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The Effect of Cross-Linking on Gas Permeability in Cross-Linked Poly(Ethylene Glycol Diacrylate)

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ABSTRACT: A series of cross-linked polymers, XLPEGDA, was prepared by photopolymerizing poly(ethylene glycol) diacrylate (PEGDA) in the presence of varying amounts of water or monofunctional poly(ethylene glycol) methyl ether acrylate (PEGMEA) to vary cross-link density. All of the polymers had essentially the same chemical composition but displayed a systematic variation in cross-link density as estimated from water swelling experiments, models such as the Flory−Rehner and modified Flory−Rehner theories, and dynamic mechanical testing. Cross-link density decreased with increasing water or PEGMEA content in the prepolymer solutions. Interestingly, gas solubility, diffusivity, and permeability were essentially independent of cross-link density for the series of materials prepared from PEGDA and water. The polymer density, fractional free volume, glass transition temperature, and polymer *d* spacing were also constant when water was used to vary cross-link density. On the basis of this result, it appears that cross-link density does not necessarily affect gas diffusion and permeation, the polymer glass transition temperature, or the fractional free volume in network polymers, and ascribing changes in these properties to changes in cross-link density alone, as is seen commonly in the literature, should be done with great care.

Introduction

Polymer modification by cross-linking has attracted interest recently in membrane-based separations of gases or vapors. Cross-linked poly(dimethylsiloxane) is used commercially as a vapor separation membrane material.[1] Cross-linking may enhance thermal and chemical resistance; this strategy has been explored to prepare pervaporation membranes that operate at elevated temperatures and high solvent activity.[2] Cross-linking can improve CO_2/CH_4 separation stability in glassy polymers, such as polyimides, by suppressing the plasticization of the polymer matrix by CO_2 or hydrocarbons.[3] Poly(ethylene oxide) (PEO) is an interesting membrane platform for the removal of CO_2 from mixtures with light gases, such as H_2, N_2, and CH_4.[4,5] Because CO_2 has an affinity for the polar ether linkages in PEO, this material exhibits high solubility and permeability selectivity for gas pairs involving CO_2 or related acid or polar gases (e.g., H_2S).[5] However, the high crystallinity of PEO ($>$70 vol %) reduces gas permeability severely.[4] For example, semicrystalline PEO exhibits a CO_2 permeability of only 12 barrers at 35 °C and infinite dilution, whereas the estimated CO_2 permeability of wholly amorphous PEO would be 140 barrers.[4] Therefore, if one could prepare membranes from amorphous PEO, then the CO_2 flux could be improved by at least 1 order of magnitude while maintaining permeability selectivity. According to Graham, cross-linked PEO is amorphous when the molecular weight of poly(ethylene oxide) segments between two cross-linking points is 1500 g/mol or less, whereas linear PEO with a molecular weight of 600 g/mol or above is highly crystalline at ambient conditions.[6] We have prepared amorphous cross-linked PEO samples exhibiting CO_2 permeability coefficients of 570 barrers at 35 °C and infinite dilution.[7] Thus, one fundamental issue is to understand the effect of cross-linking on gas transport properties. This report describes an investigation of the effect of cross-linking on gas permeation and related physical properties in polymers composed primarily of PEO (about 82 wt %).

To study the effect of cross-linking on polymer properties, the first challenge is to prepare a series of polymers with systematic variation in cross-link density without changing other properties, such as chemical composition.[8] Some early studies in this area used natural rubber, and cross-link density was varied by changing the sulfur[9,10] or peroxide[10] content used to vulcanize the polymer. For example, Barrer and Skirrow studied gas permeation and diffusion in natural rubber of various cross-link densities by varying the sulfur content used for vulcanization systematically.[9,11] Gas solubility was relatively independent of cross-link density;[9] however, gas permeability decreased as cross-link density increased, and the decrease was more pronounced for larger penetrants.[11] For example, when the sulfur content in natural rubber increased from 1.7 to 15.15 wt %, CH_4 permeability at 40 °C decreased by 1 order of magnitude, from 17.3 to 1.13 barrers. In contrast, CH_4 solubility at 60 °C changed only slightly, from 0.238 to 0.204 $cm^3(STP)/(cm^3\ atm)$, over the same range of sulfur content.[11] However, introducing polar sulfur groups during the cross-linking inevitably changes the chemical composition of the natural rubber; this factor alone could increase the glass transition temperature (T_g) and decrease the gas permeability.[12] For example, as sulfur

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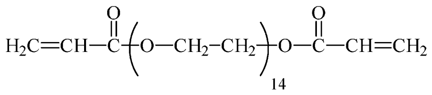
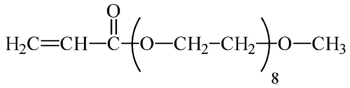
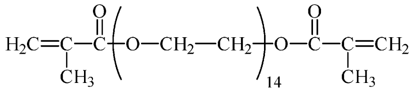
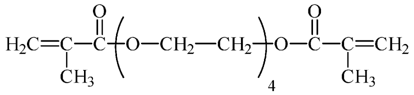
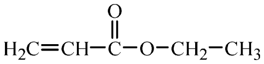
Table 1. Structures of Relevant Monomers and Cross-Linkers

Chemical	Structure
poly(ethylene glycol) diacrylate (PEGDA)	 $H_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}\left(O{-}CH_2{-}CH_2\right)_{14}{-}O{-}\overset{O}{\overset{\|}{C}}{-}CH{=}CH_2$
poly(ethylene glycol) methyl ether acrylate (PEGMEA)	 $H_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}\left(O{-}CH_2{-}CH_2\right)_{8}{-}O{-}CH_3$
poly(ethylene glycol) dimethacrylate (PEGDMA)	 $H_2C{=}\underset{CH_3}{\underset{\vert}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\left(O{-}CH_2{-}CH_2\right)_{14}{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{CH_3}{\underset{\vert}{C}}{=}CH_2$
tetra(ethylene glycol) dimethacrylate (TEGDM)	 $H_2C{=}\underset{CH_3}{\underset{\vert}{C}}{-}\overset{O}{\overset{\|}{C}}{-}\left(O{-}CH_2{-}CH_2\right)_{4}{-}O{-}\overset{O}{\overset{\|}{C}}{-}\underset{CH_3}{\underset{\vert}{C}}{=}CH_2$
ethylacrylate (EA)	 $H_2C{=}CH{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}CH_3$

content increased from zero to 16 wt %, T_g increased from about −80 °C to about +15 °C.[12] Therefore, it is difficult, if not impossible, to decouple these two factors to clearly understand the effect of cross-linking in such systems.[12,13] A similar system is poly(propylene glycol) cross-linked at the terminal hydroxyl groups with triisocyanate.[14] Decreases in hydrogen and carbon monoxide permeability were observed with increasing cross-link density achieved by increasing the content of rigid urethane-type units in these polymers.[14]

In other studies, high energy radiation has been used to cross-link semicrystalline polyethylene. Gas diffusion coefficients decreased as radiation dose increased above a certain threshold.[15] However, radiation not only cross-links the polymer, but it also affects the polymer in other ways; it can oxidize the polymer if it is radiated in the presence of O_2, crystallinity can decrease, and unsaturation and chain scission may increase.[15−17] All of these factors, along with cross-linking, contribute to changes in the gas transport properties. For example, oxidation would introduce polar groups into the polymer, which could have a significant effect on gas diffusivity.

In addition to the studies mentioned above, Barrer and co-workers prepared a series of copolymers from mixtures of tetra(ethylene glycol) dimethacrylate (TEGDM) and ethylacrylate (EA) and studied their permeability.[18] The chemical structures of TEGDM and EA are presented in Table 1. Cross-link density was controlled by changing the TEGDM content, that is, the cross-linker concentration.[18] However, changing the TEGDM content also changes the polymer chemical composition. More importantly, increasing EA content increases the concentration of chain ends ($-OC_2H_5$), which would typically increase the polymer fractional free volume and, in turn, gas permeability.[19,20]

Some researchers have even observed increases in gas permeability with increasing cross-link density.[3,21−23] For example, Siegel and Coughlin reported that gas permeability in semicrystalline polyethylene increases as cross-link density increases, probably due to the decrease in crystallinity that accompanies cross-linking.[21] Wind and co-workers employed ethylene glycol to cross-link polyimides containing carboxylic acid groups and reported an increase in CO_2 permeability from 30 to 40 barrers at 35 °C and an upstream pressure of 4.4 atm.[3]

In summary, the effect of cross-linking has not been determined clearly, although a majority of the literature reports suggest that cross-linking reduces gas permeability. However, from a simple point of view, if gas diffusion requires the collective movements of only a few repeat units in a polymer chain, then why would one cross-link junction per 20 (or more) repeat units significantly affect gas permeation? One cross-link junction per 20 repeat units is mentioned because it is within the range of values in the TEGDA/EA copolymers prepared by Barrer and co-workers[18] and the polymers considered in the current study.

