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Author(s)	Woo, Sun Young; Pandiyarajan, C. K.; Genzer, Jan
Citation	ACS applied polymer materials, 3(11), 5568-5577 https://doi.org/10.1021/acsapm.1c00890
Issue Date	2021-11-12
Doc URL	https://hdl.handle.net/2115/87252
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Type	journal article
File Information	ACS Appl. Polym. Mater. 3-11_5568-5577.pdf



Tuning the properties of surface-anchored polymer networks by varying the concentration of thermally-activated crosslinker, annealing time, and temperature in a one-pot reaction

Sun Young Woo¹, C. K. Pandiyarajan¹, and Jan Genzer^{1,2,*}

¹ Department of Chemical & Biomolecular Engineering
North Carolina State University
Raleigh, North Carolina-27695-7905, USA

² Global Station for Soft Matter
Global Institution for Collaborative Research and Education (GI-CoRE)
Hokkaido University
Hokkaido, 060-0808, Japan

ABSTRACT

We investigate the properties of surface-anchored polymer networks created via one-pot synthesis using thermally active 6-azidosulfonylhexyltriethoxy silane (6-ASHTES). 6-ASHTES is a bi-functional gelator that undergoes crosslinking and surface-anchoring reactions when annealed above 100°C. We employ a polyvinylpyrrolidone (PVP) with different molecular weights (10 - 1,300 kDa) as a model system to examine the effect of 6-ASHTES concentration, annealing time, and annealing temperatures on gel formation. A thin film of PVP/6-ASHTES mixture is deposited on a clean silicon wafer and annealed to form network layers. Spectroscopic ellipsometry measures the film thickness of the crosslinked layers from which the gel fraction and swelling ratio are determined. The gel fraction of PVP in the network can be “dialed in” by varying the annealing time, temperature, and concentration of 6-ASHTES in the PVP/6-ASHTES mixture. We use a simple Monte Carlo simulation model to describe crosslinking as a function of crosslinker concentration, reaction rate, reaction time, and polymer length. The trends obtained from the model simulations are in qualitative agreement with the experimental data.

* jgenzer@ncsu.edu

INTRODUCTION

Surface-anchored polymer networks have emerged as an exciting field of research due to their wide range of applications in coatings industries.¹⁻⁶ For example, neutral hydrophilic⁷ or zwitterionic^{8,9} polymer network films have gained enormous attention in anti-biofouling¹⁰⁻¹⁵ applications due to their swelling in aqueous media. Numerous methods have synthesized polymer brushes via “grafting to”¹⁶, “grafting from”¹⁷, and “grafting through”¹⁸ methods. Typically, surface-anchored polymer chains or polymer brushes bear reactive functional units¹⁹ and can be crosslinked with a di-functional molecule (di-thiols or di-hydro silanes), resulting in surface-anchored network layers.^{19,20} Alternatively, a precursor homopolymer or copolymer comprising cross-linkable functionality can be deposited onto a solid substrate, which is then exposed to UV light or annealing, resulting in network formation.²¹

Prucker *et al.* have recently revealed a wide range of UV- and thermally-active crosslinkers leading to the network formation via C-H insertion crosslinking (CHiC) reaction mechanism.²²⁻²⁴ Accordingly, a precursor copolymer comprising UV-active methacryloyloxybenzophenone (MABP) is deposited on the silicon or a glass substrate pre-coated with a monolayer of benzophenone containing silanes.²⁵ Upon UV irradiation, the benzophenone units present in the polymer and substrate are activated, triggering simultaneous crosslinking and surface-attachment reactions, thus creating surface-attached networks. Similar network layers can also be made by thermal means using styrene sulfonyl azides (SSAz).²⁶ Such techniques offer the ability to tune the network properties such as crosslink density, swelling, and elastic modulus of the networks in a gradient fashion. However, the method involves the complex multi-step synthesis of crosslinkers, surface-anchored, and copolymers, limiting their utility.

We recently developed a one-pot, one-step synthesis of surface-anchored network coatings using small bi-functional gelators (SBG) such as 6-azidosulfonylhexyltriethoxysilanes (6-ASHTES)²⁷ and 4-azidosulfonylphenethyltrimethoxysilane (4-ASPTMS).²⁸ The presence of sulfonylazide and alkoxy silanes enables the SBG's to undergo crosslinking and surface-attachment reactions simultaneously. These SBG's are commercially available and work with any common polymers and substrates as long as they contain C-H and/or -OH bonds in their structures. Our previous report explored the effect of temperature, concentrations of SBG's and molecular

structure of the polymers on gel formation. It allowed us to dial in a specific gel fraction of PVP/SBG's layer by adjusting temperature or concentration for a given time.

This work investigates the influence of the annealing time explicitly, the molecular weight of the polymer (*i.e.*, polyvinylpyrrolidone, PVP), and the ratio of 6-ASHTES to PVP on gel formation. We employ spectroscopic ellipsometry to measure the film thickness from which we calculate the gel fraction and swelling ratios. In addition, we use a simple Monte Carlo model to understand the gelation of PVP/6-ASHTES layers and compare it qualitatively with experimental results. We note a consistent gelation trend with simulation and experimental results and find that the molecular weight of the precursor polymer (*i.e.*, PVP) plays a critical role in the degree of crosslinking or gel fraction and has a significant effect on gel structure, *e.g.*, swelling.

EXPERIMENTAL SECTION

Materials. 6-Azidosulfonylhexyltriethoxysilane (6-ASHTES) was purchased from Gelest (Morrisville, PA). Polyvinylpyrrolidone (PVP) was acquired from Sigma-Aldrich (St. Louis, MO) and used without purification. All solvents were purchased from Fisher-Scientific (Pittsburgh, PA). Swelling experiments were performed using deionized (DI) water from the Milli-Q purification system with 10-15 M Ω ·cm product resistivity. Silicon wafer (orientation <100>, thickness 0.5 mm, and diameter 100 mm) was purchased from Silicon Valley Microelectronics (Santa Clara, CA).

Preparation of surface-anchored networks. Polymer solutions were prepared with various ratios of 6-ASHTES and PVP in methanol (the weight fraction of 6-ASHTES in the solutions ranged from 1.3 wt. % to 20 wt. %). First, a clean silicon wafer was exposed to ultraviolet/ozone (UVO) treatment for 5 mins. A layer of PVP/6-ASHTES was then deposited using a dip-coater (KSV NIMA single vessel dip coater) at a 50-100 mm/min speed. Subsequently, the sample was placed on a hot stage (FP82HT, Mettler Toledo) and annealed at 120-140°C allowing the layers to undergo crosslinking and surface attachment reactions. Limited PVP diffusion would occur under those conditions because the annealing occurred below the glass transition temperature of PVP (180°C),²⁹ although 6-ASHTES may act as a plasticizer. We note that 6-ASHTES/6-ASHTES reactions may also occur. However, we cannot distinguish those from 6-ASHTES/PVP reactions. After annealing, the sample was cooled to room temperature and then extracted in methanol for

two days, removing any unreacted or unbound materials from the silicon substrate. The initial dry thickness of the samples is ~ 60 -180 nm.

