Production of Hyperbranched Polystyrene by High-Temperature Polymerization

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Received July 15, 2004; Revised Manuscript Received October 25, 2004

ABSTRACT: An experimental investigation of the free-radical high-temperature (>300 °C) polymerization of styrene/divinyl benzene in a steady-state continuous-stirred tank reactor is reported. Under these conditions, backbiting followed by β-scission, which is the dominant chain degradation mechanism, is very aggressive. This allows for utilization of large amounts of cross-linker, thus producing hyperbranched polymers with high cross-link density, without the formation of gel. We have also shown experimentally that the propensity of the system to gel depends on the ratio between the rate of propagation and the rate of backbiting/β-scission, which can be controlled by the operating conditions, such as reaction temperature, average reactor residence time, and solvent level. Thus, through these parameters, it is possible to control the polymer molecular weight and cross-link density, as well as the occurrence of gelation. Therefore, high-temperature polymerization in a continuous-stirred tank reactor provides an economic and reliable technique for producing polymers of hyperbranched nature that can find various unique applications in polymer technology.

Introduction

Highly branched polymers have attracted a great deal of attention in recent years due to their peculiar structures[1] and rhelogical properties.[2,3] It is known that branched polymer chains have reduced viscosity when compared to linear chains of the same molecular weight, making them potentially useful in the liquid coating industry.[4,5,6] Linear, low-molecular-weight styrene−acrylic polymers properly dissolved in organic solvents are currently applied in this industry. Their molecular weight is determined as a compromise among good mechanical properties, high solids content, and viscosity values sufficiently low for spray applications. However, the continual drive toward coatings with lower volatile organic content (VOC) requires the development of new polymer structures that exhibit substantially different rheological properties than linear polymers. For this, two types of branched polymers, namely dendrimers and hyperbranched polymers, have been investigated. Dendritic polymers are defined as monodisperse, highly branched structures that are produced through sequential polymerization starting from a central multifunctional core, typically via condensation polymerization.[7] Hyperbranched polymers are highly branched, polydisperse polymers that in principle can be made either by condensation or by free-radical techniques. The high cost of polycondensation processes requires the investigation of alternative technologies. On the other hand, the classical free-radical polymerization in the presence of multifunctional comonomers leads very easily to the fomration of large-chain networks, which form insoluble gels[8] that strongly deteriorate the application properties of the polymer.

The use of free-radical polymerization with high levels of multivinyl monomers to introduce branching without gel formation has been demonstrated for styrene−acrylic polymers using high temperature[9,10] and catalytic chain transfer agents.[11] In both cases, the idea is to limit the rate of chain growth through degradation or chain-transfer reactions to retard the formation of gels. An alternative would be to use monomers, such as butyl acrylate, that exhibit chain transfer to polymer branching.[12] However, in this case, the achievement and control of the desired level of branching is difficult. Li et al.[13,14] proposed the use of a traditional chain transfer agent (CBr_4) to retard gelation in the methyl methacrylate/ethylene glycol dimethacrylate polymerization. This method is, however, less effective than catalytic chain transfer agents.[15] Gaynor et al.[16] demonstrated the production of hyperbranched polystyrene using atom-transfer copolymerization (ATRP) of styrene and *p*-chloromethylstyrene that is through a quasi-living polymerization mechanism that suppresses bimolecular termination.

In our previous work,[17,18] we have described quantitatively the thermal polymerization of styrene at high temperatures and have shown an effective method for producing low-molecular-weight polystyrene. In the present work, we exploit the specific characteristics of free-radical high-temperature polymerization, namely polymer degradation reactions, to produce hyperbranched polymers. In particular, we investigate the copolymerization of styrene/divinyl benzene in a CSTR, operated at steady state, using a broad range of reactor temperature and residence time values. The results are discussed in terms of molecular-weight distribution and gel formation, based on the previously established linear

10.1021/ma0485639 CCC: $30.25

polymerization mechanism. Before this, we need to summarize a few features of the kinetics of the free-radical polymerization of divinyl monomers, which are used in the following to interpret the obtained experimental results.

Free-Radical Polymerization of Divinyl Monomers

The Reaction Mechanism. Branched polymer chains can be formed by free-radical polymerization when branching reactions, such as chain transfer to polymer or addition to pendant double bonds in the case of divinyl monomers, are present. In the latter case, cross-links are formed when a growing polymer radical propagates with a pendant unsaturation along a polymer chain. Longer polymer chains possess higher numbers of pendant double bonds and thus exhibit a greater probability of reacting with propagating radicals than smaller chains. This leads to the accelerated growth of the largest chains in the distribution, resulting in a geometric growth of the average and polydispersity of the molecular-weight distribution, which is characteristic of cross-linking systems. Eventually, the gel point, defined as the point where the polymer chains form an infinite, percolating network, is reached. The gel point is characterized by the divergence in time of all the moments of the molecular-weight distribution whose order is larger than or equal to two (thus including the weight average molecular weight). Moreover, the gel point is associated with an abrupt transition in the physical properties of the polymer. The gel is in fact insoluble in the polymer matrix and therefore leads to a heterogeneous mixture of high-molecular-weight gel and lower-molecular-weight soluble (sol) polymer. The gel and sol fractions exhibit significantly different physical properties, particularly with respect to swelling and mechanical behavior.

When considering its formation mechanism, it is apparent that the gel is a highly cross-linked molecule that possesses a high number of pendant unsaturations and, moreover, may have multiple radicals[19] due to diffusional limitations to propagation and termination. Therefore, gels are highly reactive and continue to grow through reaction with the remaining soluble polymer chains. The largest sol molecules possess the highest number of pendant unsaturations and thus react preferentially with the gel, leading to a decrease of the average and polydispersity of the molecular-weight distribution of the remaining sol polymer.