In this work, a series of cross-linked poly(ethylene oxide) samples have been prepared by ultraviolet (UV) photopolymerization of poly(ethylene glycol) diacrylate (PEGDA, cf. Table 1) in aqueous solution. Figure 1 presents a schematic of the representative network structures in cross-linked PEGDA. By adjusting the water content in the prepolymer solutions, cross-linked poly(ethylene oxide) (XLPEGDA*XX*) samples, where "*XX*" represents the weight percent of PEGDA in the prepolymer solution, can be prepared with different

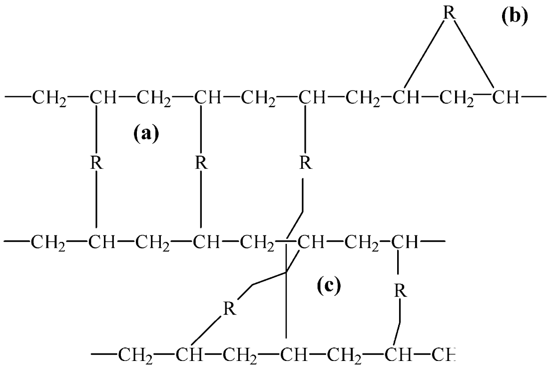


Figure 1. Schematic of representative network elements in XLPEGDA. PEGDA: $CH_2{=}CH{-}R{-}CH{=}CH_2$ (a) represents the smallest network possible in these polymers; (b) represents a wasted cross-link or loop; (c) represents an entanglement, which is permanent because of the cross-links.

cross-link densities. In general, increasing cross-link density as cross-linker concentration in prepolymer solutions increases has been very well documented for polymer systems both theoretically[24−26] and experimentally.[27,28] In XLPEGDA, only a small amount of initiator (i.e., 0.001 g initiator per 1 g PEGDA) was used to minimize the influence of initiator fragments on the chemistry of the polymers. With complete reaction of the vinyl groups in PEGDA, these amorphous polymers have the same chemical composition, independent of the cross-link density. Therefore, they are ideal models for isolating the effect of cross-linking on gas transport properties. In addition, a separate series of copolymers (PEGDA-*co*-PEGMEA) were prepared using PEGDA and poly(ethylene glycol) methyl ether acrylate (PEGMEA). Both PEGDA and PEGMEA contain about 82 wt % PEO; therefore, there is essentially no variation in chemical composition across this series of copolymers. By systematically varying PEGMEA content, one can control the cross-link density and the concentration of chain end groups in the copolymers. The effect of these changes on gas permeation properties is investigated.

Background

The steady-state permeability of a polymer to a gas A, P_A, is defined as[29]

$$P_A \equiv \frac{N_A l}{p_2 - p_1} \tag{1}$$

where N_A is the steady-state flux of gas through the film, l is the film thickness, and p_2 and p_1 are the upstream (i.e., high) and downstream (i.e., low) partial pressures of gas A, respectively. Permeability coefficients are commonly expressed in units of barrers, where 1 barrer = 10^{-10} cm^3(STP) cm/(cm^2 s cm Hg). If the diffusion process obeys Fick's law, and the downstream pressure is much less than upstream pressure, then the permeability is given by[29]

$$P_A = D_A S_A \tag{2}$$

where D_A is the average effective diffusivity and S_A is the apparent sorption coefficient, which is defined as[29]

$$S_A = \frac{C}{p} \tag{3}$$

where C is the concentration of gas dissolved in the polymer when the pressure of the gas in contact with the polymer is p. The gas solubility in rubbery polymers depends on the condensability (usually represented by the critical temperature of the gas), the interaction of the gas with the polymer matrix, and weakly on the free volume of the polymer. Diffusion of a small molecule in a polymer is often understood qualitatively to depend sensitively on free volume[30,31]

$$D_A = A \exp\left(-\frac{B}{FFV}\right) \tag{4}$$

where A is a preexponential factor, B is proportional to penetrant size, and FFV is the fractional free volume in the polymer. On the basis of this model, diffusion coefficients are strong functions of polymer free volume and penetrant size. Gas diffusivity is also determined by polymer chain flexibility, often characterized by the polymer glass transition temperature.[29]

The ideal selectivity of a membrane for gas A over gas B is the ratio of their pure gas permeabilities[29]

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left[\frac{D_A}{D_B}\right]\left[\frac{S_A}{S_B}\right] \tag{5}$$

where D_A/D_B is the diffusivity selectivity, and S_A/S_B is the solubility selectivity.

Experimental Section

Materials. Hydrogen, nitrogen, and carbon dioxide, with a purity of 99.9%, were purchased from Air Gas Southwest Inc. (Corpus Christi, TX). Methane of chemical purity (i.e., 99%) was purchased from Air Liquide America Corporation (Houston, TX). The gases were used as received. Poly(ethylene glycol) diacrylate (PEGDA: MW = 743 g/mol), poly(ethylene glycol) methyl ether acrylate (PEGMEA: MW = 460 g/mol), deuterated chloroform ($CDCl_3$), hexane, dodecane, and 1-hydroxylcyclohexyl phenyl ketone (HCPK) were purchased from Aldrich Chemical Co. (Milwaukee, WI). Poly(ethylene glycol) dimethacrylate (PEGDMA: MW = 754 g/mol) was purchased from Monomer-Polymer & Dajac Labs (Feasterville, PA). HCPK is also available under the Irgacure 184 trade name from Ciba Specialty Chemicals (Tarrytown, NY). Irgacure 2959, 2-hydroxy-1-[4-2-(hydroxyethoxy)phenyl-2-methyl-1-propanone] was purchased from Ciba. All of the solvents had a purity of at least 99%, except for the $CDCl_3$ used for nuclear magnetic resonance studies, which had a purity of 99.99%. All of the chemicals were used as received unless otherwise indicated. Ultrapure water produced by a Milli-Q water purification system (Millipore Corporation, Bedford, MA) was used throughout this study. The chemical structures of PEGDA, PEGMEA, and PEGDMA are presented in Table 1.

PEGDA Characterization. Proton nuclear magnetic resonance (^{1}H NMR)[32,33] and fast atom bombardment mass spectrometry (FAB-MS)[32,34] were used to confirm the PEGDA molecular weight. FAB-MS also provides information regarding polydispersity.

Samples for ^{1}H NMR were prepared by dissolving dry PEGDA in $CDCl_3$ at concentrations between 5 and 10 wt %. ^{1}H NMR spectra were recorded on a VARIAN INOVA-500 spectrometer operating at 500 MHz. ^{1}H NMR data are reported in ppm relative to tetramethylsilane (TMS). The spectrometer was adjusted routinely as follows: spin rate, 20 rpm; pulse width, 2.0 μs; sweep width, 9256 Hz; line broadening (for exponential multiplication), 0.1 Hz with 128 K data points. The relaxation delay was 24 s (i.e., 5T_1). ^{1}H NMR ($CDCl_3$): δ 6.43 (2 H, cis $CH_2{=}CH$), 5.82 (2H, trans $CH_2{=}CH$), 6.15 (2H, $ROOCCH{=}CH_2$), 4.32 (4H, $RCOOCH_2{-}CH_2O$), 3.73 (4H, $RCOOCH_2CH_2O$), 3.65 (4(n-2) H, $OCH_2CH_2OCH_2CH_2OCH_2$-CH_2O). The integrals for δ 6.43, δ 5.82, and δ 6.15 should be the same and equal to half of the integral of δ 4.32 or δ 3.73. The number of repeat units of ethylene oxide in PEGDA, n, can be determined based on the integral ratio of δ 3.65 to that of any of the other peaks. Therefore, the molecular weight of PEGDA can be calculated as follows:

$$M_n = \left(\frac{1}{2}\frac{\text{Integral}\cdot\delta\cdot 3.65}{\text{Integral}\cdot\delta\cdot 6.43} + 2\right) \times 44 + 126 \tag{6}$$

The FAB-MS instrument was a Finnigan MAT TSQ 700 mass spectrometer/data system. The matrix used was *m*-nitrobenzylic alcohol (MNBA). The fast atom gun (Ion Tech Model FAB-11-GG) provided xenon atoms at 7.2 keV. The instrumental resolution (M/ΔM) was 1000, and the ion source temperature was 70 °C. Typical FAB-MS results are presented as a graph of relative intensity versus mass/charge (m/z). Number (M_n) and weight average (M_w) molecular weights are calculated as follows[35]

$$M_n = \frac{\sum N_i M_i}{\sum N_i} \qquad M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i} \tag{7}$$

where N_i is proportional to the relative intensity, and M_i corresponds to m because z (charge) usually equals 1. The polydispersity index is the ratio of M_w to M_n.

