Supporting information

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

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Morphology of PVP/6-ASHTES films

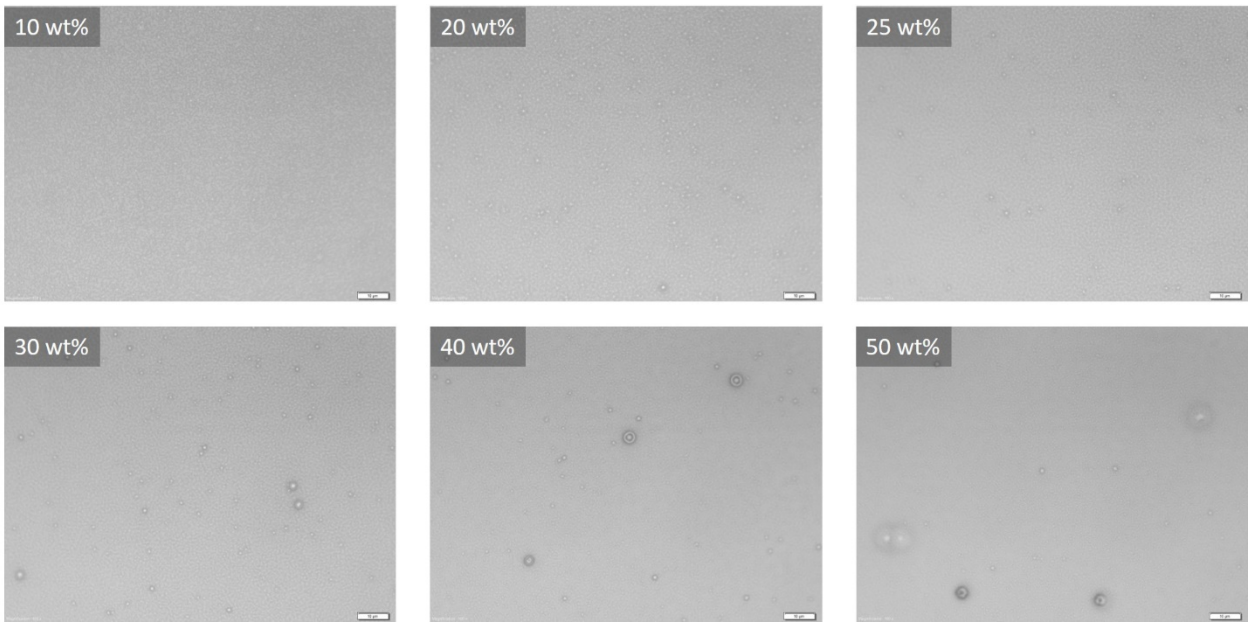

Figure S1. Optical micrographs of PVP/6-ASHTES films with various wt% of 6-ASHTES after annealing at 140°C for 5 hrs and extraction with water/methanol. The scale bar (lower right corner) in each image is 10 μm.

FTIR analysis of reaction kinetics

We used ATR-FTIR spectroscopy to monitor the disappearance of the azide group inside the polymer film. We associated this with the reaction of the sulfonyl azide moiety with the polymer. **Figure S2** plots the variation of the sulfonyl azide group vibration as a function of time at 140°C. We integrate the area under the peak at 2120-2160 cm^{-1} in the FTIR spectra and determine the fraction of activated 6-ASHTES groups for all annealing times and temperatures (*cf.* **Figure 4b**).

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We have fitted the FTIR data to a simple model relating the concentration of 6-ASHTES before ($n_{6\text{-ASHTES},0}$) and after ($n_{6\text{-ASHTES}}$) the crosslinking reaction.

$$n_{6-ASHTES} = n_{6-ASHTES,0} * e^{-k*t} \quad \text{(S1)}$$

In Equation S1 $n_{6\text{-ASHTES},0}$ is the initial concentration of 6-ASHTES before activation, k is a rate constant, and t is reaction time. Thus, Equation S1 can be rewritten in terms of a fraction of inactivated 6-ASHTES ($f_{6\text{-ASHTES}}$) as:

$$f = \frac{n_{6-ASHTES}}{n_{6-ASHTES,0}} = e^{-k*t} \quad \text{(S2)}$$

It then follows that the fraction of activated 6-ASHTES, f*, is:

$$f^* = 1 - f = 1 - e^{-k*t} \quad \text{(S3)}$$

From the fit, we can determine the rate constant (k) for each temperature.

$$k = A * e^{-\frac{E_A}{RT}} \quad \text{(S4)}$$

In Equation S4, A is a pre-exponential factor, E_A is the activation energy, R is the universal gas constant, and T is the absolute temperature.

