a particular chain belonging to the pendant material at random and moves in the direction of the gel, all the reactive groups that join the prepolymer units of type B_1 or B_2 when passing from one unit to the other will be reacted. The extent of reaction in the infinite direction, p_{inf}, will then be equal to unity. When proceeding in the direction of the chain ends, unreacted groups may be found. The directional extents of reaction on the pendant structures are then nonequal. Calculation of the extent of reaction in the direction of the finite ends ($p_A°$ and $p_B°$) is necessary in order to evaluate the molecular parameters of the pendant material. Using the definition of conditional probability, the directional extent of reaction for A and B groups on the pendant material of the gel are given by the following equations, which have been adapted from those given in ref 18:

$$p_A° = \frac{p_A[P(F_B^{in})]}{P(F_A^{out})} = \frac{p_A[1 - \nu(1 - P(F_B^{out}))]}{P(F_A^{out})} \quad (14)$$

$$p_B° = \frac{p_B P(F_A^{in})}{P(F_B^{out})} = \frac{p_B P(F_A^{out})^{f-1}}{P(F_B^{out})} \quad (15)$$

In addition to the directional extent of reaction, it is necessary to define for this new $A_f + B_2 + B_1$ system the probability of choosing from the pendant material a B group that belongs to a difunctional molecule ($\nu°$). This probability comes as a consequence of the impossibility of maintaining, in the pendant material, the same global probability defined for the whole system. Dangling ends are composed of difunctional molecules of type B_2, which have one finite and one infinite end, and monofunctional molecules (B_1), whose reactive ends are always connected to the infinite gel (see Figure 1). It is then possible to express the probability of choosing a B group belonging to a difunctional molecule in the pendant material as[21]

$$\nu° = \frac{\nu P(F_B^{out})}{1 - \nu(1 - P(F_B^{out}))} \quad (16)$$

To calculate the number-average molecular weight of pendant chains (M_{np}), we must choose chains at random and then look for the expected weight of the selected chains. This is done by selecting the root of the pendant chains and computing the expected weight looking out of A in the finite direction, $E(W_A^{out})_{fin}$:[21]

$$E(W_A^{out})_{fin} = \frac{p_A°(\nu° M_{nB_2} + (1 - \nu°)M_{nB_1}) + p_A° p_B° \nu° M_{A_f}}{1 - (f-1)p_A° p_B° \nu°} \quad (17)$$

Similarly, we may find the expected weight looking out of a B group in the finite direction, $E(W_B^{out})_{fin}$:

$$E(W_B^{out})_{fin} = p_B^{out}(M_{A_f} + (f-1)E(W_A^{out})_{fin}) \quad (18)$$

The number-average molecular weight of the pendant chains is then obtained by adding to the weight of the portion of the polyfunctional cross-linker that forms part of the pendant chains (M_A/f) the expected weight looking out of an A group in the finite direction, $E(W_A^{out})_{fin}$; thus:

$$M_{np} = \frac{M_{A_f}}{f} + \frac{p_A°(\nu° M_{nB_2} + (1 - \nu°)M_{nB_1}) + p_A° p_B° \nu° M_{A_f}}{1 - (f-1)p_A° p_B° \nu°} \quad (19)$$

To obtain the weight-average molecular weight of the pendant chains (M_{wp}), we select units of mass at random from the pendant material. Once we select a mer at random, we must look for the expected weight looking out of that mer in both directions (finite and infinite). When we move in the infinite direction, it is necessary to use the 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. Bibbó and Vallés have shown how to calculate this param-

eter.[18] The expected weight looking out of A or B now in the infinite direction is

$$E(W_A^{out})_{inf} = \frac{M_{nB_2} + C(M_{A_f} + (f-2)E(W_A^{out})_{fin}) + (1-C)(M_{A_f}/f)}{1-C} \quad (20)$$