Polymer Preparation. The prepolymer solution was prepared by adding 0.1 wt % initiator (i.e., either HCPK or Irgacure 2959) to PEGDA. After stirring, the solution was mixed with a known amount of ultrapure water to form the target composition and then sonicated for about 10 min to eliminate bubbles (Ultrasonic cleaner, Model FS60, Fisher Scientific, Pittsburgh, PA). In some experiments, N_2 was bubbled through the solution for 30 min prior to polymerization to remove dissolved oxygen. The solution was sandwiched between two quartz plates, which were separated by spacers to control film thickness. The solution was polymerized by exposure to 312-nm UV light in a UV cross-linker (Model FB-UVXL-1000, Fisher Scientific) for 90 s at 3 mW/cm^2. The solid films obtained by this process were three-dimensional networks (i.e., gels) and contained a negligible amount of low molecular weight polymer (i.e., sol) that was not bound to the network. The as-synthesized film was immersed in a large amount of ultrapure water for at least 5 days to allow any sol to diffuse out of the gels. The water was changed daily.

Fourier Transform Infrared Spectroscopy. Attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR) was used to determine the conversion of acrylate groups. The spectrometer was a Thermo Nicolet Nexus 470 (Madison, WI). For each measurement, 128 spectra were accumulated at a resolution of 4 cm^{-1}. The disappearance of acrylate double bonds because of polymerization leads to the decrease of sharp peaks at 810 cm^{-1} (ascribed to the twisting vibration of the acrylic $CH_2{=}CH$ bond),[36] 1410 cm^{-1} (deformation of the $CH_2{=}CH$ bond),[37,38] and 1190 cm^{-1} (acrylic $C{=}O$ bond).[37]

Thermal and X-ray Characterization. Thermal transitions were determined using a TA Instruments (New Castle, DE) Q1000 differential scanning calorimeter (DSC). Samples were scanned at a heating rate of 20 °C/min from −90 to 0 or 30 °C under dry N_2 purge at a flow rate of 50 mL/min. The glass transition temperature was taken as the midpoint of the heat capacity step change.

Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Bruker-Nonius D8 Advance Theta-2Theta Powder Diffractometer with Cu Kα radiation (1.54 Å). The generator was operated at 40 kV and 30 mA. The patterns were obtained by averaging scans over at least 8 h. Polymer samples were supported on a silicon wafer, which produces a sharp peak at $2\theta = 69°$. Because the diffraction range of interest for these polymers is 5−40° (2θ), the peak due to the silicon wafer support does not appear in the patterns presented in this report.

Dynamic Mechanical Analysis. Dynamic mechanical thermal analysis was performed in the vicinity of the glass transition using a Polymer Laboratories DMTA operating in single cantilever bending geometry. The polymer films had a thickness of 1 mm and were dried under vacuum at room temperature prior to measurement. The storage modulus (E') and loss tangent (tan δ) were recorded at a heating rate of 1 °C/min with test frequencies in the range of 0.1 to 10 Hz; all of the measurements were carried out under inert (N_2) atmosphere. The glass transition temperatures (T_α) were determined based on the maximum in tan δ at a frequency of 1 Hz.

Determination of Cross-Link Density. Equilibrium water swelling experiments at room temperature were used to estimate cross-link density.[39−41] After being immersed in ultrapure water for more than 5 days, the sample was wiped rapidly with a paper towel to remove surface water and the sample weight, $w_{T,1}$, was measured. The film was then dried in a fume hood at ambient conditions for 2 days, and then in a vacuum oven at room temperature for another 2 days. The weight of the dry polymer film, $w_{P,1}$, was measured. The dry film was immersed in ultrapure water again, and the procedure described above was repeated to obtain $w_{T,2}$ and $w_{P,2}$, which are the weights of the swollen film and dry film, respectively, in the second swelling experiment.

The density of dry polymer samples was determined by hydrostatic weighing using a Mettler Toledo balance (Model AG204, Switzerland) and a density determination kit.[4] The film density (ρ_p) is calculated as follows

$$\rho_p = \frac{M_A}{M_A - M_L}\,\rho_o \tag{8}$$

where M_A is the film weight in air, M_L is the film weight in the auxiliary liquid, and ρ_o is the density of the auxiliary liquid. Heptane or dodecane was used as the auxiliary liquid because poly(ethylene oxide) does not have an affinity for such alkanes.[40,41]

On the basis of these measurements and a suitable model, the following parameters could be calculated: polymer volume fraction after polymerization and before swelling (the so-called relaxed state polymer volume fraction), $v_{1,r}$; polymer volume fraction at equilibrium swelling, $v_{1,s}$; number average molecular weight between cross-links, M_c; and cross-link density, v_e.

Generally, a solvent sorbed in a polymer network exhibits its pure liquid density.[42] If volume additivity is assumed, then $v_{1,r}$ and $v_{1,s}$ can be calculated as follows

$$v_{1,r} = \frac{w_p/\rho_p}{(w_{T,r} - w_p)/\rho_2 + w_p/\rho_p} \tag{9}$$

$$v_{1,s} = \frac{w_p/\rho_p}{(w_{T,s} - w_p)/\rho_2 + w_p/\rho_p} \tag{10}$$

where ρ_2 is the density of liquid water at room temperature, w_p is the weight of dry polymer, and $w_{T,r}$ and $w_{T,s}$ represent the total weight of the polymer and solvent in the relaxed and equilibrium swollen states, respectively.

An affine deformation theory was used to estimate the number average molecular weight between cross-link junctions, M_c[39,41,43]

$$\frac{1}{M_c} = \frac{2}{M_{n,p}} - \frac{\dfrac{1}{\rho_p \bar{V}_2}\left[\ln(1 - v_{1,s}) + v_{1,s} + \chi {v_{1,s}}^2\right]}{v_{1,r}\left[\left(\dfrac{v_{1,s}}{v_{1,r}}\right)^{1/3} - \dfrac{1}{2}\left(\dfrac{v_{1,s}}{v_{1,r}}\right)\right]} \tag{11}$$

where $M_{n,p}$ is the number average molecular weight of the primary polymer chains before cross-linking, $\bar{V}_2$ is the molar volume of water (18 cm^3/mol), and χ is the Flory−Huggins interaction parameter between the polymer and water. This equation is a modification of the Flory−Rehner equation that considers the polymer system just after polymerization to be in the relaxed state, where no elastic force is present.[44] By setting $v_{1,r}$ to 1, we recover the Flory−Rehner equation. To estimate $M_{n,p}$ values in the polymers under investigation, we assume that polymerization follows two hypothetical steps: the first step is to form linear polymer chains with an average molecular weight of $M_{n,p}$ and the second step is to form cross-links among these chains.[40,45] In general, acrylate groups have high conversion and the hypothetical $M_{n,p}$ values would be large enough so that $2/M_{n,p}$ can be neglected in eq 11.[40,45] This assumption is used here. Equation 11 also assumes a Gaussian chain distribution, that is, the average number of repeat units between cross-links is presumed to be large enough that cross-linking junctions do not perturb the chain configuration.[46] For highly cross-linked polymers such as those described here, the number of repeat units between cross-links could be less than 100. Therefore, the assumption of a Gaussian chain distribution might not be valid.[39] Peppas and co-workers developed the following equation to account for deviations from a Gaussian distribution[39]

$$\frac{1}{M_c} = \frac{2}{M_{n,p}} - \frac{\frac{1}{\rho_p \bar{V}_2}[\ln(1 - v_{1,s}) + v_{1,s} + \chi v_{1,s}^{\,2}]\left[1 - \frac{1}{N}\left(\frac{v_{1,s}}{v_{1,r}}\right)^{2/3}\right]^3}{v_{1,r}\left[\left(\frac{v_{1,s}}{v_{1,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{1,s}}{v_{1,r}}\right)\right]\left[1 + \frac{1}{N}\left(\frac{v_{1,s}}{v_{1,r}}\right)^{1/3}\right]^2} \qquad (12)$$

where N is the number of links per chain (between two effective cross-link junctions) and is defined as[39]

$$N = \frac{\lambda M_c}{M_n} \qquad (13)$$

where M_n is the molecular weight of the initial monomer or cross-linker (which is PEGDA in this study) and λ is the number of links per PEGDA after polymerization, which is 4 because every vinyl group has 2 links after polymerization.[39] By combining eqs 12 and 13, M_c can be calculated if the Flory–Huggins interaction parameter between the polymer and water is known.