Calculating gel fraction. We used spectroscopic ellipsometry to measure film thickness, from which we calculated the gel fraction (P_{gel}) according to Equation 1.²⁸ The reflectivity scans were attained at a 70° angle of incidence (relative to the normal direction) in the spectral range of 400-800 nm in 60 steps (10 nm/step). These reflectivity scans were modeled using Fresnel formalism comprising a three-layer model in WVASE32 software (J.A. Woollam Co., USA). Layer 1: Si substrate layer 2: SiO₂ (1.5 nm thick); layer 3: polymer adlayer (Cauchy layer, $n = A_n + B_n/\lambda^2$, where n is the refractive index and A_n ($= 1.45$ -1.52) and B_n ($= 0.01 \mu\text{m}^2$) are fitting parameters).

The swelling ratio of surface-attached networks. The swelling of the network coatings was determined by measuring wet (or swollen) and dry (under ambient condition) layer thickness using spectroscopic ellipsometry equipped with a liquid cell. The sample containing PVP/6-ASHTES network film was immersed in a liquid cell filled with 100 ml of DI water and allowed to reach equilibrium (at least 10 min). All reflectivity scans were collected at a 70° (angle of incidence) from 400 nm to 800 nm spectral range. The swollen film thickness (d^{solvent}) was derived using an effective medium approximation (EMA).³⁰ The swelling ratio was then calculated from the ratio of swollen and dry thicknesses using Equation 2.

RESULTS AND DISCUSSION

We investigated the formation of surface-attached network coatings using a simple one-pot synthesis using PVP with various molecular weights mixed with 6-ASHTES. First, we dissolved PVP and 6-ASHTES in methanol in multiple ratios and deposited a thin layer (~ 100 nm) on a silicon wafer. Subsequently, the films were annealed at 120, 130, and 140°C at various times and extracted in methanol. **Figure S1** depicts morphologies of 6-ASHTES/PVP films with various 6-ASHTES wt% after annealing at 140°C for 5 hours and extraction in methanol. We described the crosslinking mechanism in our previous publication.²⁷ Upon annealing, the sulfonyl azide in 6-ASHTES is activated and undergoes a C-H insertion, crosslinking reaction with neighboring polymer chains. Simultaneously, the triethoxysilane head groups enable self-condensation and

condensation with the substrate hydroxy groups. Thus, the process produces surface-anchored polymer networks.

We monitored the kinetics of polymer film crosslinking on the substrate as a function of annealing time, annealing temperature, 6-ASHTES concentration, and molecular weight of PVP. We calculated the gel fraction (P_{gel}) from the change in film thickness before (d_0) and after (d) solvent extraction of the crosslinked polymer film:

$$P_{gel} = \frac{d}{d_0} \quad (1)$$

For instance, $P_{gel} = 1$ indicates a network where all precursor polymers on the substrate have been incorporated into the gel. The samples had an initial thickness of ~60 to 180 nm. We note that the initial thickness of the polymer network does not have a significant effect on gel formation.

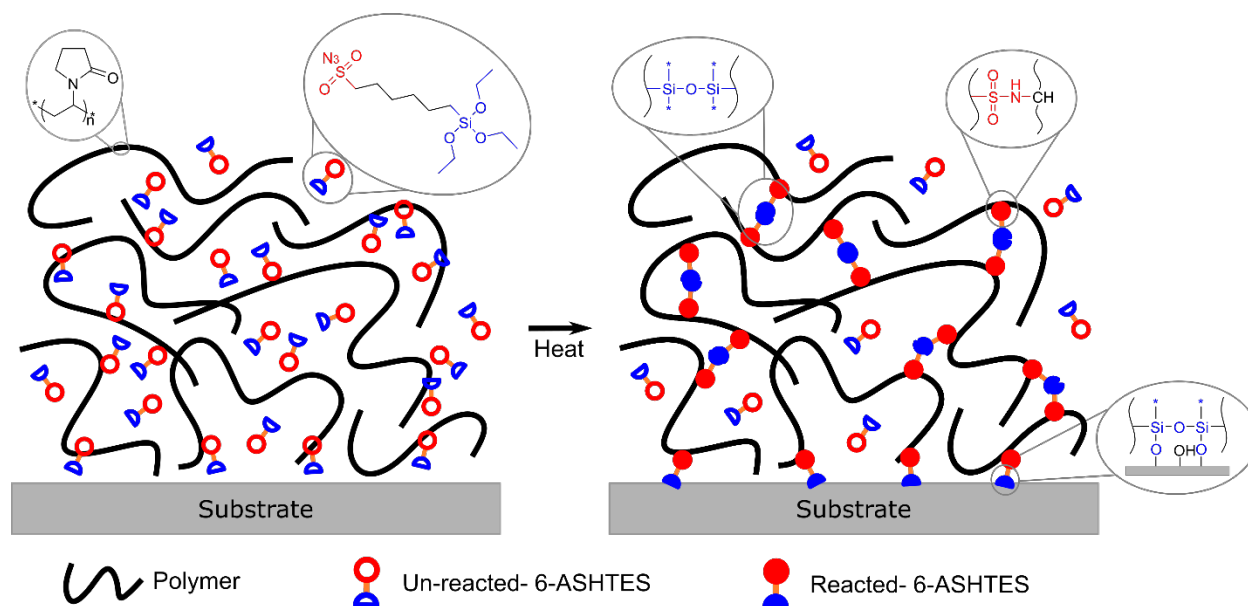


Figure 1. Generation of surface-attached PVP networks using 6-ASHTES, where the red circle and green semi-circle represent the sulfonylazide and triethoxy groups in 6-ASHTES. The open and solid symbols denote the reacted and unreacted 6-ASHTES molecules.

In **Figure 2a**, we plot the P_{gel} of polymer network as a function of annealing time at 140°C for the different molecular weights of PVP and fraction of 6-ASHTES in the gel. The molar ratio of PVP is 0.01 (open symbols) and 0.02 (closed symbols). The data shows that P_{gel} increases with increasing concentration of 6-ASHTES in the 6-ASHTES/PVP mixture and annealing time. Not

surprisingly, the crosslinking reaction proceeds faster and to greater extents with reducing the PVP molecular weight. In **Figure 2b**, we plot the P_{gel} as a function of the ratio of 6-ASHTES and VP repeat units concentration (*i.e.*, monomers). Consistently, **Figure 2b** indicates that P_{gel} depends on the concentration of 6-ASHTES at the given time. In other words, one can prepare gels with the same value of P_{gel} by adjusting the amount of 6-ASHTES in the 6-ASHTES/PVP solution and annealing time. In previous studies,²⁷ P_{gel} of the PVP network rapidly increased by raising the annealing temperature from 100°C to 140°C.