$$E(W_B^{out})_{inf} = E(W_A^{out})_{inf} - M_{nB_2} \quad (21)$$

In the system $A_f + B_2 + B_1$, we have four different species in the pendant chains: A_f acting as chain extender (A_m), A_f that constitutes a root of a pendant chain (A_o), and B_2 and B_1 dangling molecules. The expected weights for each of these molecules are[21]

$$E(W_{A_o}) = M_{A_f}/f + E(W_A^{out})_{fin} \quad (22)$$

$$E(W_{A_m}) = M_{A_f} + E(W_A^{out})_{inf} + (f-1)E(W_A^{out})_{fin} \quad (23)$$

$$E(W_{B_2}) = M_{wB_2} + E(W_B^{out})_{inf} + E(W_B^{out})_{fin} \quad (24)$$

$$E(W_{B_1}) = M_{wB_1} + E(W_B^{out})_{inf} \quad (25)$$

To calculate the weight-average molecular weight of the pendant material, it is necessary to find the weight fraction of each species in the dangling chains. The weights of species A_m, A_o, B_2, and B_1 are given by

$$a_m = [A_f]_0 M_{A_f} f P(F_A^{out})^{f-1}(1 - P(F_A^{out})) \quad (26)$$

$$a_o = [A_f]_0 M_{A_f} \sum_{i=2}^{f-1} \binom{f}{i} \frac{f-i}{f} P(F_A^{out})^{f-i}(1 - P(F_A^{out}))^i \quad (27)$$

$$b_2 = [B_2]_0 M_{nB_2} 2P(F_B^{out})(1 - P(F_B^{out})) \quad (28)$$

$$b_1 = [B_1]_0 M_{nB_1}(1 - P(F_B^{out})) \quad (29)$$

As the system under consideration is composed exclusively of pendant chains, the weight fraction of each kind of the above species in the chains is given by

$$a_m' = \frac{a_m}{a_m + a_o + b_2 + b_1} \quad (30)$$

$$a_o' = \frac{a_o}{a_m + a_o + b_2 + b_1} \quad (31)$$

$$b_2' = \frac{b_2}{a_m + a_o + b_2 + b_1} \quad (32)$$

$$b_1' = \frac{b_1}{a_m + a_o + b_2 + b_1} \quad (33)$$

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

$$M_{wp} = a_m' E(W_{A_m}) + a_o' E(W_{A_o}) + b_2' E(W_{B_2}) + b_1' E(W_{B_1}) \quad (34)$$

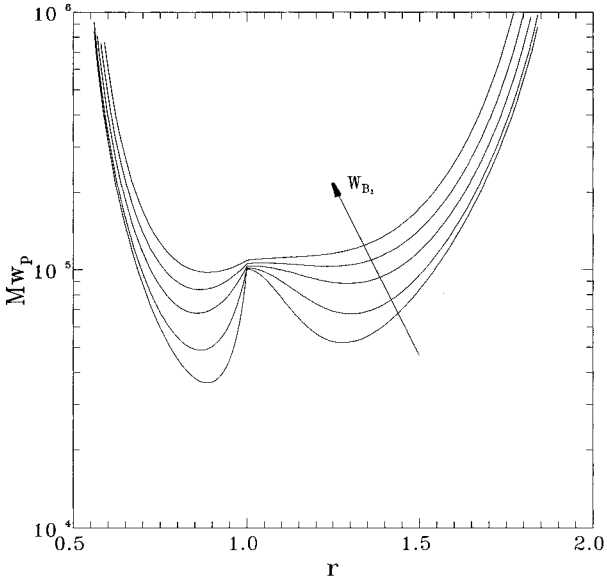

Figure 8. Weight-average molecular weight of pendant chains (M_{wp}) as a function of stoichiometric imbalance (r) at complete reaction. Networks with trifunctional cross-linker (A_3), M_A = 330.7, M_{B_2} = 10 000, M_{B_1} = 100 000, and W_{B_1} = 0.05, 0.1, 0.2, 0.3, and 0.4.