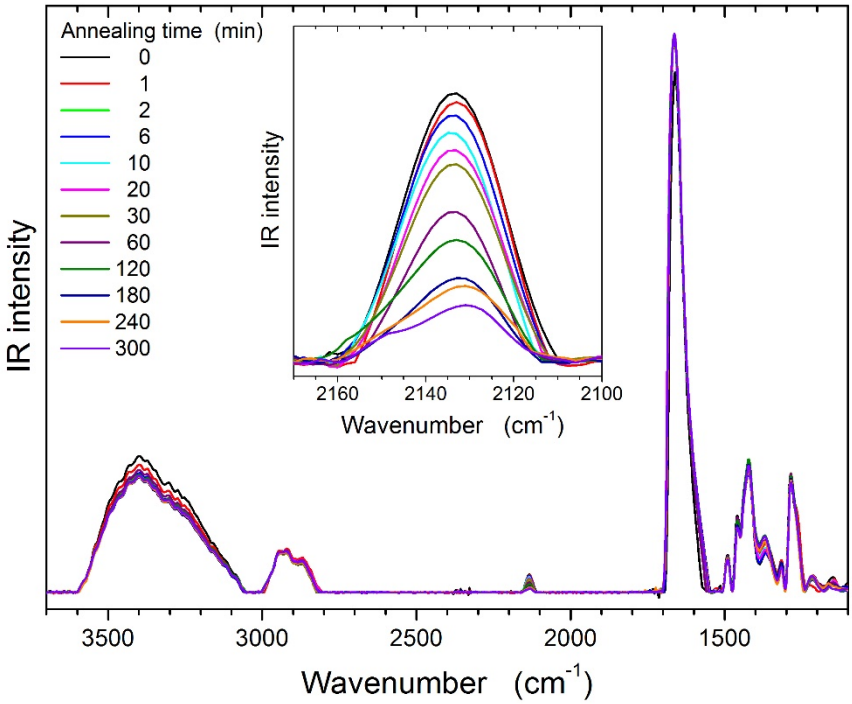

Figure S2. ATR-FTIR spectra collected from PVP/10% 6-ASHTES mixture annealed at 140°C for various times.

Figure S3 shows the fitting results from the Arrhenius dependence between k and absolute temperature (T) obtained by shifting master curve data (**Figure 4a**) and FTIR analysis (**Figure 4b**). **Table S1** lists E_A and A values estimated by fitting data from **Figure S3**. The results are consistent between the two data sets and in line with previous E_A reports obtained from studies using sulfonyl azide molecules.

Table S1. Parameters of the Arrhenius plot displayed in **Figure S3**.

	Master curve data	FTIR data
A (s^{-1})	$2.69*10^{11}$	$1.12*10^{10}$
E_A (kJ/mol)	107.07	93.62

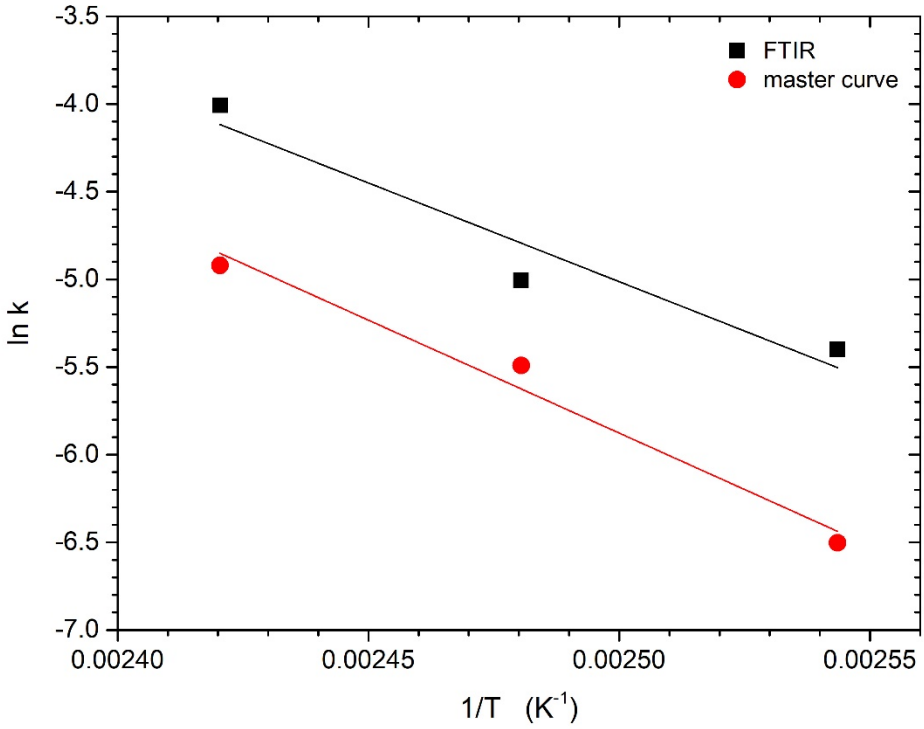

Figure S3. Arrhenius plot displaying the natural logarithm of a reaction rate constant versus the reciprocal value of the absolute temperature.

Monte Carlo model of crosslinking

We have built a simple Monte Carlo-based model that mimics (in the crudest possible way) crosslinking of polymers during the one-pot reaction. The model confirms that the molar (*i.e.*, number) ratio of the crosslinker relative to the number of "monomers" in "polymers" to be

crosslinked is the leading parameter that defines the gel fraction (P_{gel}) in the system. This notion is true regardless of the size of the "polymer."