Critical Conditions for Gelation. The theoretical understanding of the nature of the molecular-weight growth and the gel point characteristics was pioneered by Flory,[20,21,22] who applied probabilistic arguments and mean field theory to the gelation behavior of multifunctional condensation systems. These concepts were later extended to divinyl addition polymerization by Stockmayer,[23,24,25] who utilized Flory's concept of the critical primary chain length, to identify the polymerization conditions necessary for gelation to occur. An important concept in this approach is the primary chain-length distribution (PCLD), defined as the chain-length distribution that would be produced if all the cross-links in the branched chains were broken. This is simply the chain-length distribution that would result if no cross-linker was present and the polymerization was allowed to proceed under the same reaction conditions (provided that the reactivities of the divinyl and the monovinyl comonomers were equal). Stockmayer[24] related the critical value of the weight average primary chain length (P_{wc}) required for gelation, to the amount of divinyl cross-linker and the overall monomer conversion (α_c), as follows

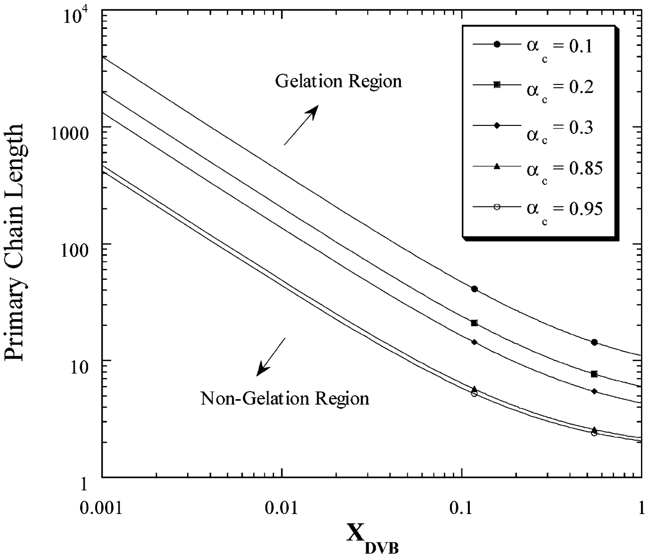

Figure 1. Critical primary chain length, P_{wc}, as a function of the fraction of DVB in the monomer feed, x_{DVB}, calculated from eq 1 for various values of monomer conversion, α_c.

$$P_{wc} = \left(\frac{1+\rho\alpha_c}{\rho\alpha_c}\right) \qquad (1)$$

where ρ represents the initial fraction of double bonds residing in the divinyl units, and in our case, it is given by

$$\rho = \frac{2\tilde{x}_{DVB}}{(1+\tilde{x}_{DVB})} \qquad (2)$$

where $\tilde{x}_{DVB}$ represents the mole fraction of DVB in the monomer feed. This derivation requires that (i) all pendant double bonds have equal reactivity, (ii) the conversion of di- and monovinyl monomers is equal, and (iii) no intramolecular cross-linking occurs. The critical values of primary chain length, as given by eq 1, are shown in Figure 1 as a function of the weight fraction of divinyl monomer in the feed stream for various monomer conversions values. Each line indicates the critical conditions for gelation for a specific monomer conversion, with the area above representing the conditions resulting in gelation and the area below representing conditions not resulting in gelation. It is seen that lower primary chain lengths are needed to cause gelation at larger monomer conversion and cross-linker weight fraction values. This can be understood by considering the fact that large primary chains require a lower cross-link density (average number of cross-links per primary chain) than small primary chains to reach a particular molecular size, as shown schematically in Figure 2. Equation 1 is remarkable in the sense that it is capable of predicting the polymer structure resulting from a process as complex as gelation using a simple relationship between only three parameters. However, this relation does not address the issue of the kinetics of gel formation, which is instead what is needed in the design of polymerization reactors. Consider for example

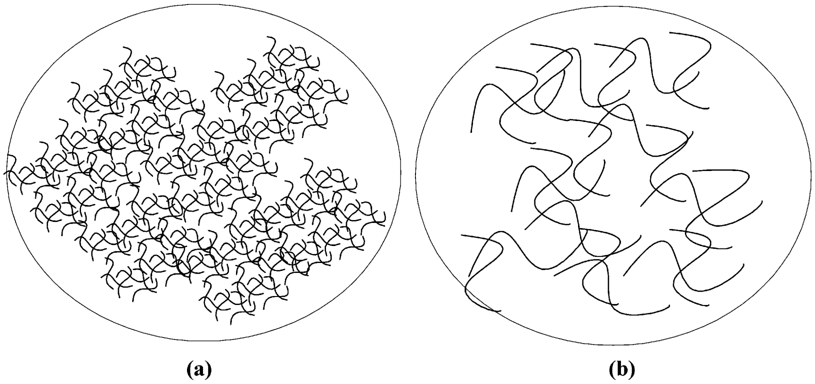

Figure 2. Schematic representation of branched polymer chains with similar molecular weight and (a) short or (b) long primary chains.

a system with a particular level of cross-linker. According to eq 1, nongelling behavior can be achieved by lowering either the primary chain length at a constant monomer conversion or the monomer conversion at a constant primary chain length. If the primary chain length is reduced, gelation is avoided and the polymer, on average, becomes more tightly cross-linked. Conversely, if the monomer conversion is lowered, the number of cross-links per chain is reduced, thus producing a less tightly cross-linked polymer. Although in both cases we prevent gel formation, it is clear that the microstructure of the two polymers is different and exhibits different properties.

