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Characterization of hydrogels formed from acrylate modified poly(vinyl alcohol) macromers

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Abstract

Poly(vinyl alcohol) was modified with pendent acrylate groups to form a macromer that was crosslinked via photopolymerization. Polymerization behavior was studied for several initial macromer concentrations using DSC and Near-IR spectroscopy. Under mild photoinitiating conditions (e.g. 0.05 wt% initiator and less than 20 mW/cm^2 of 365 nm light), the hydrogels polymerized to 100% conversion in less than 5 min. To characterize the network structure, the hydrogels formed from the acrylated poly(vinyl alcohol) macromer were compared to gels that were chemically crosslinked with glutaraldehyde and gels that were physically crosslinked by semi-crystalline regions introduced through freeze–thaw cycles. The equilibrium swelling ratio and compressive modulus were characterized for all of the resulting PVA hydrogels, and related to the network structure (i.e. $\overline{M_c}$) through a modified Flory–Rehner equation and rubber elasticity theory.

Keywords: Hydrogels; Poly(vinyl alcohol); Photopolymerization

1. Introduction

Hydrogels are water swellable, yet insoluble, crosslinked polymer networks synthesized from a variety of hydrophilic monomers. The crosslinks in these networks can be either chemical or physical, and the amount and type of crosslinks influence many of the network properties. Because of their unique properties and the ability to control and tailor these properties, hydrogels are beneficial for numerous applications. The tissue-like high water content and elastic properties make hydrogels advantageous for many biological applications, including contact lenses, controlled release matrices, and bioadhesives [1,2]. Further, the ability to imbibe large quantities of water (e.g. poly(acrylic acid)) has made hydrogels useful for many superabsorbent applications [3].

In this work, we are particularly interested in hydrogels fabricated from poly(vinyl alcohol) (PVA). Linear PVA is synthesized from vinyl acetate and available with various molecular weights and degrees of hydrolysis, which affect its solubility in water. PVA hydrogels are formed via both chemical and physical crosslinking mechanisms. Several researchers have used glutaraldehyde to chemically crosslink PVA through its pendant hydroxyl groups [4–7]. In this method, glutaraldehyde is added with a catalyst (e.g. HCl) to a PVA solution, and a rapid condensation reaction takes place forming a chemically crosslinked network. Researchers have studied the influence of the crosslinking density in relation to the final hydrogel's degree of swelling [4,7], as well as the thermodynamics [6] and permeability [5]. While this technique allows facile crosslinking of PVA, limitations exist with respect to synthesizing uniformly crosslinked networks, due to imperfect mixing and the diffusion of the glutaraldehyde in the evolving network. In addition, glutaraldehyde is toxic, and residual crosslinker is a concern for many biological applications.

In contrast to the chemically crosslinking, PVA can also be physically crosslinked by techniques that introduce crystalline regions, which act as crosslinks. Peppas and others [8–11] have extensively studied the crystallization of linear PVA from concentrated solutions. Crystalline regions are formed by repeated cycles of freezing and thawing, where each cycle takes between 4 and 48 h [8–11]. Using this method, hydrogels with up to 60% crystallinity have been formed. Many properties of these gels have been studied as a function of the degree of crystallinity, including network mesh size and diffusion [10], swelling and mechanical properties [8,9], and release of pharmaceutical agents [11].

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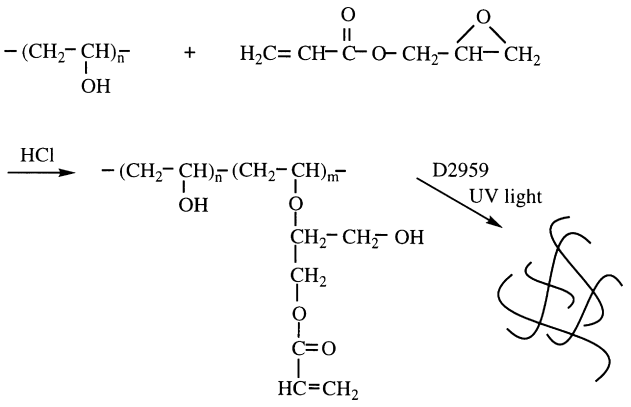

Fig. 1. Schematic of the Acr-PVA synthesis and resulting hydrogel formation.

Hickey and Peppas [10] found the gels to be stable at room temperature for several months and no additional chemical specie are incorporated that might compromise biocompatibility. However, from a mechanical and thermal perspective, the physical crosslinks are not as strong or stable as a chemically crosslinked network.

