

SUPPORTING INFORMATION FOR:

Modulating Solubility and Enhancing Reactivity of Photocrosslinkable Poly(styrene sulfonyl azide-*alt*-maleic anhydride) Thin Films

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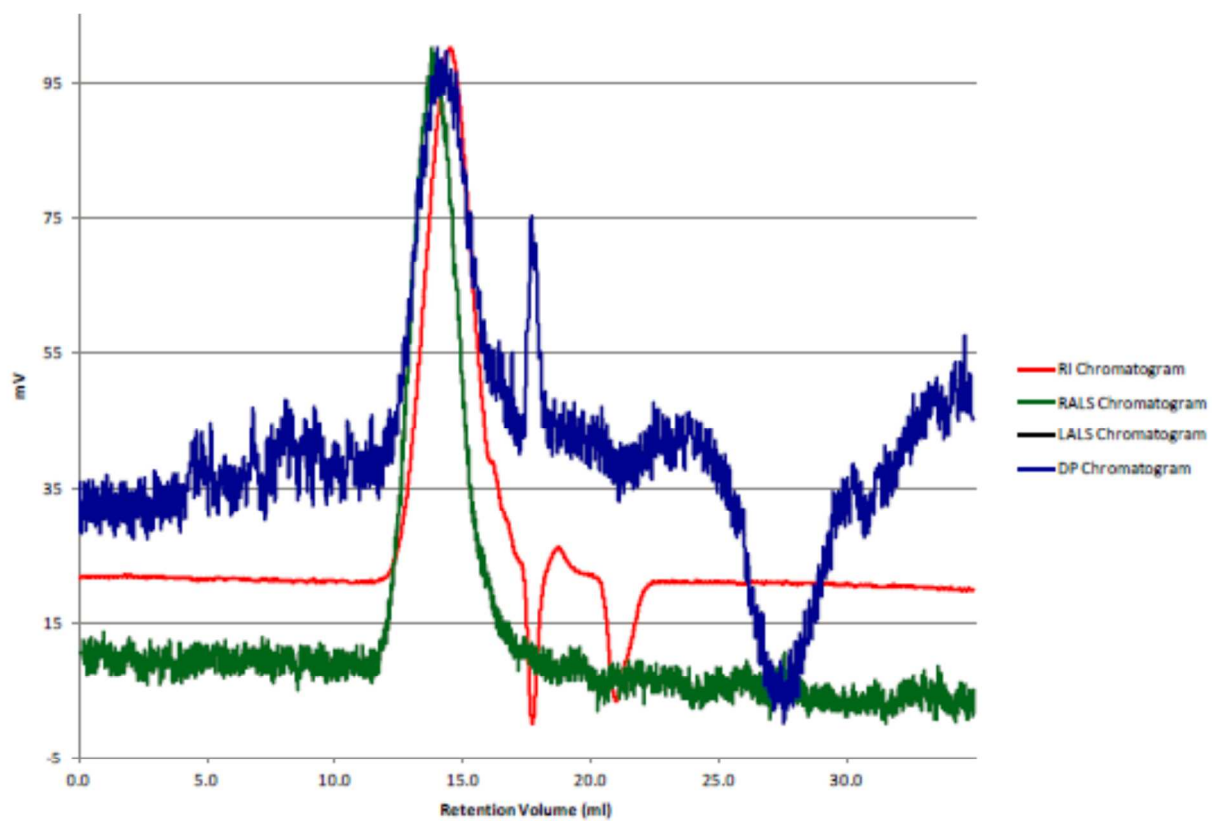


Figure S1. SEC elution curve of PSSMA as measured by multiple detectors.