Figure 8 shows the dependence of the weight-average molecular weight of the pendant chains on the stoichiometric imbalance of a system where the molecular weight of the B_2's is equal to 10 000 and M_{B_1} = 100 000. Different curves on the plot demonstrate the effect of augmenting the weight fraction of B_1 chains from 0.05 to 0.40 in the initial formulation. The molecular weight of the pendant chains is equal to that of the monofunctional B_1 chains added to the mixture only for stoichiometrically balanced networks and low values of W_{B_1}. Even for balanced stoichiometry, M_{wp} becomes larger than M_{B_1} for values of $W_{B_1} > 0.3$. Either an excess or a defect of cross-linker gives values of M_{wp} that depart rapidly from the original molecular weights of the monofunctional chains. This picture confirms conclusions from the preceding section indicating that the only way to obtain model networks with linear pendant chains of uniform structure and molecular weight is to work with stoichiometrically balanced systems and low contents of monofunctional B_1's.

We further explore the results for stoichiometrically balanced systems in Figure 9. The first plot (a) shows the dependence of M_{wp} on the weight fraction of monofunctional chains as the amount of B_1 in the initial formulation (measured as W_{B1}) is increased. Full lines correspond to the system $A_3 + B_2 + B_1$ for different molecular weights of the B_1 chains and M_{B_2} = 10 000. Dotted lines show equivalent results for the $A_4 + B_2 + B_1$ system. With low amounts of monofunctional chains, the molecular weight of the pendant chains is virtually equal to the weight of the B_1's. The range of invariance of M_{wp} with W_{B_1} increases if either M_{B_1} or the cross-linker functionality is increased. Figure 9b illustrates the situation when M_{B_1} is kept constant at M_{B_1} = 100 000 and the molecular weight of the difunctional B_2 molecules is increased from values that are considerably lower than the weight of the monofunctional chains (M_{B_2} = 10 000) to values of the order of M_{B_1} (M_{B_2} = 100 000). Values of M_{wp} remain closer to those of M_{B_1} when the molecular weight of the B_2 chains is substantially lower than M_{B_1}. In this case, for a given value of W_{B_1}, there are more B_2 than B_1 chains in the initial mixture, and this favors the formation of networks with single linear pendant chains. These results confirm the