The "polymers" are represented by "rigid sticks" of a certain length; we call it a "degree of polymerization" (DP). They remain rigid sticks with the same spatial orientation during the crosslinking process (*i.e.*, they do not change conformations like real polymers). The "polymers" are placed onto a 2D grid comprising a certain number of columns (COL) and rows (ROW). The product COL*ROW determines the total number of polymers; *e.g.*, 10 columns and 10 rows will yield 100 polymers. The example shown in **Figure S4** features COL=5, ROW=5, and DP=5. The total number of "monomer" segments in the system is then COL*ROW*DP. Each segment of each polymer is amendable towards crosslinking. Because of the 2D nature of the lattice, the crosslinking is limited only to segments of other chains that are present only in certain allowed locations. To illustrate, consider, for instance, the case below, depicting COL=5, ROW=5, and DP=5. Each segment of the original polymer is shown as "*" in **Figure S4**. The "polymer" rank number increases from the upper left to the lower right corner (horizontal direction). The first and the last segment of each "polymer" can crosslink with the last and first segments of their neighbors on the left or right of the given chain, respectively. For instance, the first segment of "polymer" #2 can react with the last segment of "polymer" #1. Concurrently, the last segment of "polymer" #2 can react with the first segment of "polymer" #3. The first segments in "polymers" #1, #6, #11, #16, and #20 (*i.e.*, first COL) are not reactive in the "horizontal direction," although they can react "vertically," *vide infra*). Similarly, the last segments in "polymers" in column 5 (*i.e.*, "polymers" #5, #10, #15, #20, and #25) can only react vertically, as will be described next. The middle segments (*i.e.*, segments 2 through DP-1) can react with the neighbors "above" (*i.e.*, direction "North") or "below" (*i.e.*, direction "South"), as long as those neighbors are available. For instance, segments 2-4 in "polymer" #6 (ROW=2, COL=1) can react with the corresponding segments 2-4 in "polymer" #1 (ROW=1, COL=1) or segments 2-4 in "polymer" #11 (ROW=3, COL=1). However, segments 2-4 in "polymer" #1 (ROW=1, COL=1) can only react with segments 2-4 in "polymer" #6 (ROW=2, COL=1). Each segment can only form a single crosslink. Thus, when segment no 3 in "polymer" #7 reacts with segment 3 in "polymer" #2, it cannot react with segment 3 in "polymer" #12. Similarly, when segment no 3 in "polymer" #7 reacts with segment 3 in "polymer" #12, it cannot react further with segment 3 in "polymer" #2.

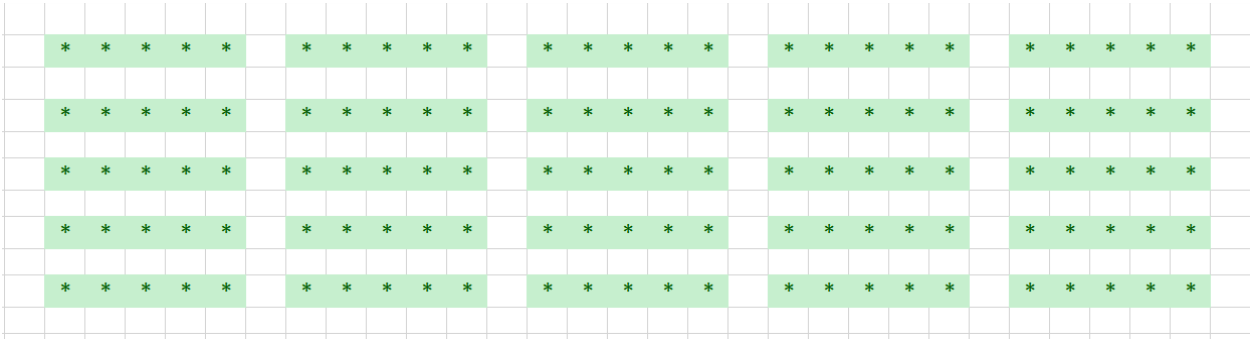

Figure S4. An example of a system with COL=5, ROW=5, and DP=5.

The reactions are governed via a Monte Carlo simulation procedure. This routine (implemented in VBA for Excel) works as follows. First, a "polymer" is selected randomly from the set of all "polymers." Then, another randomly generated number selects a segment in the chosen "polymer" that may undergo reaction. If the segment has already reacted, the process starts

from the beginning and continues until an un-reacted segment is found. If the chosen unreacted segment is the first or last segment of the "polymer," a random number decides whether to react with the "polymer" located "North"/"South" or "West"/"East" of the current location (depending on the type of the segment and "polymer" availability). If the segment of the other chain is free to react, the two segments are further scrutinized whether a reaction takes place (*vide infra*). If so, they are marked as "reacted" with a crosslink no. #. For segments 2 to DP-1, a random number decides whether reaction with the segment of the same rank in a polymer "North" or "South" (there is no "West" of "East" direction) of the current chain takes place (depending on availability). When two neighboring "polymer" segments are available for reaction, two checks are made before the actual crosslinking proceeds. Those involve the effect of temperature (*i.e.*, reaction rate) and the amount of crosslinker (relative to the overall number of segments available for crosslinking).

