Effect of Monomer Type and Dangling End Size on Polymer Network Synthesis

Jennifer H. Ward,[1,*] Kimberly Furman,[1] Nicholas A. Peppas[1,2]

[1]*School of Chemical Engineering, Purdue University, West Lafayette, Indiana 47907-2050*
[2]*Department of Chemical Engineering, The University of Texas, Austin, Texas 78712-0231*

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ABSTRACT: The design of novel biomaterials for applications in biological recognition, drug delivery, or diagnostics requires a judicious choice of preparation conditions and methods for the production of well-characterized 3-dimensional structures, preferably by benign processes. In this work, the polymerization of poly(ethylene glycol) (PEG) methacrylates was examined by kinetic gelation modeling and kinetic analysis in order to ascertain the factors affecting the resulting structure. The kinetics of the polymerization and structure of the final polymer network are strongly affected by the length of the PEG graft chain. The propagation of the polymer chains becomes increasingly diffusion limited with the incorporation of longer PEG grafts. In addition, a more heterogeneous network consisting of numerous microgel regions is produced as the length of the PEG graft is increased. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3506–3519, 2003

Key words: poly(ethylene glycol); UV free-radical polymerization; network synthesis; graft chain

INTRODUCTION

A new class of polymers for biomaterials and carriers for controlled release applications has attracted significant attention in recent years. These polymers are networks that incorporate long poly(ethylene glycol) (PEG) chains onto their main chains.[1–3] Typically, these networks are synthesized by free-radical polymerization with PEG methacrylate (MA). Therefore, the polymerization involves the reaction of a short functional group attached to a long PEG chain that does not participate in the reaction. Yet, as we will show, their configuration and thermodynamic interactions with the main network will affect the nature of the final structure that is formed. These pendent PEG chains will in turn affect the polymerization because of the volume they occupy.

PEG has numerous properties that make it ideal for biomedical applications. This polymer is nontoxic and water soluble, it is not recognized by the immune system, and it exhibits rapid clearance from the body. In addition, it has the unique ability to transfer such biological properties to other molecules to which it is covalently bound.[4] Therefore, PEG may be incorporated into a system of toxic molecules in order to render the pegylated structure nontoxic or biocompatible.

In our laboratories, we have produced 3-dimensional PEG-rich networks by free-radical polymerizations containing PEG grafts and PEG bridges. We have shown that this 3-dimensional PEG-containing structure can be used as a carrier for diffusion-controlled, drug delivery systems.[3,5] In addition, work in this laboratory has shown that tethered polymer structures or grafted PEG chains can serve as adhesion promoters for improved bioadhesion in contact with mucus.[6]

These ideas were further extended into the development of environmentally sensitive hydrogels. For example, copolymers of poly(methacrylic acid) (PMAA) grafted with PEG [P(MAA-*g*-EG)] have been developed and studied. They exhibit pH dependent swelling behavior that is due to the reversible formation/dissociation of interpolymer complexes. These polymers do not swell in acidic media because of the complexation between the acid groups of MAA and the etheric groups of PEG. However, in basic media, the system decomplexes and the gels swell to 3–20 times their size, thus allowing for the delivery of proteins.

The P(MAA-*g*-EG) system is synthesized by solution free-radical polymerization of MAA and PEG-*n*-MA (PEGMA) with a small amount of the crosslinker PEG dimethacrylate (PEGDMA). The length of the PEG chain can be varied. PEG200MA, PEG400MA, and PEG1000MA are all available com-

Correspondence to: N. A. Peppas (peppas@che.utexas.edu).
**Present address:* ExxonMobil Polymer Research Center, Baytown, TX 77520-5200.
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mercially, where the number refers to the molecular weight of the PEG chain.

The result of this polymerization is a backbone chain consisting of MAA and MA groups with the long PEG chains dangling from the MAs. In the preparation of these polymer networks, numerous factors have been examined, including the ratio of ethylene oxide to MAA and the length of the PEG chain. In particular, Peppas and Klier[2] showed that the copolymers of MAA and PEG1000MA contained more MAA repeating units (up to 5%) than the systems with the shorter PEG chains. One possible explanation of this phenomenon may be that the longer PEG chains formed coils surrounding the reactive MA group, thus limiting its reactivity.

Lowman and Peppas[7] further characterized these networks in the swollen state and found that the size of the graft chain length had little effect on the mechanical properties of the ensuing network. In a set of experiments designed to determine the elastic modulus of swollen polymer samples synthesized from MAA and PEGMA with a constant ratio of MAA to EG units of 1:1, they observed that the elastic modulus decreased slightly with increasing graft PEG molecular weight at high pH.[7] It is in this state that the complexes dissociate. The chain length of the grafted PEG chain had an effect on the network structure as it contributed to the transition from the complexed to the uncomplexed state.

The degree of complexation for the polymer samples was calculated based on a set of equilibrium swelling experiments. At pH 3.5, which is an environment for the maximum swelling for all of the gels, it was found that the maximum degree of complexation occurred for the polymer samples synthesized with PEG1000MA as compared to the gels synthesized with PEG400MA or PEG200MA. Gels with the PEG1000MA contained the largest blocks of ionizable groups between grafts; thus, these materials exhibited the highest degree of complexation.

Based on the studies of Peppas and Klier[2] and Lowman and Peppas,[7] they concluded that the best commercially available PEGMA material for the synthesis of P(MAA-*g*-EG) was PEG1000MA. Therefore, PEG1000MA has been the monomer of choice for our research group in the development of biomaterials and carriers for controlled release applications. This longer grafted PEG chain would maximize the desirable complexation between MAA and EG units in the network. Ideally, even longer PEG grafts are desired.

What has not been considered in the synthesis of these polymers is the effect of this long PEG chain on the polymerization process. In the current synthesis, only the small MA group on the end of this PEG chain is capable of undergoing radical polymerization. Therefore, it is evident that the long PEG chain will interfere sterically with the polymerization reaction of the MA sites. Our work focuses on determining the effect of the chain on the kinetics and network structure. The polymers evaluated in this study were prepared by copolymerization of PEGMA with PEGDMA as a crosslinking agent, so that our focus was the effect of the monomer length on the polymerization and the final network structure, not the complexation.

The effect of the monomer structure (i.e., the type of monomer) on the polymerization of multifunctional monomers has been studied extensively by various researchers. Dietz and Peppas[9] have conducted a very detailed analysis on the effect of increasing the monomer size and rank on the kinetics in highly crosslinked multiacrylate networks. Bowman et al.[10] have examined the effect of increasing the length between the functional groups or the rank of the monomer in PEGDMAs and have showed that increasing the length resulted in increased swelling. Anseth et al.[11] have continued the studies of increasing the rank of monomers in highly crosslinked systems. In their kinetic studies, they have found that an increase of the number of EG units between the double bonds led to a shifting of the diffusion-controlled propagation and reaction diffusion-controlled termination to higher conversions.

Because multifunctional monomers were examined so extensively, it was the purpose of this work to examine more loosely crosslinked systems. Therefore, the focus of this research is on the importance of the length of the PEG grafts on the bifunctional monomers. In order to examine the effect of the graft length on both the kinetics and the resulting polymeric network, a kinetic gelation model was developed. This model led to a better understanding of how the increased volume of the PEG graft and the subsequent steric hindrance affected the polymer network. In addition to developing the model, an experimental analysis of the copolymerization of poly(PEG*n*MA-*co*-PEG200DMA) [P(PEG*n*MA-*co*-PEG200DMA)] was completed to examine the kinetics of the reaction and the material properties.