As an alternative to the above mentioned and long-standing techniques to form PVA hydrogels, we are interested in the chemical modification of PVA to produce a photocrosslinkable macromer. In particular, the pendant alcohol group on each repeat unit is readily modified with radically polymerizable acrylate groups, and crosslinking can be modulated through a photoinitiated polymerization. Attachment of the crosslinking functionality to the PVA backbone eliminates problems associated with diffusion of the crosslinker (e.g. glutaraldehyde), while providing for a mechanism to form chemically crosslinked gels. Specifically, photopolymerization can be employed to react these multifunctional macromers and synthesize crosslinked hydrogels.

Photoinitiated polymerization provides several advantages with respect to the gel fabrication, including rapid polymerization rates under physiological conditions and spatial and temporal control of the polymerization process. These mild polymerization conditions are beneficial for many applications and allow in situ formation of the gels (for tissue adhesives), polymerization in the presence of cells (for tissue engineering), and encapsulation of drugs (for controlled release matrices).

Recently, several researchers have investigated the acrylation of PVA using acrylic acid [2,12] or acryloyl chloride [13,14]. Macromers with anywhere from 2 to 85% acrylation have been synthesized using these techniques. Chetri and Dass [12] examined the acrylated PVA macromer itself, and not the resulting crosslinked network, characterizing the macromer's glass transition temperature, heat capacity, and thermal stability. Muhlebach et al. [2] investigated photocrosslinked hydrogels formed from acrylated macromers for contact lens applications. The water content in these gels was studied as a function of the polymer molecular weight, functional groups present on the polymer chain, and irradiation conditions. Wang and collaborators [13,14] copolymerized acrylated PVA macromers with 2-hydroxy ethyl methacrylate (HEMA) for dental applications. Gels were formed via photopolymerization, and the tensile and dentine bonding strength were examined in comparison to pure poly(HEMA).

In this contribution, an acrylate modified PVA (Acr-PVA) was synthesized using glycidyl acrylate, and the resulting macromers were photocrosslinked to form hydrogels. To gain insight regarding the polymerization mechanism of these multifunctional macromers and resulting network structure of the hydrogels, several parameters were investigated. First, the influence of the initial macromer concentration on the polymerization behavior and final network swelling and mechanics was studied. Second, the properties of these radically crosslinked networks were compared and contrasted to hydrogels produced by freeze–thawing (physically crosslinked) and a condensation reaction via the addition of a small molecular weight crosslinker. Finally, a semi-crystalline network of the reactive macromer was also synthesized and subsequently photopolymerized to examine the polymerization behavior in a semi-crystalline system versus an amorphous system, as well as the influence of this pre-polymerization ordering on the final network structure. Through these studies, we aim to develop a better understanding of the polymerization behavior and hydrogel structure of radically crosslinked multifunctional PVA macromers.

2. Experimental

2.1. Materials

Poly(vinyl alcohol) (PVA) with a molecular weight range of 13–23 K (Aldrich) and 99% hydrolysis was used without further purification. Glycidyl acrylate (Sigma), glutaric dialdehyde (glutaraldehyde) (Aldrich) and hydrochloric acid (37%) (Mallinckrodt) were also used without further purification.

2.2. Macromer synthesis

An acrylate modified PVA (Acr-PVA) was synthesized (see Fig. 1) by esterification of the pendant alcohol groups on the PVA with glycidyl acrylate in an acidic aqueous environment. A 10 wt% PVA solution was prepared by heating the mixture at 80°C overnight for complete dissolution. An excess of glycidyl acrylate was slowly added, along with HCl to attain a pH of approximately 1.5. Hydrochloric acid facilitates the epoxide ring opening and the amount and time of the addition of HCl can influence the percent acrylation attained [15]. Typically, the solution was reacted for 24 h at room temperature with constant stirring. Once complete, the Acr-PVA was precipitated in acetone (Fisher), filtered, and dried in a desiccator for at least 12 h.

2.3. Gel formation

Macromer polymerization. After acrylation and drying, the Acr-PVA was then re-dissolved in DI-H_2O at 80°C at concentrations ranging from 20 to 50 wt%. The photoinitiator, 2-hydroxy-1-[4-(hydroxyethoxy)phenol]-2-methyl-1-propanone, (Darocure 2959, D2959, Ciba–Geigy), was then dissolved in the solution at a concentration of 0.05 wt%. The final solution was photopolymerized using an ultraviolet light source (Novacure, EFOS, Inc.) at an intensity ranging from 5 to 20 mW/cm^2 for 5 min or less.