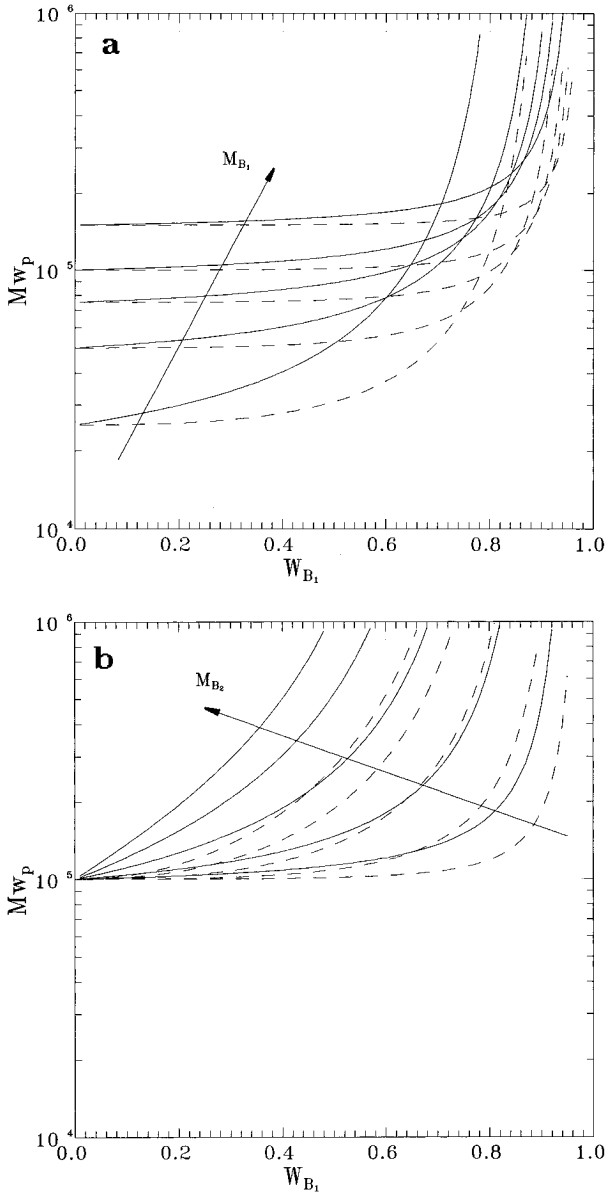

Figure 9. Weight-average molecular weight of pendant chains (M_{wp}) as a function of weight fraction of monofunctional chains (W_{B_1}) in stoichiometrically balanced networks ($r = 1$) at complete reaction ($p = 1$). (a) Same conditions as in Figure 6a. (b) Same conditions as in Figure 6b.

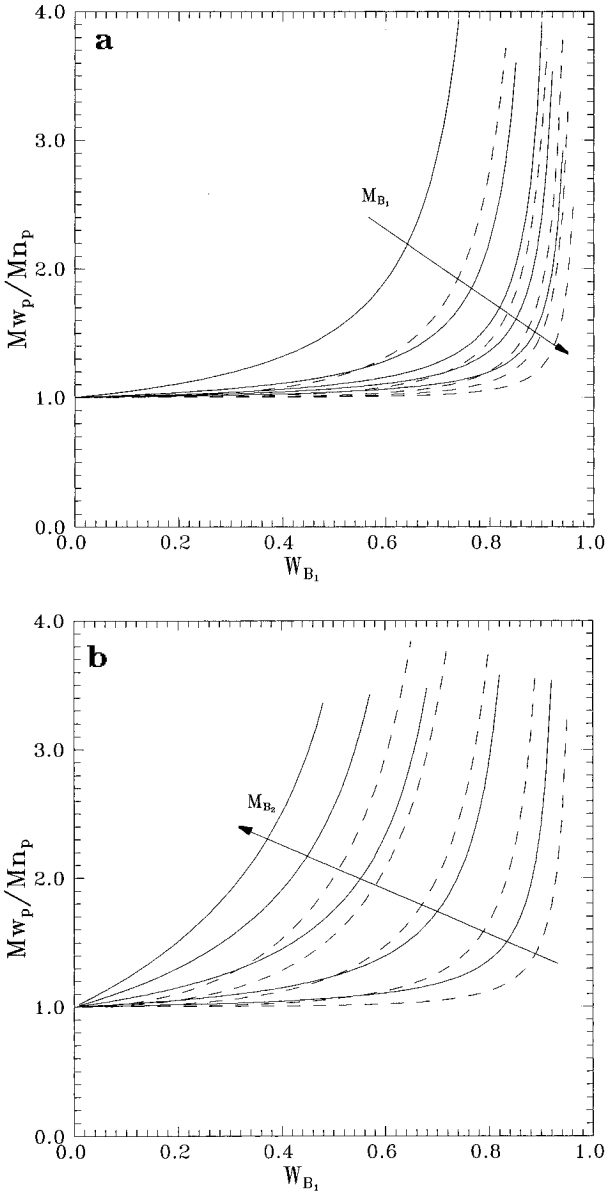

Figure 10. Polydispersity of pendant chains (M_{wp}/M_{np}) as a function of weight fraction of monofunctional chains (W_{B_1}) in stoichiometrically balanced networks ($r = 1$) at complete reaction ($p = 1$). (a) Same conditions as in Figure 6a. (b) Same conditions as in Figure 6b.

conclusions obtained from the calculations of the weight fraction of pendant chains.