Free-radical polymerization modeling

The kinetic gelation model was chosen for this study because it is a 3-dimensional model and it provided a nonmean field analysis of the polymerization. There are other types of models that have been developed to study free-radical polymerizations, including kinetic models based on mass balances.[12–15] However, for this work, we wanted to describe the structural evolution of the polymerization and the kinetic gelation model was therefore developed.

The kinetic gelation model evolved from percolation theory. However, percolation theory cannot be used for free-radical polymerization because random percolation is a static phenomenon and free-radical

polymerization is a kinetic process.[16] Therefore, Manneville and de Seze[17] proposed an extension of the percolation model, termed the kinetic gelation model, to more accurately explain free-radical polymerization. The kinetic gelation model is also often called a dynamic percolation model.[16]

Manneville and de Seze[17] studied the gelation process of a solution of bifunctional and tetrafunctional monomers in the absence of solvent. Sites in the lattice were randomly assigned to the bifunctional unit or the tetrafunctional unit. A reaction occurred by randomly selecting an active site, then randomly picking one of the first or second neighbors with available functional groups, and finally linking the two units. After this reaction, the first active site was made inactive and the second site was made active. Termination occurred when an active site reacted with another active site. The major drawback to this model was the lack of molecular movement. All of the monomers and polymers remained stationary.

Numerous researchers have improved this model by incorporating mobility, more realistic initiating mechanisms, and monomer structure.[18–29] This model provides tremendous insight into the evolving molecular structure of networks produced by free-radical polymerizations. However, the lack of molecular interactions, the realistic movement of the molecules, and the absence of a time scale can make it difficult to compare data from the model to data obtained from experiments. Numerous researchers have been able to demonstrate qualitative agreement between model results and experimental observations. Therefore, it is an acceptable model to be used in evaluating polymer network structures.

The model used in this study is based on the model proposed by Bowman and Peppas,[28,29,] but it incorporates improvements in the analysis. Their model included a more realistic initiation mechanism, a face-centered cubic lattice, and monomer and polymer movement. The face-centered cubic lattice was utilized so that there would be 12 nearest neighbors to a given site on the lattice instead of 6. In addition, both the monomers and parts of the polymer could move in the lattice, provided all bonds remained intact. Other modifications included allowing monomers to occupy more than one site. Anseth and Bowman[27] later explored the effect of monomer size on the network structure. They also investigated copolymerizations with their model and found their simulation results to be in good agreement with experimental observations.

To begin the model, the monomers and initiators were randomly distributed on the lattice. The lattice used in this study is a face-centered cubic lattice with a length of 31. In all of the simulations, 15% of the sites remained vacant to allow for movement. This allowed for reasonable mobility of the monomer molecules. In addition, periodic boundary conditions were implemented in order to neglect edge effects.

Initiators occupied two neighboring sites in the lattice. Monomers occupied a specified number of neighboring sites, depending on their relative size. Different size monomers could be implemented in a copolymerization. In addition, either one end (bifunctional monomer) or both ends (tetrafunctional monomer or crosslinking agent) of the monomer could be specified as reactive functional groups. All other sites in a monomer were unable to react. After randomly placing the initiators and monomers on the lattice, simulation of the polymerization process was initiated. During a single step in the model, three different actions took place: initiation, polymerization, and monomer and chain segment movement.

Initiation of the polymerization begins with the decomposition of the initiator molecules into radicals, as shown by eq. (1).

$$\frac{[I]}{[I]_0} = e^{-kt} \tag{1}$$

Here $[I]$ is the initiator concentration, $[I]_0$ is the initial initiator concentration, t is the time step, and k is the decay constant. Upon decomposition, the initiator split into two radicals, each occupying one site. For all of the results presented here, k was set to 0.002 (units of inverse time), unless otherwise noted. For photopolymerizations, a larger k value corresponds to a higher UV intensity, which means that more radicals will be introduced into the system in a shorter time period. The value of 0.002 was chosen based on the work of Anseth and Bowman.[27] They evaluated different values of k and found that 0.002 was representative of a relatively fast polymerization, which is typical for a photopolymerization. In these simulations, the time corresponded to the step number of the simulation (i.e., 1, 2, 3, 4, . . . , to the final step). It was not considered actual time because this is a Monte Carlo type simulation.

After eq. (1) was evaluated, all of the radicals in the system were examined. A reaction occurred if a radical was a nearest neighbor to either a reactive group or another radical. If the radical reacted with a functional group end of a monomer, propagation occurred. In this case, a bond was formed between the radical and the monomer and the radical was transferred to the monomer. If the radical reacted with another radical, termination occurred. In this case, a bond formed between both radical sites and the radicals were terminated.

One of the key steps in this model was the movement of the molecules of monomer, initiator, and polymer. The movement allows for the possibility of reactive ends becoming nearest neighbors. Movement of species occurred at every step.

Initially, 33% of the occupied sites were selected at random. Because the monomers, initiators, and polymers occupy multiple sites, only a single site within the molecule was chosen. Next, a nearest neighbor of each site was also selected at random. If that neighboring site was empty, an attempt was made to move the previously selected occupied site. A move was accepted as long as all bonds remained intact. A bond could not be broken or lengthened and all occupied sites within an initiator, monomer, or polymer had to remain nearest neighbors. Only 33% of the occupied sites, instead of all of the occupied sites, were chosen to save simulation time. Simulations took considerably longer if we attempted to move every occupied site. Movement of the molecules consumed most of the computer time. If we attempted to move more molecules, there was a considerable increase in the simulation time. The value of 33% was decided upon as an optimum in moving species and finishing a simulation in reasonable time.

EXPERIMENTAL

The monomers of PEG-*n*-MA (PEG*n*MA), where *n* refers to the molecular weight of the PEG chain, were used as received (Polysciences Inc., Warrington, PA). Monomers with PEG molecular weights of 200 and 400 were used. The crosslinking agent, PEG200 DMA (PEG200DMA), was used as received from Polysciences, Inc. The initiator was 2,2-dimethoxy-2-phenyl acetophenone (DMPA), which was purchased from Aldrich (Milwaukee, WI). Solutions of the PEG-*n*MA, PEG200DMA, and initiator were prepared. The concentration of PEG200DMA varied from 2.5 to 30 mol %. The initiator concentration was 0.1 wt %.

Kinetic studies were conducted with a differential photocalorimeter (DPC, model DPC930, TA Instruments, New Castle, DE). A sample of 2–6 mg of the monomer mixture was placed in a small aluminum pan. The pan was covered with a clear disk of polyethylene in order to prevent evaporation of the monomer. The apparatus was purged with nitrogen to prevent inhibition of the polymerization because of the presence of oxygen.

In a typical experiment, the monomer mixture in the pan was placed in the DPC, equilibrated at 30°C for 10 min, and then irradiated with UV light at 1.2 mW/cm^2 for 20 min. The heat evolved was measured as a function of time. The theoretical enthalpy of the monomer solution was then used to calculate the rate of polymerization (R_p) in units of fractional double bond conversion per second. Integration of the R_p curve versus time provided the conversion as a function of time. It was assumed that in the copolymerization of two monomers, the functional groups had equal reactivity. In other words, the theoretical enthalpy derived for a comonomer mixture was an average of the enthalpies of the individual monomers. The MA groups have an enthalpy of −13.1 kcal/mol.[30]

The mechanical properties of the polymers were measured with variable temperature dynamic mechanical analysis (DMA, model DMA 983, TA Instruments). Polymers were prepared in thin films by placing the monomer mixture with the initiator between two glass slides separated by 0.9-mm Teflon spacers. The polymerization took place under a nitrogen environment and the monomer solution was bubbled with nitrogen prior to the polymerization to remove any oxygen, which acts as an inhibitor. A spot cure UV light source (EFOS Acticure, Mississauga, ON) was used to irradiate the sample for 10 min at approximately 10 mW/cm^2.