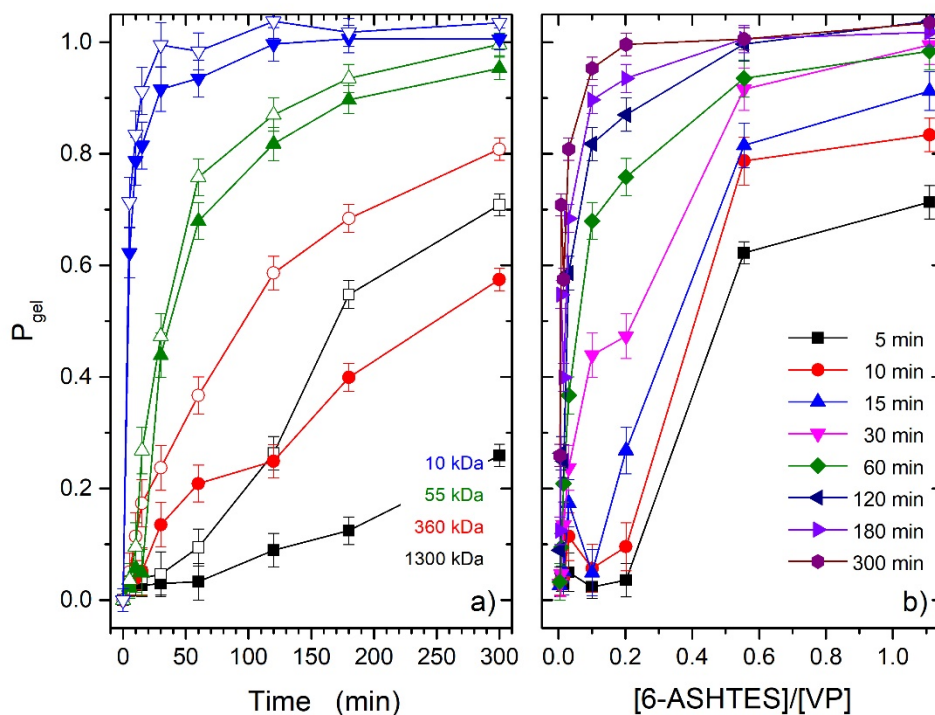


Figure 2. a) Gel fraction (P_{gel}) of PVP networks as a function of various annealing times. The gels formed by crosslinking PVP having different molecular weights with 6-ASHTES at 140°C. The open and closed symbols correspond to 0.01 and 0.02 mole fractions of PVP in 6-ASHTES/PVP films, respectively. b) Gel fraction of PVP network from left figure replotted as a function of the molar ratio of the 6-ASHTES and the total monomer for different annealing times. $[\]$ indicates a molar concentration of a given species.

It means that P_{gel} is controlled primarily by the thermal activation of the sulfonyl azide groups. These results are consistent with the current data, as shown in **Figure 3**. We replot the data of **Figure 2b** as a function of the logarithm of 6-ASHTES and VP repeat unit ratio and shift the data horizontally by using a shift factor (F^*) to produce a master plot presented in **Figure 3c**. In the abscissa, in **Figure 3** $\log([\text{activated 6-ASHTES}]/[\text{VP}]) = \log([6\text{-ASHTES}]/[\text{VP}]) + \log(F^*)$.

We repeated the above experiments with temperatures 120°C and 130°C (**Figure 3a, 3b**). The 6-ASHTES crosslinks slowly at 120°C compared with the higher temperature at the given time and form gels with low P_{gel} . The P_{gel} of the surface-anchored network can be adjusted by varying the concentration of the 6-ASHTES of polymer/crosslinker mixture, annealing time, and annealing temperature independently.

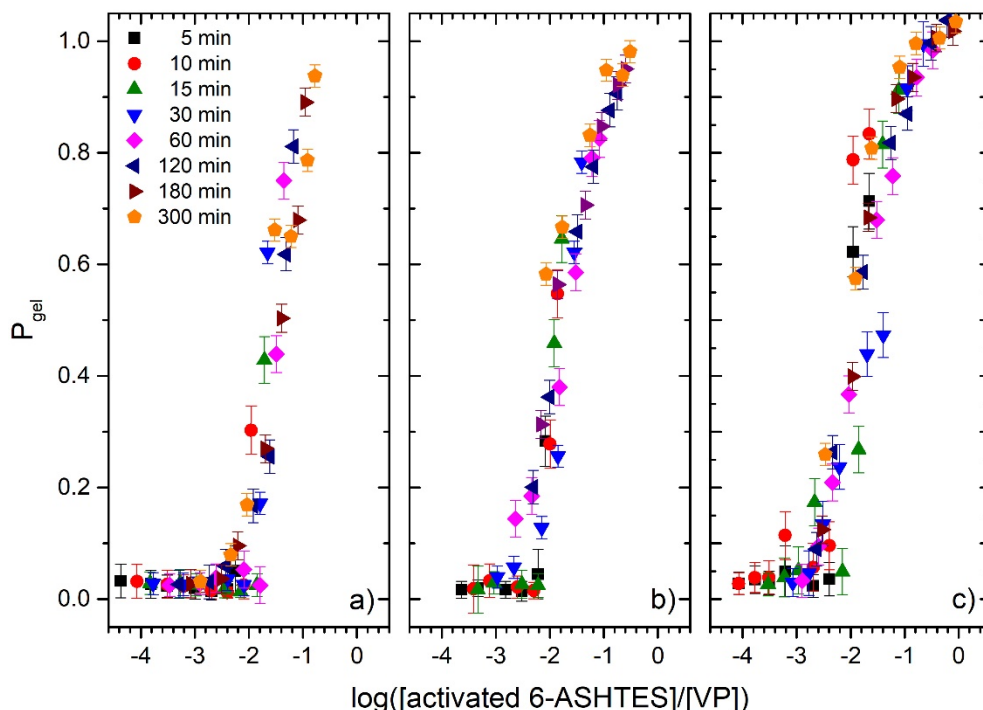


Figure 3. Gel fraction (P_{gel}) in PVP networks as a function of the logarithm of the molar ratio of the 6-ASHTES and VP units. The gels were formed by crosslinking PVP of different molecular weights and weight fractions of 6-ASHTES in PVP/6-ASHTES films for various annealing times at a) 120°C, b) 130°C, and c) 140°C. The different colors represent different gelation times. [] indicates a molar concentration of a given species.

The shift factors, F^* , needed to produce the master curves in **Figure 3** are plotted in **Figure 4a**. The shift factor F^* represents the fraction of reacted 6-ASHTES groups during the crosslinking reaction. We also used ATR-FTIR to monitor the disappearance of the sulfonyl azide group inside the polymer film and calculated the fraction of activated 6-ASHTES groups. We integrated the peak corresponding to the azide group (at vibration frequencies 2120-2160 cm^{-1}) and normalized the peak relative to the signal obtained from the same mixture before annealing (see SI section for details). The results for f^* were obtained from the FTIR analysis (see SI and ref. 25) are plotted

in **Figure 4b**. The shifted data (**Figure 4a**) and the fraction of the activated azide (**Figure 4b**) were both fitted to first-order reaction kinetics that describes the concentration of 6-ASHTES before and after the reaction (see **Equation S3** in the SI).

