Silicone-Based Hydrogels Prepared by Interpenetrating Polymer Network Synthesis: Swelling Properties and Confinements Effects on the Formation Kinetics

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ABSTRACT: In this work, interpenetrating polymer networks (IPNs) of polydimethylsiloxane (PDMS) and poly(acrylic acid) or poly(2-hydroxyethyl methacrylate) (PHEMA) have been synthesized employing a sequential method. Monomeric AAc or HEMA was introduced into the PDMS network by swelling the polymer in solutions of monomer. The polymerization of monomers was then conducted in the swollen network. The swelling properties of the IPNs were investigated by varying the monomer concentrations in the polymerization and more swelling was observed with low monomer concentrations due to the prevalence of cyclization reactions. Multi-step polymerization used to achieve IPNs with high hydrogel contents, did not improve their water uptake. The kinetics of acrylic acid polymerization was studied under various conditions. Specifically, in the presence of confinement effects imposed by the PDMS network a considerable drop in the rate of reaction was observed. The cross-linking density of the PDMS network was also studied how to affect the reaction rate. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 985–992, 2012

Key words: polydimethylsiloxane; hydrogel; interpenetrating polymer networks; swelling; polymerization kinetics; confinement effects

INTRODUCTION

Hydrogels and polysiloxanes (silicones) have many applications due to their interesting properties. Elastomers based on polydimethylsiloxane (PDMS) have special properties such as low toxicity,[1] physiological inertness,[1] good blood compatibility,[2] and good thermal,[3] oxidative,[4] and mechanical stability.[5] These unique properties have allowed PDMSs to be used in various biomedical applications such as blood pumps,[6] artificial skin,[7] cochlear implants,[8] drug delivery systems[1] etc. However, long-term applications are limited when PDMSs are in contact with tissues or the living organism due to their hydrophobicity. For this reason, different modification techniques have been used to improve the hydrophilicity of silicone polymers.[9]

Hydrogels are hydrophilic polymer networks that have a large capacity for absorbing water. Polymer hydrogels have been proposed for many applications such as the controlled delivery of medicinal drugs,[10] artificial muscles,[11] sensor systems,[12,13] and bioseparations[14] due to their good biocompatibility,[15] stimuli-responsive properties,[16] and water permeation properties.[17] The reinforcement of a polymer hydrogel is a major obstacle in potential applications because a hydrogel has poor mechanical properties in water.[18] To overcome the aforementioned problems, interpenetrating polymer networks (IPNs) of silicones and hydrogels have been synthesized. IPNs are defined as a combination of two or more polymers in the form of a network where at least one polymer is polymerized and/or cross-linked in the presence of others.[19] Like other multicomponent systems, IPNs exhibit restricted phase separation. Due to the interlocking configuration of IPNs, phase separation obtained at the end of the synthesis is immobilized and the properties of the IPN are not influenced by ageing. Thus, IPNs are well suited for the combination of highly incompatible polymer pairs.[20] The degree of cross-linking in the structure of the polymer network is critical because it dictates mechanical strength, swelling ratio, and many other properties of the polymer gel by influencing the molecular weight between cross-links (M_c). Cross-linking density diminishes due to primary cyclization, where both ends of the cross-linking agent react with the same growing polymer chain and form a loop. The cross-linking agent is a monomer with two or more double bonds and provides the structure of the polymer network by connecting long, linear chains.[21] Cyclization reactions have been thoroughly

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studied by Elliott et al.[21–24] Experimental and theoretical data obtained by modeling methods revealed that these reactions increase with an increase in the amount of solvent in the monomeric solution.

Hydrogel networks formed from poly(acrylic acid) (PAAc) have capacity of water absorption many times of their initial weight and are the basis of a class of materials called super absorbents.[21] These polymers are used in many applications including diapers,[25] personal hygiene products,[26] ion exchange resins,[27] membranes for hemodialysis[28] and ultrafiltration,[29] and controlled release devices.[21,30] The exact conditions of polymer synthesis and the kinetics of the polymerization determine the structure of the network, which in turn dictates the material's properties.[31] The kinetics of acrylic acid polymerization has been studied in the forms of solution, bulk, and precipitation.[31–34] However, an investigation on the effect of another network presence such as PDMS on AAc polymerization kinetics has not yet been conducted. The systems where such an effect may be expected are sequential full or semi-IPNs. For simultaneous IPNs, the kinetics of the reaction of both components in the starting mixture was thoroughly studied.[35] However, the kinetics of the reaction of the formation of the second linear or cross-linked polymers in first networks is so less investigated.[36–38] Sequential full IPNs of poly(2-hydroxyethyl methacrylate) (PHEMA) or PAAc/PDMS have been widely investigated by Abbasi et al., especially in terms of their biomedical applications.[8,39–42] This work involves the investigation of the effects of monomer concentration on cyclization, a novel multi-step polymerization method, and the subsequent swelling behavior of the IPNs. The kinetics of AAc polymerization was also characterized under various conditions, specifically in the presence of confinement effects imposed by the PDMS network.