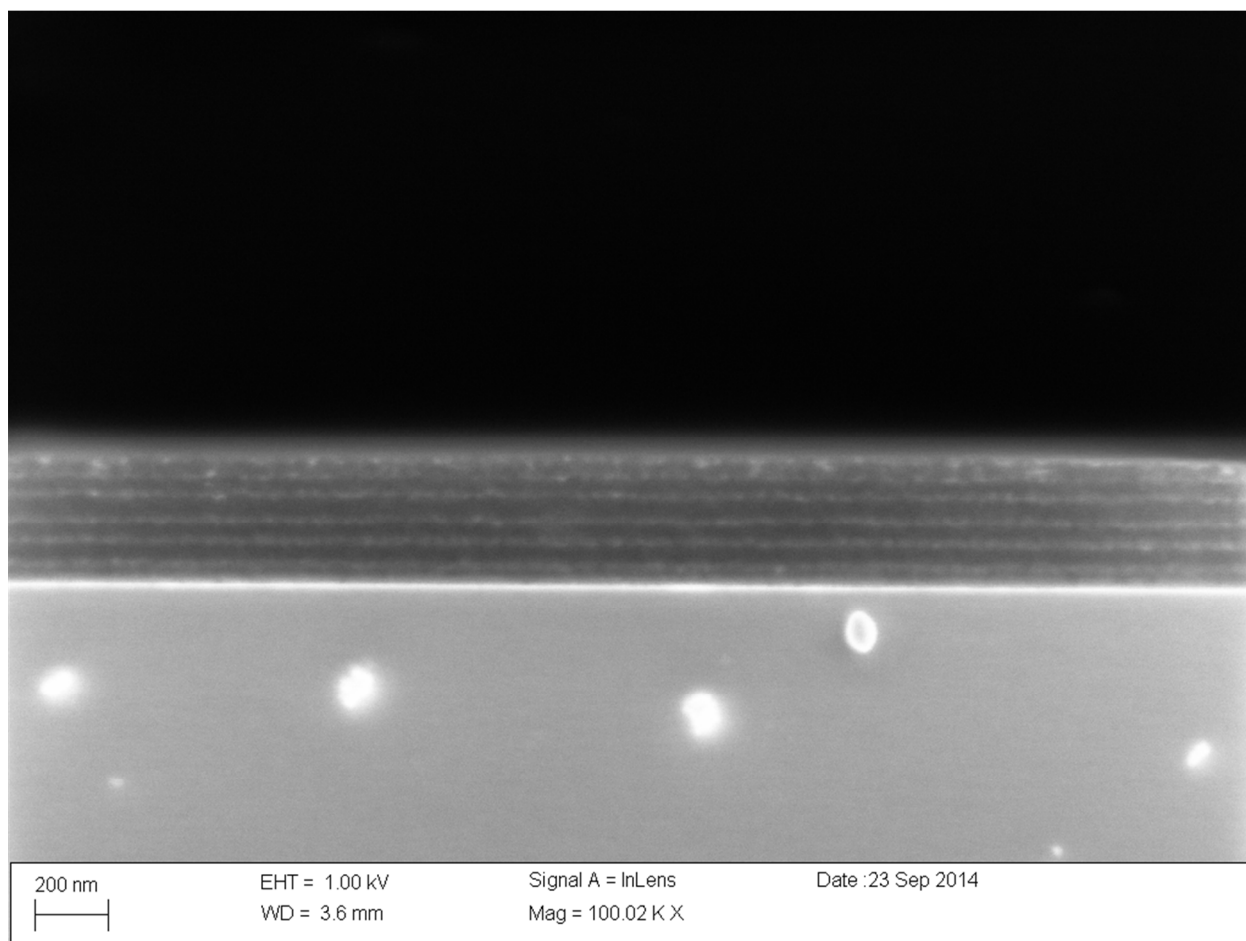


Figure S2. Original micrograph from which Figure 4 was excerpted.

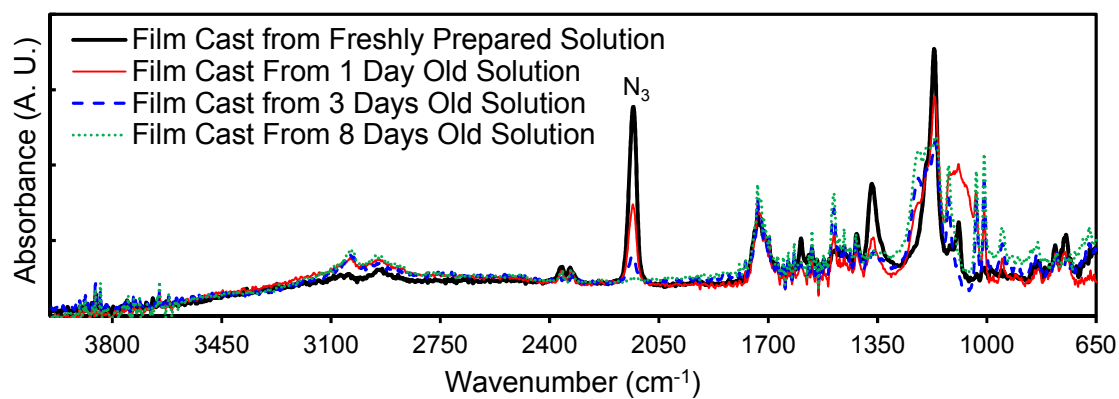


Figure S3. Transmission-mode FTIR absorption spectra of ring-opened PSSMA films prepared from solutions with different ages. Disappearance of the azide peak is observed.

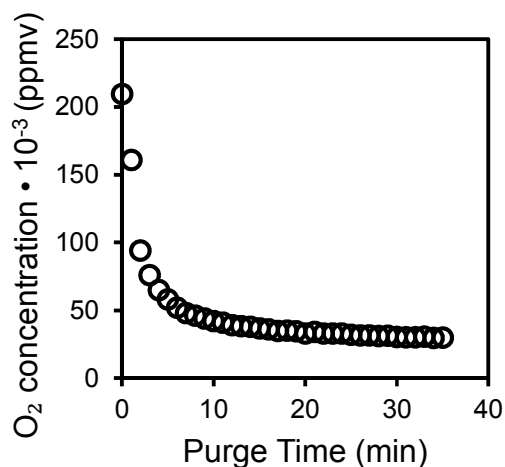
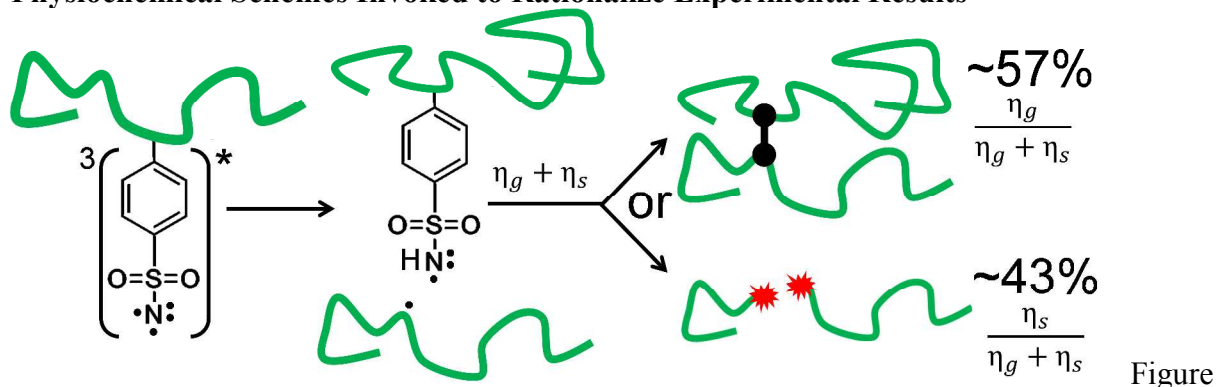