Kinetics of Chain Growth and Gel Formation. To describe the polymerization kinetics, which is the path by which the soluble polymer progresses toward the gel state, we use the numerical fractionation model introduced by Teymour and Campbell.[26] In this model, the polymer is subdivided into linear and branched chains and the latter are further subdivided into various "generations", each reflecting populations of successively larger molecular size. In particular, linear chains are defined as the zeroth generation, while branched chains formed by the combination of linear radical chains are assigned to the first generation. The second generation is produced by the combination of two members of the first, and so on for each successive generation. This means that to produce a polymer of a given generation, it is necessary to combine two radicals of the previous generation; if a radical of a particular generation combines with one of a previous one, it produces a polymer of the same generation. Such a definition of generations guarantees that, as the polymer progresses through each successive generation, it becomes geometrically larger and eventually becomes a gel. A schematic representation of the radical growth through various generations is shown in Figure 3. It is apparent from the numerical fractionation model that, in order to reach the gel point, there must be a "generation combining" mechanism, which is a process by which polymer chains of the same generation can combine to produce chains of the next generation. For example, bimolecular termination provides such a mechanism, although, in this case, in order to obtain gelation, we need the presence of chain transfer to polymer to reactivate the terminated radicals. On the other hand, if branching exists without a chain-combining mechanism, then highly branched chains are formed, but the geometric growth described above cannot take place, and therefore, gelation does not occur.[22,27,28] This, for example would be the case for chain transfer to polymer associated with termination exclusively by disproportionation.[22]

Divinyl polymerization, on the other hand, possesses two chain-combining mechanisms which convert two members of a generation into one member of the next generation. The first one is bimolecular termination by combination, and the second, which clearly dominates, is the propagation of a growing radical with a pendant double bond on a polymer chain, which leads to a single radical that belongs to the next generation. Therefore, in the case of divinyl polymerization, generational transfer, and therefore gelation, is controlled by propagation with pendant unsaturations. Thus, to produce hyperbranched polymers while avoiding gelation, we need to introduce a termination mechanism, such as, for example, an aggressive chain transfer, which stops the propagation of the radical before it connects too many chains, thus producing a gel. It is worth noting that this corresponds to a reduction of the primary chain length, thus in agreement with the conclusion given by eq 1.

Experimental Section

Steady-state CSTR equipment[17] was used for the continuous high-temperature copolymerization of styrene, with various levels of divinyl benzene (DVB), at temperatures between 300 and 330 °C. Polymerization initiation relied solely on the thermal initiation of styrene monomer. At each temperature, the effect of the DVB level on the steady-state weight average molecular weight was investigated at various residence times (RT) (between 5 and 30 min) and solvent weight percentages (between 0 and 15%). The solvent, if used, was Aromatic 150 (Exxon Chemical Co.), a mixture of aromatic hydrocarbons with a boiling point of approximately 100 °C. Styrene (Dow Chemical Co.), DVB (Aldrich Chemical Co.), and Aromatic 150 were used without further purification. The DVB was supplied as a mixture containing 80% DVB and 20% styrene. All fractions of DVB reported in this work represent the actual amount of DVB on a monomer basis, regardless of the solvent level.

One problem in the experimental analysis is the measurement of monomer conversion. Due to the high temperatures involved in the reactor operation, it was not possible to sample the monomer without altering significantly the molecular weight of the polymer. For example, the monomer evaporation unit used previously for linear polymer[17] could not be used in this case since the polymer would have further reacted in the evaporator itself. Accordingly, to compute residual monomer concentrations in the reactor, we have used the kinetic model developed and validated in our previous work.[18] The additional assumption of equal reactivity for styrene and DVB has been taken.

The molecular weights reported were determined by GPC using two Pl-gel mixed-bed columns with 10 μm poly(styrene)

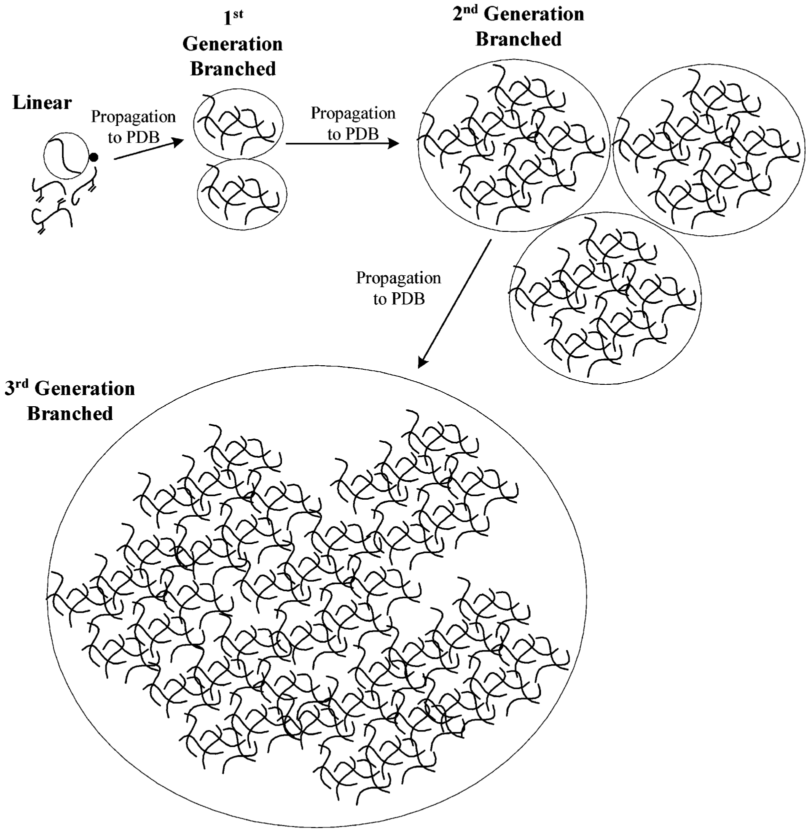

Figure 3. Schematic diagram showing the progression of soluble polymer to gelation, as described by the numerical fractionation technique.[26]