EXPERIMENTAL

Materials

AAc (Merck, Schuchardt, Germany) was purified by distillation *in vacuo*. 2-Hydroxyethyl methacrylate (HEMA) (Merck, Schuchardt, Germany), α,α′-azoisobutyronitrile (AIBN), and ethylene glycol dimethacrylate (EGDMA) (Merck, Darmstadt, Germany) were used as received. Silicone rubber and its curing agent were Silbione®4010 medical grade elastomer from Applied Silicone (Ventura, CA). All other chemicals were of reagent grade and were used as received.

Methods

PDMS preparation for swelling studies

PDMS samples were prepared by mixing raw silicone rubber with the curing agent. The elastomer component (Part A) of Silbione®4010 and the curing agent (Part B) were mixed to yield a PDMS/curing agent ratio of 100/10 wt/wt. The curing agent consisted of a dimethylsiloxane polymer, an inhibitor, and a siloxane cross-linker. After thorough mechanical stirring, the mixture was degassed. The silicone rubber strips were prepared by hot compression molding (1700 kPa, 100°C, 45 min), followed by a post curing process at 100°C and atmospheric pressure for 24 h for the establishment of physical properties. The products were immersed in toluene for 24 h to remove oligomers.

PDMS preparation for the kinetics study

PDMS films with different cross-linking densities were synthesized by mixing raw silicone rubber and the curing agent to yield PDMS/curing agent ratios of 70/10, 100/10, and 130/10 wt/wt. After thorough mechanical stirring, the mixture was spread onto a plate and a post curing process was conducted at 100°C and atmospheric pressure for 5 h for the establishment of physical properties.

IPN preparation

For the preparation of IPN, PDMS strips (1 cm × 3 cm × 1 mm) prepared by the method described in the previous section were immersed for 24 h at ambient temperature into a swelling solution consisting of AAc or HEMA monomer, AIBN, EGDMA, and toluene. The swollen samples were suspended in a sealed glass reactor containing 10 cc of monomer solution. The temperature was raised and maintained at 80°C to allow monomer, initiator, and cross-linker to react. The reaction time was dependent on the desired hydrogel content in the IPN, but the required time to complete the reaction was 3 h. The obtained IPNs were kept at 100°C for 5 h to complete the polymerization of the monomer. The IPN products were immersed in ethanol for 24 h to remove homopolymers and unreacted monomers. The specimens were dried at 50°C under vacuum for 24 h. To conduct multi-step polymerization, the above-mentioned steps for IPN formation were repeated with previously formed IPNs instead of PDMS strips. All the IPNs were prepared by one-step polymerization, unless stated otherwise.

The hydrogel content in the obtained IPNs was calculated according to the following equation:

$$\text{PAAc or PHEMA content} = \frac{w_m - w_i}{w_m} \times 100$$

where w_m is the weight of the IPN and w_i is the weight of unmodified PDMS samples. The

concentration of monomer, initiator, and cross-linker are defined as follows:

$$\text{Monomer concentration} = [\text{AAc or HEMA}] = \frac{\text{moles of monomer}}{\text{volume of solution}}\ (\text{mol/L})$$

$$\text{Mole fraction of the initiator} = [\text{AIBN}] = \frac{\text{moles of initiator}}{\text{moles of monomer}}$$

$$\text{Mole fraction of the crosslinker} = [\text{EGDMA}] = \frac{\text{moles of crosslinker}}{\text{moles of monomer}}$$

The mole fraction of the initiator and cross-linker were 0.001 and 0.01, respectively, in all experiments.

Measurement of swelling behavior

Dynamic swelling studies were performed by placing the previously dried polymer strips in distilled water, drying with filter paper, and weighing the strips on a balance at the desired time intervals. According to this procedure, the water content in the IPNs was calculated as a function of time:

$$\text{Swelling(wt\%)} = \text{water content(\%)} = \frac{w_w - w_m}{w_m} \times 100$$

where w_w and w_m represent the weight of swollen sample at a given time and dry sample, respectively.

