SUPPORTING INFORMATION

Molecular Aspects of Film Formation of Partially Cross-Linked Water-Borne Secondary Dispersions that Show Skin Formation upon Drying

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SUPPORTING EXPERIMENTAL DETAILS

Humidity Control. To prepare a saturated salt solution, the sodium chloride (NaCl) was added to 60 mL warm (about 45 °C) deionized water in a 100 mL beaker with stirring until no more salt dissolved. Additional salt was added to ensure an excess of the saturating salt. The total mass of NaCl was ca. 180g. The beaker containing the saturated NaCl solution was then placed into a fully sealed glass container in an oven preheated to 80 °C. It took at least 24 hours before being used for the film formation experiments.

SUPPORTING RESULTS AND DISCUSSION

Latex Characterization. Particle size and particle size distribution were recorded on an ALV/SP-125 light scattering spectrometer equipped with an ALV-5000 multiple tau digital time correlator and a He−Ne laser (output power = 35 mW at λ_0 = 632.8 nm) at a scattering angle of 90° at room temperature. The original dispersions of polymer nanoparticles were diluted by deionized water before characterization by dynamic light scattering (DLS). Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC) at 22 °C, using a Viscotek liquid chromatograph (TDA302) equipped with a Viscotek VE 3580 RI detector and a 2500 UV-Vis detector. Reagent grade THF containing 2.5 g L^{-1} tetra-n-butylammonium bromide (TBAB) was used as the eluent at a flow rate of 0.6 mL min^{-1}. The UV signal was collected at 300 nm for dye-labeled polymers. The columns were calibrated with linear polystyrene standards. The glass transition temperature (T_g) of each completely dry film was determined by a TA Instruments Q100 differential scanning calorimeter (DSC) on 8 ± 1 mg under N_2 at a heating and cooling rate of 10 °C/min. For most samples two or three heat-cool cycles were run: heating from -40 to 120 °C. The T_g values are taken as the midpoint temperature of the deflection on the second heating curve.

Gel Content Measurements. The gel content measurement is based on the principle of extracting the soluble part from a polymer sample and determining the soluble part gravimetrically. Coalesced film samples of the polymer dispersions were prepared by placing an aliquot of a polymer dispersion (200 μL) on a tared preheated coverslip (22 mm × 22 mm) and allowing the film to dry completely. It was then inserted into the nylon tea bag. We denote the combined weight as w_0. We denote the weight of the coverslip and the tea bag as w_1. The coverslip with its dispersion cast film was placed into the tea bag and immersed in acetone for 48 h to allow the sol component

to dissolve. The tea bag containing the polymer was removed from the solvent and allowed to dry further under vacuum for 24 h to remove any remaining solvent. The weight of this dry polymer is w_2. The gel content was calculated as shown in eq S1.

$$Gel\ content(\%) = \left(\frac{w_2}{w_0 - w_1} \right) \times 100 \qquad \text{(S1)}$$

The acetone containing the soluble part of ^{XL}Pol samples was transferred to a 35 ml (9.5 dram) vial. The solvent was removed using a rotary evaporator. The dry polymer (the sol component of XL-Pol) was collected and weighed.

UV-vis measurements. Solutions of the polymers in ethyl acetate were prepared by weighing samples with a microbalance. The sol component of ^{XL}Pol samples was isolated by the method described in Gel content measurement. Absorbance values were measured at λ_{max} for each sample (1 cm cells). Molar dye concentrations were calculated as [dye] = A(λ)/ε. These measurements used the values of molar extinction coefficients determined for dye-model-compounds: $\varepsilon_{296} = 1.1 \times 10^4$ $M^{-1}cm^{-1}$ for N-(phenanthrene-9-ylmethyl) acetamide, and $\varepsilon_{370} = 7.6 \times 10^3$ $M^{-1}cm^{-1}$ for N-acetamido-2,4-dinitrophenylhydrazine.[1] In this way, we calculated a dye content of ca. 1.9×10^{-4} mol dye per *g* for Pol.5K-Phen and ca. 1.8×10^{-4} mol dye per *g* for Pol.5K-DNP before the crosslinking reaction, and a dye content of ca. 1.8×10^{-4} mol dye per *g* for the sol component of ^{XL}Pol.5K-Phen and ca. 1.9×10^{-4} mol dye per *g* for ^{XL}Pol.5K-DNP after the reaction. Using a value of M_n = 5000 g/mol for the polymer, we estimated 1.0 dye molecules per polymer for both samples. Based on M_n = 4000 g/mol, we estimated 1.0 dye molecule per polymer for Pol.4K-Phen and 1.0 dye molecules for Pol.4K-DNP. These as-prepared polymers were then blended with an equal weight of unlabeled Pol prior to the preparation of the dispersions described below. In this way, we decreased the dye content and doubled the amount of material available.

FRET measurements and analysis. 60 μL of a secondary dispersion (containing 1:1 wt ratio of mixed Phen- and DNP-labeled nanoparticles, 30 wt % solids) was spread on a small quartz plate (20 mm × 8 mm) placed in an oven preheated to the annealing temperature. The film was allowed to dry for different times at 65 °C, 80 °C, and 95 °C. The films were then immediately measured by FRET, otherwise were moved to a fridge (~4 °C) to prevent further polymer interdiffusion prior to other measurements. The films prepared in this way have a thickness of ca. 120 μm.

