

Kinetic Gelation Modeling of Controlled Radical Polymerizations

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ABSTRACT: A kinetic gelation model has been developed that incorporates the kinetics of a living/controlled radical polymerization. Specifically, the kinetics of an iniferter polymerization were implemented in the model to determine the effect of the kinetics on the polymer structure. In particular, the replacement of the termination step with a reversible termination was examined. The model predicts the formation of more monodisperse linear polymers in the presence of an iniferter and a reversible termination reaction. When termination by combination is allowed to occur, the polydispersity increases. For cross-linking reactions, it was concluded that the iniferter only had an effect on reactions with small amounts of cross-linking agent, resulting in a delay in the gel point and a more heterogeneous structure. When the amount of cross-linking agent is increased, there is no difference in the network structure obtained by a cross-linking reaction with an iniferter versus a cross-linking reaction with the classical free-radical initiator.

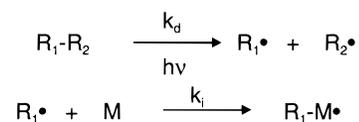
Introduction

Free-radical polymerization is a popular method for synthesizing linear and cross-linked polymers. There are several advantages to this type of polymerization, including faster reaction times, easier manufacturing techniques, and rapid formation of high molecular weight polymers.¹ However, there are drawbacks to these polymerizations and cross-linking reactions, including the lack of macromolecular structure control that can be achieved with other types of polymerization processes.²

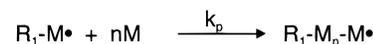
One method to attain molecular control of the polymer structure is by creating a living polymerization in which there is little or no termination. As it is well-known, Swarcz^{3,4} was the first to obtain a living polymer in the anionic polymerization of styrene with a sodium/naphthalene initiator. The idea of creating a living polymer has also been highly successful in anionic, cationic, coordination, and ring-opening polymerizations.^{5,6} Therefore, it is desired to incorporate the advantages of both a living polymerization and a free-radical polymerization in a new polymerization technique to fabricate controlled macromolecular structures. On the basis of this premise, several methods have been proposed for controlled free-radical polymerizations.^{7–18} The basic concept of these methods is to introduce a reversible termination reaction, thus enabling the system to be similar to a “living” polymerization.

Two methods currently investigated are polymerization by atom transfer radical polymerization (ATRP) and polymerization by the iniferter (*initiator–transfer agent–terminator*) technique. In the ATRP technique, termination by combination is reduced by including a metal halide complexed with some ligands. The mechanism for controlling the polymerization is the reversible homolytic cleavage of a chain end into the corresponding radical and a stable radical.⁸ Matyjaszewski and co-workers^{9,11} have been very successful at applying ATRP to create monodisperse linear polymers and block copolymers. The iniferter-based technique was introduced by Otsu,¹⁶ who polymerized styrene and methyl methacrylate in the presence of tetraethylthiuram disulfide and dibenzoyl disulfide, two typical iniferters.

Initiation:



Propagation:



Termination:

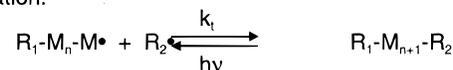


Figure 1. General mechanism for iniferter kinetics proposed by Otsu and Yoshida. For a dithiocarbamate iniferter, R_2 is a sulfur radical and R_1 is a carbon radical.

Neither one of these methods is considered truly living because termination cannot be completely eliminated.

The reactions modeled in this work are based on polymerizations with an iniferter, typically a disulfide or a dithiocarbamate molecule.¹⁷ We are interested in modeling iniferter-based reactions because of their applications in UV polymerizations. Upon heating or irradiation, the disulfide molecule forms two identical radicals which can initiate polymerization or participate in primary termination. The dithiocarbamate molecule forms two different radicals, one of which is reactive and participates in the initiation whereas the other is less or nonreactive and cannot enter initiation. Yet, it does act as a primary radical terminator. Dithiocarbamate-based reactions are the type of iniferter reactions modeled here.