DMA experiments were performed in the resonant frequency mode with an oscillation amplitude of 0.20 mm. Sample lengths were adjusted to give an average resonant frequency of 5.5 Hz. The storage (G_e') and loss (G_e'') moduli were determined for the copolymer sample. The damping factor (tan δ) is the ratio of the loss modulus to the storage modulus. The glass-transition temperature (T_g) is measured as the temperature at which tan δ is a maximum. The tan δ peak is also a measure of the heterogeneity: the wider the peak, the more heterogeneous the sample is.[31]

Modeling results

A kinetic gelation model was developed in order to examine copolymerizations of PEG*n*MA with PEG200DMA. We wanted to examine the effect of the increasing PEG graft on the network produced by the free-radical copolymerization. Monomers of PEG*n*MA occupied either two, three, or four sites on the lattice and only one end was reactive. For the crosslinking agent PEG200DMA, this monomer occupied two neighboring sites with each end being reactive.

During a simulation, every monomer was tracked. Records were kept regarding its position and reactivity and where it was in a polymer chain. Both functional groups of the crosslinking agent were tracked. For these network-producing polymerizations, the pendent double bond reactivity was extremely important and it was used to characterize the network. A pendent double bond was formed when one end of a crosslinker monomer reacted in a polymer chain, leaving the other reactive end dangling from the polymer chain and free to react. When this pendent double bond reacted, a cycle formed. Figure 1 illustrates the three types of cycles: primary cycle, secondary cycle, and crosslink. The formation of primary and secondary cycles results in a very heterogeneous structure because of the formation of microgel regions. These cycles do not contribute to the overall structure of the polymer. Only the formation of crosslinks leads to an expansion of the polymer network.

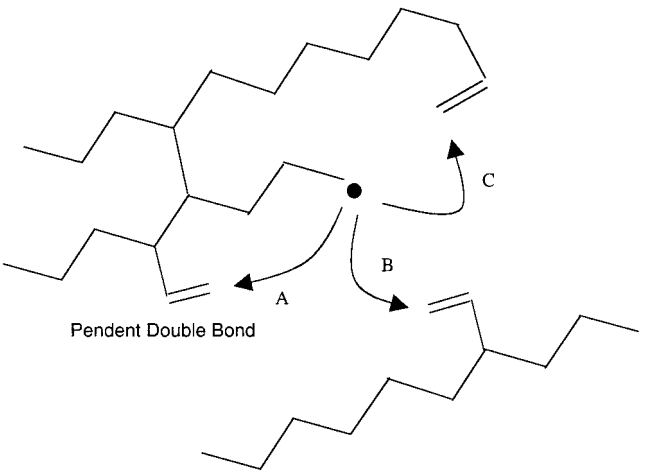

Figure 1 Three types of cycles can form in a polymer network when a pendent double bond reacts with a free radical. Primary cycles are formed according to reaction A, crosslinks are formed according to reaction B, and secondary cycles are formed according to reaction C.

In the first scenario, a copolymerization with 50% crosslinking agent was considered. The length of the second comonomer was varied between two, three, and four neighboring sites. In Figure 2(a) the reactivity of the pendant double bonds is followed during the reaction. At every conversion, the fraction of primary cycles, secondary cycles, and crosslinks was determined. In all of the copolymerizations, more primary cycles were formed than any other type of cycle. This was due to the close proximity between a pendent double bond and a radical on the same primary chain. Adding a crosslinking agent into the primary chain resulted in a pendent double bond that was extremely close to the radical. Therefore, the chance of a reaction between the two was increased. If a primary cycle was not formed right away, the chance of a crosslink or secondary cycle forming increased because the radical and pendent double bond on the same primary chain became further apart. The radical had a better chance of reacting with a pendent double bond on a separate chain. Figure 2(a) shows this trend of an increasing fraction of crosslinks and secondary cycles as conversion increased. The fraction of crosslinks peaked and then decreased at the highest conversions because all of the different polymer molecules linked together. As the polymer molecules became linked, the network expanded the entire lattice and secondary cycles formed more often.

Figure 2(a) also presents the results for copolymerizations with increasing PEG graft lengths. It was evident that increasing the graft length increased the fraction of primary cycles. The long four-site PEG graft hindered the reactions between different chains to form crosslinks. This resulted in a very high fraction of primary cycles. Examination of this polymer network revealed numerous microgel regions of polymers. The long graft hindered the reactions that would have linked the microgel regions. The final network structure was very heterogeneous because of the presence of numerous microgel regions.

For the same copolymerization simulations, Figure 2(b) displays the weight-average molecular weight (X_w) as a function of conversion. The point at which X_w diverged corresponded to the point where the polymer extended from one end of the lattice to the other. This is commonly referred to as the gel point. Increasing the graft length from two sites to three sites delayed the gel point from 25 to 30% conversion. A drastic delay in the gel point was observed when the graft length was increased to four sites. For this copolymerization, the X_w did not start to increase until 70% conversion. This was another indication of the formation of numerous microgel regions that were not all connected.

For the next set of simulations, the amount of crosslinking agent was decreased to 10%. Figure 3(a) displays the pendent double bond reactivity for these copolymerizations with a graft chain length of two, three, or four sites. Overall, there were less primary cycles formed with 10% crosslinking agent than with 50% crosslinking agent. This was expected because, with less crosslinking agent, there were fewer pendant double bonds in the primary chain. The same trend with the increasing length of the graft chain that was observed with 50% crosslinking agent was observed here. A longer graft chain led to an increase in the number of primary cycles because the grafts caused a larger hindrance for the radicals to react with pendent double bonds on different chains.

Figure 3(b) shows the X_w value as a function of conversion for these copolymerizations with 10% crosslinking agent. There was a significant delay in the gel point as compared to the previous copolymerizations because of the decrease in the amount of crosslinking agent. Again, the longer graft chains led to a delay in the gel point, which corresponds to the formation of more primary cycles. Because more primary cycles had formed, more microgel regions were present, which made the network more heterogeneous.

As the concentration of crosslinking agent was decreased, the polymer backbone contained more grafts. One of the easiest reactions that occurred in the presence of a crosslinking agent was the formation of a primary cycle. The radical on the end of a propagating chain was in very close proximity to a pendent double bond on the same chain. As the concentration of crosslinking agent was decreased, there were less pendent double bonds. Instead, grafts were positioned next to each other, as illustrated in Figure 4. In the radicals and functional groups that were close enough