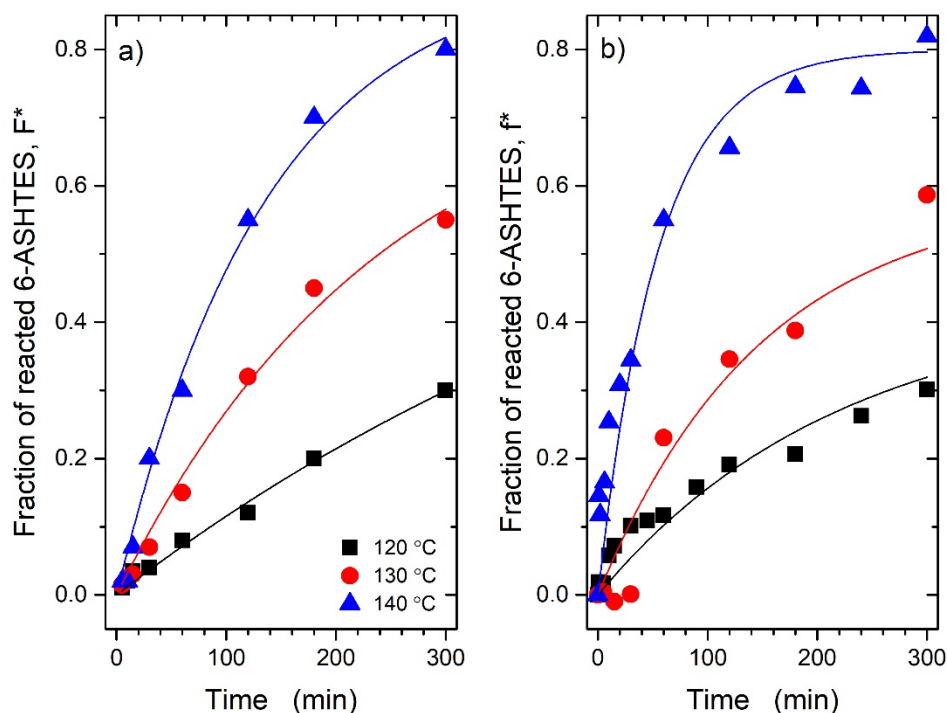


Figure 4. The fraction of reacted 6-ASHTES (F^* and f^*) as a function of annealing time at 120°C (black), 130°C (red), and 140°C (blue). The weight fraction of 6-ASHTES was 10%. a) F^* was obtained by shifting the data sets in Figure 2b horizontally. b) f^* was obtained from ATR-FTIR spectra collected from PVP/6-ASHTES samples. The concentration of [activated 6-ASHTES] = F^* [6-ASHTES] or [activated 6-ASHTES] = f^* [6-ASHTES].

Using the ATR-FTIR data, we monitored the consumption of the sulfonyl azide groups. In the kinetic model (see SI), we assumed that this process translated directly to the formation of sulfonyl amide linkers. We admit that this may not be the case. We do not have means of monitoring the concentration of sulfonyl amide bonds. We also assumed that the siloxane bonds crosslinked faster than the reaction involving sulfonyl groups. We provided evidence of this in our previous paper.²⁷ However, the high reactivity of siloxane bonds may result in clusters involving more than just two 6-ASHTES molecules. Hence, the fraction of reacted 6-ASHTES may not represent the actual density of the crosslinking points. The fractions of reacted 6-ASHTES obtained by shifting the P_{gel} data sets (*cf.* F^* in **Figure 4b**) and those extracted from FTIR-ATR

analysis (*cf.* f^* in **Figure 4b**) exhibit a similar dependence on annealing time and activation energy (*cf.* **Figure S2**, **Table S1**). This observation gives us confidence that the number of silane molecules in the condensed clusters does not vary among experiments.

We made samples containing 10 wt% of 6-ASHTES with various PVP molecular weights to investigate the surface-attached network swelling behavior in deionized water. All samples were annealed between 5 min and 1440 min at 140°C. The gel fractions of samples are plotted in **Figure 5a**. P_{gel} of the two highest PVP molecular weights (*i.e.*, 360 and 1,300 kDa) increase considerably with increasing time and reach a plateau, indicating final crosslinking. However, 10 and 55 kDa PVP layers do not show a plateau in 1440 min annealing time.

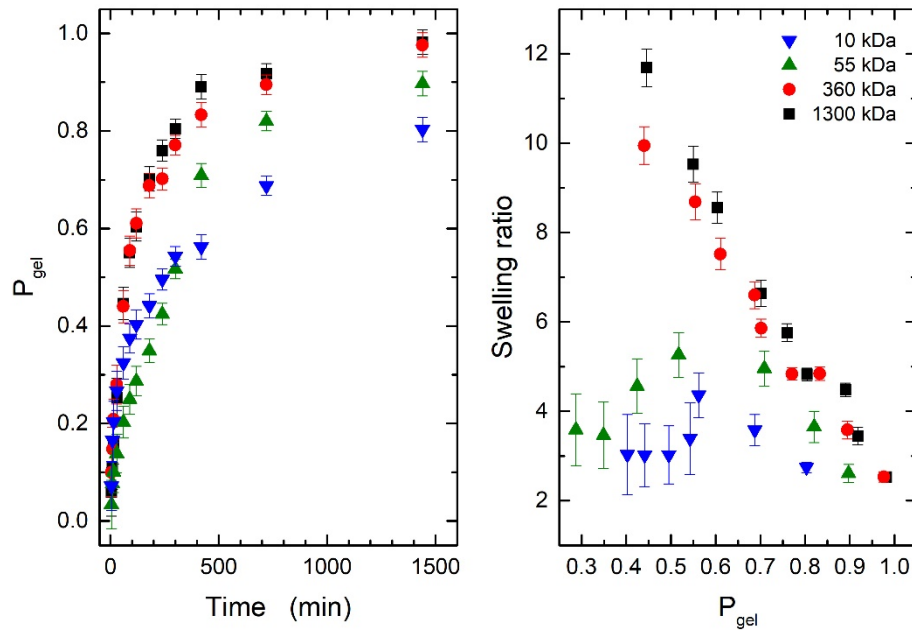


Figure 5. Gel fraction of PVP networks as a function of time (left) and swelling ratio (right) of PVP network as a function of P_{gel} . All samples contained 10 wt% 6-ASHTES and were crosslinked by annealing at 140°C.

We define the swelling ratio, α^{solvent} of the polymer network by Equation (2):

$$\alpha^{\text{solvent}} = \frac{d^{\text{solvent}}}{d} \quad (2)$$

d is the dry thickness of PVP, and d^{solvent} is the thickness of the same polymer layer after swelling in water. The swelling ratio increases with decreasing P_{gel} , as expected (*cf.* **Figure 5b**). At high P_{gel} ($>0.7 \sim 0.8$), the swelling ratio has the same dependence on P_{gel} for all molecular weights

increasing with decreasing gel fraction. However, at low P_{gel} (<0.7), the swelling ratio of 10 and 55 kDa samples deviates from this trend. We further support this trend by plotting P_{gel} (cf. **Figure 6**) and the swelling ratio (cf. **Figure 7**) from gels prepared by crosslinking PVP of various molecular weights with 6-ASHTES with concentrations ranging from 5 to 20 wt%.