beads, with a single Pl-gel preparative guard column.[17] In all cases, polymer concentration was measured using a refractive-index detector. It is well-known[29] that GPC cannot be used to measure the absolute molecular weights of branched polymers. In particular, since the hydrodynamic radius of a branched polymer chain is lower than that of a linear chain of the same molecular weight, GPC underestimates the true molecular weight of the branched polymer. Therefore, the molecular-weight values reported in this work should be regarded as qualitative, and will be used only to describe the qualitative trend of the molecular-weight distribution in connection with the gelation process. In this context, the same relation between M_w and GPC retention time developed earlier[17] for linear chains has been used.

Results and Discussion

Characterization of the Gel Point in a CSTR. We have investigated the performance of the continuous reactor and, in particular, the average molecular weight of the produced polymer as a function of temperature, average residence time, cross-linker weight fraction, and solvent percentage in the feed. In all previous studies in the literature, gelation has been investigated using a batch reactor, where the gel point is simply defined as the time where a gel phase first appears. This cannot be done in a continuous reactor. In this work, we have observed the reactor behavior at steady state (which required for each experiment to undergo a transient equal to 3−6 times the average residence time, depending on the degree of branching) as a function of one of the operating conditions mentioned above, while keeping the others fixed and defined as critical value for gelation the one where the first occurrence of a gel phase was observed. This is illustrated in Figure 4 where the average molecular weight in the sol phase at steady state is shown as a function of the weight fraction of cross-linker in the feed stream, at 316 °C, 15 min residence time, and 15% solvent by weight in the feed stream. It can be seen that the molecular weight of the sol polymer increases with increasing level of DVB, until a value of approximately $x_{DVB} = 0.106$, where the slope of the molecular weight with respect to the cross-linker level tends to diverge, which seems to indicate that the system is approaching the gel point. This is consistent with the observation that at the two

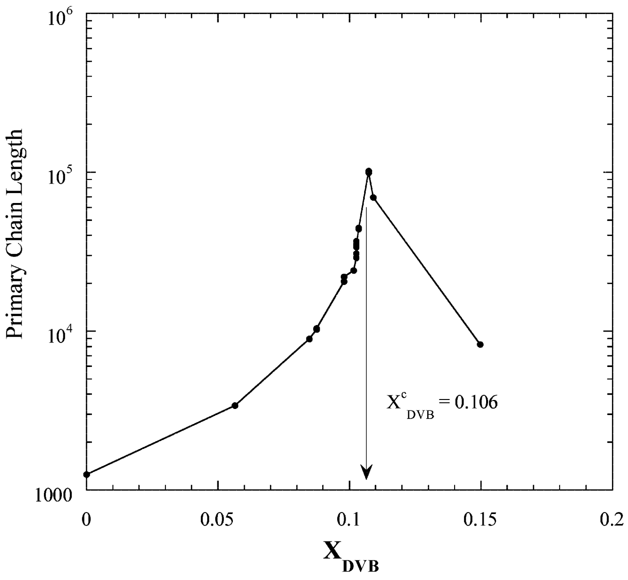

Figure 4. Average molecular weight, M_w, as a function of the weight fraction of DVB in the monomer feed, x_{DVB}, for experimental runs at 316 °C, 15 min residence time, and 15% solvent. The arrow indicates the critical value of x_{DVB} at the gel point.

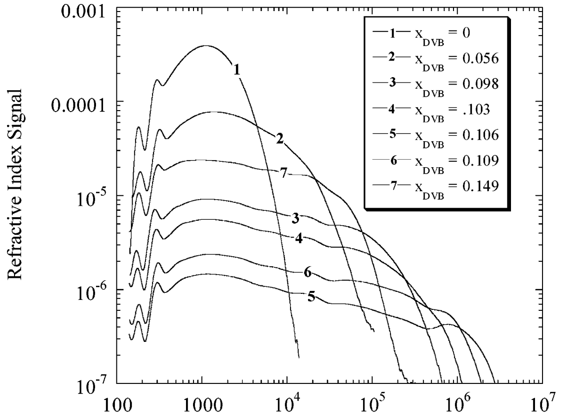

Figure 5. GPC distributions for values of the cross-linker weight fraction in the feed.

higher DVB levels, i.e., 0.109 and 0.149, a massive formation of gel was observed in the reactor outflow, which forced discontinuation of the reactor operation before steady-state conditions could be achieved. The fact that in these two last conditions the reactor actually operated in the presence of a gel is confirmed by the data shown in Figure 4, which indicate that beyond 0.106 the molecular weight of the soluble polymer decreases. This is the typical post-gel behavior of the sol polymer described earlier, and it is due to the fact that the higher-molecular-weight polymer chains have the larger number of reactive double bonds and therefore the higher probabilities to be incorporated in the reactive gel. We can therefore conclude that the critical cross-linker level leading to gelation is approximately 0.106 or, more precisely, between 0.106 and 0.109. In all the following experiments, the critical DVB concentration has been defined as the value leading to the largest molecular weight before the appearance of gel.