Figure 1 describes the main steps of iniferter-based polymerization reactions. The goal of this work was to develop a model that could be used to examine the molecular structure of a polymer synthesized by this new “living”/controlled radical technique. In particular, it was desired to determine the effect of the iniferter on network-producing polymers synthesized by ultraviolet light free-radical polymerizations. The model chosen was the kinetic gelation model which is a

percolation or random walk model. This type of model provides tremendous insight into the molecular structure. In particular, it can provide insight on the effect of the new kinetics on both linear polymerizations and network-producing polymerizations. Much of the experimental work with iniferters to date has focused on developing monodisperse linear polymers and block copolymers, but little is known about the effect on polymer network synthesis.

Kinetic Gelation Model

The model utilized in this work is based on the Flory–Stockmayer theory,¹⁹ which is identical to percolation on a Cayley tree. Manneville and de Seze²⁰ developed one of the first percolation models examining free-radical polymerizations. In their original model, bifunctional and tetrafunctional units were randomly placed on a lattice. Reaction occurred by randomly selecting an active site and linking it to a randomly selected available functional group that was a first or second neighbor. The active site was then transferred to the new site. The major drawback to this model was the lack of molecular movement. Since this work, numerous researchers have proposed various methods to improve the model.^{21–27} Bansil and co-workers²¹ incorporated solvent and monomer mobility in their model. Solvent sites could exchange positions with nearest-neighbor sites occupied by solvent or by unreacted monomer. They were also able to compare their simulation results with experimental observations of vinyl–divinyl polymerizations showing that the model followed the same overall trends as the experiments. Bowman and Peppas²⁶ further refined the kinetic gelation model by incorporating a more realistic initiation mechanism and more movement of the monomers and polymers. Occupied sites could be moved to an empty nearest-neighbor site as long as all bonds remained intact.

Model Details. In our model, at the start of the polymerization, monomers and initiators are distributed randomly on a face-centered-cubic lattice of length 31. A face-centered-cubic lattice was chosen over a cubic lattice because it allows 12 nearest neighbors instead of six. Periodic boundary conditions are also implemented to eliminate edge effects.

Initiators occupy two neighboring sites on the lattice and monomers occupy any predetermined number of neighboring sites. All of the simulations presented here are for polymerizations containing 1% initiator, a typical initiator concentration. In addition, 15% of the sites remain empty to allow for monomer and polymer movement.

In this model, the initiator decomposes into two radicals based on the following half-life equation:

$$\frac{[I]}{[I]_0} = \exp(-kt) \quad (1)$$

Here, $[I]$ is the initiator concentration, $[I]_0$ is the initial initiator concentration, t is the simulation step, and k is a constant. The key parameter in this equation is the constant k , low values of which indicate that radicals are introduced into the system slowly corresponding to the situation of decreasing UV light intensity.

At every time step during the simulation, the radicals and their nearest neighbors are monitored to determine whether a reaction will take place. Reaction occurs when a radical is a nearest neighbor to a functional group of

a monomer or a radical on a polymer chain. During the reaction, a new bond is formed between the reacting neighbors, and the radical is transferred to the neighbor. Also during each step, 33% of the occupied sites are moved. For simulation efficiency, we did not move all of the molecules as we found that moving 33% of the molecules was adequate. After an occupied radical site was chosen (site A), one of the 12 nearest neighbors was also randomly chosen (site B). The criteria for moving were the following: (i) site B must be empty, and (ii) all of the bonds to which the molecule at site A was attached must remain intact and not be broken, shortened, or lengthened.