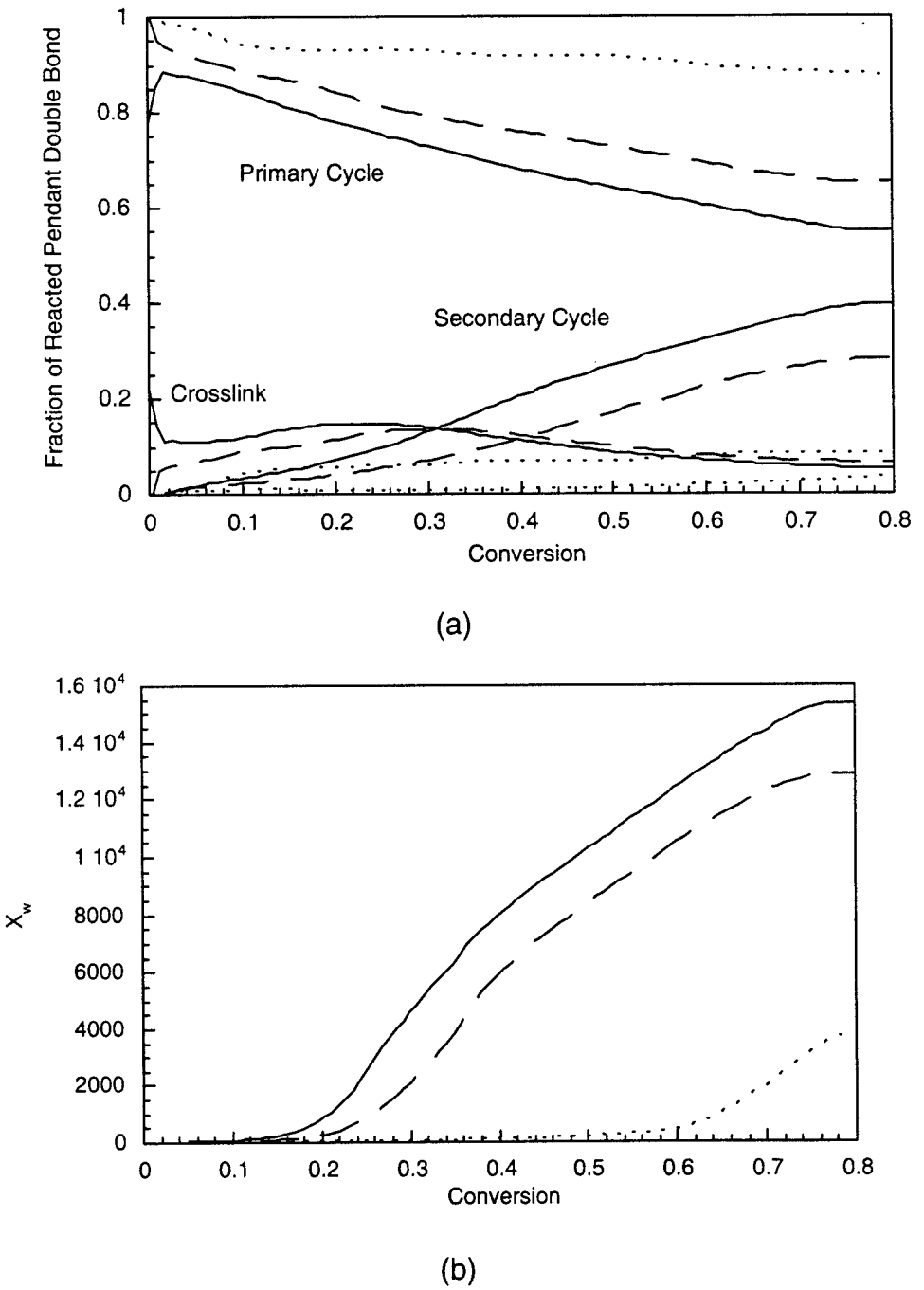

Figure 2 The (a) pendent double bond reactivity and (b) weight-average number of sites occupied (X_w) as a function of conversion for simulations with 50% crosslinking agent (two sites) and 50% monomer with only one reactive end and occupying (—) two, (– –) three, and (- - -) four sites.

to each other to react, this made movement very difficult.

In the case of the smallest graft, the rate of propagation was slowed the least. The monomers were smaller and more mobile and the grafts on the backbone did not hinder propagation as much. Figure 3(a) shows that this resulted in more crosslinks. After the network expanded the lattice, the rate of propagation decreased quickly because movement was restricted.

For the longest graft, both the rates of propagation and termination were decreased because of the lack of mobility caused by the large molecules and the large grafts on the polymer backbone.

The kinetic gelation model provided useful insight into the effect of increasing the PEG graft length on the copolymerization. A small increase would hinder polymerization somewhat and cause a more heterogeneous polymer network. At some point, as the size of

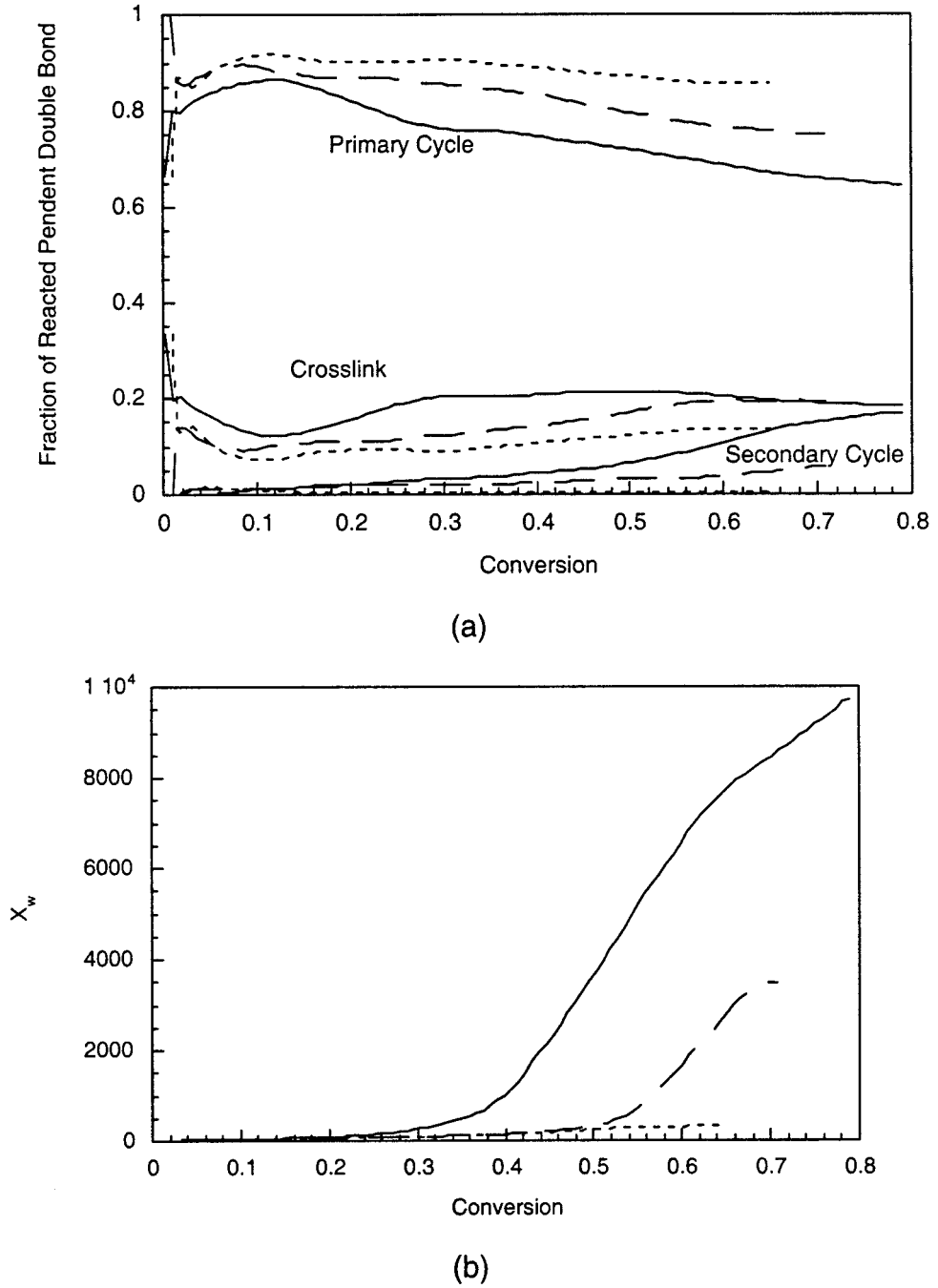

Figure 3 The (a) pendent double bond reactivity and (b) weight-average number of sites occupied (X_w) as a function of the conversion for simulations with 10% crosslinking agent (two sites) and 90% monomer with only one reactive end and occupying (—) two, (– –) three, and (- - -) four sites.

the graft was increased, the changes in the copolymerization were quite drastic. The gel point was delayed significantly and the network became a series of microgel regions instead of a more homogeneous, crosslinked network.