The pre- and post-gel behavior of the sol MWD can be best understood by considering the steady-state distributions obtained at the increasing conversion values indicated in Figure 4, as shown in Figure 5. In accordance to the previous observations, it is seen that as the amount of DVB is increased from 0 to 0.106, i.e., curves 1−5, both the average and the broadness of the MWD increases. In particular, the tail of the distribution continuously progresses to higher molecular weights, producing polymers with higher polydispersity. Once the critical cross-linker level of $x_{\mathrm{DVB}} = 0.106$ is exceeded, the first molecules of gel are formed, and these start to consume preferentially the highest-molecular-weight sol polymer. This can be clearly seen by the recession of the high-molecular-weight tail at $x_{\mathrm{DVB}} = 0.109$ (curve 6), which proceeds even further at $x_{\mathrm{DVB}} = 0.149$ (curve 7). This corresponds to the significant decrease of the average of the sol polymer molecular-weight distribution shown in Figure 4.

As mentioned above, the general behavior of the distributions shown in Figure 5 is due to the fact that the overall rate of propagation through pendant double bonds is highest for the largest polymer chains. It is this chain-length dependence of the branching reaction that causes the severe broadening in the distribution observed in Figure 5 and inherently makes unfeasible the production of monodispersed, highly branched polymers by free-radical polymerization.

Role of the Operating Conditions. To interpret the effect of the reactor operating conditions on the behavior of these highly branched systems, we need to deepen our analysis by considering the kinetic mechanism that underlies this polymerization process. In the case of linear-chain polymerization systems, i.e., without cross-linker, it was found that in the temperature range between 260 and 345 °C, polymer degradation reactions become significant and compete with propagation and termination. Hydrogen abstraction by the chain end radical from the third, fifth or seventh carbon down the chain (backbiting) followed by β-scission was identified as the primary chain-formation and molecular-weight controlling mechanism. Random hydrogen abstraction through chain transfer to polymer, followed by β-scission, was also found to be present but to a much lesser extent. Moreover, ^{13}C NMR analysis has confirmed[30] the absence of tertiary branch points, indicating that the propagation of tertiary radicals formed by chain-transfer events is negligible. Therefore, it was concluded,[17,18] in the temperature range mentioned above, that the molecular weight of the linear polymer is controlled by the ratio between the rate of propagation and the rate of backbiting/β-scission, given by the following relation:

$$D_{\mathrm{n}} \propto \frac{k_{\mathrm{p}}[M]}{k'_{\mathrm{BB}}} \tag{6}$$

where D_{n} is the average number degree of polymerization, $[M]$ is the monomer concentration and k_{p} and k'_{BB} are the rate constants for the propagation and the backbiting/β-scission reactions, respectively.

From the equation above, it is seen that the molecular weight is controlled by the polymerization temperature and the monomer concentration. Increasing the reaction temperature decreases the average degree of polymerization, D_{n}, for two reasons. First, the activation energy for the backbiting/β-scission reaction is higher than that of propagation, thus making backbiting/β-scission relatively more important at higher temperatures. Second, higher temperatures result in higher monomer conversion, consequently lowering the monomer concentration. In addition, process conditions, such as residence time and solvent level, affect significantly the monomer concentration, independently of the reaction temperature and, therefore, also the molecular weight.

Since the reactivity of DVB is very similar to that of styrene, we expect also that for the high-temperature styrene−DVB polymerizations considered in this work, the dominating mechanism competing with chain growth is backbiting followed by β-scission. Accordingly, the average polymer molecular weight, as well as the critical gelation conditions, are controlled by a single kinetic parameter defined as the ratio between the rate of propagation and the rate of backbiting/β-scission, as given by eq 6. Since in the context of linear chains we have seen that the relative rate of propagation compared to backbiting/β-scission can be decreased by increasing the reaction temperature, the reactor residence time, or the solvent level, we expect that these actions would lead in the case of branched chains to lower molecular weight and to reduced tendency to gel. It is worth noting that the propagation-to-backbiting/β-scission rates ratio controls the average length of the primary chain distribution and therefore also in the frame of the statistical approach, i.e., eq 1, this parameter is expected to control the gelation behavior. Although these findings are based on qualitative kinetic arguments, they will be seen to be supported by the experimental observations discussed in the following.

The effect of reaction temperature on the gelation behavior at 5, 15, and 30 min average residence times is shown in parts a, b, and c of Figure 6, respectively. The data refer to experimental runs conducted without or with 15% solvent in the feed stream. It is apparent that the reaction temperature has a significant effect on the steady-state molecular weight as a function of the amount of cross-linker. In particular, it is seen that as the temperature increases the average molecular weight for a given DVB percentage decreases and the critical level of DVB leading to gelation increases. It is to be noted that high-temperature operation, through the backbiting/β-scission reaction, is very efficient in producing highly branched polymer chains, while avoiding gelation.

The effect of solvent percentage in the feed can be illustrated by a comparison of the dotted and solid curves in the same figures. It is clear that the addition of solvent lowers the average molecular weight for any given level of DVB and thus retards gelation. The evaluation of the effect of the residence time requires a comparison of the data on the different parts (a−c) of Figure 6. To facilitate the comparison, the average molecular-weight data have been plotted in Figure 7a−c as a function of the DVB level for various values of the residence time at 300, 316, and 330 °C, respectively. The data agree also in this case with the above kinetic analysis, showing that as the average residence time increases the average molecular weight decreases and gelation is retarded. An increase in the reactor residence time decreases the monomer concentration and thus, according to eq 6, lowers the primary chain length, leading to a lower molecular weight and a retardation in gelation.