Condensation crosslinking. Glutaraldehyde was added dropwise to a 20 wt% PVA solution with a small amount of HCl to catalyze the reaction. The solution was stirred vigorously and quickly poured into disk templates ($D =$ 11.1 mm, $t = 1$ mm) needed for subsequent testing (e.g. swelling and compressive modulus). The solutions were reacted for 30 min in the templates.

Physical crosslinking. Crystallinity was introduced into samples of PVA by using the freeze–thaw process [8–11]. Thin films of 20 wt% Acr-PVA and initiator solutions were frozen for 24 h at −15°C, and subsequently thawed at room temperature for another 24 h. This cycle was repeated at least twice, and as many as nine times. After the freeze–thaw process was complete, some of the samples were further processed via photopolymerization to produce chemical crosslinks in addition to the crystalline regions in the gels. Differential scanning calorimetry (DSC) was used to characterize the percent crystallinity in the physically crosslinked gels. Using a scan rate of 10°C/min and a theoretical heat of 138.6 J/g for a 100% crystalline sample [16], the physically crosslinked gels formed from the acrylated macromer were found to contain ~2% crystallinity.

2.4. Characterization

Macromer. The percent acrylation of the PVA macromers was determined using ^{1}H-NMR (Varian VXR-300S), and all spectra were collected in D_2O. The –CH=CH_2 protons (two doublets and one split doublet at 5.6–6.4 ppm) were ratioed by the PVA backbone protons (–CH_2–) and (–CH–) at 1.4–1.8 ppm and 3.8–4.1 ppm to calculate the percent acrylation. Depending on the reaction conditions, ^{1}H-NMR revealed that between 7 and 20% acrylation was attainable. For all the studies in this work, the typical reaction scheme was used, and 7% acrylation was attained.

Polymerization. The polymerization behavior of the Acr-PVA was monitored using differential scanning calorimetry (DSC) (Perkin–Elmer DSC-7) to measure the polymerization rate and near infrared spectroscopy (NIR) (Nicolet Magna-IR 750 Spectrometer Series II, with an auxiliary experiment module) to quantify the conversion. The DSC head was modified with quartz windows to allow for the transmission of initiating light, and a high intensity light source equipped with a 365 nm band-pass filter was used to initiate the polymerization. The light intensity was varied between 5 and 20 mW/cm^2 in this study. The polymerizations were carried out in air at 25°C. Since the polymerization of the Acr-PVA macromer solution is an exothermic reaction, the heat released by the sample is directly proportional to the rate of polymerization. To prevent evaporation, plastic lids were placed over the samples in the DSC pans prior to polymerizing.

NIR was used to monitor the conversion of the pendant acrylate groups as a function of time. The acrylate peak appears between 6140 and 6210 cm^{-1}. A light source was placed in the IR chamber with the sample and a series of scans was performed during irradiation. NIR is particularly advantageous for studying the polymerization of hydrogels since samples up to a couple of mm in thickness can be used, as well as samples that have high water contents.

Hydrogels. Equilibrium swelling studies were performed to measure the sol fraction, equilibrium swelling ratio, and to calculate the average molecular weight between crosslinks ($\overline{M_c}$). One millimeter thick disks with a diameter of 11.1 mm were polymerized and placed into a sink of deionized water to swell for 24 h. After equilibrium swelling was reached, the disks were placed in a vacuum oven for 24 h to dry completely and subsequently weighed. $\overline{M_c}$ was calculated using the Peppas–Merrill equation, which is a modified Flory–Rehner equation for highly swollen gels that are polymerized in solution [17,18].

$$\frac{1}{\overline{M_c}} = \frac{2}{\overline{M_n}} - \frac{\bar{v}}{V_1}\frac{[\ln(1-\upsilon_{2,s}) + \upsilon_{2,s} + \chi_1\upsilon_{2,s}^2]}{\upsilon_{2,r}\left[\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)\right]} \quad (1)$$