Apparatus

Study of the kinetics of polymerization

Reaction rate profiles were obtained using a differential scanning calorimeter (DSC) (Netzsch, F3 200 DSC). A hermetically sealed aluminum pan containing monomer solution with or without PDMS film was placed in a DSC cell with an empty reference pan. The cell was then heated at a high rate of 20°C/min to 77°C to prevent polymerization and at a low rate of 5°C/min to achieve the desired isothermal reaction temperature of 80°C and control the increase in temperature. Once the cell reached the desired reaction temperature, the nitrogen purge was turned on and the reaction was allowed to begin. DSC was used to measure the heat flow from the sample pan relative to heat flow from the reference pan over time. To analyze the data, a linear baseline corresponding to heat flow at the end of the reaction was chosen. Dividing the total heat flow measured by DSC over the course of the polymerization by the heat flow due to the reaction at an indicated time (the difference between the measured heat flow at any given time and the baseline heat flow), gives the reduced polymerization rate (W_{red})[36] for the indicated time. The measured rate of polymerization is equal to the first derivative of the double bond conversion, x, with respect to time. Thus, x was determined as a function of reaction time by integration of the curve W_{red} versus time. The limiting conversion was equal to 1 because no heat was released when the temperature was increased up to 130°C (more than the glass transition temperature of PAAc).

Scanning electron microscopy

The morphology of IPNs was studied by scanning electron microscopy (SEM) of freeze fractured samples using a LEO 440-i SEM operating at 15 kV. The broken samples were stained with OsO_4. All samples were sputter-coated with a thin layer of gold before viewing to enhance conductivity.

RESULTS AND DISCUSSION

Swelling of the IPNs

Effect of monomer concentration on swelling

Figures 1 and 2 show the swelling behavior of IPNs containing PDMS/PHEMA and PDMS/PAAc over time and with different hydrogel contents. The water content of all IPNs increased with time up to a value that remained approximately constant and was identified as the equilibrium swelling ratio. Obviously, a greater amount of hydrogel leads to more swelling.

Figure 3 compares the equilibrium swelling ratio of PDMS/PHEMA and PDMS/PAAc IPNs, which shows more hydrophilic behavior of AAc. In comparison with HEMA, acrylic acid has less polarity, but more ability of hydrogen bonding.[43] Acrylic acid has hydrophilic carboxyl group and can be ionized in the water (Fig. 4). It has been shown that, copolymerization of AAc with nonionizable HEMA

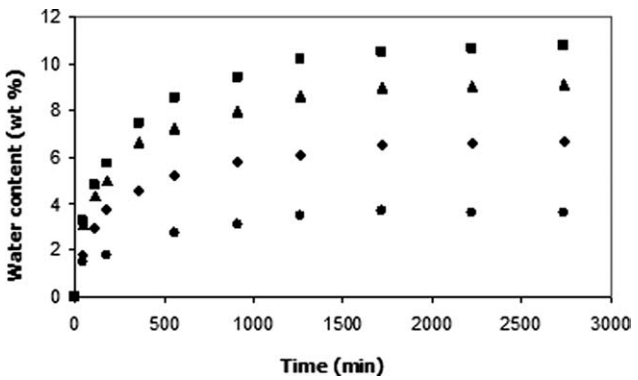

Figure 1 Swelling behavior of IPNs containing various amounts of PHEMA ([monomer] = 2 mol/L). 7.8 wt % (●), 20 wt % (◆), 30.8 wt % (▲), and 39.16 wt % (■).

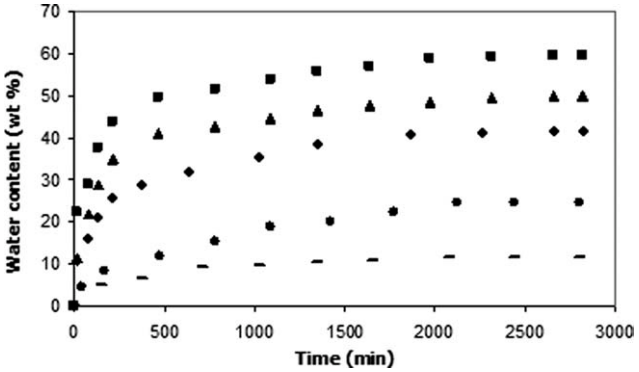

Figure 2 Swelling behavior of IPNs containing various amounts of PAAc ([monomer] = 2 mol/L). 10.7 wt % (–), 17.3 wt % (●), 22.2 wt % (◆), 27.7 wt % (▲), and 34.8 wt % (■).

resulted in less swellable polymers. The equilibrium swelling ratio decreased from 7.3 for ionized PAAc to 2.0 for P(AAc-*co*-HEMA) with 55 mol % AAc to 45 mol % HEMA.[44] In another study, water contact angle of PHEMA was reported 63°.[45] The grafting of PAAc was carried out onto nanocomposites based on poly(carbonate-urea)urethane and polyhedral oligomeric silsesquioxanes (POSS). Water contact angle of the film decreased from 100 to 33.4°, when a confluent layer of PAAc covered the surface of nanocomposite.[46] Therefore, PDMS/PAAc IPNs are expected to be more hydrophilic, with higher equilibrium swelling ratio.