In the experiments above, we have in fact seen that very high levels of cross-linker can be used without the danger of gelation. For example, at 330 °C and 30 min residence time, which corresponds to the highest rate of backbiting/β-scission, the amount of DVB that the system can tolerate without gelation is over 25%. This level of DVB is unusually high, especially considering the high monomer conversion and that it can be appreciated by comparison with other systems described in the literature. Li et al.[13,14] investigated the copolymerization of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA) at 70 °C. They investigated experimentally the gelation dynamics using varying amounts of EGDMA and chain-transfer agents. Subsequently, Gossage[31] used the numerical fractionation technique to simulate the gelation dynamics, MWDs, and cross-link density of the same system. It was found experimentally that gelation occurred at EGDMA levels below 5 wt% and, in most cases, below 1 wt%, depending on conversion. The calculated cross-link density, defined as the number of cross-links relative to the number of monomer units, was on the order of 10^{-4}−10^{-3}. This is indeed much lower than that obtained in the experimental run of $x_{\mathrm{DVB}} = 0.25$ mentioned above, where, on average, one cross-link is present for every four monomer units, i.e., a cross-linked density equal to about 0.25, which is indeed representative of a hyperbranched polymer.

Modeling the Experimental Data. A detailed kinetic model of high-temperature polymerization of vinyl−divinyl monomer mixtures of the same type of the one developed earlier in the absence of divinyl monomers, i.e., for linear chains,[17] is currently not possible.

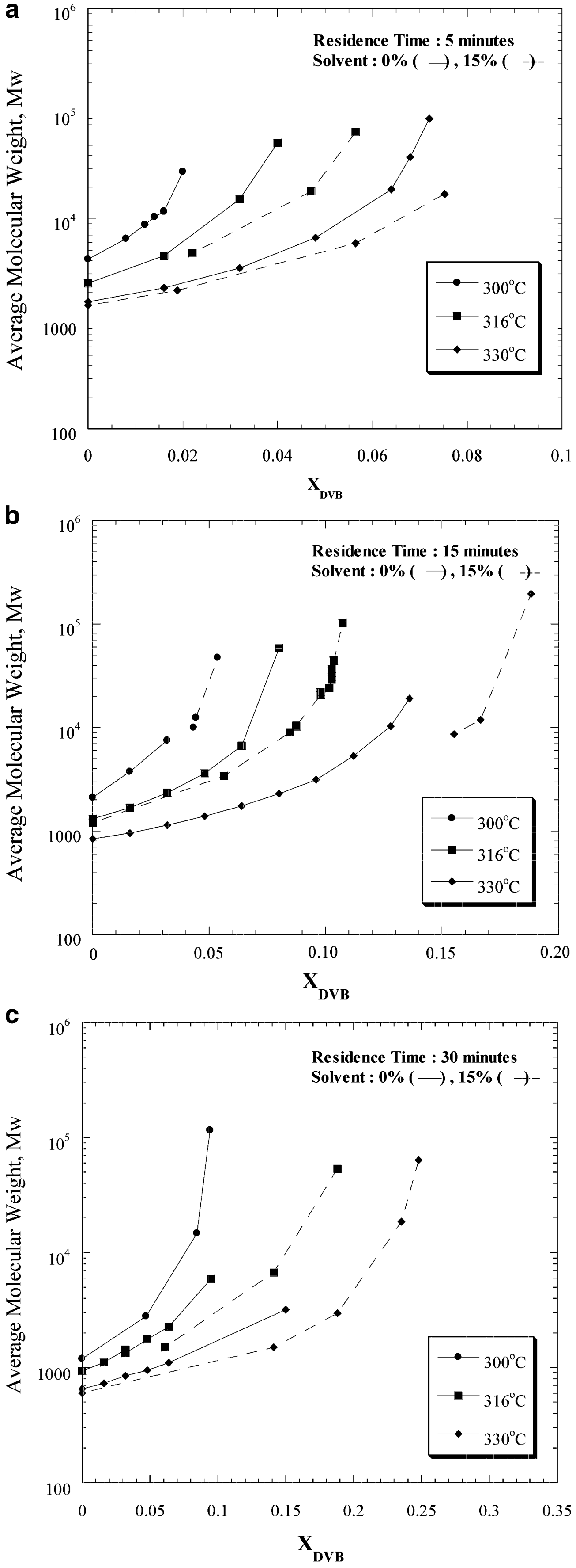

Figure 6. Average molecular weight, M_w, as a function of the weight fraction of DVB in the monomer feed, x_{DVB}, for various temperatures and weight percentage solvent equal to 0% (—) or 15% (- - -); residence time: (a) 5, (b) 15; (c) 30 min.