In this equation, $\overline{M_n}$ is the number average molecular weight in the absence of any crosslinking; $\bar{v}$ the specific volume of the polymer; V_1 the molar volume of the solvent; $\upsilon_{2,s}$ the equilibrium polymer volume fraction; $\upsilon_{2,r}$ the polymer volume fraction after crosslinking but before swelling; and χ_1 is the polymer solvent interaction parameter. Values of χ_1 for PVA in water have been reported in the literature [19], and from this data, a χ_1 of 0.49 was used. The crosslinking density, ρ_x, was calculated from [18]

$$\rho_x = \frac{1}{\bar{v}\overline{M_c}} \quad (2)$$

Finally, the network mechanical properties were measured using a dynamic mechanical analyzer (DMA) (Perkin–Elmer DMA-7) with a parallel plate accessory. Polymer solutions were photopolymerized in 1mm thick sheets and equilibrium swollen. Upon reaching equilibrium, disks ($D = 5.1$ mm) were cut from the sheet, and compression tests were performed at a rate of 100 mN/min. The compressive modulus (K) was calculated by fitting a line through the initial linear section of the data (2–10% strain). The compressive modulus was related to the network structure ($\overline{M_c}$) through the rubber elasticity theory [20,21] which accounts for chain ends, but not cycles or other

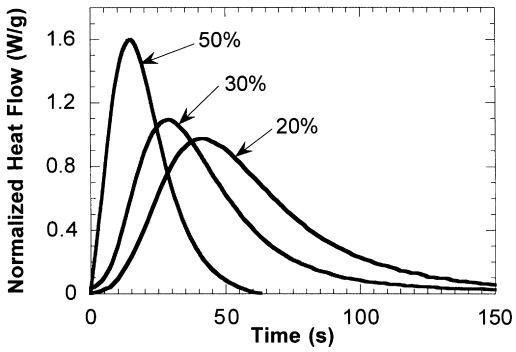

Fig. 2. Polymerization behavior as a function of time for three different concentrations of Acr-PVA in water. Polymerizations were initiated with 0.05 wt% D2959 and 20 mW/cm^2 of UV light.

network imperfections.

$$\frac{1}{\overline{M_c}} = \frac{3K(1-2\nu)}{2(1+\nu)\rho RT(\upsilon_{2,s})^{1/3}} + \frac{2}{\overline{M_n}} \quad (3)$$

Here, ρ is the density of the polymer; ν Poisson's Ratio, and T is the temperature of the gel.

3. Results and discussion

Typically, multifunctional monomers (e.g. hexamethylene diacrylate and trimethylol propane trimethacrylate) are low molecular weight specie that are encapped with functional groups that can be homopolymerized to produce highly crosslinked polymer networks [22–24]. These materials have found applications in numerous coatings and solvent-free processing of polymer films. During the polymerization of these monomers, several characteristic features of the reaction behavior are readily observed and include: autoacceleration and autodeceleration; low gel point conversion; limiting double bond conversion; unequal reactivity of functional groups; and trapping of radicals. In contrast to more typical multifunctional monomers, the Acr-PVA macromer studied here has a relatively high molecular weight and contains several pendant double bonds per chain

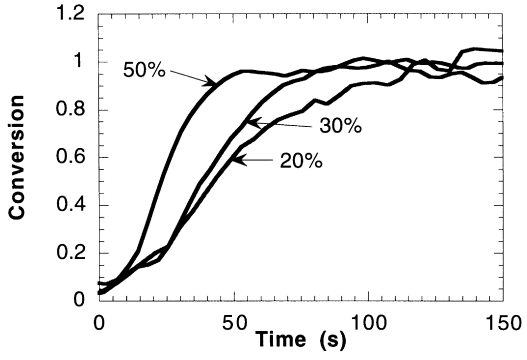

Fig. 3. Conversion as a function of polymerization time for three different concentrations of Acr-PVA in water. Polymerizations were initiated with 0.05 wt% D2959 and 11 mW/cm^2 of UV light.

(i.e. several crosslinking double bonds per molecule). Both of these features can significantly influence the overall polymerization behavior and ultimate network structure. Thus, the polymerization behavior of the multifunctional Acr-PVA macromers was investigated using both DSC and NIR.

In Fig. 2, the normalized heat flow, which is proportional to the rate of polymerization, is shown as a function of polymerization time for several different concentrations of the Acr-PVA macromer in water. Since many of the applications that we are pursuing require polymerization under physiological conditions, the polymerizations were initiated with 0.05 wt% D2959 and 20 mW/cm^2 of UV light (i.e. cytocompatible initiating conditions [25]) and were conducted in the presence of atmospheric oxygen. Since these radical polymerizations are inhibited by oxygen, which typically leads to an initial lag time, time zero corresponds to the first detectable heat flow and not the initial exposure of the solution to the initiating light. Typical lag times due to oxygen inhibition were 5–80 s, depending on the macromer solution concentration, with more dilute solutions exhibiting greater lag times.