The effective number of chains in the networks per unit volume, or the effective number of network junctions per unit volume, v_e (mol/cm^3), is given by[46]

$$v_e = \frac{\rho_p}{M_c} \qquad (14)$$

It would be interesting to compare the value of v_e to the number of theoretical network junctions, which is defined as the number of chains when PEGDA reacts completely and forms a perfect network without dangling ends.[46,47] The theoretical number of network junctions, v_t (mol/cm^3), is given by[40,46–48]

$$v_t = 2c \qquad (15)$$

where c (mol/cm^3) is the concentration of cross-linking agent (i.e., PEGDA) in the dry polymer, and the constant, 2, indicates that every PEGDA forms two junctions. On the basis of eqs 14 and 15, the theoretical molecular weight between cross-links, $M_{c,ideal}$, is[40,46]

$$M_{c,ideal} = \frac{M_n}{2} \qquad (16)$$

In addition to solvent swelling experiments, cross-link density can also be estimated from mechanical properties, such as elastic modulus measured using dynamic mechanical testing. The following equation is often used[49]

$$v_e = \frac{E'}{3RT} \qquad (17)$$

where E' is the elastic modulus in the rubbery plateau, R is the gas constant, and T is the temperature at which E' is evaluated (room temperature in our case). The value of v_e from this model typically overestimates the effective cross-link density because this model accounts for the effect of chain entanglements in addition to cross-linking.[50]

Permeation and Sorption Measurements. Pure gas permeability in XLPEGDAs was determined using a constant volume/variable pressure apparatus.[51] The flux and permeability were calculated from the pressure rise in a downstream vessel of known volume. In this study, all of the samples were masked partially using impermeable aluminum tape on the upstream and downstream faces as described previously.[4]

The CO_2 and CH_4 solubility coefficients of the polymers were determined using a dual-volume, dual-transducer apparatus based on the barometric, pressure-decay method.[52,53] The detailed procedure is described elsewhere.[4] Special care was taken to make the sorption measurements in the XLPEGDA samples as accurate as possible because, in this rather polar material, gas solubility is low.[4]

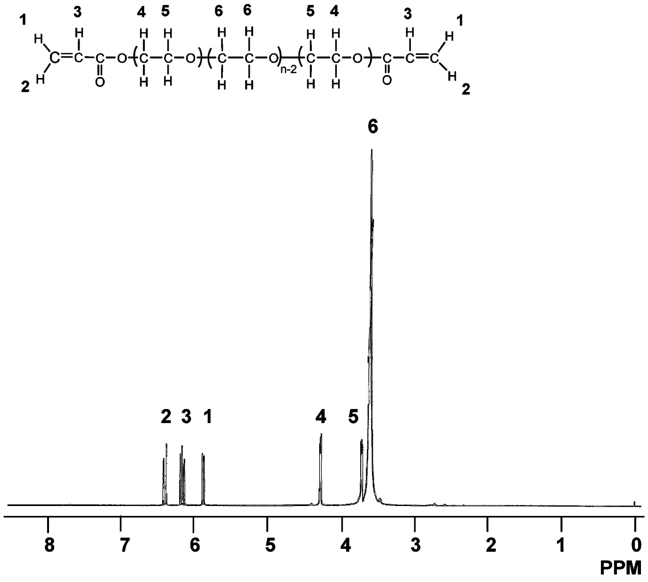


Figure 2. ^{1}H NMR spectrum of PEGDA.

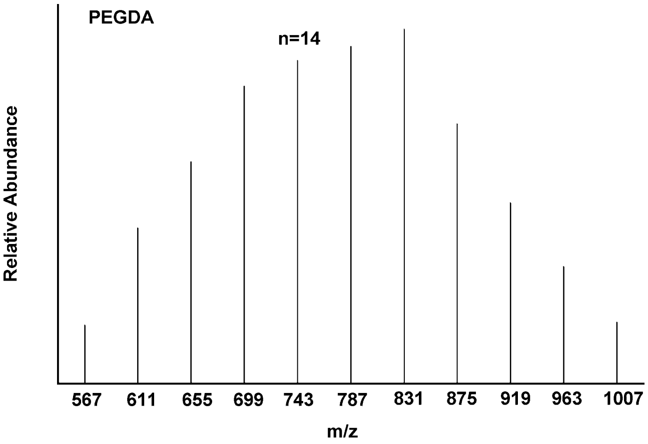


Figure 3. Fast atom bombardment mass spectrum in the range m/z 500–1100 for PEGDA. Ionized PEGDA forms a series of peaks at m/z values of 567, 611, 655, 699, 743, and so forth. The peak at 743 corresponds to PEGDA with 14 ethylene oxide units.

Results and Discussion

PEGDA Molecular Weight Characterization. On the basis of information from the supplier, the PEGDA sample used in these studies has an average molecular weight between 699 and 743 g/mol. Because the molecular weight and its distribution will inevitably affect the polymer network structure, it was important to confirm the molecular weight and obtain the polydispersity index. Figure 2 presents the ^{1}H NMR spectrum of PEGDA. The average number of ethylene oxide repeating units is 14, and based on eq 6, the number average molecular weight is 743 g/mol, which is consistent with the specification provided by the supplier. Figure 3 presents a FAB-MS spectrum, where signals corresponding to noise have been neglected. Using eq 7, we find that the number average molecular weight is 730 g/mol, and the polydispersity index is 1.08. The M_n values estimated by NMR and FAB-MS are similar, and the polydispersity value suggests a narrow distribution of molecular weight. This result is consistent with the typical process for making poly(ethylene oxide)-based materials by ring-opening polymerization of ethylene oxide; usually performed under living polymerization conditions, the method yields materials with low values of polydispersity.[54]

Polymerization Conditions. Polymerization of acrylate monomers under UV light, that is, UV radiation curing, is a well-established technology in industry.[55] Acrylate double bonds often exhibit very high reactivities, mainly because of large propagation rate constants and relatively low termination rate constants.[55] Both acrylate groups of PEGDA are expected to have similar reactivities,[46] with the reaction of more than 90% of the acrylate groups occurring within a few seconds under typical polymerization conditions.[55] In this study, prepolymer solutions were exposed to UV for 90 s to ensure full reaction of the acrylate groups. The effect of UV exposure time on polymerization of these materials is reported separately.[56]

Typical initiators for acrylate monomers are aromatic ketones.[55] Because water was used as the solvent, two initiators were used: water insoluble HCPK and water soluble Irgacure 2959. Both initiators undergo an α-cleavage process upon exposure to UV radiation, forming a benzoyl (for HCPK) or substituted benzoyl (for Irgacure 2959) radical and a counter radical.[57] Both radicals formed in each case are active for initiating polymerization.[57] Consequently, both initiators lead to high reaction rates and a high degree of conversion during polymerization.[57] The amount of initiator used is critical. Introducing a high concentration of initiator in the curing solution produces a polymer with a nonuniform structure across its depth because of too much UV absorption on the top surface layer, which is closer to the UV source.[55] In this study, the initiator amount was 0.1% relative to the weight of PEGDA. Mercury lamps, with an average wavelength of 312 nm, were used because the initiators have high absorption in this range.[58]

In general, cross-linked polymers contain an infinite network (gel) and a sol fraction that is not attached to the network. The gel fraction typically approaches 1 as the extent of reaction of the monomer reaches 100%.[46] In our studies, the weight of PEGDA added for polymerization was always very close to the weight of dried polymer after washing, suggesting that very little sol was formed. For example, for a polymer prepared from 35 wt % PEGDA and 65 wt % H_2O, the weight of the dry polymer sample, after repeated extraction with water to remove the sol as described earlier, was 98% of the weight of the PEGDA added. FTIR-ATR was used to probe the amount of unreacted acrylate groups in the dry polymer samples. Figure 4 compares a typical spectrum of a polymer prepared from 20% PEGDA and 80% H_2O (XLPEGDA20) with that of liquid PEGDA. The spectra for other polymers are very similar to that of XLPEGDA20 and are not shown for brevity. All of the characteristic peaks for the acrylate groups (i.e., those at 812, 1190, and 1410 cm^{-1})[36−38] practically disappear in the IR spectrum of the polymer, which indicates that the reaction conversion of PEGDA is close to 100%. Additionally, the spectra taken from the two sides of the polymer sample are shown to be almost identical, so there is no measurable effect of film depth on polymerization for the range of thicknesses considered in this study. As a result, film thickness should not play an important role in other physical properties, such as water uptake and gas permeation. Additionally, this result confirms that sufficient initiator was used to perform the polymerization.

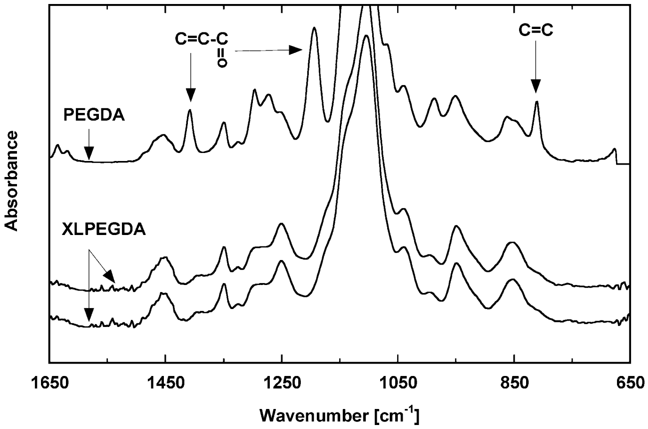


Figure 4. FTIR spectra of liquid PEGDA and each side of a solid XLPEGDA20 film. For the solid polymer film, one side was exposed directly to UV light and the other side was positioned opposite to the UV source. This film has a thickness of about 500 μm. These spectra have been displaced vertically for clarity.

The polymers prepared should have similar theoretical cross-link density and chemical composition. However, higher contents of diluent during polymerization would increase intramolecular cross-link-forming loops, which do not contribute to the elastic force of the network; these structures are called wasted cross-links, as illustrated in Figure 1.[46] In this way, the effective cross-link density in this series of polymers can be manipulated by varying the amount of water content in the prepolymer solution.