Figure S4. Oxygen content in exposure chamber after various N₂ purge times as measured by directing the outflow through a Model 810 O₂ meter (Illinois Instruments). A purge time of at least 30 minutes was used for all exposures performed in the N₂ purged chamber.

Physiochemical Schemes Invoked to Rationalize Experimental Results



S5. Hydrogen abstraction by triplet nitrene from a polymer C-H bond to yield free radicals. Grafting is a possible network outcome via radical-radical recombination. Scission is also a possible network outcome.¹⁻³ Values provided are those calculated for PSSMA/MK blend films.

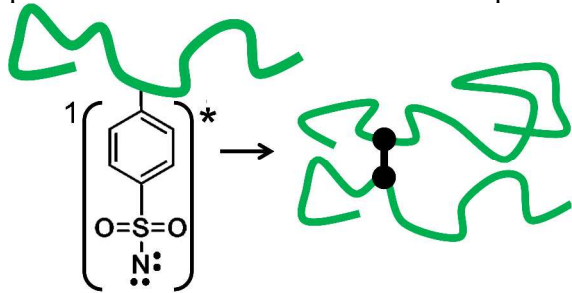


Figure S6. Insertion of singlet nitrene into a polymer C-H bond to yield a crosslink. Scission is not a network outcome.¹

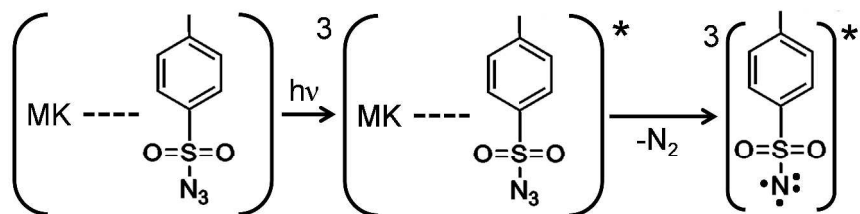


Figure S7. Excitation of a ground-state complex between Michler's ketone and PSSMA to generate triplet state sulfonyl nitrenes.^{4, 5}

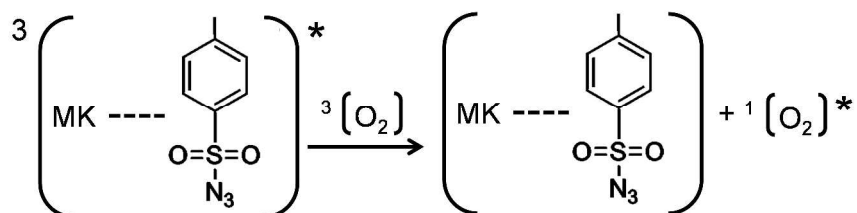


Figure S8. Energy transfer from excited MK-PSSMA charge transfer complexes to ground state oxygen to generate excited, singlet oxygen.

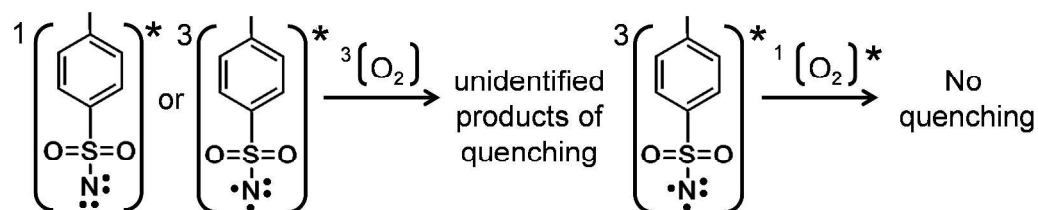


Figure S9. Singlet- and triplet-excited nitrenes are quenched by ground state oxygen and preclude reactions with polymer, but are not quenched by singlet oxygen because it is already electronically excited.

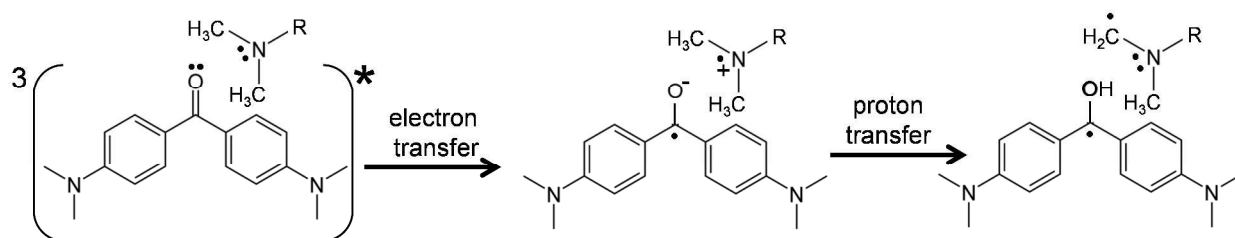


Figure S10. Photoreduction of MK by electron transfer from tertiary amine followed by proton transfer from methyl group.⁶⁻⁸ This mechanism is far less likely to generate radicals on the PSSMA backbone than a hydrogen abstraction mechanism.