From the data in Fig. 2, several important characteristics should be noted. Interestingly, despite the fact that these solutions contain anywhere from 50 to 80% water, autoacceleration is present from the onset of polymerization, which is attributed mainly to the relatively high viscosity of the solution arising from the high macromer molecular weight (13–23 K). In addition, the polymerization behavior (e.g. total polymerization time, magnitude and time of the rate maximum) depends strongly on the initial macromer concentration. Increasing the macromer concentration increases the initial reactive group concentration and the solution viscosity, and these effects are readily observed in Fig. 2. First, as the concentration of double bonds is increased, the overall heat flow and polymerization rate is increased; however, diffusion limitations during the polymerization lead to further complexities in the rate behavior. For example, the polymerization rate does not scale simply by the concentration of reactive groups, as the time of occurrence of the rate maximum and total polymerization time shift to higher values with increasing water content. The decreasing macromer concentration and increasing water concentration lead to lower solution viscosities and higher mobilities during polymerization which act to delay the onset of autoacceleration (increases the polymerization time) and autodeceleration (shifts the time and conversion of the rate maximum). Finally, even at this relatively slow rate of photoinitiation (e.g. 0.05 wt% D2959 and 20 mW/cm^2), the polymerizations are complete in 1–3 min, which is important for several applications (e.g. tissue adhesives).

In addition to characterizing the polymerization rate behavior with DSC, NIR was used to monitor the total double bond conversion as a function of time for solutions of the Acr-PVA macromer, and the results are shown in Fig. 3. NIR is a particularly valuable experimental tool for characterizing polymerizations in aqueous solutions and

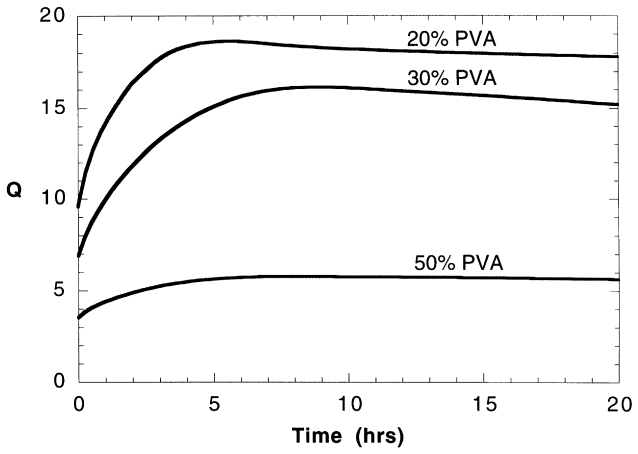

Fig. 4. Swelling behaviors as a function of time for three different initial macromer concentration of Acr-PVA.

samples of appreciable thickness. The polymerizations were initiated with 0.05 wt% D2959 and ~11 mW/cm^2 of UV light. In general, a typical S-shaped curve is observed where oxygen inhibition is followed by autoacceleration and then autodeceleration [24]. In addition, the trends observed in Fig. 3 with respect to the polymerization time, onset of autoacceleration, and time of the rate maximum as a function of macromer concentration are consistent with those seen with the DSC in Fig. 2. However, in contrast to the homopolymerization of low molecular weight multifunctional monomers, the solution polymerization of the Acr-PVA macromers leads to 100% conversion of the double bonds within a few minutes [24]. Diffusion limitations with respect to macro-radicals attached to the macroscopic network (influencing k_t) and pendant double bonds on the high molecular weight macromers (influencing k_p) dominate the overall polymerization behavior due to the limited mobility of the chains. However, the solution polymerizes to form a rubbery, swollen hydrogel with mobility that allows complete conversion of the functional groups.

While difference in the macromer solution concentration lead to dramatically different polymerization behavior, structural differences in the network may also result. To compare the network structures produced under the above polymerization conditions, the equilibrium swelling ratio and the mechanical modulus of the gels were measured, and the results were used in conjunction with two different theories to calculate the average molecular weight between crosslinks, $\overline{M_c}$ Hydrogels were synthesized by photopolymerization of Acr-PVA macromer solutions at different concentrations, and the gels were subsequently swollen to equilibrium in deionized water.

Table 1
Network properties of Acr-PVA as a function of initial macromer concentration

wt% PVA	Q	Compressive modulus (kPa)	$\overline{M_c}$ (g/mol)[a]	$\overline{M_c}$ (g/mol)[b]
20	18	55	5530	8990
30	15	94	5160	8980
50	5.5	371	1155	8890

[a] Calculated from the Peppas–Merrill equation.
[b] Calculated from the rubber elasticity theory.