Experimental analysis of P(PEG*n*MA-*co*-PEGDMA)

In conjunction with the modeling of the copolymerization, differential scanning calorimetry (DSC) was used to determine the kinetics of the copolymerization. The mechanical properties of P(PEG*n*MA-*co*-PEGDMA) were also determined.

Polymerization kinetics

The DPC analysis of the copolymerization provided a detailed analysis of the kinetics. A typical free-radical polymerization comprises three steps: initiation, prop-

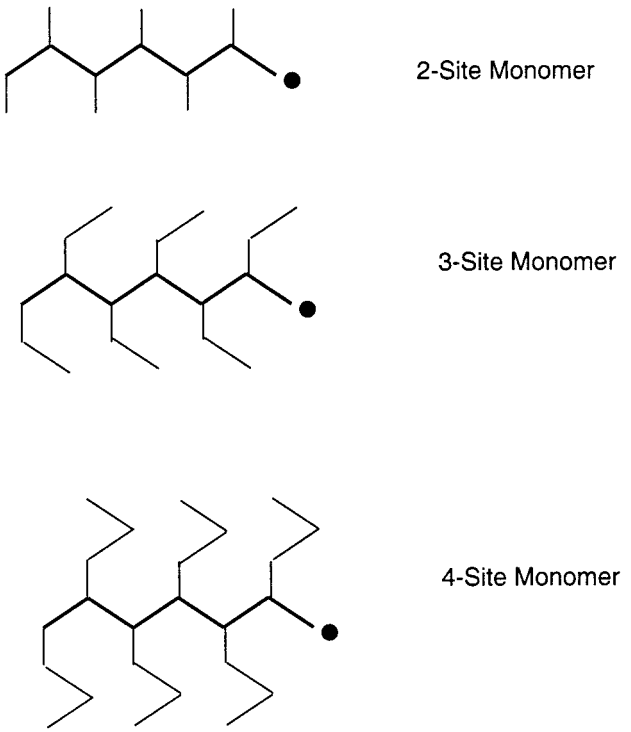

Figure 4 A schematic of the propagating polymer with the backbone chain (bold line) and the increasing graft length for the kinetic gelation model with two-, three-, and four-site monomers.

agation, and termination. Based on these steps, it is possible to set up a mass balance of the monomer. The monomer ([*M*]) disappears in the initiation step and the propagation step:

$$-\frac{d[M]}{dt} = R_p + R_i \tag{2}$$

Here R_p represents the rate of propagation and R_i is the rate of initiation. In these polymerizations, the rate of propagation is much faster than the rate of initiation, so R_i is neglected. The derivatio of R_p is further written as

$$R_p = k_p[M]\left(\frac{R_i}{2k_t}\right)^{1/2} \tag{3}$$

where k_p is the propagation kinetic constant, [*M*] is the concentration of monomer, and k_t is the termination kinetic constant. An assumption is made that the rate of initiation of the radicals is equal to the rate of their termination. For UV polymerizations, the rate of initiation is expressed as

$$R_j = 2\phi\varepsilon I_0[A]b \tag{4}$$

where ϕ is the efficiency, ε is the molar absorptivity, I_0 is the incident light intensity, [*A*] is the concentration of the species that undergoes photoexcitation, and *b* is the thickness. All of the values in eq. (4) were known for conditions of the DPC experiments. The efficiency of DMPA was assumed to be 0.6.

The normalized heat flows for the copolymerization of PEG200MA with various amounts of the crosslinking agent PEG200DMA are shown in Figure 5. The monomer mixture was kept isothermal at 30°C for 10 min prior to turning on the UV light. At the 10-min

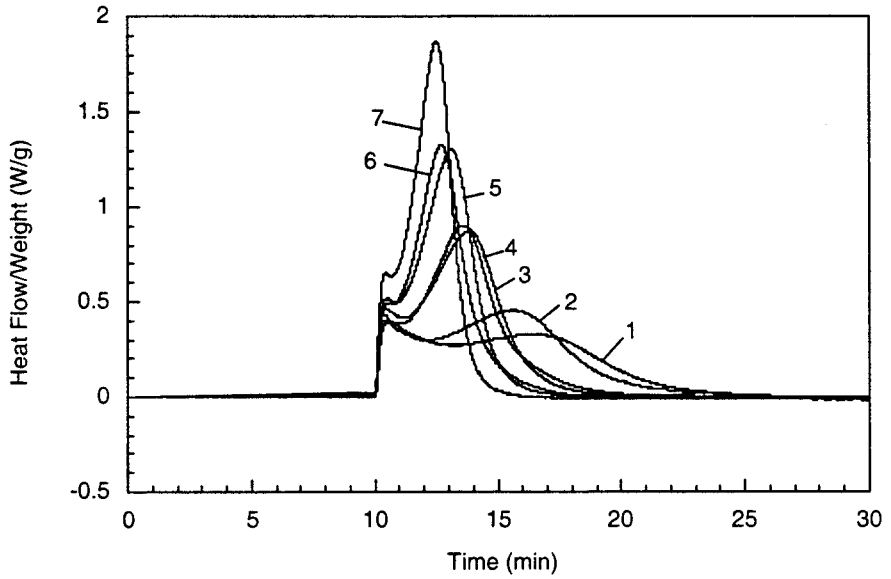

Figure 5 The normalized heat flow as a function of time during the copolymerization of PEG200MA with the crosslinking agent PEG200DMA. The different runs correspond to different amounts of the comonomer/crosslinking agent PEG200DMA: 2.5 (curve 1), 5.0 (curve 2), 10.0 (curve 3), 15.0 (curve 4), 20 (curve 5), 25 (curve 6), and 30 mol % (curve 7).