Interpolating Between Photochemical Conversion Data Points

Photochemical conversion in neat PSSMA films exposed to broadband irradiation was well described by a thin-film, first order rate equation with a single rate constant, $k\epsilon$:⁹

$$p = 1 - \exp(-k\epsilon D_{UV}), \quad (\text{S1})$$

where k is a quantum yield with units J/mol, and ε is the molar absorptivity of PSSMA at the exposure wavelengths.

Directly excited azides obey this relationship because their photolysis is unimolecular and not coupled to other chemical species present in the film. Eq. S1 does not describe photochemical conversion when multiple reaction rates are present, which is typically encountered when photolysis involves multiple chemical species in a solid, glassy film. For example photoreduction of benzophenone in glassy polymer films is generally well-described by equation featuring a ln-normal distribution of rate constants.¹⁰ This is the dispersive kinetics model of Albery et al.,¹¹ which is

$$p_i = 1 - (\pi)^{-1/2} \int_{-\infty}^{+\infty} \exp(-x^2) \exp[-k_i \varepsilon_i D_{UV} \exp(\gamma_i x)] dx, \quad (S2)$$

where i refers to the species of interest, ε_i is its molar absorptivity, x is a transform variable, k_i is an average conversion efficiency, and γ_i describes the spread of its distribution. We used Eq. S2 to interpolate between photochemical conversion points for MK photolysis in PSSMA/MK blend films. The constants that best fit our data are shown in Table S1.

MK Content	$k_{MK} \varepsilon_{MK} (\text{cm}^2 \text{J}^{-1})$	γ_{MK}
2.5 wt. %	2.154	4.2
5 wt. %	1.798	3.3
10 wt. %	0.205	4.9
20 wt. %	0.059	6.4

Table S1. Constants used in Eq. S2 to interpolate between benzophenone conversion data points in PSSMA/MK blend films.

For the case of sensitized azide photolysis in PSSMA/MK blend films, the ability of an azide group to be converted depends on its proximity to a sensitizing MK molecule. Some blend compositions are incompletely sensitized, which means that 100% photolysis of azide groups is not achievable even for very long exposure times. For this reason Eq. S2 was modified as

$$p_i = p_{i,\infty} \left[1 - (\pi)^{-1/2} \int_{-\infty}^{+\infty} \exp(-x^2) \exp[-k_i \varepsilon_i D_{UV} \exp(\gamma_i x)] dx \right]. \quad (S3)$$

where $p_{i,\infty}$ implies a maximum possible photochemical conversion of species i . The constants which best fit our azide photolysis data are shown in Table S2.

MK Content	$k_A \varepsilon_{MK} \text{ (cm}^2\text{J}^{-1}\text{)}$	γ_A	$p_{A,\infty}$
2.5 wt. %	0.001	10.7	0.62
5 wt. %	0.046	7.8	0.96
10 wt. %	0.939	5.1	0.92
20 wt. %	4.795	3.8	0.97

Table S2. Constants used in Eq. S3 to interpolate between azide conversion points in PSSMA/MK blend films.

Eqs. S2 and S3 use a unimodal distribution of rate constants, and strictly represent first-order reaction processes. The relatively high values of γ_i present in Tables S1 and S2 for some blend compositions indicates that photochemical conversion is likely not unimodal and/or first-order. Therefore, the use of Eqs. S2 and S3 to interpolate between photochemical conversion datapoints should be considered as largely empirical and physical trends should not be ascribed to its best-fit parameters. The purpose of using Eqs. S2 and S3 to interpolate between photochemical conversion datapoints is to generate inputs to the statistical gelation model, so that the efficiencies of grafting and scission can be extracted from the sol fraction data.

Statistical Gelation Models For Simultaneous Scission/Grafting Reactions

Charlesby-Pinner Equation

We seek to understand sol fraction data obtained at various doses using a gelation model that enables extraction of physically meaningful parameters. Specifically, from the experimental data we wish to determine the number of grafting events, η_g , and the number of scission events, η_s , for every photochemically-activated azide group in PSSMA and benzophenone group in MK.

For the simpler case of neat PSSMA, we first considered using a modified Charlesby-Pinner equation¹² used previously to model the gelation of polymers bearing pendant benzophenone groups.³ This equation can be written as

$$\omega_s + \sqrt{\omega_s} = \frac{\eta_s}{2\eta_g} + \frac{1}{f\eta_g p} \quad (\text{S4})$$

where ω_s is the sol fraction, f is the number of functional side groups on a weight average polymer, and p is fraction of azide groups that have been photochemically converted in the neat PSSMA polymer. As a check of this equation we calculated ω_s values for $f = 50$, $\eta_g = 0.35$, and various values of η_s and p . As shown in Figure S11, ω_s decreases with p , and the result for $\eta_s = 0$ of ω_s becoming infinitesimally small with even low values of p is consistent with expectations for polymer gelation. The values of η_g and η_s can be determined by linear regression of Eq. S4 to real sol fraction data plotted as $\omega_s + \sqrt{\omega_s}$ vs. p^{-1} , which is also shown in Figure S11. Non-linearity in real sol-fraction data plotted in this format is typically attributed to the polydispersity at low-conversion differing from the random distribution represented by Charlesby-Pinner theory.¹³ Unfortunately, the effects of MK present in the PSSMA/MK blends cannot be accounted for in this equation, so we considered an alternative approach.