The dynamic swelling behavior is shown in Fig. 4, where it can be noted that all of the gels rapidly reach their equilibrium swelling (in ~9 h). In addition, the swelling ratio decreases slightly after reaching equilibrium, which is attributed to the relatively high sol fraction in these gels (i.e. ~35%), and this sol fraction does not appear to be dependent on the initial macromer concentration. Furthermore, differences in the network structures are readily observed from the overall swelling behavior. First, the equilibrium degree of swelling, Q, decreases from ~18 to ~15 to ~5.5 as the macromer solution concentration increases from 20 to 30 to 50 wt%. Since these gels underwent the same photoinitiation process and react to 100% conversion, the differences in the swelling behavior were related to differences in the network structure. $\overline{M_c}$ was calculated using these Q values and Eq. (1), and differences in the network structure are readily apparent. The calculated $\overline{M_c}$ varied from ~5530 to ~5160 to ~1155 g/mol as the macromer solution concentration increased from 20 to 30 to 50 wt%. Assuming 100% efficiency of the crosslinking double bonds, a theoretical $\overline{M_c}$ value was calculated ($\overline{M}_{c,theory} = 616$ g/mol) and compared to the experimental values. The differences in these values are likely related to the high sol fractions and the presence of network imperfections (e.g. cycles) that are inherent in radical crosslinking polymerizations. In general, the presence of solvent leads to higher cyclization as the local pendant double bond concentration increases relative to the bulk double bond concentration [26].

The compressive modulus (K) of the equilibrium swollen samples was also measured and the results are shown in Table 1. As the initial macromer concentration was increased from 20 to 30 to 50 wt%, the magnitude of K in the resulting gel increased from 55 to 94 to 371 kPa, respectively. The mechanics of the gel are related to the crosslinking density (ρ_x) and the amount of water present ($\upsilon_{2,s}$) in the gel, and thus, the increased crosslinking that results at higher macromer solution concentrations leads to a higher compressive modulus in the gel. Thus, from a practical standpoint, the gel modulus can be varied through simple changes in the initial macromer concentration.

From the experimentally measured compressive modulus and Q, $\overline{M_c}$ was calculated from the Peppas–Merrill equation (Eq. (1)), as well as the rubber-elasticity theory (Eq. (3)), and the results are shown in Table 1. As discussed above, the Peppas–Merrill equation quantifies the differences in the network crosslinking density as a function of macromer concentration. However, rubber-elasticity theory predicts only slight variations in the average molecular weight between crosslinks. In addition, the $\overline{M_c}$ values calculated

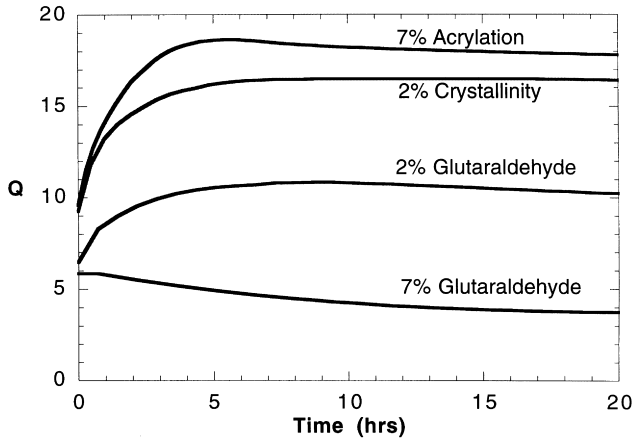

Fig. 5. Swelling behavior as a function of time for PVA hydrogels formed via three different crosslinking mechanisms.

from the rubber-elasticity theory are all higher than those calculated from the swelling behavior, as well as the theoretically predicted value ($\overline{M}_{c,theory} = 616$ g/mol). The higher values for $\overline{M}_c$ calculated from the rubber elasticity theory, as compared to the Peppas–Merrill equation, may be related in part to the greater influence of cyclization on the swelling behavior as compared to the mechanical behavior.