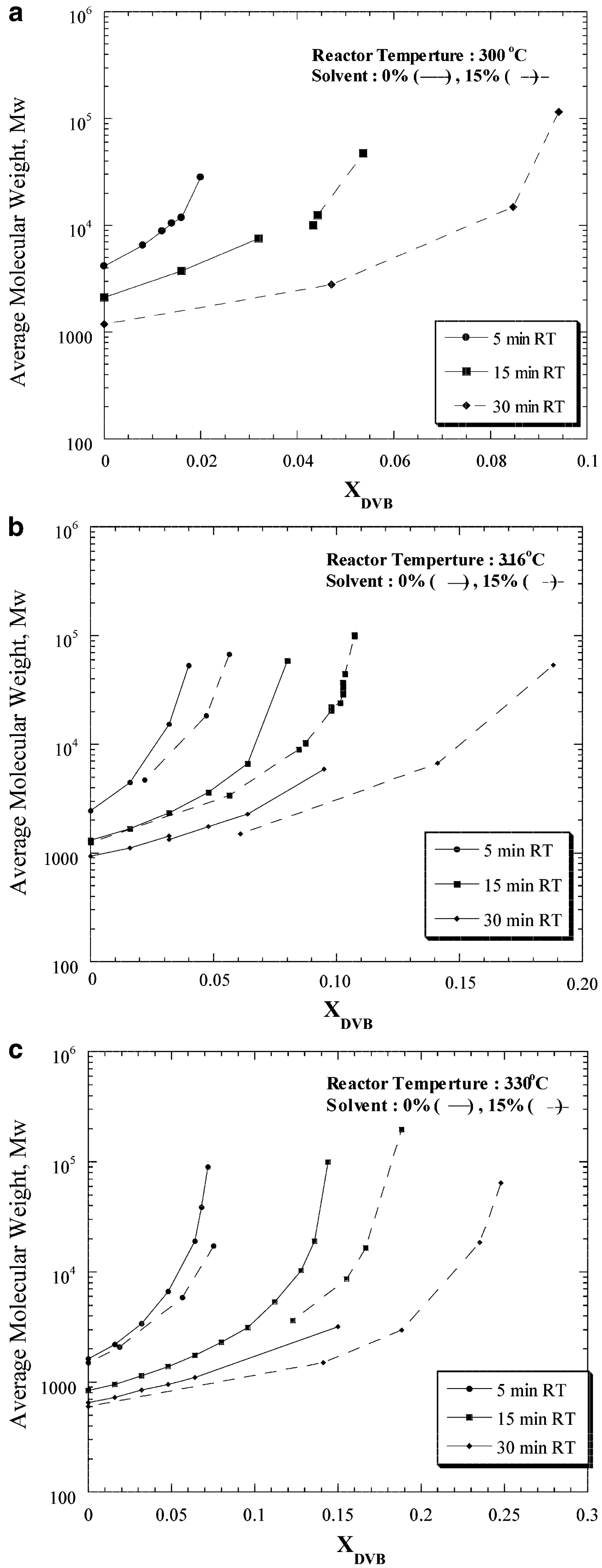

Figure 7. Average molecular weight, M_w, as a function of the weight fraction of DVB in the monomer feed, x_{DVB}, for various residence times and weight percentage solvent equal to 0% (—) or 15% (- - -); temperature = (a) 300, (b) 316, and (c) 330 °C.

The main problem is the description of the topology of these highly branched polymers in mathematical terms. For example, we cannot describe where each branch originates from another branch of the polymer and how many monomer units this contains. This means that, in the case of random scission, we cannot determine the size of the two resulting fragments. In the case of backbiting, we cannot account for apparently important phenomena, such as backbiting to a unit on a different primary chain in the same macromolecule, or the fact that backbiting cannot occur on growing branches which are not sufficiently long. In the case of ethylene polymerization, which is characterized by long-chain branching with random β-scission, the branching density is much lower and the problems above become less severe. So, for example, they have been ignored by Lammel[32] and Pladis and Kiparissides,[33] who simply assumed a uniform probability distribution of fragments resulting from random scission, as is the case for linear chains. This approach has been improved by Hutchinson[34] by introducing a hyper-geometric function to describe the distributions of branches in the fragment to at least partially account for the topology of these macromolecules. None of these approaches would, however, be appropriate to describe the highly cross-linked polymers considered in this work.

On a lower level of detail, we can compare our experimental results with the Flory−Stockmayer theory to verify the possibility of using eq 1 as a tool for interpreting the behavior of this complex system. This equation requires knowledge of the weight average primary chain length, P_w, and the monomer conversion, α_c, to calculate the critical cross-linker level, ρ. The former has been estimated from the molecular weight of polystyrene with 0% cross-linker at each specific experimental condition. Monomer conversion has been estimated from the kinetic model previously developed for polystyrene.[17] In both cases, we assume that styrene and DVB exhibit the same reactivity, which has been, for example, shown by Malinsky and Klaban[35] and Story,[36] although contradictory results have also been reported in the literature.[37] In addition, it should be noted that Figure 1 shows that the sensitivity of the gel point to the conversion level at the high monomer conversions (>90%) considered in this work is quite low.

The critical value of the ρ parameter leading to gelation has been computed from eq 1 and translated into a critical weight fraction of DVB, x^C_{DVB} for each combination of temperature, residence time, and solvent level investigated experimentally. The obtained values are summarized in Table 1 and are compared with the corresponding experimental values in Figure 8. In the same figure are also shown the experimental values of the critical weight fraction of cross-linker in the monomer feed for the methacrylate/ethylene glycol diacrylate systems reported by Matsumoto[42] and Walling.[38] It is worth noting that the experimental conditions adapted in these studies resulted in lower monomer conversion and cross-linker concentration values at the gel point than those reported in this work. This confirms that high-temperature continuous free-radical polymerization provides a unique technique for producing highly branched polymers without gelation. In addition, it should be considered that the reaction conditions in a CSTR are significantly different from those in a batch reactor. A CSTR operated at steady state is characterized by constant monomer, radical, and polymer concentrations, resulting in a homogeneous instantaneous primary chain-length distribution. In contrast, in a