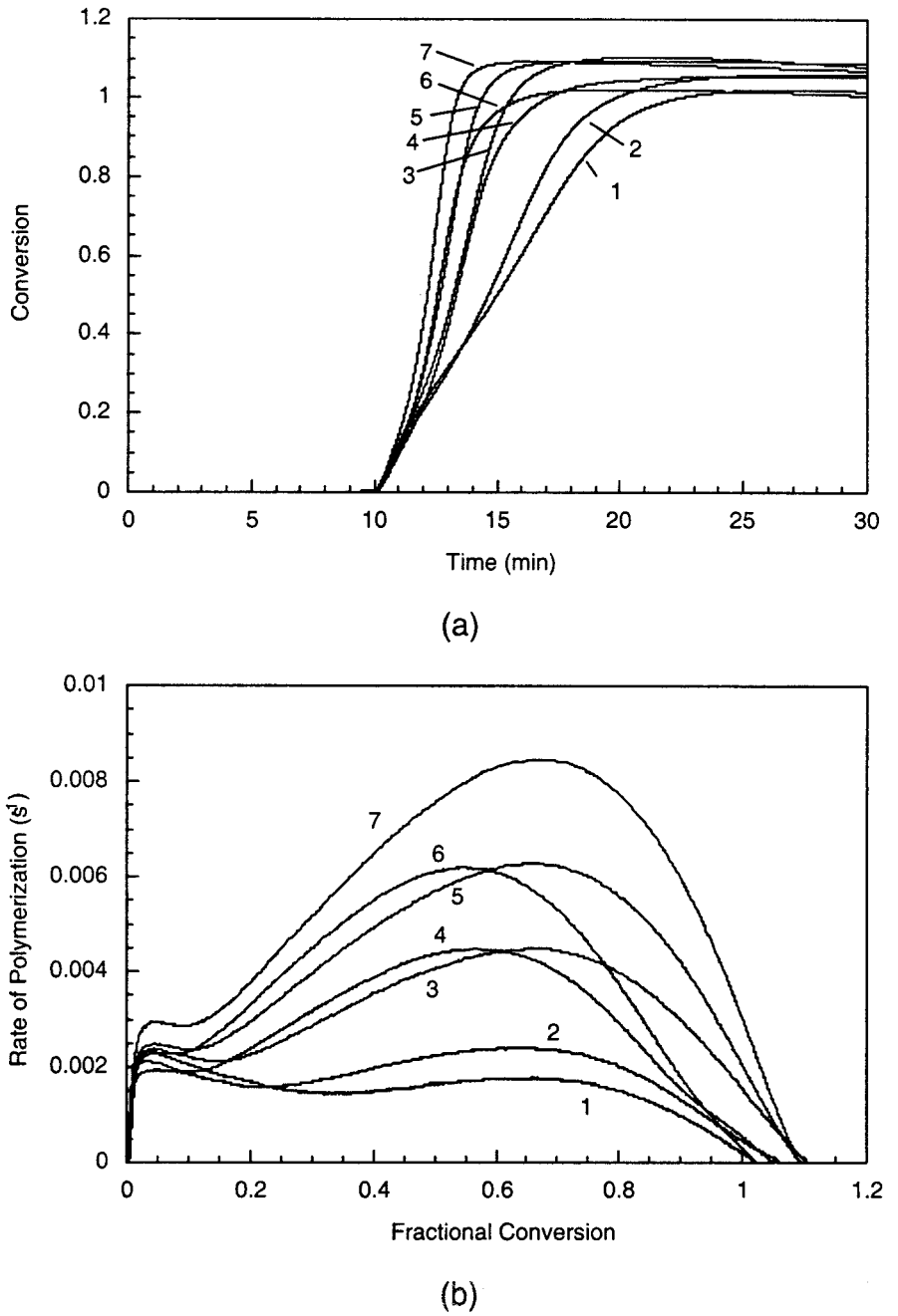

Figure 6 (a) The conversion as a function of time and (b) the rate of polymerization as a function of conversion during the copolymerization of PEG200MA with the crosslinking agent PEG200DMA. The different runs correspond to different amounts of the comonomer/crosslinking agent PEG200DMA: 2.5 (curve 1), 5.0 (curve 2), 10.0 (curve 3), 15.0 (curve 4), 20 (curve 5), 25 (curve 6), and 30 mol % (curve 7).

mark, the sample was irradiated with 1.2 mW/cm^2 UV light. There was a sharp increase in the heat flow, corresponding to an exothermic reaction. The copolymerization with the greatest amount of PEG200DMA had the highest peak and returned to zero heat flow the fastest. As the amount of PEG200DMA was decreased, the peak height decreased and the reaction lasted longer.

These data were used to calculate the value of R_p and the conversion. Figure 6(a) displays the conversion profiles and Figure 6(b) displays the results for R_p as a function of conversion. The copolymerizations with the larger concentrations of PEG200DMA exhibited an increase in R_p even as the monomer was consumed. This is known as an autoacceleration phenomenon. Another interesting feature of these polymerizations was the decrease in R_p between 5 and 20% conversion before the autoacceleration effect.

The decrease in R_p at low conversion was attributed to the diffusion-controlled termination. In order for

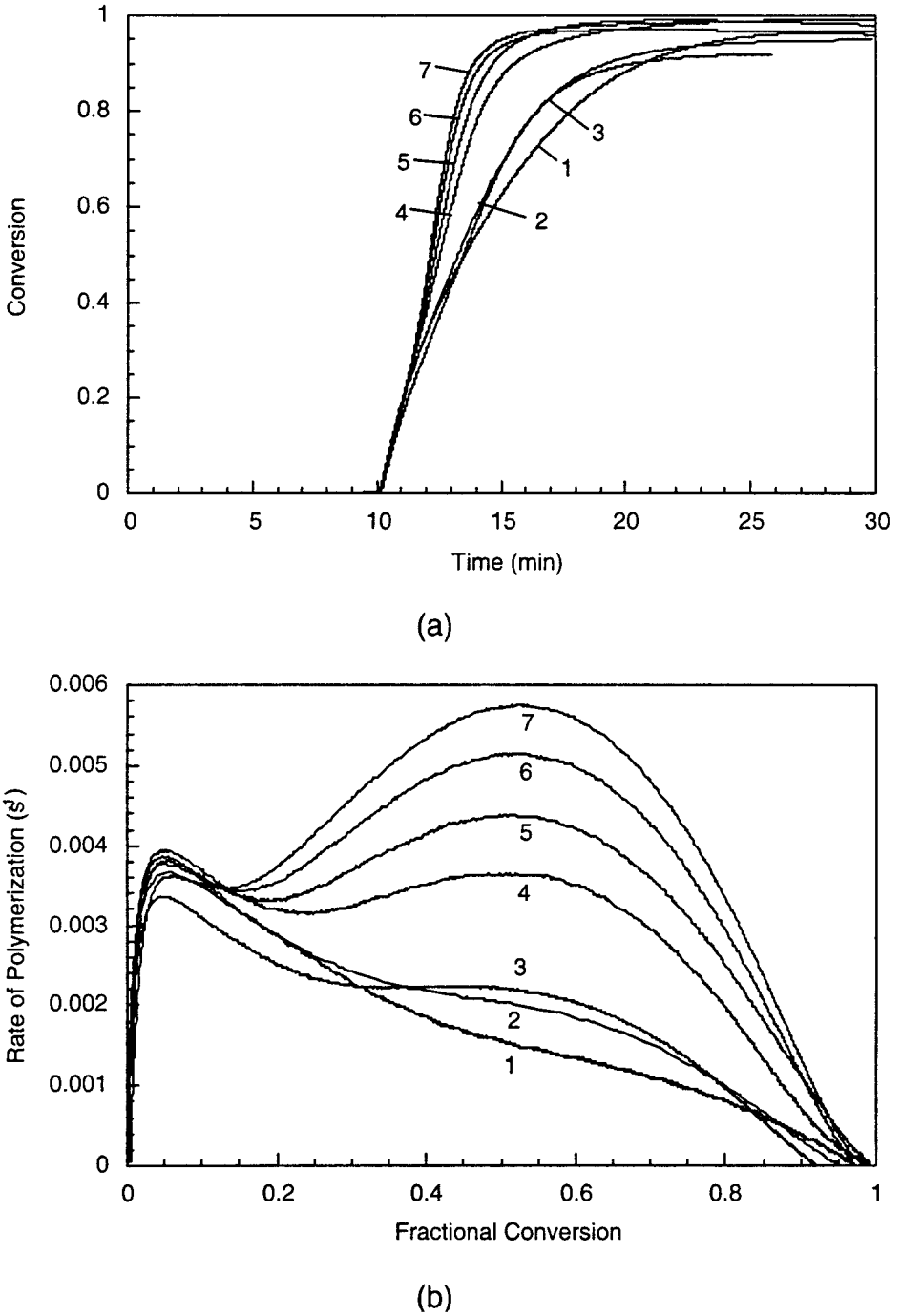

Figure 7 (a) The conversion as a function of time and (b) the rate of polymerization as a function of conversion during the copolymerization of PEG400MA with the crosslinking agent PEG200DMA. The different runs correspond to different amounts of PEG200DMA: 2.5 (curve 1), 5.0 (curve 2), 10.0 (curve 3), 15.0 (curve 4), 20 (curve 5), 25 (curve 6), and 30 mol % (curve 7).

termination to occur, the propagating polymer chains must first undergo translational diffusion in order to be in proximity to each other. Next, segmental diffusion occurs where the two chains rearrange so that the radical ends are close enough to react. Finally, the chemical reaction of the two chains occurs. During a polymerization, the viscosity drastically increases in the transition from a low viscosity monomer system to a very viscous polymer system. As the polymer concentration increases, the medium becomes a poorer solvent. Thus, the randomly coiled propagating chains become smaller and it is easier for segmental diffusion to occur. At the same time, this increase in polymer concentration increases the viscosity and the chains become entangled, making translational diffusion more difficult.