Figure 5 presents the equilibrium swelling ratio of IPNs by percent for different amounts of PHEMA at two levels of monomer concentration. When the curves in the figure are compared, more swelling is observed for lower monomer concentrations at the same content of hydrogel. However, one-way analysis of variance (ANOVA) with a probability value of 95% showed no significant difference between two

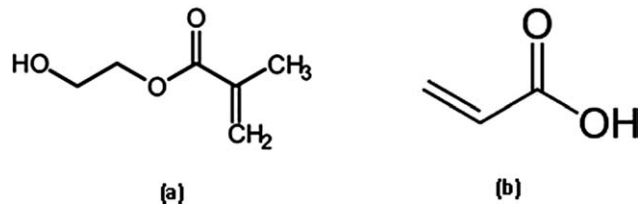

Figure 4 Molecular structure of (a) 2-hydroxyethyl methacrylate and (b) acrylic acid.

curves ($P > 0.05$). To produce densely cross-linked networks, a multi-vinyl monomer was employed as the cross-linking agent, which resulted in pendant double bonds on the growing polymer chains. These pendant double bonds can react with propagating radicals by two different reaction mechanisms including primary cyclization and cross-linking. In primary cyclization reactions, a pendant double bond reacts intramolecularly with the radical on its own propagating chain and then continues to propagate. In cross-linking reactions, a pendant double bond reacts intermolecularly with another growing polymer chain.[24] Therefore, not all of the double bonds on cross-linking agents react to form cross-links. Potential cross-linking is lost due to intramolecular cyclization, where both ends of the cross-linking agent react with the same growing polymer chain, forming a loop structure.[21] The rate of monomeric double bond consumption and the rate of propagation decreases with increasing solvent concentration. Consequently, the radicals propagate away from the pendant double bonds more slowly and the distance between a radical and the functional groups on the same chain will grow gradually. The slow-growing radical chain will have an increased chance of encountering pendant double bonds, causing more cyclization. However, the

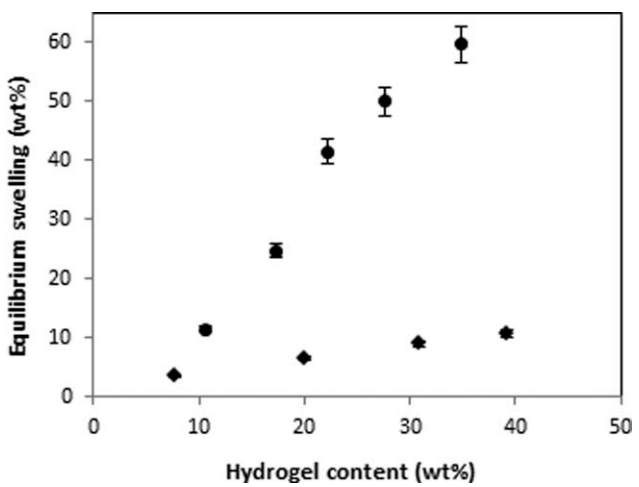

Figure 3 The equilibrium swelling ratio of IPNs containing various amounts of PHEMA (◆) and PAAc (●) with a monomer concentration of 2*M*.

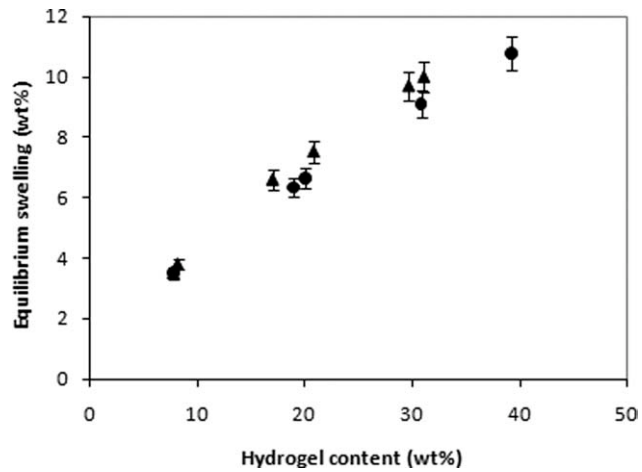

Figure 5 The equilibrium swelling ratio of IPNs containing various amounts of PHEMA with a monomer concentration of 1*M* (▲) and 2*M* (●).