DSC and WAXD Results. Figure 5a and b present wide-angle X-ray diffraction patterns for semicrystalline poly(ethylene oxide) and a representative XLPEGDA sample, XLPEGDA50. The diffraction patterns of other XLPEGDA samples are very similar to that of XLPEGDA50, except for a slight shift in the position of the amorphous halo. The PEO WAXD pattern exhibits sharp characteristic peaks for PEO crystals at 2θ values around 17−19° and 22−24°, which is consistent with previous reports.[59] However, those peaks are absent in the XLPEGDA pattern, which clearly indicates the amorphous nature of XLPEGDA samples at room temperature. Because of short range order, these cross-linked polymers exhibit a broad halo. The d spacing, which corresponds to the position of the diffraction maximum, can be calculated using Bragg's Law[59]

$$d = \frac{\lambda}{2 \sin \theta} \tag{18}$$

where λ is the wavelength of Cu Kα radiation (1.54 Å), and θ is the angle of the reflection peak. The results are summarized in Table 2, and there is no significant effect of prepolymer composition (i.e., effective cross-link density) on d spacing. d spacing has been used widely to characterize the spacing between polymer chains, and it has been related to gas permeability.[60]

Figure 6 presents differential scanning calorimetry thermograms (first scan) for various XLPEGDA samples. The glass transition temperatures recorded in Table 2 represent the midpoints of the transitions in Figure 6. Second DSC scans were performed for XLPEGDA100 and XLPEGDA80, and the T_g values were very consistent between the two scans, reflecting a lack of thermal

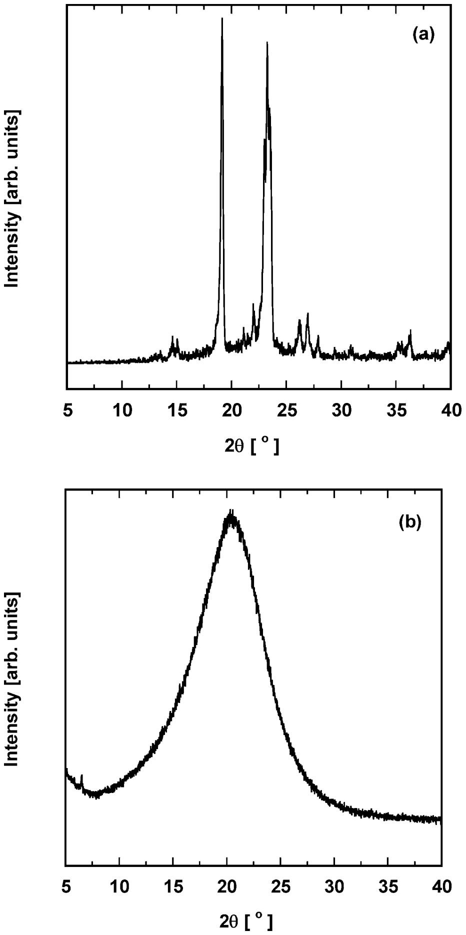


Figure 5. Wide-angle X-ray diffraction patterns for a film of (a) semicrystalline poly(ethylene oxide)[59] and (b) cross-linked poly(ethylene oxide) (XLPEGDA50).

history effects on T_g for these rubbery polymers. The calorimetric T_g values for all of the polymers fall within a very narrow range, which suggests that T_g is not dependent on the effective cross-link density; a similar result is obtained for the glass transition temperatures determined via dynamic mechanical testing (T_α, see Table 2). The T_g values will be discussed further after calculations of effective cross-link density are presented.

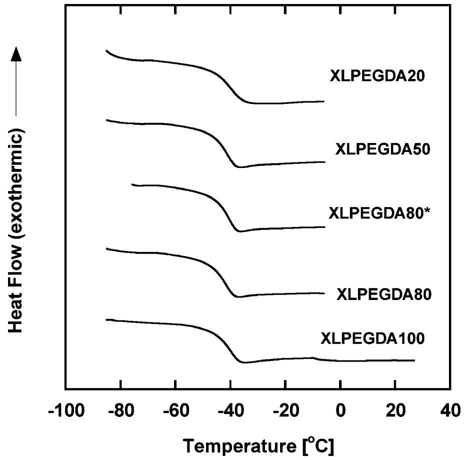


Figure 6. First scan differential scanning calorimetry thermograms of XLPEGDAs. All of the polymers were prepared using HCPK as the initiator, except XLPEGDA80*, which was prepared using Irgacure 2959 as the initiator. Additionally, the inhibitor was removed and N_2 was bubbled through the prepolymer solution of XLPEGDA80* to determine the influence of these variables on the properties of the final polymer. The thermograms have been displaced vertically for clarity.

Generally, high molecular weight PEO is highly crystalline.[54] However, the cross-linked polymers do not crystallize in the temperature range of the DSC experiments, which was between −90 and 30 °C. Because crystallization does not occur at temperatures below T_g, it can be concluded that PEO crystals are not present in the XLPEGDAs. A unit cell of a PEO crystal contains four PEO chains with a 7/2 helix structure, that is, each chain in the unit cell has seven repeating units that undergo two turns in the unit cell.[61] In XLPEGDA there are, on average, only seven ethylene oxide units per acrylate group, so the acrylate linkages appear to behave as defects introduced regularly into the PEO backbone of XLPEGDA. These defects apparently disrupt the efficient packing of seven consecutive ethylene oxide units as needed to form a crystal unit cell. Additionally, cross-linking may reduce the possibility that four PEO chains could be co-located with sufficient conformational freedom to arrange perfectly into a unit cell. Thus, PEO crystal formation is suppressed. For comparison, the unreacted cross-linker, PEGDA, does

Table 2. Physical Properties and Structural Characteristics of Cross-Linked Polymers

properties		XLPEGDA100	XLPEGDA80	XLPEGDA50	XLPEGDA20
d-spacing (Å)		4.3	4.2	4.3	4.2
$v_{1,r}$		1.0	0.771	0.459	0.175
ρ_p (g/cm^3)		1.183 ± 0.005	1.188 ± 0.005	1.181 ± 0.005	1.176 ± 0.005
FFV		0.118	0.117	0.119	0.124
T_g (°C)		−40	−42	−41	−42
$T_{\alpha,1\,\mathrm{Hz}}$ (°C)		−35	−34	−34	−34
$v_{1,s}$		0.618 ± 0.004	0.536 ± 0.001	0.424 ± 0.001	0.293 ± 0.007
Q (%)[a]		62	86	140	240
χ		0.656 ± 0.015	0.649 ± 0.014	0.638 ± 0.012	0.626 ± 0.004
M_c[b] (g/mol)	F−R	125	255	903	
	M1	125	195	304	
	M2	502	631	962	
	E′	155	228	486	
v_e[b] × 10^3 (mol/cm^3)	F−R	9.5	4.6	1.3	
	M1	9.5	6.1	3.9	
	M2	2.4	1.9	1.2	
	E′	7.6	5.2	2.4	

[a] $Q = (1 - v_{1,s})/v_{1,s} \times 100\%$. [b] F−R: Flory−Rehner theory as shown in eq 11 when $v_{1,r} = 1$; M1: the model based on eq 11; M2: the model based on eq 12; E′: the model based on eq 17.

crystallize; it has a melting temperature between 12 and 17 °C, according to Aldrich.

Cross-Link Density. Water swelling results are presented in Table 2. The dry sample weight after the second cycle of soaking in water was essentially the same as the dry weight after the first equilibration with water, suggesting no significant sol fraction removal during these steps (if, in fact, there was any sol present in the materials following polymerization and extraction). Except for XLPEGDA20, the water uptake was the same in both swelling experiments. For XLPEGDA20, the film swollen just after the polymerization appears opaque, and contains about 80 wt % (or 82 vol %) water. However, in the second swelling experiment, the film becomes transparent, and the water content of the film is only 71 vol %.[56] This phenomenon has been observed in other systems, and it is ascribed to phase separation during cross-linking because of excess diluent and/or excessive cross-linking.[62,63] In such samples, a macroporous structure is formed during polymerization, which leads to the opaque character and high water sorption in initial water uptake measurements.[56,63] However, this structure in a rubbery polymer collapses during the first drying, and the material becomes a nonporous film that sorbs less water upon subsequent soaking.[63] In all cases, the water uptake after the second hydration step was used to calculate cross-link density. In some glassy polymers, the formation of such a macroporous structure can be sustained during drying.[63] However, this effect has not been reported in rubbery polymers.