To incorporate an iniferter, several modifications were made to model the kinetics. First, when the initiator decomposes, it forms a carbon and a sulfur radical. Only the carbon radical may initiate propagation with the functional group of a monomer. The sulfur radical only reacts with carbon radicals on polymer chains. After a new carbon–sulfur bond has formed in the polymer chain, it may decompose into two radicals:

$$\frac{[P_n-R_s]}{[P_n-R_s]_0} = \exp(-k_s t) \quad (2)$$

Here, $[P_n-R_s]$ denotes the concentration of C–S bonds in polymer chains and k_s is the constant characteristic of the bond breakage process. Finally, to fully incorporate a “living” system, termination between two carbon radicals of polymer chains was not allowed, although the effect of the termination on the structure was investigated fully.

A variety of parameters are recorded during the reaction in order to investigate the structure. In addition to determining the functional group conversion at every time step, the number of sites occupied by the polymers is also tracked. The number-average number of sites, X_n , and the weight-average number of sites, X_w , occupied by the polymers are then calculated. The polydispersity index (PDI) for these systems is the ratio of X_w to X_n . This PDI will not be the same as that recorded experimentally because in the model, only the number of sites on a lattice occupied by the polymer is calculated. For network-producing polymerizations, we are interested in the heterogeneity of the structure. Therefore, the formation of cross-links is monitored throughout the polymerization.

Results and Discussion

As mentioned previously, the goal of this work was to examine the effect of an iniferter-based initiator on the molecular structure of the ensuing linear and cross-linked chains. Therefore, the model was used to investigate various scenarios including linear polymerizations and network-producing polymerizations. For the linear polymerizations, the system consisted of only bifunctional monomers. In previous work on controlled radical polymerizations,^{21–27} it has been shown that incorporating a reversible termination reaction resulted in more monodisperse polymers. Therefore, the polydispersity index was an important parameter to examine in this case. To validate the model, it was necessary to determine the effects of the iniferter and the reversible termination step on the polydispersity of the polymers.

For network-producing polymerizations, cross-linking agents were added to the system. Experimentally, it is not clear what the effect of the iniferter is on a cross-

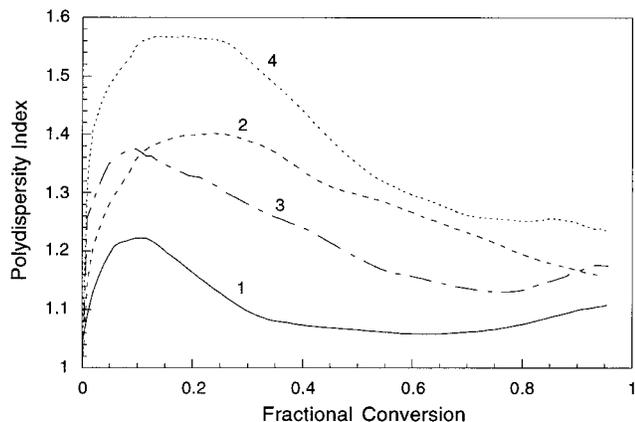


Figure 2. Polydispersity index results for linear polymerizations with single site bifunctional monomers for different values of k and k_s . The parameters for the different curves are as follows: (1) $k = 0.02$, $k_s = 0.02$; (2) $k = 0.02$, $k_s = 0.002$; (3) $k = 0.002$, $k_s = 0.02$; and (4) $k = 0.002$, $k_s = 0.002$.

linked system. Therefore, the model is able to provide tremendous insight as to the heterogeneity of the structure, the final conversion, and the presence of trapped radicals.

In the case of linear polymerizations, we first investigated the effect of the decomposition constants k and k_s on the linear polymer size. In this model, all monomers occupied one site on the lattice and were bifunctional. In addition, the system was assumed to be truly living without termination by combination. The different cases investigated were $k = 0.02$ and $k_s = 0.02$, $k = 0.02$ and $k_s = 0.002$, $k = 0.002$ and $k_s = 0.02$, and $k = 0.002$ and $k_s = 0.002$. For these simulations, a larger k value means that initiating radicals are introduced into the system rapidly whereas a larger k_s value indicates that the C–S bond on the polymer will dissociate into two radicals quickly. The values of k were chosen on the basis of the previous work of Bowman and Anseth, who also studied the effect of the initiator decay constant.^{26,27} The number-average, X_n , and the weight-average, X_w , number of sites occupied by the polymers were calculated as functions of the monomer conversion. The polydispersity index, PDI, was also calculated as the ratio of the weight average to the number average.