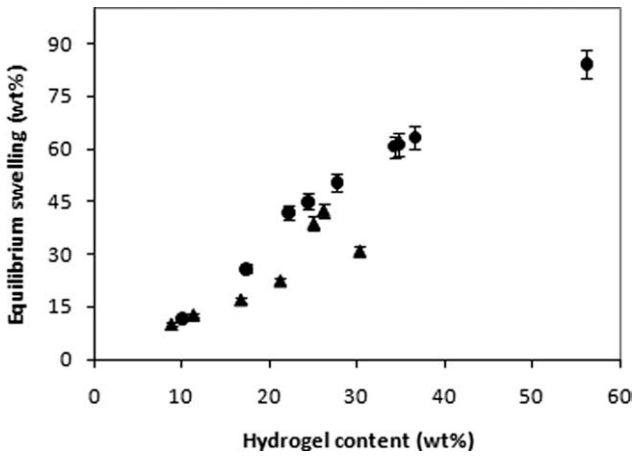

Figure 6 The equilibrium swelling ratio of IPNs containing various amounts of PAAc with a monomer concentration of 1*M* (▲) and 2*M* (●).

growing radical is surrounded by more monomer units when little or no solvent is present. The radical is able to add repeat units rapidly and does not have a significant amount of time to react with pendant double bond and cyclize. The pendant double bond will then have an increased chance of cross-linking. Therefore, primary cyclization, unlike cross-linking reactions, is facilitated by increasing the amount of solvent or decreasing the concentration of monomer. When a polymer system possesses more cross-links, the overall structure is held together tightly, adding rigidity and enhanced mechanical strength, while reducing the subsequent swelling. When a polymerization includes more cyclizations, the overall network structure is filled with rings and the polymer chains on the backbone are able to swell and move further apart.[23] Therefore, a higher monomer concentration leads to lower hydrogel swelling. However, the confinement effects imposed by the PDMS network may not allow the swelling of the hydrogel or IPN to increase beyond a certain extent and may result in the absence of significant differences in the swelling of IPNs prepared by different concentrations of monomer, as shown in Figure 5.

Further analysis discloses identical swelling equilibrium for both monomer concentrations with hydrogel content of approximately 10%, which is contrary to the statements made above. As explained in section "IPN preparation," the preparation of IPNs with low hydrogel content is achieved on stopping the reaction in its early stages. In the early stages of polymerization, the rate of the reaction is low and the radical chain grows slowly. Thus, there is an increased and approximately similar chance of cyclization, regardless of the operational conditions of the reaction media. As the polymerization progresses, the reaction rate increases and the monomer concentration can show its effect on cyclization.

Effect of multi-step polymerization on swelling

Figure 6 shows the equilibrium swelling ratio of IPNs containing various amounts of PAAc and monomer concentrations of 1 and 2*M*. A comparison of the data reveals that IPNs prepared with a lower monomer concentration undergo less swelling despite the presence of more loop structures in their networks due to cyclization. To obviate this contradiction, we refer to the multi-step polymerization method used for the preparation of IPNs with PAAc contents of >10% and monomer concentrations of 1*M*. Due to a slower polymerization rate in comparison with HEMA, lower concentration of AAc (1*M*) could not achieve the hydrogel content of >15% in the IPN, even by extending the reaction time for a complete polymerization as far as possible. Therefore, to reach a higher hydrogel percentage in the IPN, a novel method referred to as multi-step polymerization was applied. Figure 7 shows the SEM micrograph obtained from cross-section of PDMS/PAAc IPN containing 20 wt % of PAAc. The PAAc-rich phase appears as lighter, discrete spheres that are surrounded by PDMS as a continuous phase. In multi-step polymerization, IPNs are already formed and are swollen in monomeric solution. Acrylic acid monomers are attracted to the PAAc-rich domains (Fig. 7) in the IPN. Thus, these monomers do not distribute throughout the network to produce more hydrophilic areas. Accumulation of AAc monomers in PAAc-rich domains and their subsequent polymerization create tight areas that are less able to swell. The underlying curve in Figure 6 represents IPNs formed with a monomer concentration of 1*M*, which contain hydrogel contents of 10, 17–26, and 30% and synthesized by one, two, and three-step polymerization, respectively. Interestingly, due to the