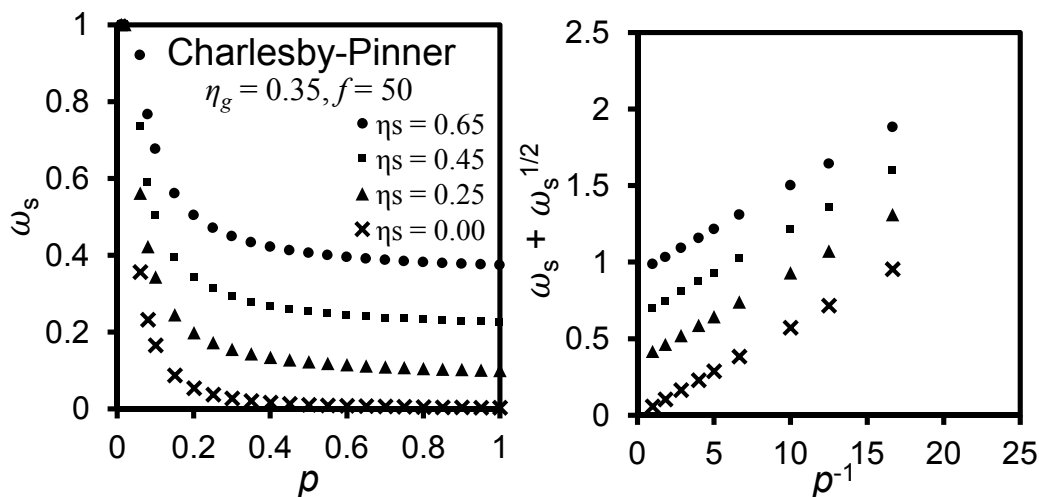


Figure S11. Predictions of sol fractions using Eq. S4.

Gelation of PSSMA

To develop a predictive understanding of gelation for our specialized systems that returns physically realistic values of ω_s , we adapted the Miller-Macosko gelation theory to account for the effects of simultaneous gelation and scission in neat PSSMA and PSSMA/MK blends. For the former case, we consider that grafting reactions do not decrease the functionality of the polymer being grafted to. As in the original Miller-Macosko work, the probability that any functional group chosen at random leads outwards to a finite chain, $P(F^{out})$, is

$$P(F^{out}) = \eta_g p P(F^{in}) + 1 - \eta_g p \quad (S5)$$

where $P(F^{in})$ is the probability that all arms on a PSSMA lead to finite chains. Chain scission has the effect of reducing the weight-average number of arms leading out for every scission event, and therefore increasing $P(F^{in})$. Thus

$$P(F^{in}) = P(F^{out})^\alpha \quad (S6a)$$

where

$$\alpha = \frac{2f}{2+f\eta_s p} \quad (S6b)$$

α represents the weight-average functionality of an initially randomly dispersed polymer undergoing scission reactions, where $\eta_s p$ is the likelihood of any given functional group causing scission. For example, a polymer with $f = 50$ and $\eta_s = 0.5$ would be halved ($\alpha = 25$) when $p = 0.08$; it would be reduced to only $\alpha = 10$ as p reaches 0.32. Note that relatively few scission and grafting reactions are needed to convert even a monodisperse polymer to a randomly distributed one.¹⁴

Combining Eqs. S5 and S6, $P(F^{out})$ can be determined by numerically finding the roots of

$$\eta_g p P(F^{out})^\alpha - P(F^{out}) + 1 - \eta_g p = 0 \quad (S7)$$

which lie between 0 and 1 for polymers with a finite gel fraction. If a root of $P(F^{out})$ does not exist between 0 and 1, the polymer does not possess a gel fraction ($P(F^{out}) = 1$, $\omega_s = 1$). A randomly chosen polymer will be part of the sol if all of its arms lead out to finite chains. Thus

$$\omega_s = P(F^{in}) \quad (S8)$$

Calculated ω_s values for the polymer network formation are shown in Figure S12 for $f = 50$, $\eta_g = 0.35$, and various values of η_s and p . Finite gel fractions are obtained at sufficiently high p . For $\eta_s = 0$ the ω_s values obtained are similar to those obtained from Eq. S4, albeit slightly smaller and the relationship between $\omega_s + \sqrt{\omega_s}$ and p^{-1} is non-linear.