Figure 2 shows the results for the linear living polymerizations with various constants. As the values of k and k_s increase, X_n and X_w decrease, as does the PDI (Figure 2). As k decreases, initiating radicals are more slowly introduced into the system, and X_n and X_w are larger because there are fewer propagating polymer chains. The monomers are more evenly distributed on the polymer chains when there are more propagating polymer chains present in the system at the same time. A large value of k_s strongly affects the PDI because the C–S bond is quickly decomposed into two radicals, and the chains are allowed to propagate. As k_s is decreased, the rate of propagation of a particular chain is slowed down due to the presence of the terminal C–S bond leading to a more disperse system.

The next step in the modeling predictions was to investigate the effect of termination on the molecular weight and polydispersity of the polymers. This was done by assigning a probability of termination. For example, if a propagating carbon radical is a nearest neighbor to another propagating carbon radical, the chance of a bond forming between the two sites and terminating the polymer is defined by the probability.

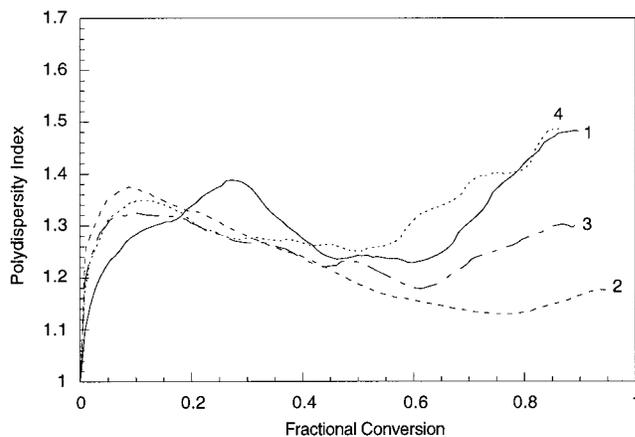


Figure 3. Polydispersity index as a function of monomer conversion for linear polymerizations with the classical free-radical kinetics (1), with an iniferter present and no termination (2), with an iniferter and 50% probability for termination (3), and with an iniferter and 100% probability for termination (4).

In addition, results from polymerization with an iniferter with varying probabilities for termination were compared with the results for a polymerization with conventional free-radical kinetics, including termination by combination. The results from the cases modeled are shown in Figure 3.

From Figure 3, it is evident that termination plays a primary role in the evolving structure of the linear polymers. If termination is impeded in the presence of the iniferter, X_n , X_w , and the PDI all decrease. There is a dramatic decrease in the average number of sites occupied by the polymer when there is no termination. However, if the probability of termination occurrence is increased to 50% or 100%, X_n and X_w begin to approach the values reported in a polymerization with the classical free-radical kinetics and no iniferter present. The PDI is also greatly affected by the elimination of termination. By decreasing the probability for permanent termination of polymer chains, all of the polymer chains continue to propagate, and the monomers are more evenly added to the chains. If even only a fraction of the chains are allowed to terminate, the remaining monomers will only add to the remaining propagating chains, resulting in a more disperse system. This also skews the average number of sites occupied by the polymers because a few chains will be relatively short while others will continue to grow and become very large.