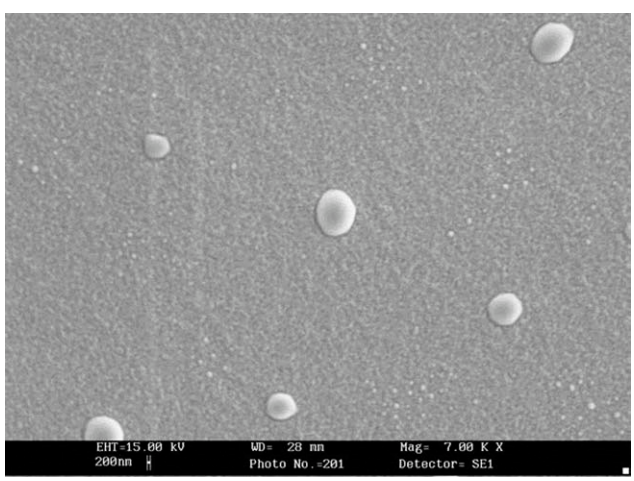

Figure 7 SEM micrograph obtained from OsO_4-stained cross-section of PDMS/PAAc IPNs with a PAAc content of 20 wt %.

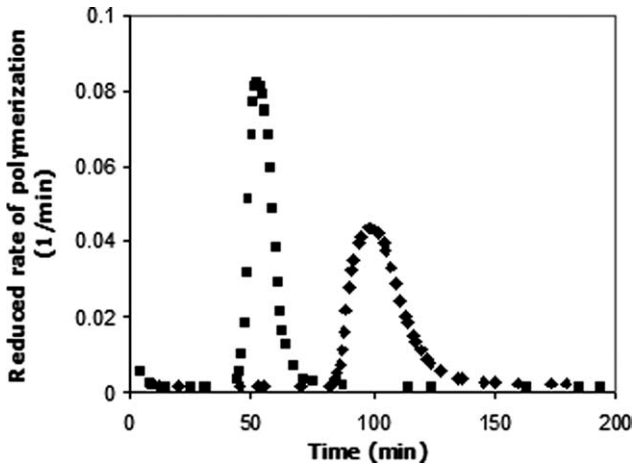

Figure 8 Reduced rate of AAc polymerization over time with a monomer concentration of 2*M* (◆) and 2.5*M* (■). The reaction temperature is 80°C.

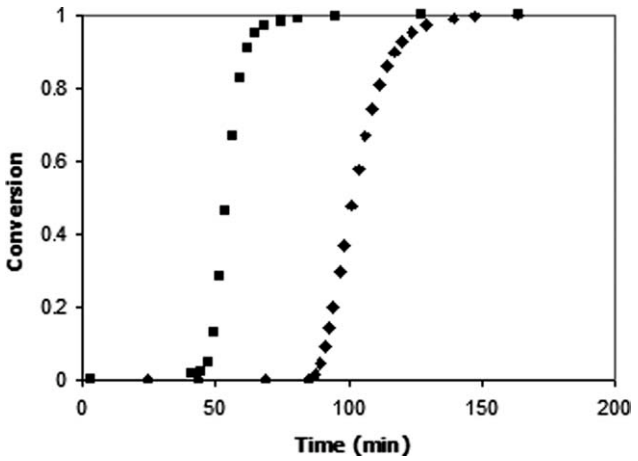

Figure 9 Conversion profiles of AAc polymerization with a monomer concentration of 2*M* (◆) and 2.5*M* (■). The reaction temperature is 80°C.

creation of much tighter PAAc domains, a dramatic drop in swelling was observed when three-step polymerization was used to achieve a hydrogel content of 30% in the IPN. Using one-way ANOVA, no significant difference was found when IPNs with hydrogel contents of about 25% in two curves were compared ($P > 0.05$). However, the difference becomes significant considering that we would expect more swelling for IPNs with monomer concentration of 1*M*.

Kinetics of acrylic acid polymerization

Effect of monomer concentration on the rate of polymerization

In Figure 8, the reduced rate of precipitation polymerization of AAc[32,33] is plotted as a function of time for specific monomer concentrations (2 and 2.5*M*) and Figure 9 gives the corresponding conversion-time profiles. The induction time for the reaction may be caused by inhibitor that remained in the monomer and acted as a primary radical scavenger, leading to a delay in initiation.