The calculation of cross-link density is very sensitive to the value of the Flory−Huggins interaction parameter (i.e., χ), which varies with temperature and polymer concentration.[64] In previous studies of poly(ethylene oxide) cross-linked either by acrylate groups,[41,65] peroxide,[66] γ radiation,[67−69] or other methods,[70] the χ value was taken to be the same as that of linear poly(ethylene oxide). Two χ values are used in the literature. The first value, 0.426, was determined by osmotic pressure measurements and found to be nearly constant for polymer volume fractions from 0.04 to 0.20.[69] The second χ value, 0.45, was measured by light scattering for a dilute solution of PEO in water.[71] However, these values might not be appropriate for the polymers prepared in this study because they have polymer volume fractions of 0.30−0.60 at equilibrium with water. The corresponding χ value would need to be obtained from linear PEO/water solutions at similar volume fractions. Furthermore, XLPEGDA contains about 18 wt % ethyl-ester linkages that might affect χ values. Another method for χ determination is based on the use of the stress−strain relationship to estimate cross-link density, and then combining this result with water swelling studies to determine χ.[38,72] The χ values obtained in this manner for the PEO/water system are about 0.50 at 25 °C for polymer volume fractions between 0 and 0.2.[38,72] The underlying assumption in this approach is that cross-link density calculated from mechanical properties and solvent swelling should be consistent. However, the inconsistency between these two approaches has been well documented, possibly because polymer chain disentanglement occurs during mechanical testing, but not in solvent swelling studies, according to some researchers.[27,39]

In a companion paper,[56] χ values in XLPEGDA have been determined carefully as a function of water content using water vapor sorption experiments. Here, we propose a simple method to estimate the χ values between XLPEGDAs and water. Flory noted that the relaxed state for a polymer network should be that just after polymerization from the prepolymer solution.[44] Therefore, XLPEGDA20 would be in the relaxed state at a water content of 80 wt % (or 82 vol %) if there was no phase separation. Because the maximum water uptake of nonporous XLPEGDA20 is only 71 vol % in the second swelling experiment (i.e., at thermodynamic equilibrium), it should be reasonable to assume that there is no elastic force present in this film when it is in equilibrium with water (i.e., after being dried and re-swollen in water). Thus, eqs 11 and 12 reduce to the Flory−Huggins model for liquid water swelling (i.e., $a = 1$) in this case

$$\chi = \frac{\ln a - \ln(1 - v_{1,s}) - v_{1,s}}{{v_{1,s}}^2} = \frac{-\ln(1 - v_{1,s}) - v_{1,s}}{{v_{1,s}}^2} \tag{19}$$

The χ value obtained by this analysis is 0.626 ± 0.004, which is somewhat higher than that discussed above for linear PEO. One possible reason for the difference could be the higher polymer content in XLPEGDA20 (0.29 volume fraction), compared with polymer volume fraction of 0.20 or less when χ values of 0.426 or 0.45 are reported. Also, XLPEGDA contains hydrophobic ethyl ester linkages that could reasonably act to increase the χ value for water in these samples relative to that in linear PEO.

In a study of water vapor sorption in XLPEGDA20, at a water vapor activity (i.e., a) of 0.94, the polymer volume fraction is 0.57.[56] Because of the lack of elastic force in this polymer at the swollen state, the Flory−Huggins model, eq 19, can be used to estimate the χ value of the polymer and H_2O at $v_{1,s}$ of 0.57. The χ value obtained is 0.652 ± 0.004. An empirical equation could be used to correlate χ with polymer volume fraction[40,45,64]

$$\chi = \chi_0 + \chi_1 v_{1,s} \tag{20}$$

where χ_0 and χ_1 are adjustable constants. Because we have two χ values of XLPEGDA20 and H_2O at two $v_{1,s}$ (i.e., 0.29 and 0.57), the values of χ_0 and χ_1 can be calculated and are 0.599 ± 0.009 and 0.0926 ± 0.020, respectively. Because all of the polymers have very similar chemical compositions, the χ values of the polymers and H_2O could be reasonably regarded as very similar. Therefore, the χ values for the other polymers can be calculated using eq 20; they are reported in Table 2, which also presents the effective cross-link density calculated from eqs 11 and 12. Additionally, cross-link density is estimated from dynamic mechanical testing based on eq 17. All of these models suggest that decreasing the cross-linker concentration in the prepolymer solutions decreases the effective cross-link density or increases the molecular weight between cross-links (M_c). For example, as water content in the prepolymer solution increases from 0 to 50 wt %, the effective cross-link density decreases by about 50%. The M_c value of XLPEGDA20 could not be calculated using eq 11 (M1) or 12 (M2), as discussed above. However, dynamic mechanical testing shows that XLPEGDA20 has the highest M_c value among the samples considered. It seems that eq 12 might be more suitable for this system. The ideal M_c is 370 g/mol according to eq 16.

However, M_c values from the modified Flory–Rehner theory (eq 11) are only 125 g/mol for XLPEGDA100, which corresponds to less than 3 ethylene oxide units. Instead, the M_c values (e.g., 502 g/mol) given by eq 12 appear to be more realistic. However, it should be noted that the formation of permanent entanglement in the polymers could reduce the M_c values.

The trend of decreasing υ_e with decreasing cross-linker content in the prepolymer solution has been well documented in other cross-linked polymer systems, such as 2-hydroxyethyl methacrylate polymerized with ethylene glycol dimethacrylate,[40] ethylene glycol monomethacrylate polymerized with ethylene glycol dimethacrylate,[47] acrylamide polymerized with *N,N′*-methylenebis(acrylamide),[27,28] and poly(acrylic acid) with poly(ethylene glycol) diacrylate.[25] For example, in copolymers of ethylene glycol monomethacrylate (EGMM) with ethylene glycol dimethacrylate (EGDM) at an EGDM concentration of 0.11×10^{-4} mol/(cm^3 polymer), as water content in the prepolymer solution increases from 20 to 65 vol %, the water uptake in the copolymer increases from 46 to 61 vol %, and the effective cross-link density measured from mechanical properties decreases from 0.91×10^{-3} to 0.24×10^{-3} mol/cm^3.[47] Such behavior is usually explained by the increase in cyclization (i.e., wasted cross-links) during gel formation at low cross-linker concentration in the prepolymer solution.[28] Therefore, even though the diluent content does not affect the cross-linker reaction conversion, the increase in ineffective cross-links at higher diluent content is significant enough to change the effective cross-link density.

Density and Glass Transition Temperature. The density can be used to estimate the fractional free volume as follows[73]

$$FFV = \frac{V - V_o}{V} \tag{21}$$

where V is the polymer specific volume at the temperature of interest, and V_o is the specific occupied volume at 0 K, which is estimated as 1.3 times the van der Waals volume.[73] The *FFV* values in Table 2 are very similar for all polymers because of the similar density and chemical composition. So, varying the cross-link density does not change the fractional free volume in these materials.

Interestingly, all of the XLPEGDAs exhibit similar glass transition temperatures from both DSC and dynamic mechanical measurements, indicating that T_g is independent of the effective cross-link density. It is customary to relate T_g to free volume at temperatures above T_g by the following equation[5]

$$FFV = FFV(T_g) + \alpha_r(T - T_g) \tag{22}$$

where *FFV* and *FFV*(T_g) are the fractional free volumes of the polymer at temperatures T and T_g, respectively, and α_r is thermal expansion coefficient for the free volume in the rubbery state. This approach has been employed to explain the change of T_g in cross-linked natural rubbers, for example.[74] By assuming that *FFV*(T_g) is independent of the cross-link density and α_r is constant, the experimental values of free volume measured for these polymers can be related to the observed (invariant) values of T_g. Thus, from the standpoint of free volume, T_g in these polymers would not be expected to change because the measured fractional free volume is essentially independent of the amount of water in the prepolymer.

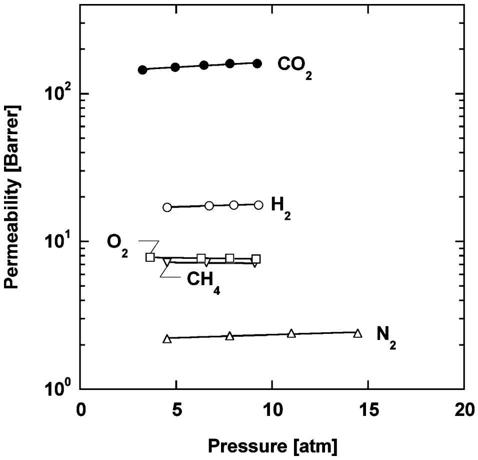


Figure 7. Pure gas permeability in XLPEGDA50 as a function of upstream pressure at 35 °C.

Gas Transport Properties. Figure 7 presents the permeability coefficients of four gases (i.e., N_2, CH_4, H_2, and CO_2) in XLPEGDA50 at 35 °C as a function of upstream pressure. The dependence of permeability on pressure follows typical behaviors of rubbery polymers.[75] For light gases such as N_2, H_2, and CH_4, permeability remains almost the same as pressure varies; for more condensable penetrants such as CO_2, permeability increases as pressure increases. Other XLPEGDAs exhibited similar behavior; however, the data are not shown for brevity.