Table 1. Experimental Operating Conditions and Corresponding Critical Weight Fraction of DVB in the Feed, x^C_{DVB}, Measured Experimentally and Calculated through Eq 1

temperature (°C)	residence time (min)	% solvent	experimental		calculated
			M_{w0}[a]	x^c_{DVB}[b]	x^c_{DVB}[b]
300	5	0	4125	0.024	0.0122
300	15	0	2100	na[c]	0.0295
300	30	15	1185	na[c]	0.0446
316	5	0	2475	0.044	0.0204
316	15	0	1321	0.088	0.0393
316	15	15	1200	0.107	0.0444
316	30	0	900	na[c]	0.0607
316	30	15	800	0.217	0.0712
330	5	0	1610	0.075	0.0323
330	5	15	1525	0.080	0.0348
330	15	0	832	0.147	0.0679
330	15	15	780	0.195	0.0744
330	30	0	650	na[c]	0.0922
330	30	15	625	0.256	0.0982

[a] M_{w0} = molecular weight without DVB. [b] x^c_{DVB} = critical weight fraction of DVB in the feed. [c] na = insufficient data to estimate gel point.

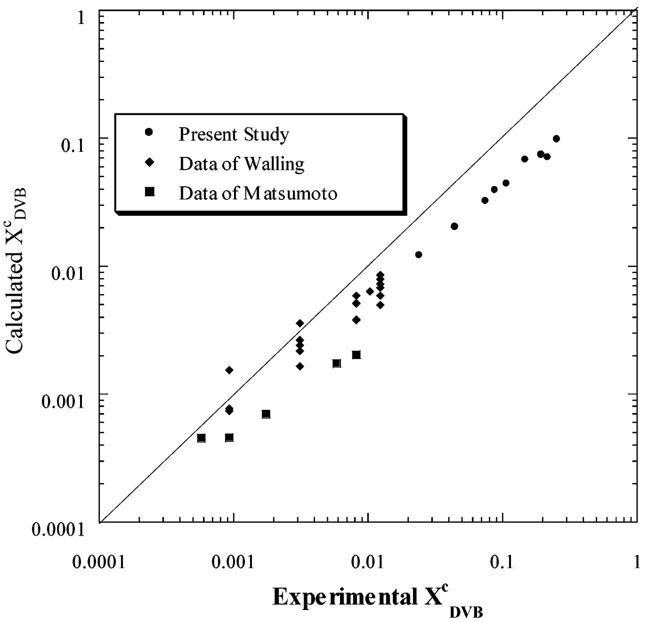

Figure 8. Critical values of the weight fraction of DVB in the feed, x^C_{DVB}, calculated using eq 1 compared to those measured experimentally: (●) this work, (■) Matsumoto,[41] (◆) Walling.[38]

batch reactor, these concentrations change continuously over time, resulting in an inhomogeneous primary chain-length distribution. Nevertheless, all the experimental data compare similarly to the predictions of the Flory−Stockmayer theory. In particular, in Figure 8, it is seen that the trend predicted theoretically is similar to the experimental one, although the critical amount of cross-linker necessary for gelation is consistently underestimated. Note that the experimental data reported in this work provides the possibility of checking the reliability of eq 1 for cross-linker concentration values larger than those considered in previous literature studies.

The reasons for this discrepancy between theoretical and experimental results, which has already been evidenced in the literature,[39−41] have been discussed by Matsumoto.[42] The Flory−Stockmayer equation utilizes certain assumptions, such as that the pendant and monomer double bonds have equal reactivity and that all pendant double bond reactions result in cross-link formation, but of course, any deviations from these assumptions reduces the predictive abilities of the model. For example, cyclization reactions, namely primary and secondary intramolecular cyclization, both result in cross-links that do not increase the molecular weight. The former describes the situation whereby a growing radical adds to a pendant double bond on the same primary chain. The latter refers to a growing radical that reacts with a pendant double bond on a different primary chain within the same polymer molecule. The importance of intramolecular cyclization for the styrene/DVB system has been discussed by Soper et al.[43] On the other hand, Story[38] analyzed the importance of primary cyclization as being responsible for the formation of microgel regions for this system. Considering the importance of backbiting in our system, primary cyclization is expected to occur to some extent. Therefore, the extent to which these reactions occur will delay the gelation point as compared to theory. Another important reason for the delayed gelation as indicated by Matsumoto[42] is the excluded volume effect, whereby a reduced concentration of pendant double bonds are available for reaction due to diffusional difficulties of highly cross-linked chains.

Conclusions

In this study, we have investigated the behavior of styrene/DVB high-temperature (>300 °C) polymerization in a steady-state CSTR, with specific reference to the polymer MWD and the gel formation. Under these conditions, backbiting followed by β-scission is the dominant mechanism in stopping chain growth, while bimolecular termination is negligible by comparison. It has been demonstrated that, as a consequence of this aggressive chain degradation mechanism, large amounts of cross-linker can be utilized, producing polymers with high cross-link density and potentially hyperbranched nature without gelation. We have also shown experimentally that the propensity of the system to gel depends on the ratio between the rate of propagation and the rate of backbiting/β-scission, which can be controlled by the reaction operating conditions. In particular, it has been demonstrated that by increasing the reaction temperature, the reactor residence time, or the solvent level, one can delay the occurrence of gelation and decrease the average molecular weight, that is, produce more highly branched polymers. Therefore, high-temperature polymerization in a CSTR provides an economic and well-controllable technique for producing polymers of hyperbranched nature that can find various unique applications in polymer technology.

Finally, a comparison of the experimental results with those of the classical Flory−Stockmayer model has shown that the latter underestimates the critical cross-linker concentration values needed to provoke gelation. This is a significant finding since it confirms previous results reported earlier in the literature, but under completely different operating conditions.

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MA0485639