Further examination of Figures 8 and 9 reveals that autoacceleration occurred, i.e., the polymerization rate increased with increasing monomer conversion over a portion of the conversion profile. In bulk polymerizations, this phenomenon is typically attributed to the gel effect. The polymerization rate increases over time due to a decrease in the termination rate as the reaction medium becomes increasingly viscous. The polymerization rate begins to decrease only when the monomer is sufficiently depleted and/or when propagation becomes diffusion-limited.[31]

Because radical mobility and the nature and extent of the gel effect vary with solution concentration, the kinetic features of the polymerization depend strongly on the initial monomer concentration, which is evident from Figure 8. An increase in the monomer concentration raises the overall rate of the reaction. It also reduces the induction time due to better competition with the inhibitor, allowing the reaction to initiate.

Effect of cross-linking agent on the rate of polymerization

A higher reaction rate can be achieved in the presence of a cross-linking agent, which is evident from the plot in Figure 10. The increase in the slope of the curve over time is more substantial in the presence of cross-linker, indicating a larger autoacceleration due to more severe diffusional limitations.

Effect of PDMS network on the rate of polymerization

Generally, the kinetics of IPN formation is so less investigated in the literature. The kinetics of the

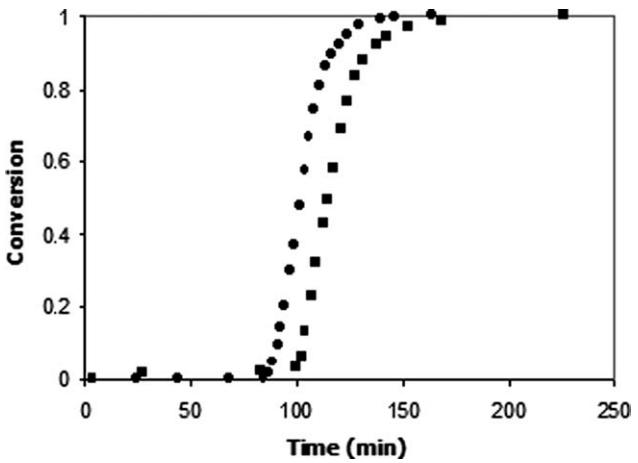

Figure 10 Conversion profiles of AAc polymerization with (●) and without (■) cross-linking agent ([cross-linker]/[monomer] = 0.01).

polymerization of styrene and methyl methacrylate in beforehand prepared networks based on the methyl methacrylate copolymer with dimethacrylate tridecaethyleneglycol and styrene with dimethacrylate ethylene glycol were studied and the termination constant was found lower as compared with bulk polymerization.[37,38] Peculiarities of formation kinetics of sequential semi-IPNs based on cross-linked polyurethane with different cross-linking density and linear polystyrene (PS) and polybutylmethacrylate (PBMA) was also studied. Maximum value of the reduced reaction rate in the presence of prefabricated network ($W_{red,N}$) was increased in comparison with pure styrene and BMA ($W_{red,P}$) due to a decreased termination constant as confirmed in previous works. Increasing the cross-linking density of the host network reduced $W_{red,N}$. Two reasons were supposed. First, in viscous media the role of diffusion processes in polymerization is very important. Diffusion may affect not only the chain termination but initiation reaction as well. Increasing viscosity of the media diminishes the constant of decomposition of the initiator and efficiency of initiation. The important role plays so called "cage" effects preventing the diffusion separation of a radical couple. Second, a tighter network would lower the amount of monomers in semi-IPNs diminishing of polymerization rate.[36]

But, our results suggest that the presence of the PDMS network in the reaction media lowers the polymerization rate (Fig. 11). The reaction media was a combination of the enclosed solution (the solution inside of the PDMS network) and the free solution encompassing the network. As a result, the overall rate of polymerization is impressed by both the solutions. Introducing the PDMS network into the monomeric solution and diffusion of the solution into the network reduces the overall monomer concentration in the medium, which results in a decreased reaction rate. Lower monomer concentration can also increase the induction time by affecting the initiation reaction. However, with similar monomer concentrations, the rate of polymerization is expected to increase in the enclosed solution compared with free solution due to confinement effects imposed by the network. Evidently, an increase in the reaction rate due to confinement effects is dominated by the drop in monomer concentration, which reduces the reaction rate.