Polydispersity of the pendant chains is very sensitive to the presence of branches in these chains. A departure of this parameter from unity indicates that pendant chains are losing their linear structure and are becoming branched. Parallel to the behavior of M_{wp}, Figures 10 and 11 show the effect of W_{B_1} or r, respectively, on the polydispersity of the pendant chains. Polydispersity is very close to unity in formulations with relatively low M_{B_2} and high M_{B_1}. Figure 10a shows that, in some cases, it is possible to obtain linear pendant chains of constant molecular weight for stoichiometrically balanced networks with initial weight fractions of B_1 molecules up to 0.50. On the other hand, when M_{B_2} gets closer to the molecular weight of the monofunctional chains, polydispersity in the pendant material increases (Figure 10b). Either an excess or a defect of cross-linker gives a departure of polydispersity from unity. In this case, an excess of cross-linker gives an abrupt change in polydispersity values, as can be seen in Figure 11. A defect of cross-linker also leads to polydisperse pendant chains but with a weaker effect.

When a more precise characterization of the pendant chains is needed, other molecular parameters can be used to estimate the perfection of the pendant structure. The numbers of branch points and chains per molecule, as well as the average molecular weight of the longest chain in one pendant chain, can be calculated following a similar approach.

IV. Conclusions

In a naive analysis of the system $A_f + B_2 + B_1$, it may be wrongly assumed that networks are always formed by elastically active chains made of B_2 molecules and pendant chains composed of B_1 molecules. However, a more careful study shows that this situation takes place only under certain formulation conditions.

In this paper, we have analyzed the behavior of the molecular structure of the network as a function of the stoichiometric imbalance, the initial weight fraction of monofunctional chains in the mixture, and the relative

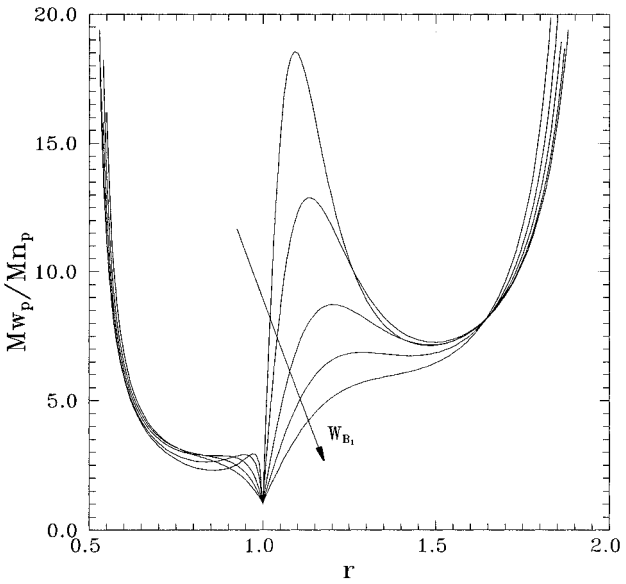

Figure 11. Polydispersity of pendant chains (M_{wp}/M_{np}) as a function of stoichiometric imbalance (r) at complete reaction. Networks with trifunctional cross-linker (A_3), $M_A = 330.7$, $M_{B_2} = 10\,000$, $M_{B_1} = 100\,000$, and $W_{B_1} = 0.05$, 0.1, 0.2, 0.3, and 0.4.

weights of the B_2 and B_1 chains. We have put special emphasis on some variables of interest to us: the weight fraction of pendant chains (W_p), the weight-average molecular weight of pendant chains (M_{wp}), and the polydispersity. The study was oriented to find formulations that allow us to obtain networks with pendant chains composed of linear molecules with known and uniform molecular weight.

A first analysis indicates that networks are more perfect when the formulations are stoichiometrically balanced. Either a defect or an excess of cross-linker leads to networks with much more complex pendant chains. A more detailed inspection of the results from stoichiometrically balanced networks shows that, even in this condition, there exists a limiting amount of monofunctional chains that can be added to the mixture if the objective is to obtain networks with uniform linear pendant chains of constant molecular weight.

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