The results of linear polymerizations demonstrate the same trends that other researchers have observed and predicted when implementing a reversible termination in the reaction. Xia and Matyjaszewski¹⁰ demonstrated that lower polydispersities were obtained for styrene, methyl acrylate, and methyl methacrylate when polymerized by ATRP using AIBN/CuBr₂/2dNbipy as the initiating system. Furthermore, they showed higher polydispersities for PMMA at higher temperatures due to slower deactivation as compared to propagation. Our simulations showed that slower deactivation, or smaller k_s , resulted in higher polydispersity. In addition, in ATRP, only a few percent of the polymer chains undergo termination, also contributing to the lower PDI.⁸ In their paper on living radical polymerizations, Greszta and co-workers⁷ discuss the synthesis of well-defined polymers. Their kinetic analysis demonstrated that a low concentration of growing radicals in dynamic equilibrium with

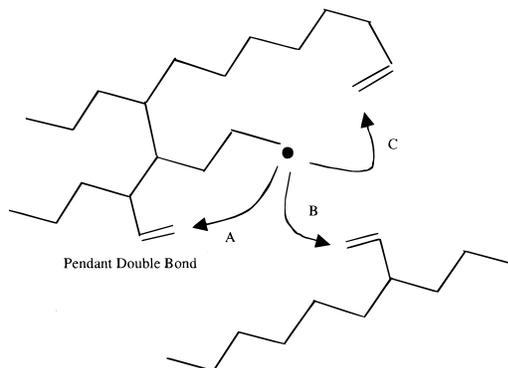


Figure 4. Different types of cycles that can form in a polymer network when a pendant double bond reacts. (A) is a primary cycle, (B) is a cross-link, and (C) is a secondary cycle.

dormant species is necessary for monodisperse samples. Our model is also in agreement with this analysis, as the simulations with the lowest k and k_s had the lowest PDI. All of these instances give credibility to the model for use in a “living”/controlled radical polymerization.

The next step in our analysis was the incorporation of cross-linking agents into the model to examine the effect of the iniferter on polymer network formation. The network structure was inferred by investigating the pendant double-bond reactivity. A pendant double bond is formed when one end of the cross-linking agent monomer reacts with a polymer chain, leaving the other reactive end dangling from the polymer chain. When this pendant double bond reacts, a cycle forms. There are three different types of cycles (primary cycles, cross-links, and secondary cycles) as illustrated in Figure 4. When cross-links form, the network is expanding the system. However, when primary or secondary cycles form, the network is not growing and microgel regions are forming, resulting in a more heterogeneous network.

To analyze the structure of various polymer networks, we carried out copolymerizations with varying amounts of cross-linking agent. The cross-linking agent occupies two neighboring sites on the lattice, and each end is reactive. Although the other comonomer also occupies two neighboring sites, only one end is reactive. The formation of pendant double bonds is monitored and their reactivity tracked. The constants for all of these polymerizations were $k = 0.002$ and $k_s = 0.02$. This implies that the C–S bond on the polymer will dissociate faster than the C–S bond in the original iniferter or initiator. The values of k and k_s were investigated as in the linear case, but only results for $k = 0.002$ and $k_s = 0.02$ are presented here. The same conclusions were drawn for the other values.

Figure 5 displays the results of a polymerization/cross-linking reaction with 10% cross-linking agent. This figure displays how the pendant double bonds react and what fraction of the reacted double bonds forms a primary cycle, a cross-link, or a secondary cycle as a function of double-bond conversion. Three different polymerizations are examined: polymerization with the classical free-radical kinetics without iniferter, polymerization with an iniferter but without termination, and polymerization with an iniferter and a 50% probability for termination. The incorporation of an iniferter results in more primary cycles at the beginning of the reaction. This implies that more microgel regions are formed, and the network is more heterogeneous. This happens because the sulfur radicals are reacting with the poly-