To compare the inherent permeability of polymers to various gases, we used the following empirical equation to estimate the penetrant permeability at infinite dilution (i.e., upstream pressure, $p_2 = 0$), $P_{A,o}$[75]

$$P_A = P_{A,o}(1 + m\Delta p) = P_{A,o}(1 + mp_2) \tag{23}$$

where P_A is the permeability coefficient at an upstream pressure p_2, m is an adjustable constant, and Δp is the difference between the upstream and downstream pressure, $\Delta p = p_2 - p_1$. Because the downstream pressure, p_1, is much less than upstream pressure, p_2, Δp can be replaced by p_2. The results of this calculation are recorded in Table 3. There is no significant trend in gas permeability with effective cross-link density of the polymer networks. N_2 permeability remains almost the same, and the permeability of the other penetrants increases slightly with decreasing cross-link density. The selectivity of gases relative to N_2 is calculated and recorded in Table 3. It appears that selectivity increases slightly with decreasing cross-link density.

The gas permeability of these amorphous polymers are compared with those of semicrystalline poly(ethylene oxide) (S–C PEO) in Table 3. In general, S–C PEO exhibits permeability coefficients that are about 1 order of magnitude lower than that of the XLPEGDAs because of the highly crystalline nature of S–C PEO.[4] If one applies standard models to describe the effect of crystallinity on gas permeability, then the data for S–C PEO can be used to estimate the gas permeability in the amorphous regions of the semicrystalline polymer. These permeability values are reported as those corresponding to Am PEO in Table 3. Interestingly, the permeability of Am PEO is very close to that of the XLPEGDA samples. It is also noteworthy that the

Table 3. Pure Gas Permeability and Selectivity over N_2 at 35 °C and Infinite Dilution[a]

	$P_{A,o}$ (barrer)				$m \times 10^3$ (atm^{-1})				selectivity		
polymer	N_2	CH_4	H_2	CO_2	N_2	CH_4	H_2	CO_2	CH_4/N_2	H_2/N_2	CO_2/N_2
XLPEGDA100	2.2 ± 0.3	5.8 ± 0.6	15 ± 2	110 ± 10	−11 ± 15	−2 ± 14	6 ± 24	19 ± 13	2.6 ± 0.5	6.8 ± 1.3	50 ± 8
XLPEGDA80	2.1 ± 0.1	6.7 ± 0.4	15 ± 1	110 ± 7	3 ± 6	3 ± 9	1 ± 5	28 ± 9	3.1 ± 0.2	7.1 ± 0.6	52 ± 4
XLPEGDA50	2.1 ± 0.1	7.9 ± 0.9	16 ± 2	138 ± 14	10 ± 6	−4 ± 15	9 ± 17	19 ± 16	3.8 ± 0.5	7.6 ± 1.0	66 ± 7
XLPEGDA20	2.2 ± 0.2	7.3 ± 0.7	18 ± 2	145 ± 16	18 ± 10	8 ± 10	13 ± 11	24 ± 14	3.4 ± 0.4	8.6 ± 1.2	66 ± 9
S−C PEO	0.25 ± 0.02	0.60 ± 0.05	1.8 ± 0.1	12 ± 1					2.4 ± 0.3	7.2 ± 0.7	48 ± 6
Am PEO	3.0	7.1	21	143					2.4	7.2	48
XLPEGDMA		4.7 ± 0.7	14 ± 1	83 ± 14		8 ± 14	0	22 ± 16			

[a] Note: S−C PEO: semicrystalline poly(ethylene oxide); Am PEO: estimated amorphous phase poly(ethylene oxide); and XLPEGDMA: cross-linked poly(ethylene glycol) dimethacrylate.

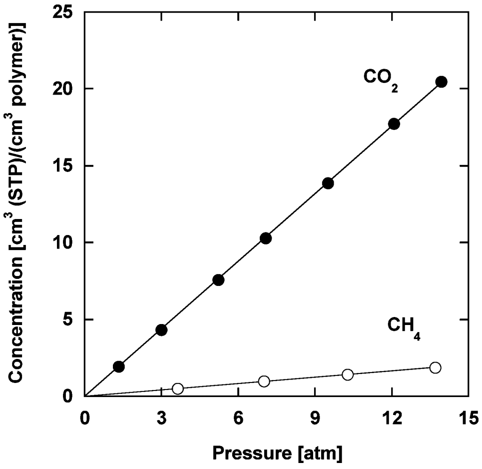


Figure 8. CO_2 and CH_4 sorption isotherms in XLPEGDA50 at 35 °C.

permeability selectivity of other gases over N_2 is quite similar in the XLPEGDAs and semicrystalline PEO. CO_2/N_2 selectivity has been characterized extensively in various PEO-containing materials, such as block copolymers of polyamide-*b*-PEO (PEBAX)[51] and cross-linked polymers prepared from poly(ethylene glycol) methacrylates.[76] These PEO-containing materials exhibit CO_2/N_2 selectivity values in the range of 50−70 at 35 °C,[5] which are consistent with the CO_2/N_2 selectivity values for the XLPEGDAs, as illustrated in Table 3. Gas permeability in XLPEGDAs is also compared with that in a cross-linked polymer (XLPEGDMA) prepared using poly(ethylene glycol) dimethacrylate (PEGDMA, $n = 14$). This polymer was prepared in a procedure similar to the XLPEGDAs, and no solvent was used. The PEGDMA molecular weight was about 750 g/mol according to the manufacturer and confirmed using NMR and FAB-MS. In general, XLPEGDMA exhibits lower gas permeability than the XLPEGDAs.

Considering the remarkable difference in water uptake among these polymers, it is interesting to observe so little change in gas permeability. To further understand the gas transport properties, we performed CH_4 and CO_2 sorption experiments. Figure 8 presents the sorption isotherms of CO_2 and CH_4 in XLPEGDA50 at 35 °C. For typical rubbery polymers, these isotherms would be linear for low sorbing gases, such as CH_4, and exhibit mild positive curvature for highly sorbing gases, such as CO_2. However, both isotherms are well described by straight lines (i.e., Henry's law) over the pressure range considered in this study, such that the gas solubility is given by the slope of the line that best describes the data and passes through the origin. The same behavior is observed for the other polymers in this series, and the results are presented in Table 4. All of the polymers exhibit similar solubility values for CO_2 and CH_4, in contrast to the significant variation in water solubility in these polymers (cf. Table 2). Therefore, cross-link density or elastic force does not play a role when the penetrant is sparingly soluble in the polymer. In this regard, cross-linking should not be important even for gas sorption at high pressure because the volume fraction of sorbed penetrant in these polymers is always low. For example, the volume fraction of CO_2 in XLPEGDA50 is only 0.038 at the highest CO_2 pressure considered (i.e., 14 atm). The volume fraction is calculated by

$$v_{2,s} = C\bar{V}_2/(22\,414 + C\bar{V}_2) \tag{24}$$

where $\bar{V}_2$, the partial molar volume of the penetrant, is taken to be 45 cm^3/mol for CO_2.[4] The observation is consistent with previous reports of gas sorption in cross-linked polymers, where gas sorption was shown to be independent of cross-link density.[18,76,77]

Diffusion coefficients of CO_2 and CH_4 at infinite dilution were calculated based on eq 2, and they are recorded in Table 4. It appears that the difference in cross-link density among these polymers does not have a significant impact on the gas diffusion coefficients. This conclusion is quite different from those of previous studies,[18,76] although the results are not necessarily in conflict. For example, one study regarding the effect of cross-link density on gas diffusion is based on copolymers prepared from tetra(ethylene glycol) dimethacrylate (TEGDM) and ethylacrylate (EA).[18] Table 5 presents some physical properties including CO_2 solubility and diffusivity at 60 °C in this series of copolymers. As EA content increased from 40% to 80%, CO_2 solubility remained almost unchanged but CO_2 diffusivity increased by about 300% while cross-link density decreased by about 60%. Such changes in effective cross-link density are very similar to the changes in the XLPEGDA polymers considered in this study. It would be tempting to conclude that the increased CO_2 diffusivity in copolymers of TEGDM and EA (TEGDM-*co*-EA) is due solely to the decrease in cross-link density, which was stated in the reference.[18] However, this may not be the case. The decrease in cross-link density in TEGDM-*co*-EA is accompanied by a significant decrease in glass transition temperature and density, which results partly from the copolymer effect, that is, the addition of EA increases the concentration of chain ends, which is well-known to decrease T_g and increase the fractional free volume, regardless of whether the system is cross-linked.[7] As such, the role of cross-link density on gas diffusion in TEGDM-*co*-EA is not unambiguous and needs to be examined carefully.