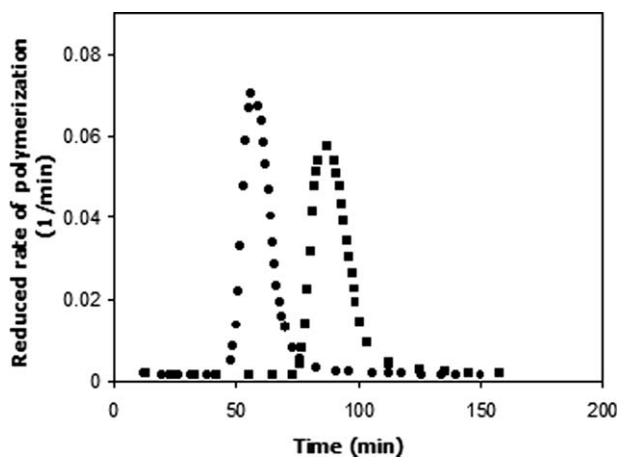

Figure 11 Reduced rate of AAc polymerization over time with (■) and without (●) the presence of the PDMS network having a total PDMS/curing agent composition of 70/10, [AAc] = 2.5*M*.

TABLE I
Hansen Solubility Parameters of PDMS, Toluene, and AAc

Materials	Hansen solubility parameters $(MPa)^{1/2}$			
	$\delta_{dispersion}$	$\delta_{polarity}$	$\delta_{hydrogen\ bonding}$	δ_{total}
PDMS	15.9	0	4.1	15.5
Toluene	18	1.4	2	18.16
AAc	17.7	6.4	14.9	24

Since PDMS and AAc are chemically different components, toluene, as a solvent of PDMS, was used to carry AAc into the network. Table I represents Hansen solubility parameters of PDMS, toluene, and AAc.[43,47] Regarding to this table, dispersion and polar interactions in toluene are more similar to acrylic acid than PDMS. Also empirically, PDMS is soluble in toluene but not in acrylic acid.[48,49] Therefore, the AAc concentration is supposed to be lower inside the network compared with the free solution.[50] On the other hand, the initiator, AIBN may tend toward the area with lower monomer concentration, as it is hardly soluble in pure AAc. The reduced concentration of the initiator in the free solution would lower the reaction rate and increase the induction time, while its high amount inside the network may not promote the polymerization due to the severe cage effect. Cage effect hinders the initiation reaction, which in turn, lengthen the induction time.

Effect of PDMS network with different cross-linking densities on the rate of polymerization

The effects of different cross-linking densities of the PDMS network were also examined on the kinetics of polymerization, which is shown in Figure 12. The leftmost curve is associated with the network prepared by a PDMS/curing agent ratio of 130/10 wt/wt. The other curves indicate ratios of 70/10 and 100/10 wt/wt, respectively. A greater amount of curing agent leads to a higher cross-linking density and tighter network. The overall rate of polymerization is influenced by both the free and enclosed solution, as already mentioned. As the network becomes tighter, the termination constant decreases besides a lower efficiency of

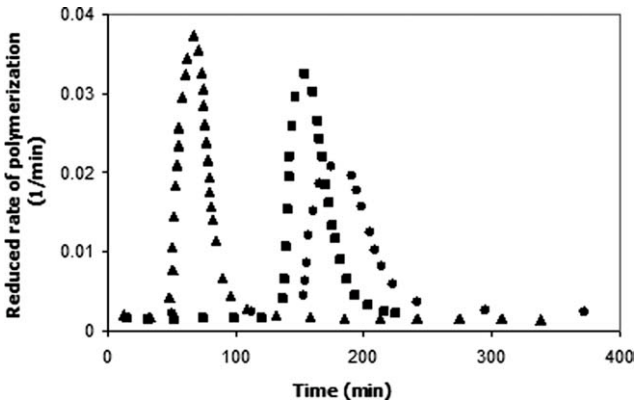

Figure 12 Reduced rate of AAc polymerization in the presence of the PDMS network with a total PDMS/curing agent composition of 70/10 (■), 100/10 (●), and 130/10 wt/wt (▲), [AAc] = 2*M*.

initiation. Moreover, the amount of solution diffused into the network decreases and minimizes the influence of the PDMS network on the overall rate of the reaction. Therefore, competition between these factors indicates how the cross-linking density of the PDMS network affects the reaction rate. The data presented in this figure suggests that the highest rate of polymerization is achieved with a PDMS/curing agent ratio of 130/10 wt/wt and the lowest rate occurs with a ratio of 100/10 wt/wt.

CONCLUSIONS

With identical hydrogel contents of more than ~ 10%, more swelling was observed for lower monomer concentrations due to cyclization reactions. Multi-step polymerization decreased the swelling of IPNs due to tightening of PAAc domains. The rate of polymerization increased with monomer concentration and adding the cross-linker, but it decreased in presence of the PDMS network. The cross-linking density of the PDMS network affected the reaction rate and was associated with the amount of solution that diffused into the network and the extent of the gel effect inside the network.

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