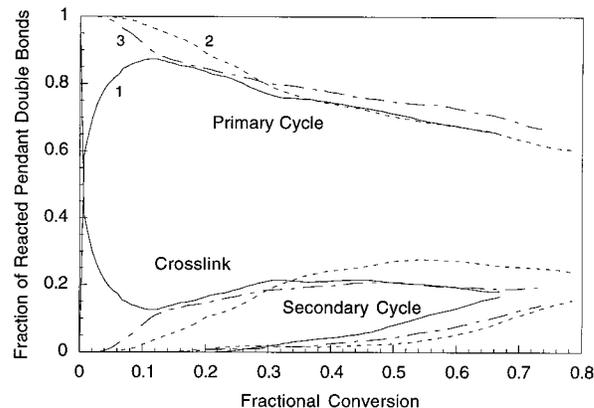


Figure 5. Pendant double-bond reactivity as a function of conversion for a copolymerization with 10% cross-linker and 90% monomer. Results are for polymerizations with conventional kinetics (1), with iniferter kinetics and no termination (2), and with iniferter kinetics and a 50% probability for termination (3).

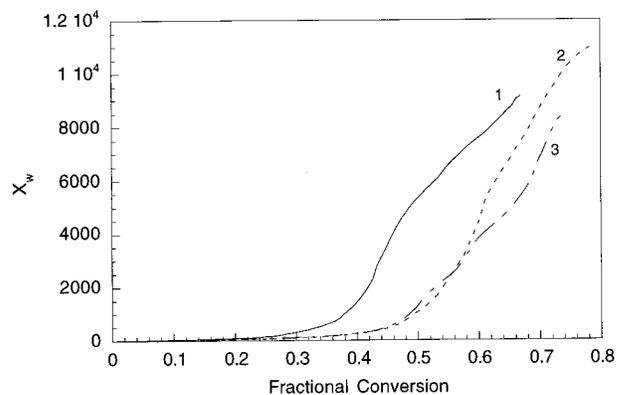


Figure 6. Weight-average number of sites occupied by the polymers, X_w , as a function of conversion for a copolymerization of 10% cross-linker and 90% monomer. Results are for polymerizations with conventional kinetics (1), with iniferter kinetics and no termination (2), and with iniferter kinetics and a 50% probability for termination (3).

mer chains, and then when the C–S bond in the chain breaks, the carbon radical will react with the closest reactive group, which, in this case, is more likely to be a pendant double bond on the same primary chain. In addition, increasing the probability of termination in the iniferter polymerizations does not decrease the formation of the primary cycles at the beginning of the reaction. It is the presence of the C–S bonds in the polymer chains that is affecting the pendant double-bond reactivity and not the termination reaction.

The gel point of the polymerization was also examined. Figure 6 displays the weight-average number of sites, X_w , occupied by the polymers as a function of conversion for the three different polymerizations. When X_w starts to increase rapidly, the polymer is expanding the entire lattice and forming a gel. From the figure, it is observed that the iniferter delays the gel point. This correlates to the formation of more primary cycles. When more primary cycles form, there are more microgel regions, and the system is not growing and spanning the lattice, thus delaying the gel point. The delay in the gel point is observed in the iniferter polymerizations regardless of whether or not termination is allowed to occur.

The next step was to incorporate more cross-linking agent. Figure 7 displays the pendant double-bond

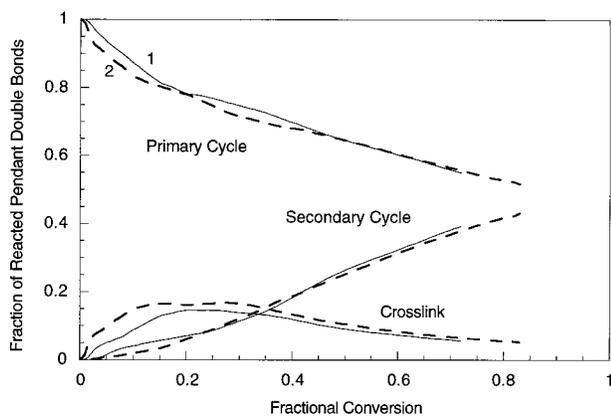


Figure 7. Pendant double-bond reactivity as a function of conversion for a copolymerization with 50% cross-linking agent (2-sites, both ends reactive) and 50% monomer (2-sites, one end reactive). Results are for polymerizations with conventional kinetics (1) and with iniferter kinetics (2).