To further characterize the structure of networks formed from radically polymerizing Acr-PVA, these networks were compared to networks synthesized from more widely used crosslinking techniques, specifically, chemical crosslinking through condensation with glutaraldehyde [4–7] and physical crosslinking with crystalline regions introduced by freeze–thawing [8–11]. A 20 wt% solution of 7 mol% acrylated PVA macromer was photopolymerized to from a crosslinked gel and compared to gels formed by crosslinking a 20 wt% PVA solution with 7% glutaraldehyde and 2% glutaraldehyde. In addition, a physical network was formed by freeze thawing of 20 wt% solution of 7 mol% acrylated PVA to introduce 2% crystallinity, and the gel was subsequently photopolymerized to induce chemical crosslinking. The equilibrium volume swelling behavior as a function of swelling time for gels produced from these various crosslinking methods is shown in Fig. 5. From these results, several comparisons can be made regarding the influence of the crosslinking mechanism on the overall network structure as inferred from the equilibrium swelling ratio.

In general, the overall swelling behavior in crosslinked networks is a function of the crosslinking density (e.g. $\overline{M}_c$) and chemistry (e.g. χ_1). If the variations in the networks chemistry are assumed minor (i.e. since only the chemistry of the crosslinks is changed), then differences in the equilibrium swelling are mainly attributable to variations in the network structure. In these systems, the equilibrium volume swelling ratio, Q, varies from ~4 to 18, and several comparisons are noteworthy.

First, in examining the swelling of hydrogels formed by the reaction of 2 or 7 mol% glutaraldhyde (GA) with linear PVA, the expected trend of decreasing swelling with increasing crosslinker is observed. However, the theoretical equilibrium swelling ratio, calculated from Eq. (1) for ideal networks crosslinked with 2 and 7% glutaraldehyde would be 6.6 and 4.5, respectively, whereas the experimentally measured Qs are 10 and 4, respectively. Thus, the 2% GA network swells to a higher Q than predicted theoretically, which is mainly attributed to the 5% extractable sol fraction that is present. Whereas, the 7% GA network swells slightly less than predicted and has no extractable portion, and is thus behaving similar to an ideally crosslinked network.

Network gelation by the reaction of glutaraldehyde with the pendant hydroxyl groups on linear PVA proceeds by a mechanism that is dramatically different from the chain polymerization of pendant double bonds attached to PVA chains. Glutaraldehyde is a low molecular weight compound with a relatively high diffusivity in the solution, and polymerization proceeds by random and homogeneous crosslinking of any two aldehyde and alcohol functionalities. In contrast, the gelation of Acr-PVA occurs by the initiation of radicals that propagate through unreacted double bonds attached to the high molecular weight macromer until termination. Additionally, enhanced reactivity of double bonds near the propagating radical may result in extensive cyclization and inhomogeneities in the network structure. The complex structural evolution of networks formed during the polymerization of multifunctional monomers has been studied extensively by several researchers [22–24]. Here, the functionalization of a relatively high molecular weight macromer with reactive pendant double bonds, Acr-PVA, provides an interesting system to compare and contrast networks formed from multifunctional monomer photopolymerizations, as well as networks formed from condensation polymerization.

Upon photopolymerization of the Acr-PVA solution, a gel was formed with a relatively high sol fraction (~35%) and swelled nearly 18 times its volume in water. This high Q and extractable sol fraction are both indicators of the nonidealities of the chain crosslinking process (e.g. unequal reactivity of the double bonds and extensive cyclization). For an ideal network, where all of the pendant double bonds react to form chemical crosslinks, a 7% Acr-PVA macromer would lead to a network with a Q of ~5.5 (calculated from Eq. (1)). In addition, comparison of Q values for networks formed from the photopolymerization of Acr-PVA to the gelation of linear PVA with 2 or 7% GA, indicate the higher efficiency of the glutaraldehyde crosslinking. Thus, while an Acr-PVA macromer provides advantages with respect to the rapid synthesis of crosslinked gels through photopolymerization without the addition of any small molecular weight crosslinkers, the resulting network is more loosely crosslinked than networks formed with glutaraldehyde at comparable crosslinker concentrations.

To provide further insight regarding the parameters influencing the network structural evolution during the photopolymerization of Acr-PVA, a physically crosslinked network

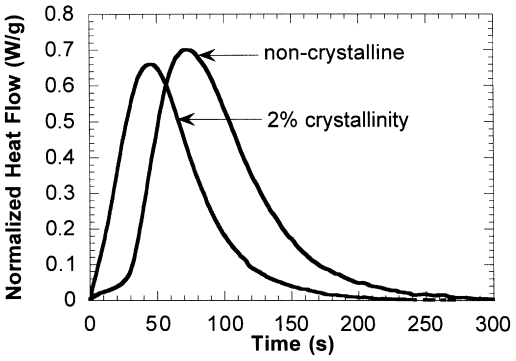

Fig. 6. Polymerization behavior as functional of time for 20 wt% Acr-PVA solutions in non-crystalline and semi-crystalline gels. Polymerizations were initiated with 0.05 wt% D2959 and 18 mW/cm^2 of UV light.