To include a finite probability of the crosslinking reaction as a function of temperature, we assume that the reaction is of the first order. The likelihood of forming a new crosslink will be proportional to the reaction probability of the crosslinker given by Equation (S5)

$$x = x_0(1 - e^{-k*MCS}) \tag{S5}$$

In Equation (S5), k is the reaction rate, x is the concentration of the reacted x-link units, x_0 is the initial concentration of the crosslinked units, MCS is the "time" in Monte Carlo steps. See discussion below. The k follows the typical Arrhenius dependence on absolute temperature (T) via:

$$k = A * e^{-\frac{E_A}{k_B T}} \tag{S6}$$

We do not know the hopping prefactor (A) and the activation energy (E_A) values. We use k as a measure of the reaction temperature and employ it as an input parameter. We assume that the crosslinking reaction takes place with a certain probability equal to $(1 - e^{-k*MCS})$. Technically, this is accomplished by generating a random number RND ($\in$(0,1]) and letting the reaction take place when $RND < (1 - e^{-k*MCS})$. Although the crosslinking reaction requires two reactions (*i.e.*, one with each monomer), we assume that the reaction probability is the same for both reactions. It is an oversimplification. Yet, given the many assumptions, we have made in this simplistic model, this postulation is reasonable.

After we determine whether the reaction can take place based on temperature (or k), we further scrutinize whether the reaction is allowed based on the current concentration of the crosslinking molecules [X] and the available (*i.e.*, unreacted) monomers in the polymers [M]. To this end, we evaluate a crosslinking ratio (CR) as:

$$CR = \frac{[X]}{[X]+[M]} = \left(1 + \frac{[M]}{[X]}\right)^{-1} \tag{S7}$$

We then generate a random number RND and compare it to CR. If RND<CR, the crosslinking reaction is allowed to proceed. If the reaction takes place, we decrease [M] by two and [X] by one and continue the process until we either have no crosslinks or free monomers left or we reach the pre-determined number of MC steps (200-500 in most cases). We define the gel fraction as a ratio of crosslinked polymers relative to the total number of polymers. At low gel

fractions, the polymers may form individual domains. At higher gel fractions, the crosslinked domains will create a percolating network. We repeat the procedure 30 times and average the results to obtain sufficient statistics.

We assign a corresponding time to each MC Step according to the kinetic Monte Carlo scheme:

$$\tau_1 = -\frac{ln(RND)}{k} \tag{S8}$$

$$\tau_j = \tau_{j-1} - \frac{ln(RND)}{k} \qquad j > 2 \tag{S9}$$

Figure S5 shows the time dependence in the Monte Carlo model on the number of Monte Carlo steps.[1,2]

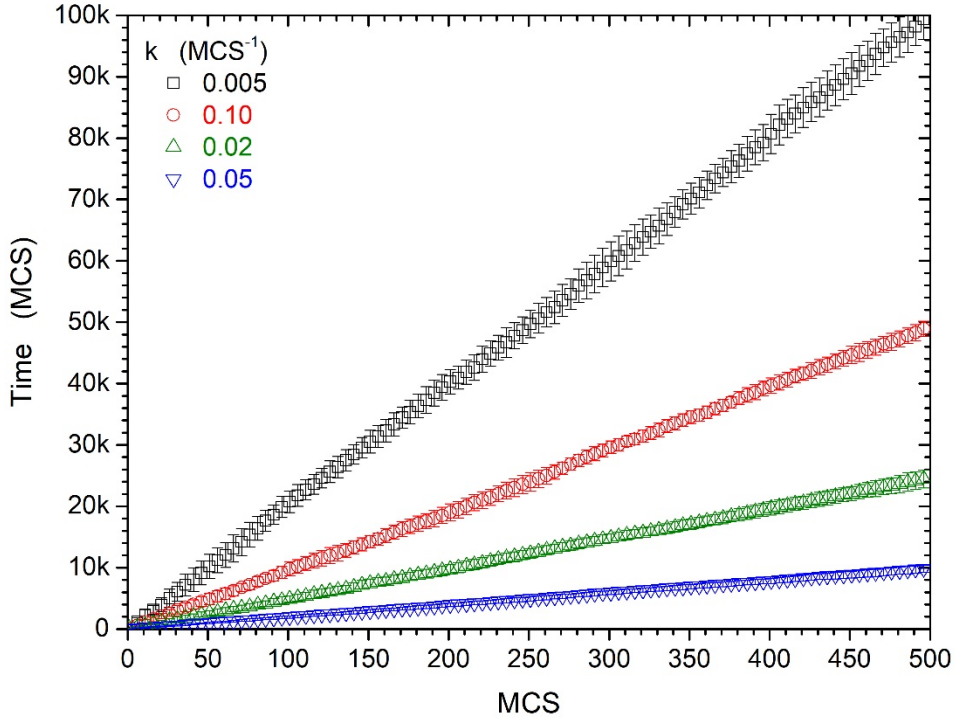

Figure S5. "Time" vs. Monte Carlo Steps in computer simulations. The slope is k^{-1}, as expected from Equations S8 and S9.