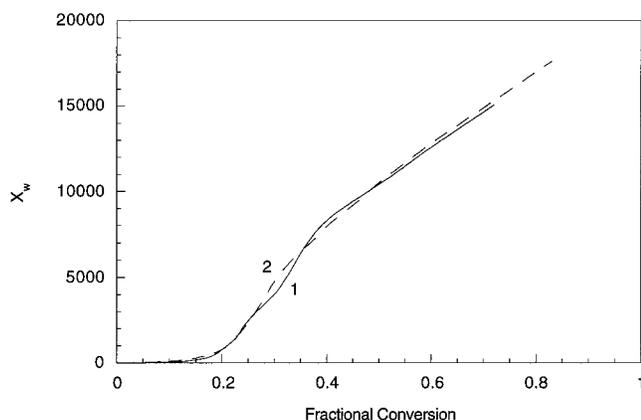


Figure 8. Weight-average number of sites occupied by the polymers, X_w , as a function of conversion for a copolymerization of 50% cross-linking agent and 50% monomer. Results are for polymerizations with conventional kinetics (1) and with iniferter kinetics (2).

reactivity for polymerizations with 50% cross-linking agent with and without the iniferter present. The simulations indicate little difference between a polymerization with the conventional kinetics and one with iniferter kinetics. The gel points are also the same (see Figure 8). Therefore, it appears that the presence of an iniferter has little effect on the pendant double-bond reactivity, and thus we can conclude that the structures are very similar. In this case, there are more pendant double bonds present, and the system is so tightly cross-linked that eliminating termination will not change the final structure.

In all of the data of iniferter polymerizations presented here, it was assumed that the C–S bond in the polymer would dissociate at a faster rate than the initiator ($k < k_s$). In the next simulations, the effect of k and k_s on the network structure was examined. For the polymerizations with 10% cross-linking agent, the values of k and k_s were reversed. Figure 9 displays the pendant double-bond reactivity for polymerizations with the following parameters: $k = 0.002$ and $k_s = 0.02$, $k = 0.02$ and $k_s = 0.002$, and $k = 0.002$ and $k_s = 0.002$. If the initiator dissociates faster than the C–S bond in the polymer ($k > k_s$), less primary cycles form at low conversion. In this case, more propagating chains are introduced at the lower conversions, allowing for the pendant double bonds to react and form cross-links with

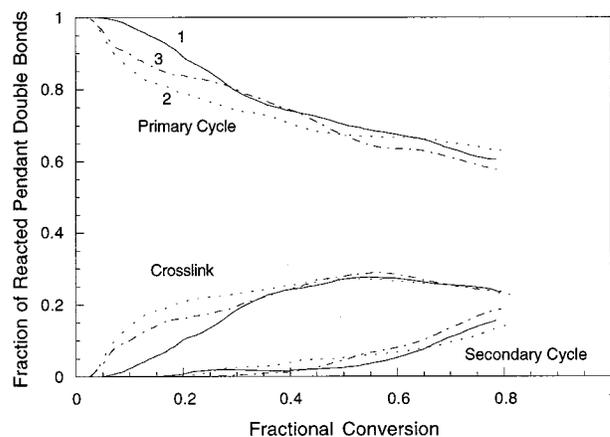


Figure 9. Pendant double-bond reactivity for a polymerization with 10% cross-linking agent and various values of k and k_s : (1) $k = 0.005$, $k_s = 0.02$; (2) $k = 0.02$, $k_s = 0.002$; and (3) $k = 0.002$, $k_s = 0.002$.

other chains instead of forming primary cycles with the same chain. Even though less primary cycles are formed in this scenario, there are still a larger fraction present than in polymerizations without an iniferter present. The other scenario presented in this figure is when the initiator and the C–S bond in the polymer both dissociate at the same rate ($k = k_s$). The results for the pendant double-bond reactivity fall between the other two scenarios.