To assess the effect of chain end groups, we prepared a series of copolymers from PEGDA and PEGMEA (i.e.,

Table 4. CO_2 and CH_4 Solubility, Diffusivity, Solubility Selectivity, and Diffusivity Selectivity in XLPEGDAs at 35 °C and Infinite Dilution

polymer	S_A (cm^3(STP)/(cm^3 atm)) CH_4	CO_2	$D_A \times 10^7$ (cm^2/s) CH_4	CO_2	S_{CO_2}/S_{CH_4}	D_{CO_2}/D_{CH_4}
XLPEGDA100	0.11 ± 0.02	1.3 ± 0.1	4.0 ± 0.8	6.2 ± 0.6	12 ± 2	1.6 ± 0.4
XLPEGDA80	0.13 ± 0.02	1.4 ± 0.1	3.9 ± 0.6	6.1 ± 0.4	11 ± 2	1.6 ± 0.3
XLPEGDA50	0.14 ± 0.02	1.5 ± 0.1	4.3 ± 0.8	7.2 ± 0.7	10 ± 1	1.7 ± 0.4
XLPEGDA20	0.14 ± 0.02	1.4 ± 0.1	4.0 ± 0.7	7.6 ± 0.8	10 ± 1	1.9 ± 0.4

Table 5. Physical Properties and Structural Characteristics of Copolymers Prepared from Mixtures of Tetra(ethylene glycol) Dimethacrylate (TEGDM) and Ethylacrylate (EA)[18]

EA (mol %)	density (g/cm^3)	T_g (°C)	M_c (g/mol)	$\nu_e \times 10^3$ (mol/cm^3)	S_{CO_2} (cm^3(STP)/(cm^3 atm))	$D_{CO_2} \times 10^8$ (cm^2/s)
20	1.231		430	2.88		
40	1.226	79	470	2.63	1.03	3.6
60	1.217	65	520	2.36	0.84	5.9
80	1.192	2	750	1.60	0.94	15

PEGDA-*co*-PEGMEA) and compared them with the XLPEGDAs. These two series of polymers have very similar chemical composition, with approximately 82 wt % overall ethylene oxide content. Therefore, any difference in the physical properties of these two series of polymers should not be due to differences in chemical composition. As PEGMEA content in PEGDA-*co*-PEGMEA increases, cross-link density decreases and methoxy chain end-group concentration increases. Dynamic mechanical data for these copolymers (i.e., E' values at 25 °C) were used to estimate cross-link density based on eq 17, and the results are compared with those of the XLPEGDAs in Figure 9a. Interestingly, the dependence of cross-link density on PEGDA content in the prepolymer solutions in both series of polymers seems to follow the same trendline. In contrast, Figure 9b shows that CO_2 permeability at 35 °C and infinite dilution in these two series of polymers exhibit completely different trends. In PEGDA-*co*-PEGMEA, as PEGDA content decreases from 100% to 30 wt %, the CO_2 permeability increases by more than 200%, from 110 to 320 barrers. However, in the XLPEGDAs, as PEGDA content in the prepolymer solution decreases from 100% to 20%, CO_2 permeability changes only from 110 to 140 barrers. This distinct difference clearly suggests that cross-link density does not play an important role in the gas permeability of these materials. Instead, the concentration of methoxy chain end groups is the determining factor influencing gas permeability. The presence of methoxy chain end groups can increase the polymer fractional free volume, decrease the polymer glass transition temperature, and increase the polymer permeability to gases; the detailed analysis was presented elsewhere.[7] In general, the comparison of PEGDA-*co*-PEGMEA and the XLPEGDAs suggests that the effect of cross-link density per se on permeation properties has perhaps been overestimated. The widely referenced work on gas transport in TEGDM-*co*-EA is an example, as discussed above.[18]

The apparent overestimation of the effect of cross-link density also exists in the literature when evaluating changes in T_g.[50,78] For example, an empirical equation has been generalized for copolymers prepared from divinyl benzene (mole fraction = n) and styrene. The change in T_g with varying divinyl benzene content, ΔT_g, is described assuming that all of the vinyl groups in divinyl benzene participate in the cross-linking[78]

$$\Delta T_g = T_g(n) - T_g(n = 0) = 586n \qquad (25)$$

This equation successfully modeled the T_g change among the copolymers examined, and the authors concluded that the change was due solely to variations in the cross-link density.[78] However, an increase in divinyl benzene content would inevitably decrease the concentration of chain end (i.e., methyl) groups from the vinyl monomers and would result in an increase in T_g based upon free volume theory, as illustrated above. Equation 25 fails to discern the effect of cross-link density from other influential factors, such as chain end group concentration. The assumption that changes in T_g are due solely to differences in cross-link density needs to be reevaluated.

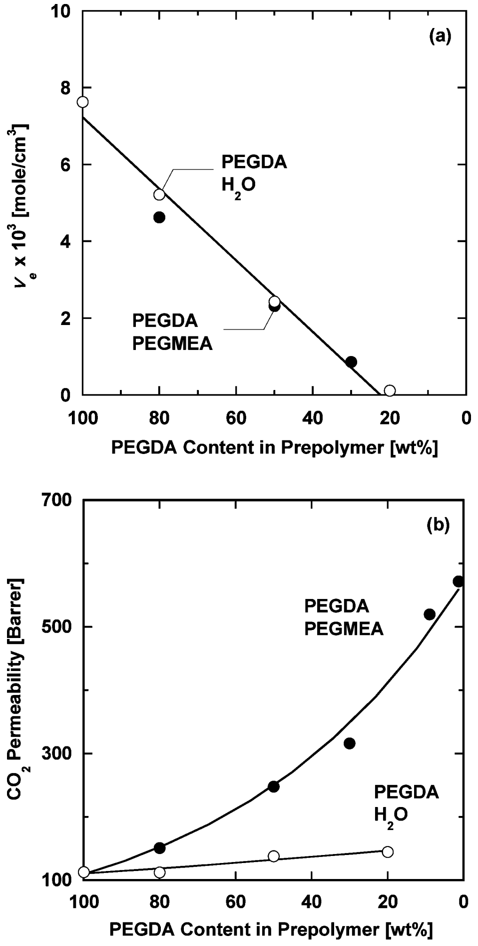


Figure 9. Effect of PEGDA content in the prepolymer solutions containing PEGDA/H_2O or PEGDA/PEGMEA on (a) effective cross-link density and (b) CO_2 infinite dilution permeability at 35 °C.

Table 6. Effect of Initiator and Inhibitor on the Physical Properties of XLPEGDA80

film	density (cm^3/g)	T_g (°C)	$v_{1,s}$	infinite dilution permeability (barrer)[a] N_2	CH_4	H_2	CO_2
PEGDA as received; HCPK initiator	1.188	−42	0.536	2.1	6.7	15	110
inhibitor-removed and N_2 bubbled PEGDA; Irgacure 2959 initiator	1.188	−40	0.531	2.0	6.6	16	113

[a] Gas permeability was measured at 35 °C.

Effect of Initiator and O_2 on Polymerization. The effect of initiator and the presence of O_2 during polymerization on the physical properties of XLPEGDA polymers was investigated. Two initiators were compared, hydrophobic HCPK and hydrophilic Irgacure 2959. O_2 is a well-known inhibitor for free radical polymerization.[55] In our preparation protocol, the prepolymer liquid is sandwiched between two quartz plates, which can prevent the ingress of O_2 into the system during polymerization. However, there is always some dissolved O_2 in the prepolymer solutions because they are prepared at ambient conditions. One way to remove O_2 is to bubble N_2 through the prepolymer solution.[79] Commercial PEGDA also contains about 100 ppm monomethyl ether hydroquinone (MEHQ),[80] which is an inhibitor to prevent PEGDA from polymerizing. MEHQ can be removed using inhibitor removers purchased from Aldrich. For this study, four films of XLPEGDA80 were prepared: (1) 0.1 wt % HCPK; (2) 0.1 wt % HCPK, O_2 and MEHQ removed; (3) 0.1 wt % Irgacure 2959; (4) 0.1 wt % Irgacure 2959, O_2 and MEHQ removed. FTIR spectra of all of these films are very similar and suggest that the conversion of acrylate groups is essentially complete in all cases. All four films exhibit nearly the same density and water swelling ratio, resulting in similar estimated fractional free volume and effective cross-link density values. Additionally, gas transport properties and T_g values were measured for Film 4 and compared with those for Film 1, as illustrated in Table 6. In general, there is no significant difference in any measured property due to the difference in initiators nor the presence of free radical inhibitors such as O_2 and MEHQ.

Conclusions

A series of cross-linked polymers was prepared using prepolymer solutions containing poly(ethylene glycol) diacrylate (PEGDA) and H_2O. By adjusting the water content of the prepolymer solutions, we could vary the cross-link density in the resulting polymers systematically while maintaining the same chemical composition; cross-link density decreased as water content in the prepolymer solution increased. FTIR showed essentially total disappearance of vinyl groups during polymerization, indicating complete reaction of the PEGDA. For the prepolymer solution containing 80 wt % H_2O, phase separation was observed during polymerization.

Gas solubility and permeability in these polymer networks were measured, and diffusivity was calculated. Interestingly, these properties were essentially independent of cross-link density, which is in contrast to the general notion that higher cross-link density leads to lower gas diffusivity and permeability. However, such behavior is consistent with the fact that many of the physical properties in these polymers, such as density, fractional free volume, glass transition temperature, and *d* spacing, were independent of cross-link density. On the basis of this result, it appears that cross-link density does not necessarily affect gas diffusion and permeation, the polymer glass transition temperature, nor the fractional free volume in network polymers, and ascribing changes in these properties to changes in cross-link density alone, as is commonly seen in the literature, should be done with great care. That is, the changes in gas diffusion and permeability often observed with cross-linked systems are more the result of T_g changes than cross-link density changes.

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