Figure S6 depicts a snapshot of a crosslinked system involving 5*5 = 25 chains, each having a DP=5. A total of 20 crosslinkers produced a system comprising 20 crosslinked and 5 free chains. By definition, a gel is a system of chains crosslinked so that they form a percolation pathway. Examining the crosslinked polymers below reveals that the crosslinked polymers do not form a single percolated network. Instead, we detect the formation of: 2 networks comprising 2 chains each, 1 network comprising 3 chains, 1 network comprising 6 chains, and 1 network made of 7 chains. For the sake of simplicity, we take any crosslinked polymer (*i.e.*, whether a part of the larger percolation cluster or linking only a few chains) to be part of the network/gel. We define a gel fraction as the fraction of the original "polymers," in which at least one segment was attached

to another “polymer.” While not a perfect network, these crosslinked regions, as illustrated below, provide a representative picture of network formation in randomly crosslinked chains.

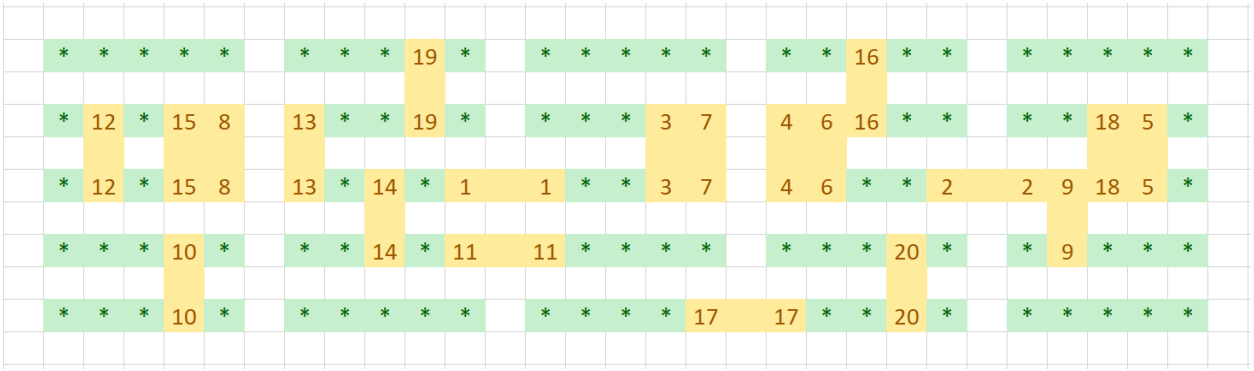

Figure S6. A system with COL=5, ROW=5, DP=5 crosslinked with 20 crosslinks.

Figures S7-S10 plot P_{gel} versus reaction time for polymers with different degrees of polymerization (DP) and crosslinker/monomer ratios, [X]/[M], at various values of k. For each k and [X]/[M], P_{gel} attains a unique value at a given reaction time, regardless of the molecular weight of the polymer.