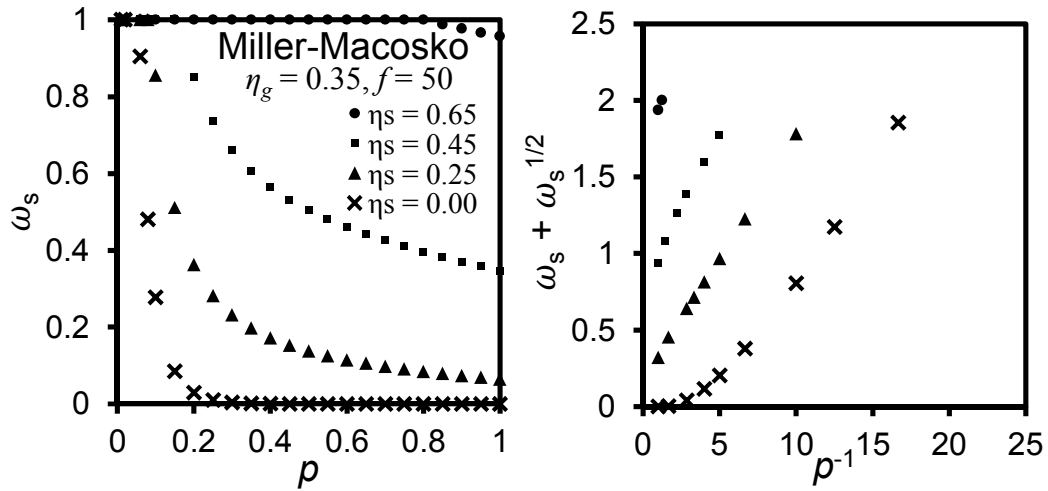


Figure S12. Predictions of sol fractions using Eqs. S5-S8.

Through similar arguments as above and in Ref. ¹⁵, the weight average molecular weight of polymer prior to gelation can be obtained as

$$M_W = M_{Wi} \frac{1 + \eta_g p}{1 - \alpha \eta_g p} \quad (S9)$$

where M_{Wi} is the initial weight average molecular weight of PSSMA. Note that M_W will still increase with equal probabilities of scission and grafting; these reactions result in a product with

a higher weight-average molecular weight. M_W diverges to infinity when the denominator in the right side of Eq. S9 is equal to zero. Therefore the critical conversion necessary to form a gel is

$$p_{Gel} = \frac{2}{f(2\eta_g - \eta_s)} \quad (S10)$$

Physically realistic values of η_g and η_s lie between 0 and 1 and their sum is less than 1. Since M_W/M_{Wi} is highly dependent on α , Eq. S10 is only strictly valid for polymers with a random initial distribution.

Alternative Initial Distribution Functions

We utilized a relatively simple expression for α in Eq S6b based on a random initial distribution ($D = 2$), even though PSSMA is not randomly distributed ($D = 1.47$). Other expressions for α are available to represent other distributions, such as:

An expression for initially monodisperse polymers by Montroll and Simha:¹⁴

$$\alpha = 1 + \frac{2(1-\eta_s p)[(1-\eta_s p)^f - 1 + \eta_s p f]}{(\eta_s p)^2 f}. \quad (S11)$$

An expression for initially monodisperse polymers by Charlesby and Pinner:¹²

$$\alpha = \frac{2}{(\eta_s p)^2 f} [\exp(-\eta_s p f) + \eta_s p f - 1]. \quad (S12)$$

An expression for “pseudo-randomly” distributed starting polymers by Charlesby and Pinner:¹²

$$\alpha = \frac{2}{\eta_s p} \left[1 - \frac{\ln(1 + \eta_s p f)}{\eta_s p f} \right]. \quad (S13)$$

An expression for a generalized Poisson-type initial distribution by Inokuti that reduces to Eq. S6b for $D = 2$:¹⁶

$$\alpha = \frac{2}{\eta_s p} \left[1 - \frac{D}{\eta_s p f} \left(1 - \left[1 + \frac{\eta_s p f (D-1)}{D} \right]^{\frac{-1}{D-1}} \right) \right]. \quad (S14)$$

Due to the simple, modular nature of formulating closed form expressions within the Miller-Macosko framework, any of the expressions above could be substituted for Eq. S6b. To ascertain whether using an alternative expression for α would alter our analysis we first plotted α vs. $\eta_s p$ for a polymer with $f = 50$ and different initial distributions in Figure S13. For different initial molecular weight distributions, α differs by, at most, 3.6. To gauge the influence of the initial molecular weight distribution being uniform or random on the polymer degree of polymerization and sol fraction, these expressions for α were applied into Eqs. S5-S9 for specified values of η_s and η_g . It can be observed from Figure S14 that the initial distribution significantly affects the rise in molecular weight just prior to gelation, but that post-gelation properties are not very sensitive to whether an initial distribution is random (a.k.a. “most probable”) or uniform.

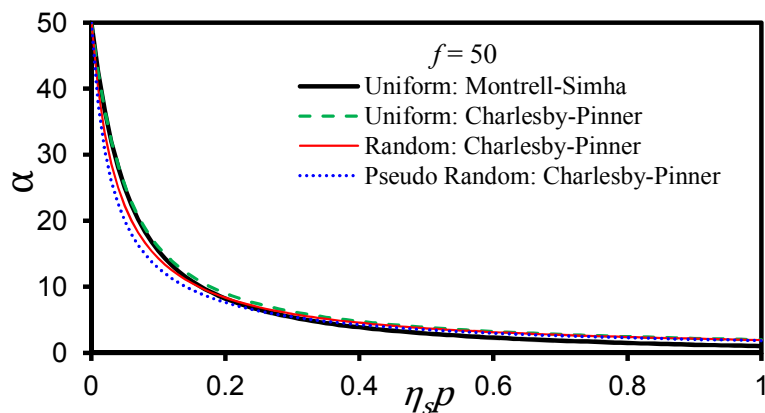


Figure S13. Number of arms leading out from a weight average polymer for various degrees of scission.