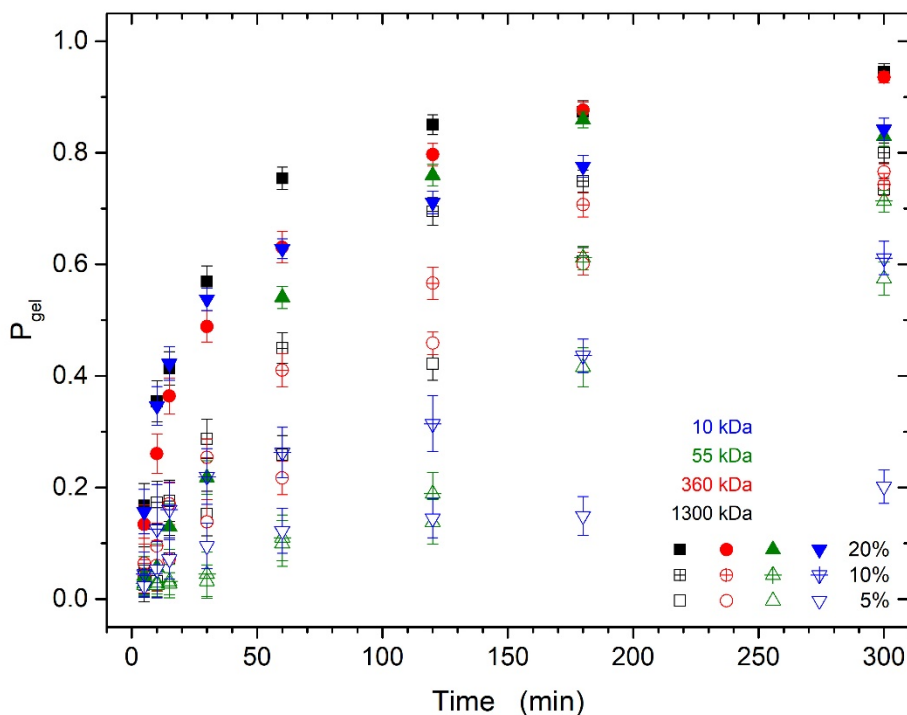


Figure 6. Gel fraction (P_{gel}) of PVP networks prepared by reacting PVP of various molecular weights and PVP/6-ASHTES concentrations at 140°C at multiple times. The different colors represent different molecular weights of PVP. Open, crossed, and closed symbols correspond to the weight percent of 6-ASHTES in the 6-ASHTES/PVP mixture ranging from 5 to 20%.

Figure 6 plots the corresponding P_{gel} dependence on crosslinking time. Gels made of higher molecular weight PVP (360 and 1300 kDa) and higher weight fraction of 6-ASHTES exhibit a steady increase in P_{gel} independent of the molecular weight of PVP. However, gels prepared from low molecular weight PVP (10 and 55 kDa) and lower weight fraction of 6-ASHTES feature a larger scatter in P_{gel} as a function of annealing time. **Figure 7** displays the swelling ratios of the gels formed by crosslinking PVP of various molecular weights with 6-ASHTES with concentrations ranging from 5 to 20 wt%. As in **Figure 5b**, the swelling ratio for PVP polymers with high molecular weight and high concentration of 6-ASHTES increases steadily with decreasing the P_{gel} . However, the swelling ratio in gels prepared from lower molecular weight

PVP or lower concentration of 6-ASHTES does not increase considerably with decreasing P_{gel} . Later in the paper, we present the results of a simple computer simulation model, which demonstrates that P_{gel} increases with reaction time and attains the same value for polymers crosslinked with the same weight fraction of the crosslinker, regardless of the molecular weight of the polymer. We attribute the behavior described in the data in **Figure 6** and **Figure 7** to imperfect gels with heterogeneities in their structure. Ellipsometry measures the average thickness of the swollen film. It cannot detect local inhomogeneities in the film structure. Therefore, one needs to consider measuring both P_{gel} and the swelling ratio to characterize the gel structure fully. We conclude that shorter polymers cannot form homogeneous, uniformly crosslinked networks.

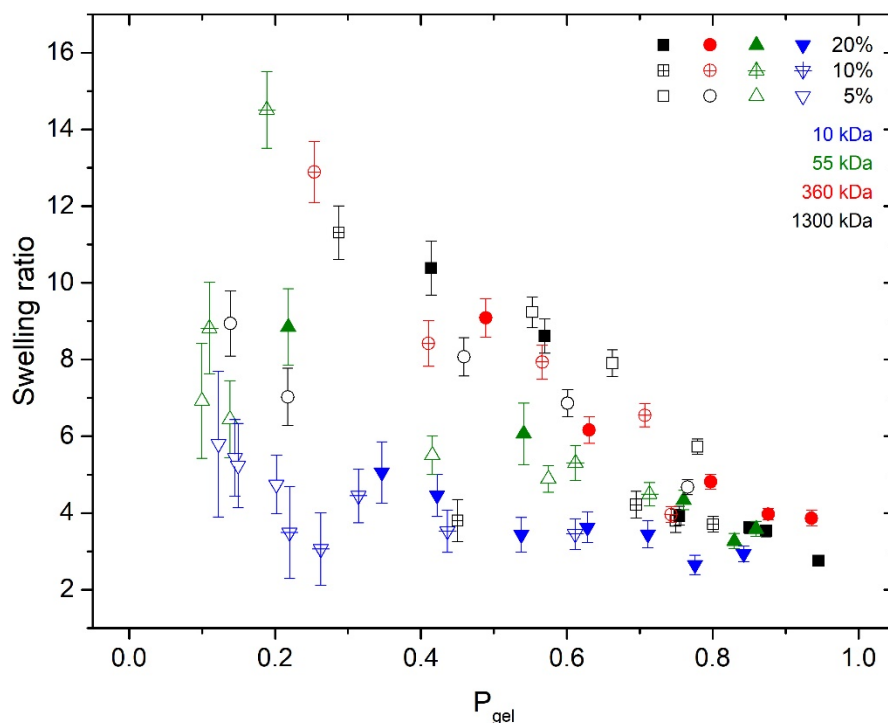


Figure 7. The swelling ratio of PVP networks prepared by reacting PVP of various molecular weights and PVP/6-ASHTES concentrations at 140°C at different times. The different colors represent different molecular weights of PVP. Open, crossed, and closed symbols correspond to the weight percent of 6-ASHTES in the 6-ASHTES/PVP mixture ranging from 5 to 20%.

We developed a simple Monte Carlo kinetic model that describes crosslinking in our system (see SI for more information). We use the model to confirm the scaling we employed in interpreting the experimental data and provide more insight into the effect of the molecular weight of polymers on gel properties. We provide the details of the model in the SI document.

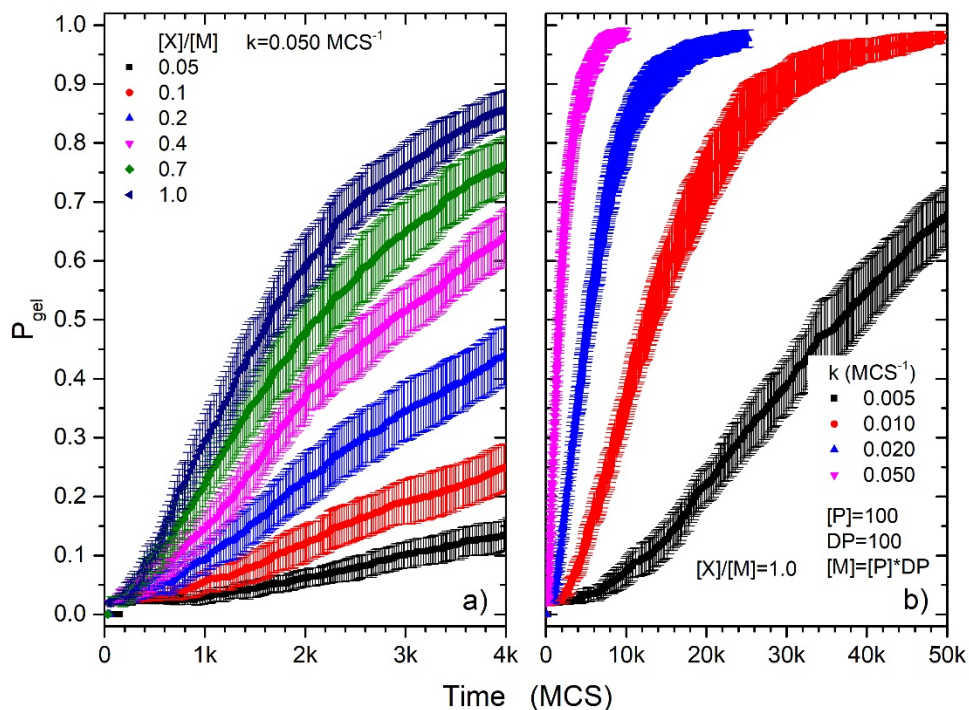


Figure 8. Gel fraction of gels (P_{gel}) as a function of Monte Carlo steps (MCS), equivalent to time. a) P_{gel} for various ratios of crosslinker ([X]) and monomer ([M]) and constant reaction rate (k), number of polymers, and degree of polymerization. P_{gel} increases with increasing $[X]/[M]$. b) P_{gel} for values of k and constant $[X]/[M]$ and a constant number of polymer and degree of polymerization. P_{gel} increases with increasing k .