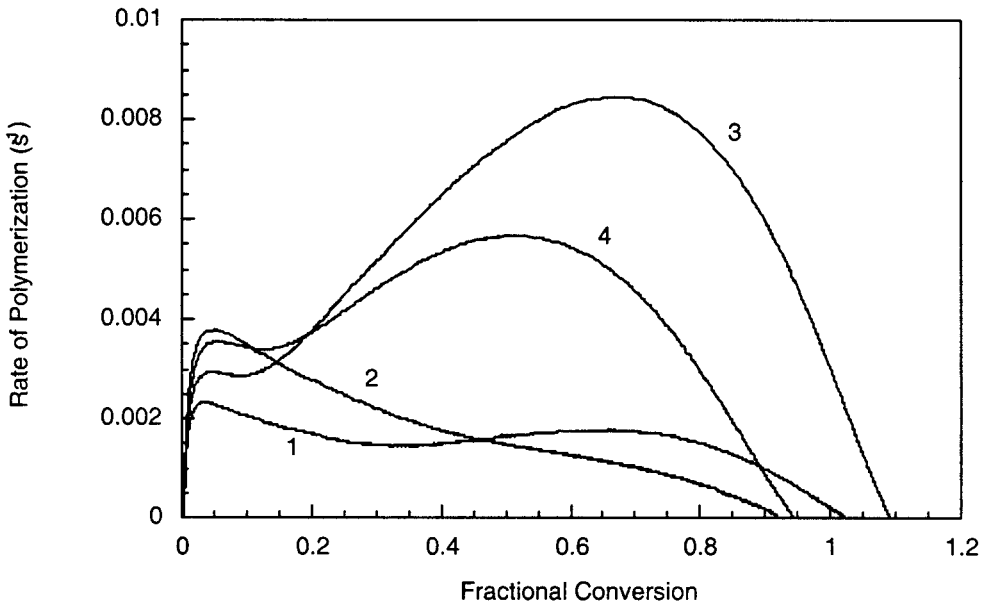

Figure 8 A comparison of the rate of polymerization for the copolymerizations of PEG200MA with 2.5 mol % PEG200DMA (curve 1), PEG400MA with 2.5 mol % PEG200DMA (curve 2), PEG200MA with 30 mol % PEG200DMA (curve 3), and PEG400MA with 30 mol % PEG200DMA (curve 4).

During the early stages of the polymerization, the initial increase in segmental diffusion is greater than the decrease in translational diffusion, causing the k_t value to increase, which in turn decreases the polymerization rate . If the segmental and translational diffusion exactly counterbalanced each other, k_t would remain constant. The slope of this decrease in the first 20% conversion was largest for the fraction with the least amount of crosslinker and the most PEG200MA. The increase in the amount of PEG200MA most likely created more entanglements of the PEG chains and decreased the translational diffusion because the PEG grafts were closer to each other. The decrease in R_p also occurred for a longer time in the system with the most PEG200MA, another indication that the presence of the PEG chains increased the translational diffusion.

Between 10 and 30% conversion, the various copolymerizations exhibited an increase in R_p and autoacceleration began. Autoacceleration is typically observed in crosslinked regions. As the polymer network formed, it became increasingly difficult for two longer propagating chains to diffuse toward each other and terminate. Instead, propagation with the functional group on the smaller, more mobile monomer occurred at a much faster rate, which led to the increase in R_p. As the amount of crosslinking agent was increased, the R_p increased faster and to a higher value. An increased amount of the crosslinking agent resulted in a more highly crosslinked polymer network. This made the solution more viscous during the polymerization and hindered termination, thus increasing the R_p. Eventually, at high conversion, enough monomer had been consumed that the rate of propagation decreased and termination began to dominate.

In the next set of experiments, the kinetics for the copolymerization of PEG400MA with the crosslinking agent PEG200DMA was determined. The same mole percent concentrations of PEG200DMA were used in these copolymerizations as in the copolymerizations with PEG200MA.

The corresponding conversion profiles and R_p data as a function of conversion are shown in Figure 7. A very prominent autoacceleration effect was evident with the copolymerizations containing the most PEG200DMA. At the lowest concentration of PEG200DMA, there was no autoacceleration effect and only a steady decline in R_p from the initial value. For this case, the copolymerization consisted mainly of the longer grafts of PEG400MA. This larger monomer slowed down the rate of propagation and therefore the R_p did not increase as it did in the copolymerizations with a lower concentration of PEG400MA.

In order to make a comparison with the kinetic gelation modeling results, the copolymerizations of P(PEG200MA-*co*-PEG200DMA) and P(PEG400MA-*co*-PEG200DMA) were compared. Figure 8 shows a comparison of the different copolymerizations with 2.5 and 30 mol % PEG200DMA. A summary of the various kinetic data for the copolymerizations is compiled in Tables I and II.

Increasing the graft length had a prominent affect on the kinetics. In all of the copolymerizations, there was a stronger autoacceleration and higher maximum R_p in the copolymerizations with PEG200MA than

TABLE I
Kinetic Data for Copolymerizations of PEG200MA and PEG200DMA

PEG200DMA (mol %)	Initial R_p (s^{-1})	$R_{p,max}$ (s^{-1})	Conversion at $R_{p,max}$ (%)	Final Conversion (%)
2.5	2.25×10^{-3}	1.75×10^{-3}	68	102
5	2.13×10^{-3}	2.42×10^{-3}	65	106
10	2.36×10^{-3}	4.49×10^{-3}	68	108
15	1.94×10^{-3}	4.48×10^{-3}	57	105
20	2.48×10^{-3}	6.28×10^{-3}	66	109
25	2.28×10^{-3}	6.2×10^{-3}	55	101
30	2.94×10^{-3}	8.46×10^{-3}	69	107

$R_{p,max}$, maximum R_p during autoacceleration.

with PEG400MA. However, the initial R_p was higher for the copolymerizations with the longer PEG400MA.

The kinetic gelation modeling results indicated that the longer grafts resulted in more primary cycles, a delay in the gel point, and a plateau in the number of radicals, an indication of an increased rate of termination relative to propagation. Because the R_p decreased with increasing graft length, that also meant that there was an increase in the rate of termination relative to the rate of propagation. In addition, the higher R_p at the low conversion for the longer grafts corresponded with the formation of more primary cycles in the beginning, as shown in the modeling results. As mentioned earlier, primary cycles form faster when the radical is closest to the pendent double bond. Increasing the graft length increased the probability for primary cycles, which caused the initially higher R_p in the kinetic experiments.

One concern in these experimental calculations was the reported conversions that were over 100%. This was most likely attributable to the assumption of the theoretical enthalpy. If the enthalpy were increased by 5%, the final conversion would be decreased by 5%, which would then lead to a more reasonable result. Another assumption made in these calculations for the copolymerizations was the lack of distinction in the reaction of a functional group on the PEGMA monomer and a functional group on the PEGDMA monomer. The theoretical enthalpy used in these systems was based on this assumption and calculated based on the initial concentration. In an ideal copolymerization, where $r_1 = r_2$, the monomers show equal reactivities toward each other and the final copolymer has a random distribution with the same concentration as the feed. This equal reactivity assumption was considered valid in this case because the functional groups on both monomers were MA groups attached to PEG chains.