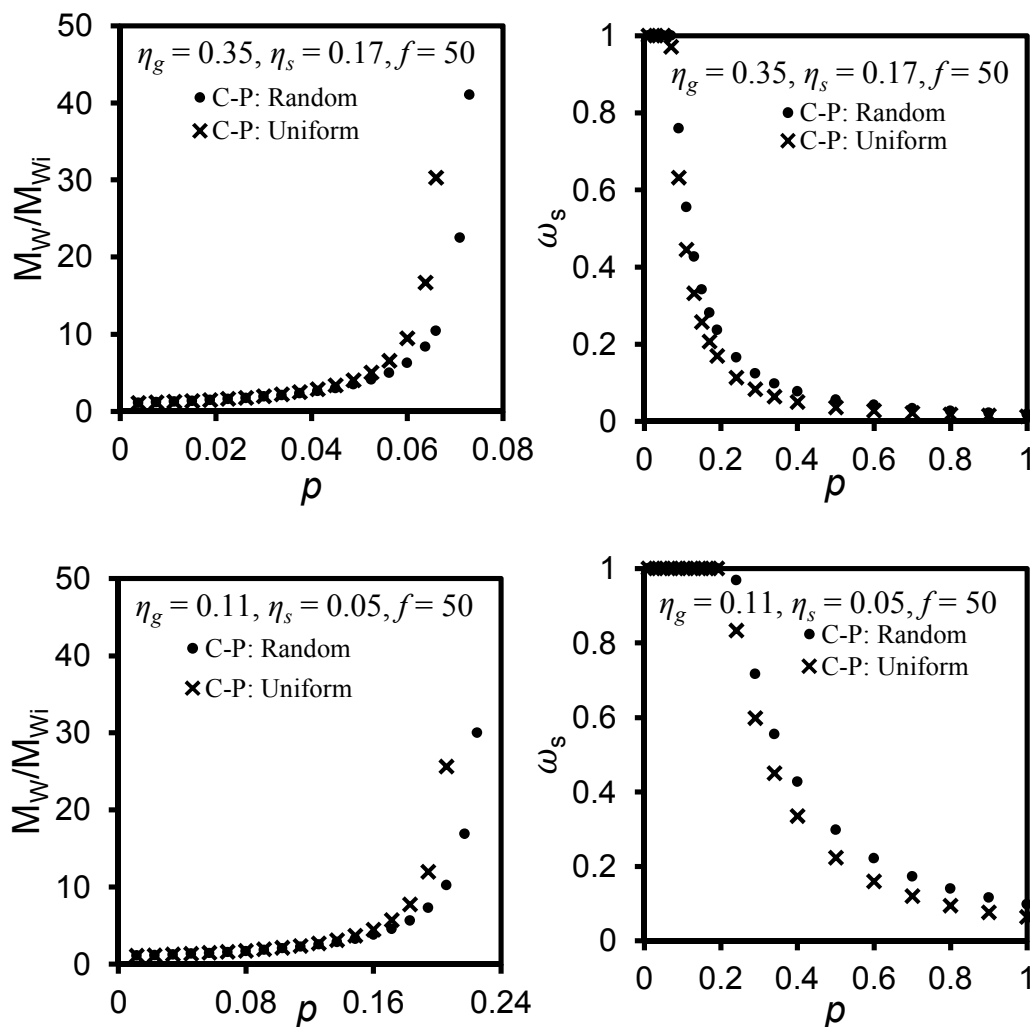


Figure S14. Weight average degree of polymerization and sol fraction predictions for various scission/grafting likelihoods, and initial molecular weight distributions.

Gelation of PSSMA/MK Blends

The addition of a photoactive blend component, MK, suggests that additional probabilistic parameters and formulae will be needed to predict sol fractions. In this model we consider MK to be bound to PSSMA as part of a charge transfer complex, with its ability to sensitize azide groups implicitly represented by p , the fraction of azide groups which have been photolyzed. We consider that the photoreduction of MK may cause chain scission, via hydrogen

abstraction reactions, and enhance the grafting of nitrenes, via the generation of radicals. Starting with the probability $P(F_A^{out})$ that any “azide” group chosen at random on PSSMA leads outwards to a finite chain, it can be shown that

$$P(F_A^{out}) = \underbrace{\eta_g p(1 + r\eta_{gB}p_B)}_{\text{probability A grafts}} P(F_A^{in}) + \underbrace{1 - \eta_g p(1 + r\eta_{gB}p_B)}_{\text{probability A does not graft}} \quad (\text{S15})$$

where the parenthetical term is a virial-like correction that potentially improves the grafting likelihood with increasing MK content. p_B is the fraction of benzophenone groups in MK which have been photoreduced, r is the initial ratio of benzophenone to azide groups, and η_{gB} characterizes the influence of MK photoreduction on PSSMA’s grafting reactions. p is the fraction of azide groups which have been photolyzed. $P(F_A^{in})$ is the probability all arms on a given PSSMA lead to finite chains; as before the number of arms on PSSMA are reduced by scission according to

$$P(F_A^{in}) = P(F_A^{out})^\alpha \quad (\text{S16a})$$

where

$$\alpha = \frac{2f}{2 + \underbrace{\eta_s p f}_{\text{scissions by PSSMA}} + \underbrace{\eta_{sB} p_B r f}_{\text{scissions by MK}}} \quad (\text{S16b})$$