In **Figure 8**, we plot the gel fraction (P_{gel}) as a function of the MCS while varying the ratio of the concentration of the crosslinker ([X]) to monomer (**Figure 8a**) and the rate constant (k) while keeping the concentration of monomers ([M]) the same. Overall, P_{gel} increases with increasing the $[X]/[M]$ ratio and increasing k . Increasing the reaction time (MCS in computer simulations) further promotes the two trends. We have verified that these trends hold for other $[X]/[M]$ ratios and a different number of polymers and different degrees of polymerizations. The results are in qualitative agreement with the trends in our experimental data, which reveal that P_{gel} increases with increasing the crosslinker concentration in polymer/crosslinker mixture and increasing the reaction temperature. In the simulations and experimental data, we detect that P_{gel} follows a sigmoidal trend with time (or MCS). It initially increases gradually, then the rate of P_{gel} rise increases, and finally, it levels off at longer times (or MCS).

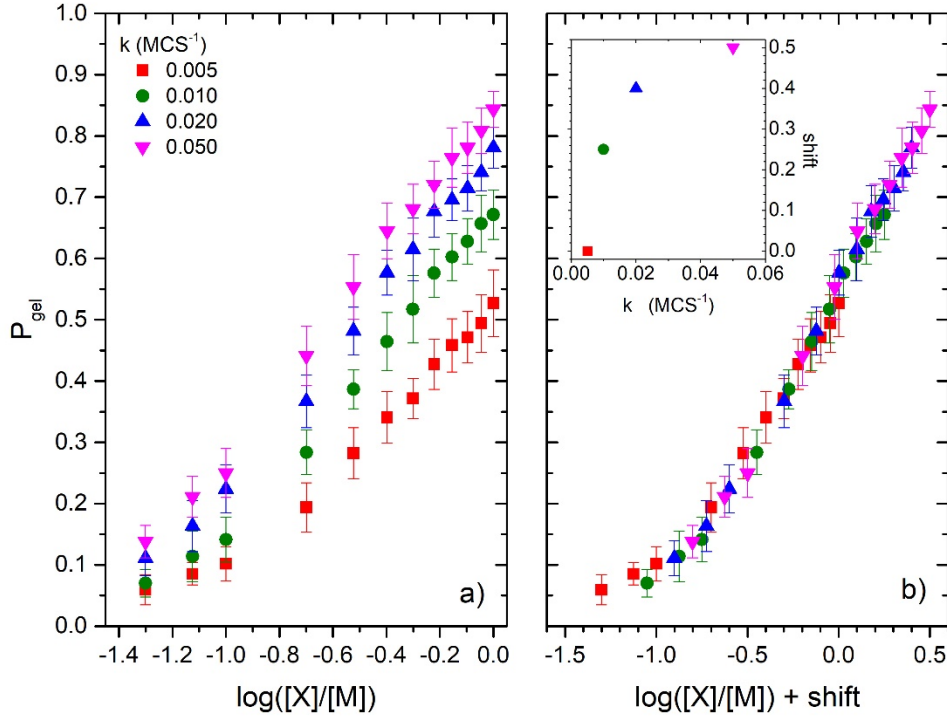


Figure 9. a) Gel fraction of gels (P_{gel}) as a function of $\log([X]/[M])$ for various reaction rates (k) and a fixed number of polymers and degree of polymerization after 200 Monte Carlo steps. b) Same data as in **Figure 9a**), except that the abscissa has been replotted as $\log([X]/[M]) + \text{shift}$. The values of the shift factor as a function of k are displayed in the inset to **Figure 9b**.

In **Figure 9a**, we plot P_{gel} as a function of the crosslinker concentration $[X]$ and the monomer concentrations $[M]$ for different temperatures (*i.e.*, k values) after 200 MCS. We plot P_{gel} as a function of the log of $[X]/[M]$. Increasing the temperature (or k) gives rise to a higher value of P_{gel} for a given value of $\log([X]/[M])$. This behavior is understandable as the crosslinking rate and P_{gel} increase with increasing temperature (or k). **Figure 9b** plots the data from **Figure 9a** by shifting the abscissa by a given amount (*i.e.*, shift) to produce master plots. We plot the “shift” values as a function of k in the inset to **Figure 9b**. The physical meaning of “shift” can be understood as a correction to the number of crosslinkers activated to participate in crosslinking. Hence, $\log([X]/[M]) + \text{shift}$ can be written as $\log(10^{\text{shift}}[X]/[M])$, where $10^{\text{shift}}[X]$ is the number of activated crosslinkers.

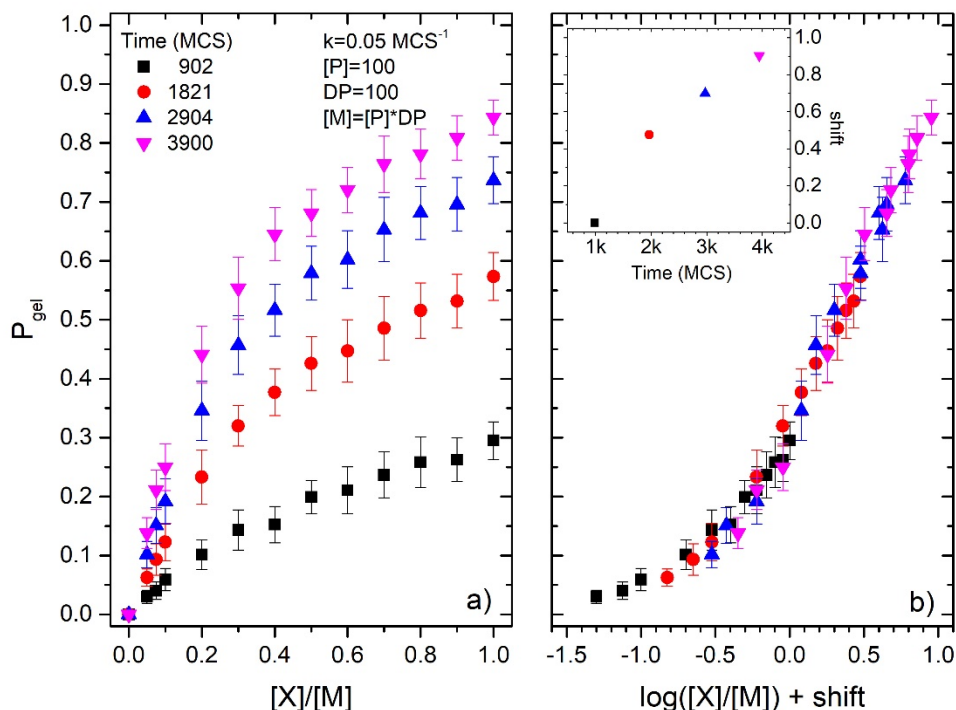


Figure 10. a) Gel fraction of gels (P_{gel}) as a function of $\log([X]/[M])$ for various reaction MCS for a fixed value of k and a fixed number of polymers and degree of polymerization (DP) after 200 MCS. b) Same data as in **Figure 10a**, except that the abscissa has been replotted as $\log([X]/[M]) + \text{shift}$. The values of the shift factor as a function of MCS are displayed in the inset to **Figure 10b**.