Mechanical properties of P(PEG-*n*-MA-*co*-PEG200DMA)

Variable temperature DMA experiments were conducted to examine the mechanical properties of the copolymers. Only polymers with higher concentrations of PEG200DMA were evaluated. As the amount of crosslinking in a copolymer is increased, the T_g increases. The DMA experiments work best for polymers with a higher T_g.

Figure 9 shows the tan δ as a function of temperature for specimens of crosslinked polymers prepared from either PEG200MA or PEG400MA with 50 mol % PEG200DMA. Because each copolymer had a different T_g, the temperature is shown as $T - T_g$ so as to normalize the data. The polymer with PEG200MA had a T_g of 12 ± 3°C whereas the polymer with PEG400MA had a considerably lower T_g of −28 ± 5°C. The standard for measuring the heterogeneity of the material from tan δ is to calculate the width of the peak at one-half the maximum tan δ. Figure 9 shows

TABLE II
Kinetic Data for Copolymerizations of PEG400MA and PEG200DMA

PEG200DMA - (mol %)	Initial R_p (s^{-1})	$R_{p,max}$ (s^{-1})	Conversion at $R_{p,max}$ (%)	Final Conversion (%)
2.5	2.04×10^{-3}	—	—	92
5	3.67×10^{-3}	—	—	95
10	3.48×10^{-3}	2.31×10^{-3}	48	95
15	3.95×10^{-3}	3.66×10^{-3}	51	99
20	3.87×10^{-3}	4.38×10^{-3}	52	98
25	3.78×10^{-3}	5.14×10^{-3}	52	96
30	3.62×10^{-3}	5.75×10^{-3}	53	99

$R_{p,max}$, Maximum R_p during autoacceleration.

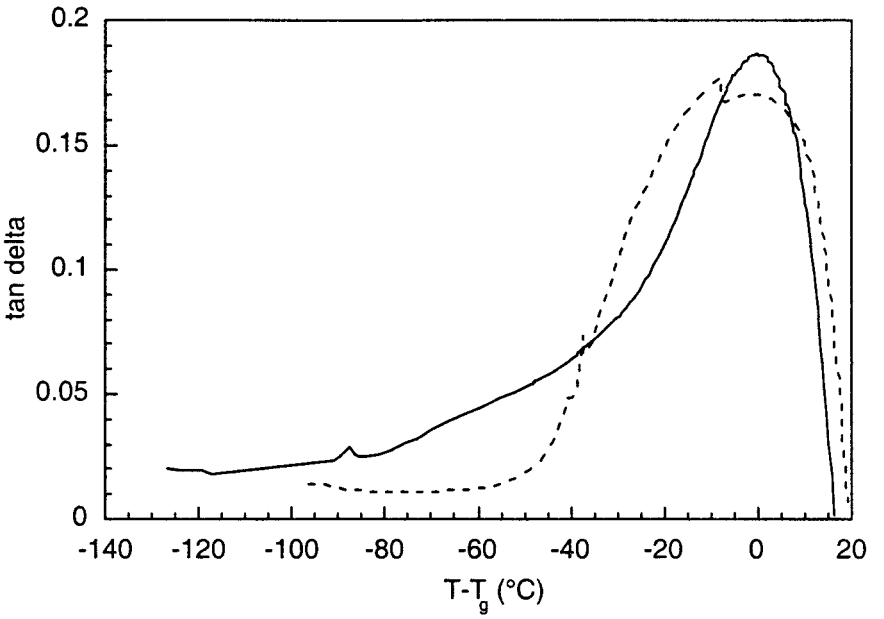

Figure 9 The damping factor (tan δ) as a function of the effective temperature above the glass-transition temperature (T_g) for a polymer network sample prepared from (—) 50 mol % PEG200MA and 50 mol % PEG200DMA and (- - -) 50 mol % PEG400MA and 50 mol % PEG200DMA.

that the system with PEG400MA has a slightly wider peak, indicating a more heterogeneous sample.

More highly crosslinked systems prepared from 75 mol % PEG200DMA were also examined (Fig. 10). For the copolymers with PEG200MA, the T_g was 42 ± 3°C whereas the copolymer with PEG400MA had a T_g of 12 ± 2°C. The tan δ peaks for the two different polymer systems were not significantly different. However, the tan δ was higher for the polymer containing PEG200MA. For the highly crosslinked polymers, there was little effect of the monomer length on the overall heterogeneity; however, there was a significant decrease in the T_g with the longer PEG400MA.

Incorporating longer PEGMA chains into the polymeric system resulted in a decrease in the mechanical properties and strength of the material. The long, nonreactive dangling end inhibited polymerization enough to weaken the material. As the amount of crosslinking agent was increased, there were fewer

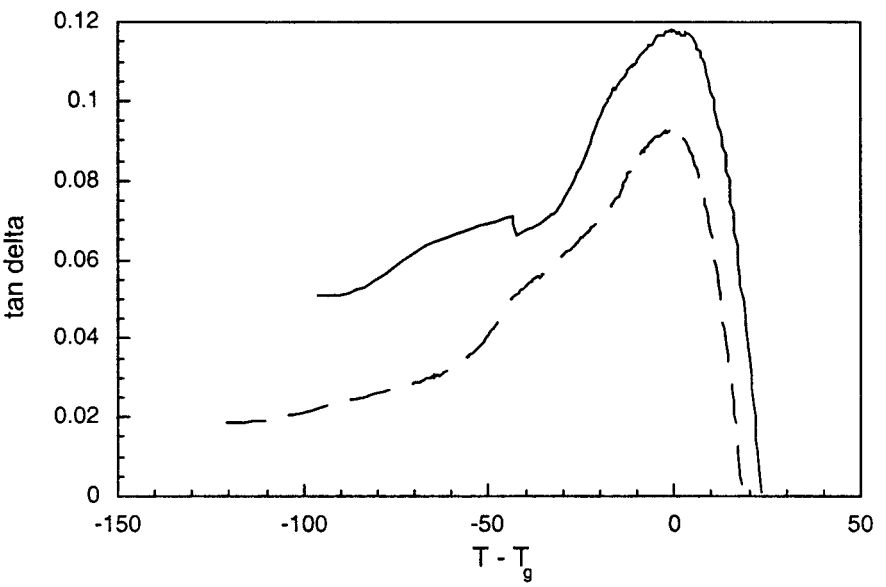

Figure 10 The damping factor (tan δ) as a function of the effective temperature above the glass-transition temperature (T_g) for a polymer network sample prepared from (—) 25 mol % PEG200MA and 75 mol % PEG200DMA and (- - -) 25 mol % PEG400MA and 75 mol % PEG200DMA.

grafts along the primary chains and the heterogeneity of the polymer was not affected as much.

CONCLUSIONS

In this article, we examined the effect of long, nonreactive PEG grafts on polymerization kinetics, mechanical properties, and network structure formation. Copolymerizations of either PEG200MA or PEG400MA and PEG200DMA as the crosslinking agent were considered. The kinetic gelation simulations showed that increasing the graft length resulted in more primary cycles and microgel regions in the polymer network in addition to more trapped radicals. This was in agreement with the kinetic studies, which concluded that the longer grafts slowed the rate of polymerization and resulted in lower final conversion. In both copolymerizations, if the amount of the crosslinker was increased, the rate of polymerization increased and a prominent autoacceleration effect was observed, which was mainly due to the presence of fewer grafts along the backbone. There are benefits to incorporating the longer PEGMA chains into a polymeric system for specific biomedical applications; however, there is a trade-off in that there are more trapped radicals and a degradation in material properties.

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