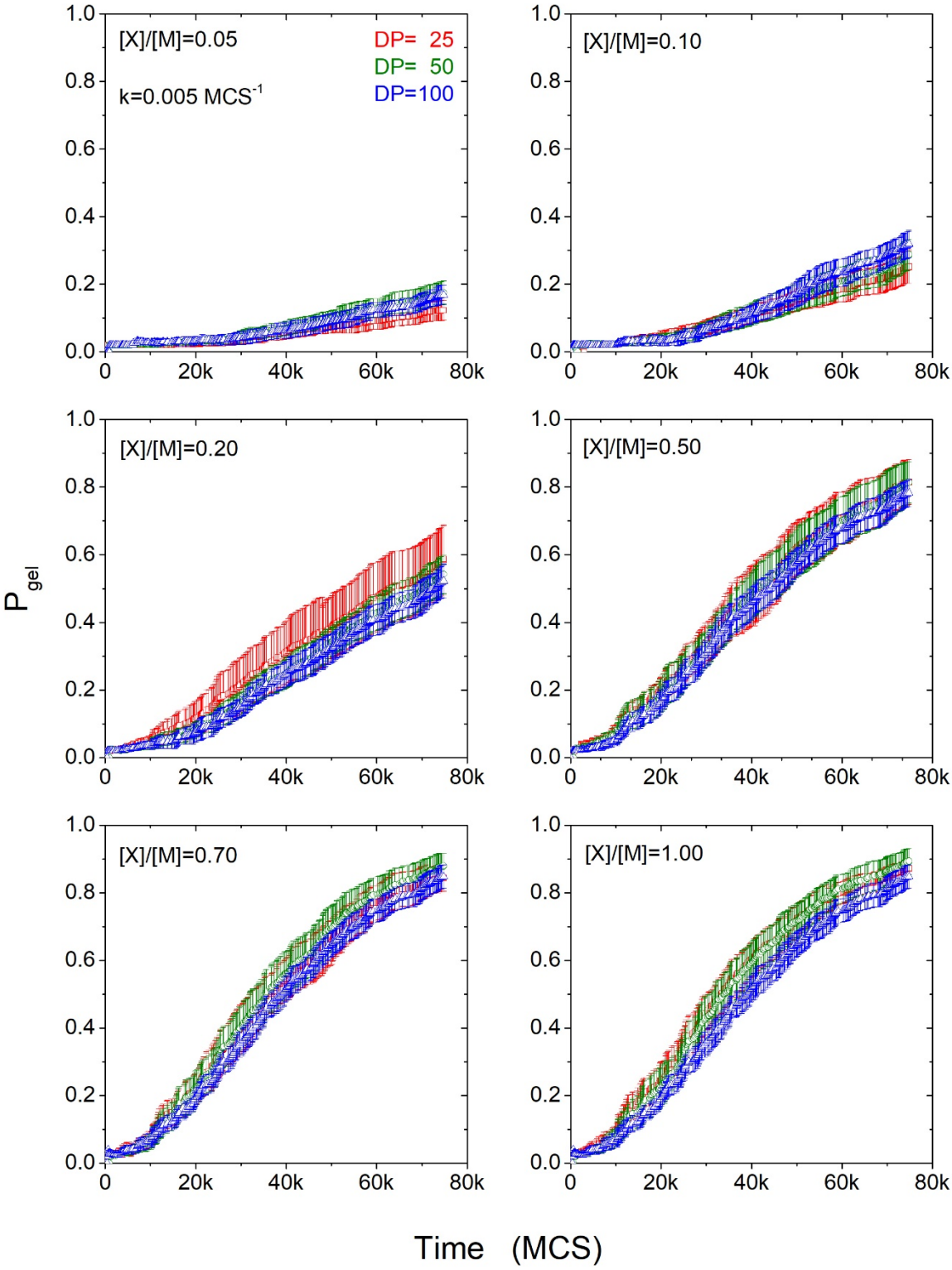

Figure S7. P_{gel} as a function of the reaction time of polymers with different degrees of polymerization (DP) and crosslinker/monomer ratios, [X]/[M], at k=0.005 MCS^{-1}.