Figure 10a plots P_{gel} as a function of the $[X]/[M]$ ratio from different MCS while keeping k , the number of polymers, and their degree of polymerization constant. P_{gel} increases with increasing $[X]/[M]$ and increasing the polymerization time (or MCS). This behavior is consistent for all numbers of polymers and degrees of polymerization. **Figure 10b** plots the data from **Figure 10a** by shifting the abscissa by a given amount (*i.e.*, shift) to produce master plots. The values of “shift” as a function of MCS are plotted in the inset to **Figure 10b**. The physical meaning of “shift” can be understood as a correction to the number of crosslinkers activated to participate in crosslinking. As noted previously, $\log([X]/[M]) + \text{shift}$ can be written as $\log(10^{\text{shift}}[X]/[M])$, where $10^{\text{shift}}[X]$ denotes the number of activated crosslinkers.

Finally, in **Figure 11** we plot P_{gel} as a function $\log([X]/[M]) + \text{shift}$ for crosslinking reaction performed with polymers having three different degrees of polymerization (25, 50, 100) at three different temperatures (or k), equal to: a) $k=0.01$, b) $k=0.02$, and c) $k=0.05$. The values of “shift” as a function of MCS are plotted in the insets to **Figures 11a-Figure 11c**. The physical meaning

of “shift” remains the same; *i.e.*, $\log([X]/[M]) + \text{shift}$ can be written as $\log(10^{\text{shift}}[X]/[M])$, where $10^{\text{shift}}[X]$ is the number of activated crosslinkers.

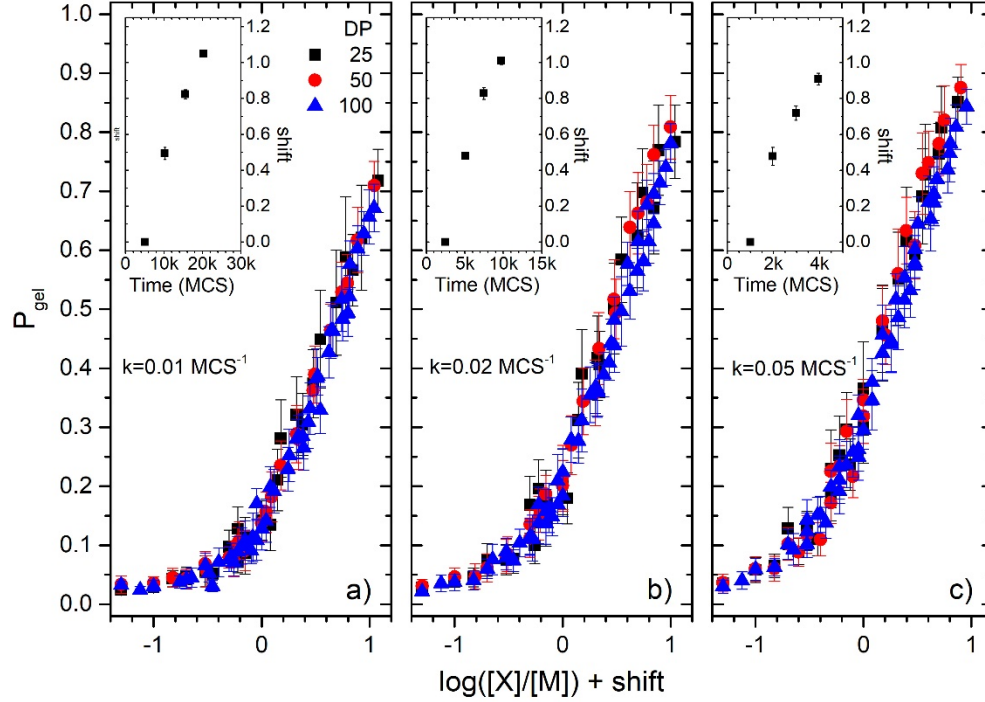


Figure 11. a) Gel fraction of gels (P_{gel}) as a function of $\log([X]/[M]) + \text{shift}$ for various degrees of polymerization (DP) and three different rate constants: a) $k=0.01$, b) $k=0.02$, and c) $k=0.05$. The values of the shift factor as a function of MCS are displayed in the insets to **Figure 11a-Figure 11c**.

Finally, we return to the discussion of gel properties as a function of the molecular weight of the parent polymers. In **Figure 12**, we plot P_{gel} as a function of reaction time for $k=0.01 \text{ MCS}^{-1}$ and polymers having different molecular weights. We plot the data for three $[X]/[M]$ ratios; the complete data set featuring four different k values and six $[X]/[M]$ values are shown in the SI information section. The data in **Figure 12** show for a given $[X]/[M]$ ratio, P_{gel} exhibits universal dependence on time. To connect $[n_6\text{-ASHTES}]/[\text{VP}]$ to the weight fraction of 6-ASHTES, we write:

$$w_X = \frac{m_X}{m_X + m_M} = \frac{[X]M_X}{[X]M_X + [M]M_M} = \frac{\frac{[X]}{[M]}M_X}{\frac{[X]}{[M]}M_X + M_M} \quad (3)$$

After some algebra, Eq. (3) reduces to:

$$\frac{[X]}{[M]} = \frac{M_M}{M_X} \left(\frac{w_X}{1 - w_X} \right) \quad (4)$$

$$\frac{[6-ASHTES]}{[VP]} = \frac{M_{VP}}{M_{6-ASHTES}} \left(\frac{w_{6-ASHTES}}{1-w_{6-ASHTES}} \right) = 0.314 \left(\frac{w_{6-ASHTES}}{1-w_{6-ASHTES}} \right) \quad (5)$$

We have previously determined that P_{gel} depends on the ratio of crosslinker and the number of crosslinkable units in the polymer. Regardless of the molecular weight, gels formed at a given weight fraction of the crosslinker should exhibit the same P_{gel} . The data shown in **Figures 5-7** show that networks formed with a low molecular weight/low crosslinker density are imperfect.