of Acr-PVA was produced through repeated freeze–thaw cycles of a 20 wt% solution of 7 mol% Acr-PVA. The resulting physically crosslinked network contained 2% crystallinity, as measured by DSC. While the % crystallinity is low compared to other studies of physical gels formed from linear PVA [8–11], the value is reasonable considering the low molecular weight of our PVA macromer (13–23 K) and the fact that 7% of the pendant hydroxyl groups were acrylated. After formation of the physical gel, the network was photopolymerized to examine the influence that ordering in the crystalline regions might have on the crosslinking efficiency. The final network Q was ~16, and ~10% lower than the gel polymerized from a non-crystalline solution of Acr-PVA. The lower swelling results from the combined physical and chemical crosslinking present in the gel.

In addition to comparing the swelling behavior of networks formed from the photopolymerization of non-crystalline macromer solutions to those formed in semi-crystalline physically crosslinked gels, we were also interested in how the polymerization behavior might be altered by photopolymerizing the Acr-PVA in a semi-crystalline (i.e. semi-ordered) system. To perform these studies, DSC was used to monitor the reaction behavior, and Fig. 6 contains the heat flow as a function of time for two such systems. Both systems contained 20 wt% Acr-PVA; however, one was a liquid solution and the other was a semi-crystalline physically crosslinked gel. In the semi-crystalline gel, there are two additional effects that influence the overall polymerization behavior compared to the polymerization of the homogenous, macromer solutions. First, the sample is already a physically crosslinked gel with an infinite viscosity, which leads to greater restrictions in mobility from the onset of the photopolymerization. Second, the semi-ordering of the chains in crystalline regions can lead to higher concentrations of double bonds locally, compared to the bulk, and influence the crosslinking kinetics and polymerization rate. Since there was only 2% crystallinity in these physically crosslinked gels, the viscosity effects dominated any effects that might result from ordering in the system.

Table 2
Network structure of 20 wt% solutions as function of crosslinking mechanism and percent crosslinker

Polymer	Gel fraction (%)	$\overline{M_c}$ (g/mol)[a]	$\overline{M_c}$ (g/mol) theoretical	ρ_x (mol/l)
7% Acr-PVA	64	5530	616	0.229
2% Crystallinity	63	4835	–	0.262
2% Glutaraldehyde	95	2845	1100	0.446
7% Glutaraldehyde	100	215	308	5.902

[a] Calculated from the Peppas–Merrill equation.

Finally, in addition to examining the swelling behavior as a function of crosslinking mechanism, $\overline{M_c}$ and ρ_x were calculated from the Q data (data in Fig. 5), and the theoretical $\overline{M_c}$ was calculated from Eq. (1). The results are summarized in Table 2. Many of the differences in network structure that result from these three crosslinking methods are illustrated in this table. First, the gel fraction varies widely between these methods from ~60 to 100%. The gel fraction is a measure of the ideality of the crosslinking mechanism, and the radical chain crosslinking mechanism is less ideal than the GA crosslinking. The gel fraction, in combination with network imperfections, results in large structural differences, as the crosslinking density varies from 0.229 mol/l for radically crosslinked network to 5.902 mol/l for the 7 mol% GA crosslinked network. In addition, when comparing the experimental values to the theoretical values, the GA networks are closest to ideal, and the crosslinking density in the radically polymerized networks is nearly 9 times lower than the theoretical maximum for these macromers. Overall, a comparison of these differences implies that the choice of crosslinking method can greatly influence the resulting polymer network structure in several different aspects.

5. Conclusions

Linear PVA was modified with glycidyl acrylate to form a macromer that was radically crosslinked with a photoinitiated mechanism. The reaction behavior of the Acr-PVA macromer was dependent upon the initial macromer concentration, and in general, these systems photopolymerize to 100% conversion in just a few minutes. Differences in the reaction behavior were related to differences in the resulting network structures. Swelling and mechanical tests confirmed that different crosslinking densities are achieved by variations in the initial macromer concentration. For comparison, PVA was crosslinked with glutaraldehyde, and Acr-PVA was crosslinked in a semi-crystalline state. These studies verified the imperfections and structural differences in the photocrosslinked networks. The short reaction times and versatility in the network properties allow for the potential use of these PVA gels in many applications.

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