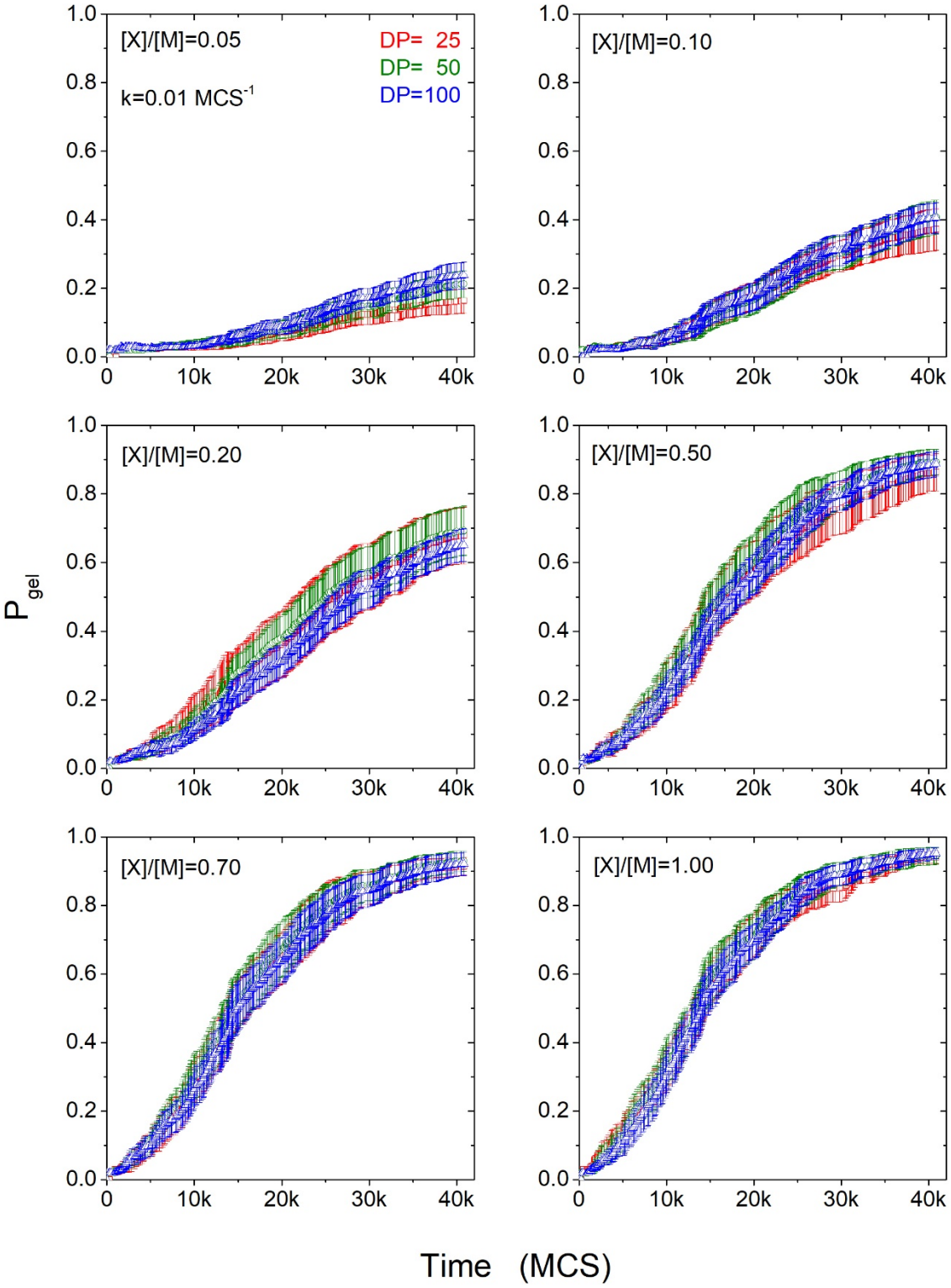

Figure S8. P_{gel} as a function of the reaction time of polymers with different degrees of polymerization (DP) and crosslinker/monomer ratios, [X]/[M], at k=0.01 MCS^{-1}.

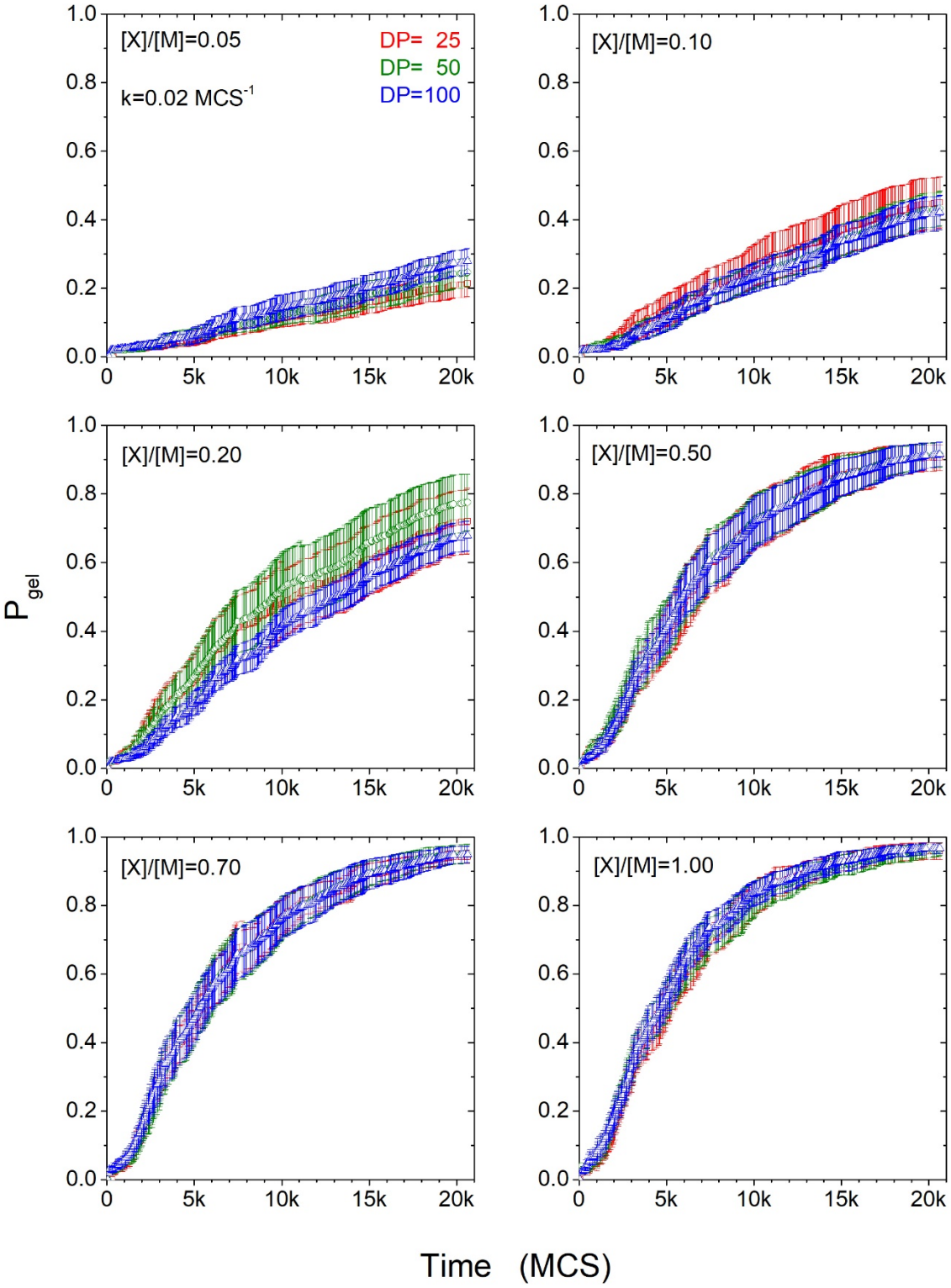

Figure S9. P_{gel} as a function of the reaction time of polymers with different degrees of polymerization (DP) and crosslinker/monomer ratios, [X]/[M], at k=0.02 MCS^{-1}.