In Eq. S16b, η_{sB} is the likelihood for a photoreduced benzophenone to cause scission, p_B is the fraction of benzophenone groups in MK which have been photoreduced, and r is the initial ratio of benzophenone to azide groups. Since $\omega_s = P(F_A^{in})$, Eqs. S15 and S16 may be combined to yield

$$0 = \eta_g p(1 + r\eta_{gB}p_B)\omega_s - \omega_s^{\frac{2 + \eta_s p f + \eta_{sB} p_B r f}{2f}} + 1 - \eta_g p(1 + r\eta_{gB}p_B). \quad (\text{S17})$$

Realistic values for η_g , η_s , η_{gB} , and η_{sB} lie between 0 and 1, the sum of η_g and η_s should be less than or equal to 1, and the sum of η_{gB} and η_{sB} should be less than or equal to 1. These

constraints arise from our expectation that, at most, only one grafting or scission outcome is possible for each photolyzed azide or photoreduced benzophenone group. The MK contents stated in the manuscript are relative to ring-closed PSSMA; due to the ring-opening reaction slightly lower MK contents were employed in the blend model.

Ring-Closed PSSMA MK Content	Ring-Opened PSSMA MK Content	r
2.5 wt. %	2.1 wt. %	0.015
5 wt. %	4.2 wt. %	0.031
10 wt. %	8.5 wt. %	0.066
20 wt. %	17.3 wt. %	0.150

Table S3. Anticipated effect of ring-opening reaction on MK content and stoichiometric ratio r .

Regression Analysis of Gelation Data

To fit the experimental observations to the gelation models detailed above, we first express the model equations in terms of the measured quantities. For example, by combining Eqs S5-S8, the modified Miller-Macosko model for the gelation of PSSMA can be written as:

$$1 - \omega_s^{1/\alpha} - \eta_g p (1 - \omega_s) = 0, \quad (\text{S18})$$

where $\alpha = 2f/(2 + f\eta_s p)$. Based on the values of ω_s and p determined as a function of dose, we solved Eq. S18 for the best-fit values of η_g and η_s using an implicit orthogonal distance regression algorithm (ODR)¹⁷ from SciPy.¹⁸ This approach was repeated on both the data collected under ambient and N₂ purged conditions. The resulting best-fit values and standard errors are given in Fig. 6b in the text. However, because the fit parameters are strongly correlated, it is not appropriate to derive confidence regions associated with the fit directly from the standard errors. Therefore, we employed a standard bootstrap method to estimate the 95% confidence regime for each condition. To do so, the residuals in both p and ω_s associated with the best fit parameters were randomly assigned to the measured values and the resulting values

were refit using Eq. S18. This process was repeated 1000 times for each condition. The smallest elliptical regions that contain 95 % of the η_g and η_s determined in the manner are shown in Fig. 10 for under ambient (red) and N₂ purged (blue) conditions. The same numerical approach was also applied to the statistical model for gelation of PSSMA/MK blends by solving Eq. S17 for η_g , η_s , η_{gB} , and η_{sB} based on the observations of ω_s , p , and p_b at all MK compositions. The best-fit values are provided Fig. 9. To estimate the 95 % confidence region for η_g and η_s , the same bootstrap procedure was used, while holding η_{gB} and η_{sB} constant at their best-fit values. Again, the predicted 95 % confidence ellipse is shown in purple in Fig. 10.

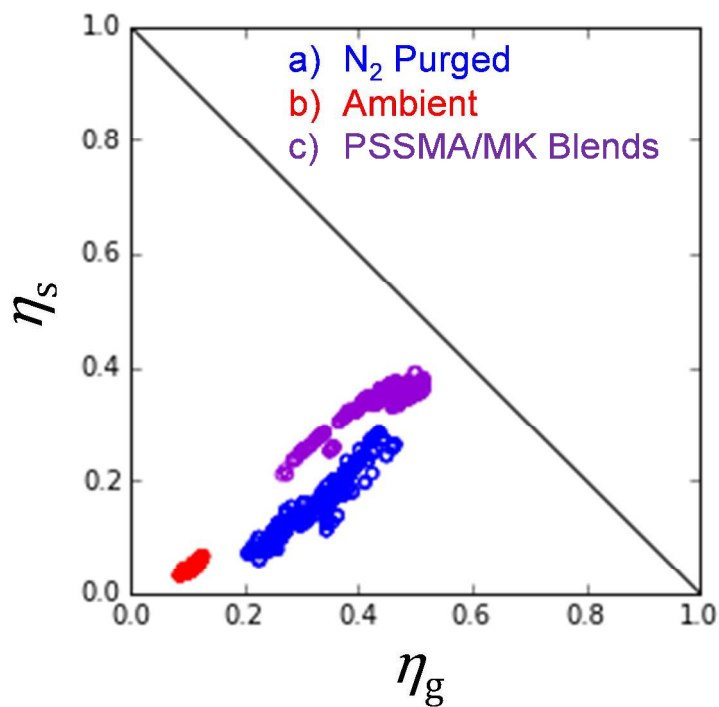


Figure S15. The raw results of bootstrap analysis of the gelation models to the photochemical gelation data. The elliptical regions defined by this analysis were used to construct Fig. 10 in the main manuscript.

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