Conclusions

A kinetic gelation model has been developed to examine the structures of polymeric systems polymerized with “living”/controlled radical techniques. For linear polymerizations, it was shown that eliminating the termination between two carbon radicals results in more monodisperse systems. In addition, increasing the rate of the reversible reaction with the sulfur radical when an iniferter is present results in a lower polydispersity index. For network-producing polymerization/cross-linking reactions, it was found that the change in kinetics only has an effect on loosely cross-linked networks. There are more primary cycles and microgel regions and a delay in the gel point in the presence of the iniferter. However, for more highly cross-linked system, there is very little difference between the structures produced in the presence and in the absence of an iniferter. Changing the kinetics does not alter the pendant double-bond reactivity. Thus, to control polymer network formation for more tightly cross-linked systems, the pendant double-bond reactivity must be controlled in some other manner.

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References and Notes

- (1) Odian, G. *Principles of Polymerization*; Wiley: New York, 1991.
- (2) Vogl, O.; Jaycox, G.; Hatada, K. *J. Macromol. Sci., Chem.* **1990**, *A27*, 1781.
- (3) Szwarc, M. *Nature* **1956**, *178*, 1168.
- (4) Szwarc, M.; Levy, M. *J. Am. Chem. Soc.* **1956**, *78*, 2657.

- (5) Matyjaszewski, K. *Cationic Polymerizations: Mechanism, Synthesis, and Applications*; Marcel Dekker: New York, 1996.
- (6) Ivin, K.; Saegusa, T. *Ring Opening Polymerization*; Elsevier: New York, 1984.
- (7) Greszta, D.; Mardare, D.; Matyjaszewski, K. *Macromolecules* **1994**, *27*, 638.
- (8) Patten, T. E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901.
- (9) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.
- (10) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7692.
- (11) Shipp, D. A.; Wang, J.-L.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 8005.
- (12) Granel, C.; Dubois, P.; Jerome, R.; Teyssie, P. *Macromolecules* **1996**, *29*, 8576.
- (13) Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules* **1997**, *30*, 2190.
- (14) Ajayaghosh, A.; Francis, R. *Macromolecules* **1998**, *31*, 1436.
- (15) Otsu, T.; Yoshida, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 127.
- (16) Otsu, T.; Yoshida, M.; Tazaki, T. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 133.
- (17) Otsu, T.; Matsumoto, A. *Adv. Polym. Sci.* **1998**, *136*, 75.
- (18) Sebenik, A. *Prog. Polym. Sci.* **1998**, *23*, 875.
- (19) Stockmayer, W. H. *J. Chem. Phys.* **1944**, *12*, 125.
- (20) Manneville, P.; de Seze, L. In *Numerical Methods in the Study of Critical Phenomena*; Della Dora, J., Demongeot, J., Lacolle, B., Eds.; Springer: Berlin, 1981.
- (21) Bansil, R.; Herrmann, H. J.; Stauffer, D. *Macromolecules* **1984**, *17*, 998.
- (22) Herrmann, H. J.; Landau, D. P.; Stauffer, D. *Phys. Rev. Lett.* **1982**, *49*, 412.
- (23) Boots, H.; Pandey, R. B. *Polym. Bull.* **1984**, *11*, 415.
- (24) Kloosterboer, J.; van de Hei, G.; Boots, H. *Polym. Commun.* **1984**, *25*, 354.
- (25) Bowman, C. N.; Peppas, N. A. *J. Polym. Sci., Polym. Chem.* **1991**, *29*, 1575.
- (26) Bowman, C.; Peppas, N. *Chem. Eng. Sci.* **1992**, *47*, 1141.
- (27) Anseth, K. S.; Bowman, C. N. *Chem. Eng. Sci.* **1994**, *49*, 2207.

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