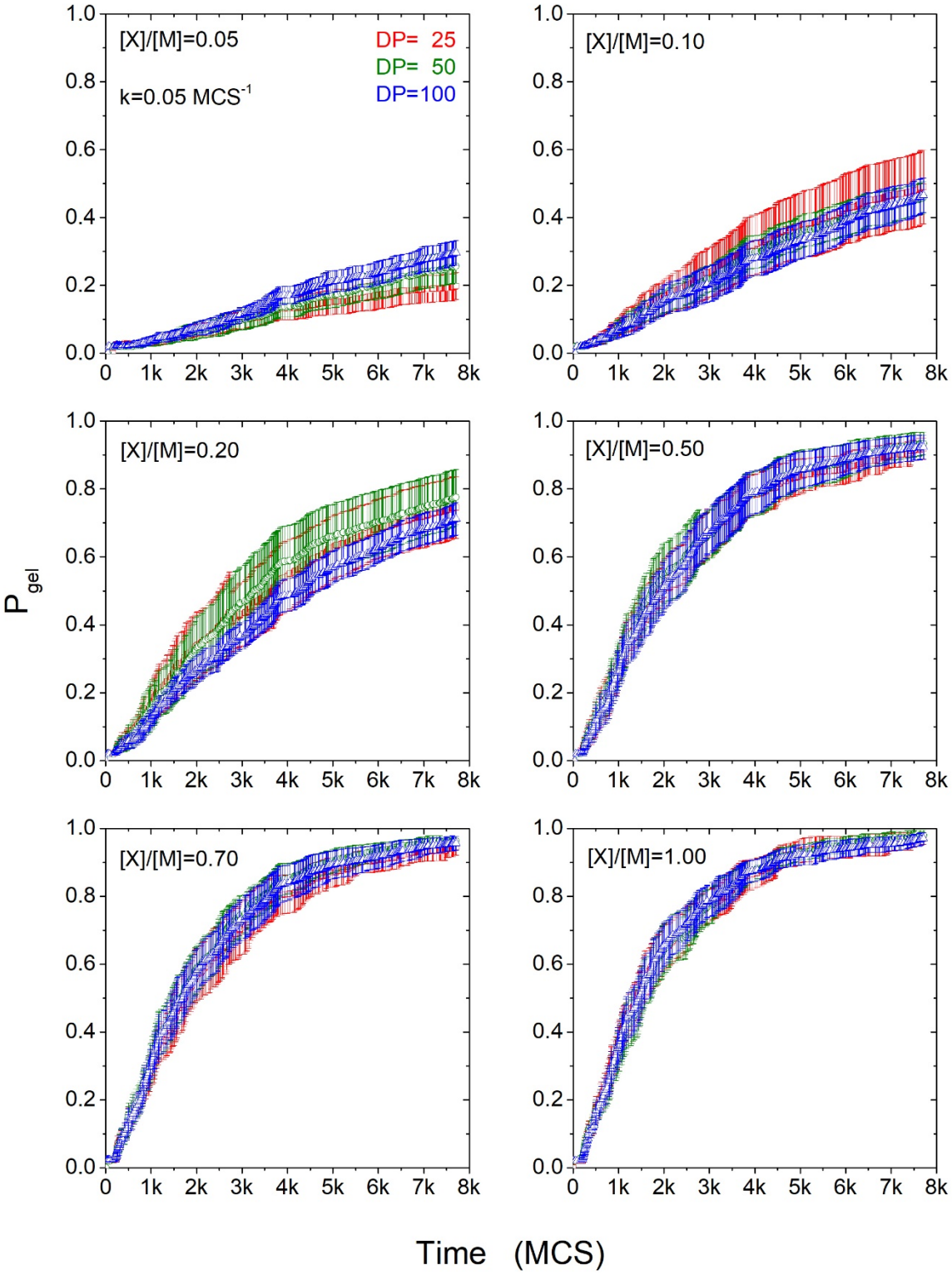

Figure S10. P_{gel} as a function of the reaction time of polymers with different degrees of polymerization (DP) and crosslinker/monomer ratios, [X]/[M], at k=0.05 MCS^{-1}.

References

(1) Serebrinsky, S. A. Physical time scale in kinetic Monte Carlo simulations of continuous-time Markov chains. *Phys. Rev E* **2011**, *83*, 037701.

(2) Andersen, M.; Panosetti, C.; Reuter, K. A practical guide to surface kinetic Monte Carlo simulations, *Frontiers in Chemistry* **2019**, *7*, Article no. 202.