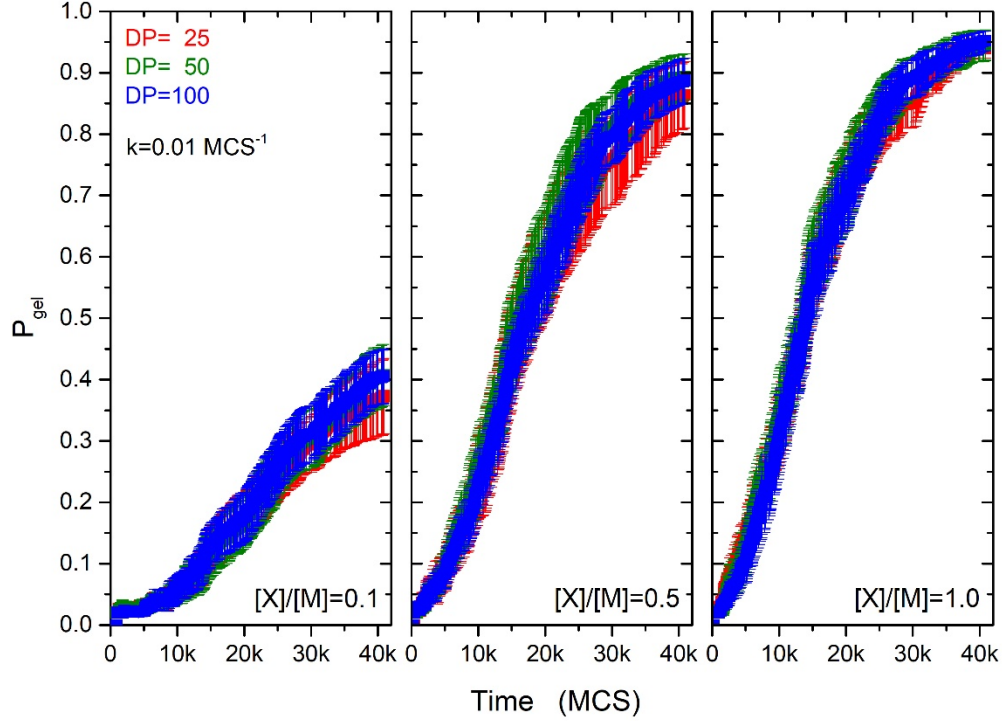


Figure 12. a) Gel fraction of gels (P_{gel}) as a function of time at various degrees of polymerization (DP). We used $k=0.01$, and varied the crosslinker/monomer ratio $[X]/[M]$ varied from 0.1, to 0.5, to 1.0.

We recognize that the model has limitations. It assumes that the polymers exist as rigid rods resting without motion on a 2D lattice. We further consider that the crosslinkers featured bi-functional crosslinkers that link two neighboring chains. Despite these limitations, our results confirm that a specific value of P_{gel} can be “dialed in” by varying the concentration of the crosslinker (X), the annealing time (or MCS), and the annealing temperature (k) independently. We confirmed that a unique value of P_{gel} could be “dialed in” at a given $\log([X]/[M])$ + shift. The physical meaning of the shift factor is $10^{\text{shift}[X]}$; it represents the number of activated crosslinkers.

We established the dependence of the shift factor on temperature, crosslinker concentration, and annealing time. Overall the simulation studies confirm the findings in our experimental studies.

CONCLUSION

In this work, we study the kinetics of formation of the surface-anchored poly(vinylpyrrolidone) (PVP) networks using a thermally active bi-functional crosslinker 6-azidosulfonylhexyl triethoxysilane (6-ASHTES), at various 6-ASHTES concentrations, PVP molecular weight, annealing temperature, and annealing time. 6-ASHTES also acts as an anchoring agent that immobilizes the crosslinked PVP on the surface (although some PVP may attach to the substrate via H-bonds). We evaluate the gel fraction (P_{gel}), i.e., the amount of polymer left on the substrate after crosslinking relative to the initial amount, and swelling ratio of the substrate-anchored gel in water using spectroscopic ellipsometry. We show that P_{gel} data collected from samples with various polymer: crosslinker ratios annealed at different temperatures and times can be collapsed onto universal master plots. This concentration-time-temperature superposition reveals that P_{gel} in the gel can be adjusted by tailoring the amounts of polymer and crosslinker, the reaction conditions, the annealing temperature, and the annealing time. We evaluate the activation energy for crosslinking from the shifting factor of the master curves and the disappearance of sulfonyl azide as monitored by ATR-FTIR. We use swelling experiments to study the gel structure. While gels made of high molecular weight PVP form uniform networks, gels prepared from low molecular weight PVP and low concentrations of 6-ASHTES are heterogeneous. We also developed a simple Monte Carlo model that simulates the formation of crosslinked networks as a function of the concentration of the crosslinking agent, the molecular weight of the “polymer,” and temperature. The simulation data can be collapsed on similar master curves as the experimental data. While we only report experimental data for PVP in this work, we have evidence that networks can be formed from other polymers as long as they contain C-H bonds. This result opens up possibilities for creating functional polymeric networks using commodity polymers without specialized chemical synthesis. This work may open the door to many potential applications, including (but not limited to) functional coatings, selective membranes, and many others.

Associated content

Supporting information

The supporting information is available free of charge on the ACS Publications website.

Image analysis of 6-ASHTES/PVP films. ATR-FTIR analysis of reaction kinetics. Monte Carlo Model of crosslinking reaction. (PDF)

Acknowledgments

This work was supported by a grant NSF DMR-1809453. Partial support from the S. Frank and Doris Culberson funds is appreciated. The authors thank Dr. Erik Santiso (NC State University) for fruitful discussions.

Conflict of Interest

The authors declare no conflict of interest.

Author Information

Corresponding author

*E-mail: jgenzer@ncsu.edu

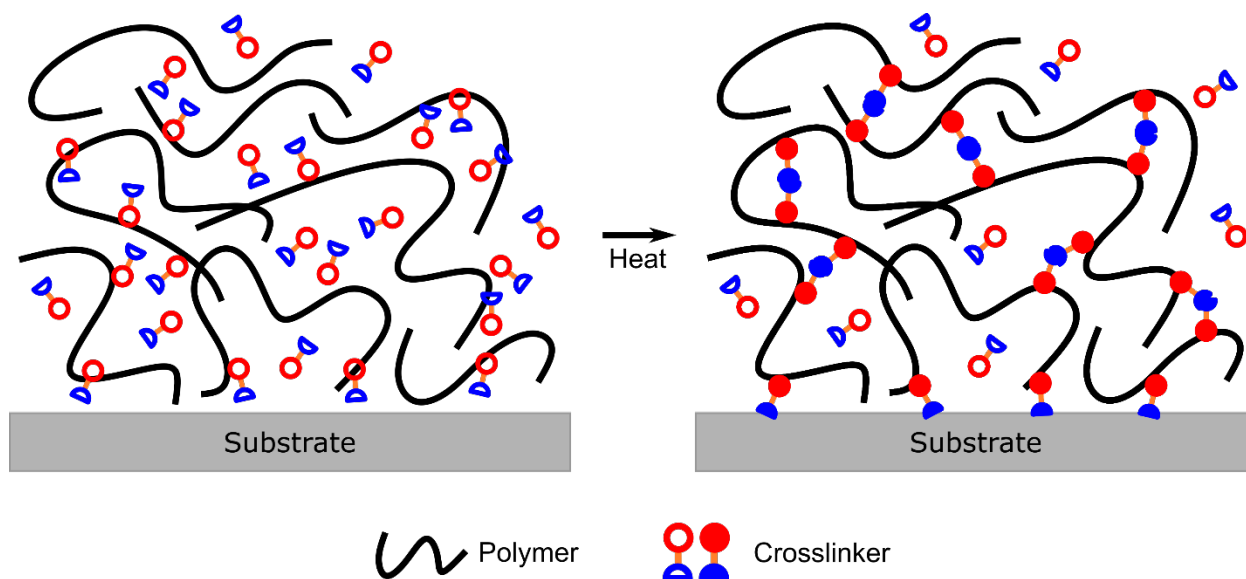
ORCID: Jan Genzer: 0000-0002-1633-238X

ORCID: C.K. Pandiyarajan: 0000-0002-8954-9141

Keywords

Hydrogel, substrate-anchored network, gel fraction, one-pot reaction, poly(vinylpyrrolidone), sulfonyl azide, 6-ASHTES.

TOC figure



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