Solvent-cast films were prepared from the ethyl acetate solution of the initial film, cast from the same dispersion (1:1 wt ratio of mixed Phen- and DNP-labeled nanoparticles). The films on quartz

plates were placed directly on a high mass (2 cm thick) aluminum plate in an oven preheated to the annealing temperature and then annealed for 24h.

As described in Ref 2, we found an additional fluorescence associated with polymer labeled with the 2,4-DNP chromophore. We refer to the donor fluorescence decay curves measured on samples containing DNP acceptor as I_D. To accommodate the background fluorescence, we introduce an additional term into the fitting function

$$I_D = B_1 exp((-(t')/\tau_D) - 2\gamma(t'/\tau_D)^{(1/2)}) + B_2 exp(-t'/\tau_D) + B_3 exp((-(t')/\tau_B) \qquad \text{(S2)}$$

Here B_3 represents the contribution of the background fluorescence to the decay profile. We calculated the value of $\tau_B = 1.5$ ns, by exponentially fitting the decay profiles of polymer labeled with the 2,4-DNP chromophore. Measured decay profiles were fitted to eq (S2) (with $\tau_D = 44$ ns and $\tau_B = 1.5$ ns) using the Levenberg-Marquardt algorithm. The B_3 remains approximately the same at ca. 0.20. The fit function was convoluted with the IRF before comparing with measured decay profiles. Data analysis allows for a small correction due to scattered light. The quality of the fit of the data was determined by χ^2 which was always less than 1.5. We then subtracted the contribution of the background fluorescence described by the B_3 term to obtain values of $I_D(t')$ (eq (S2)) to calculate values of Φ_{ET}.

Calculation of Pecl, t Number. The Pecl, t number can be calculated using eq (S3). In the equation, H is the thickness of the wet film (m), $\dot{E}$ is the initial evaporation rate of water (ms^{-1}), and D_h is the diffusion coefficient of the latex particles ($m^2\ s^{-1}$).

$$Pe = \frac{H\dot{E}}{D_h} \qquad \text{(S3)}$$

The values of H, E, and D_h can be estimated either from experimental results or derived from the Stokes-Einstein equation. For all formulations, the volume fraction of latex particles to water is approximately 30%. The height of the wet film was calculated by the volume of dispersion divided by the casting area. The evaporation rates of all samples were similar, so we only show a profile of Pol.4K-Phen/DNP. To simplify the calculation, we estimated the evaporation rate from the gradient of the fast-drying region from Figure S1 as the concentration of water is proportional to the integrated absorbance. The evaporation rate is ca. 1.6×10^{-6} m/s. The diffusion coefficients of the Pol.4K-Phen/DNP and ^{XL}Pol.4K-Phen/DNP particles were calculated from DLS by the Stokes-Einstein equation model are approximately 3.2×10^{-12} $m^2\ s^{-1}$ and 2.4×10^{-12} $m^2\ s^{-1}$. Hence the

Pecl, t number for Pol.4K-Phen/DNP and ^{XL}Pol.4K-Phen/DNP would be 60 and 79 respectively at the start of drying, thus being in a region where an accumulation of particles and skin formation is likely to occur.

SUPPORTING FIGURES

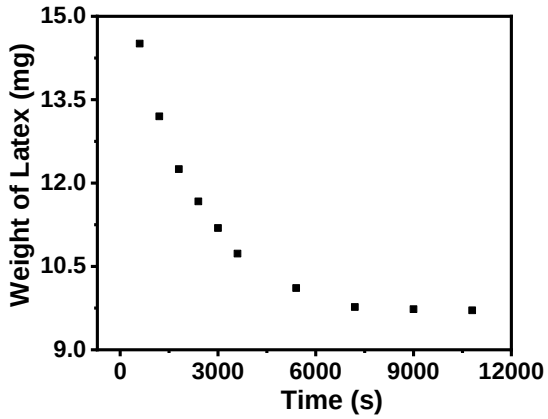


Figure S1. Mass loss as a function of time for the Pol.4K-Phen/DNP drying at 80 °C in the oven. The evaporation rate of water was obtained in the initial linear region.

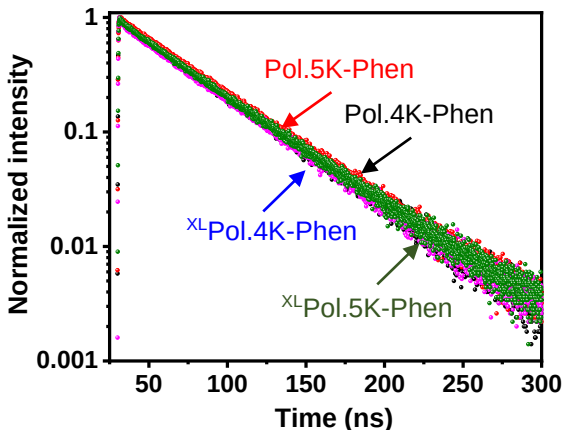


Figure S2. Normalized donor fluorescence decay profiles $I_D(t)$ of the as-prepared dispersion of Pol.4K-Phen, ^{XL}Pol.4K-Phen, Pol.5K-Phen, and ^{XL}Pol.5K-Phen.

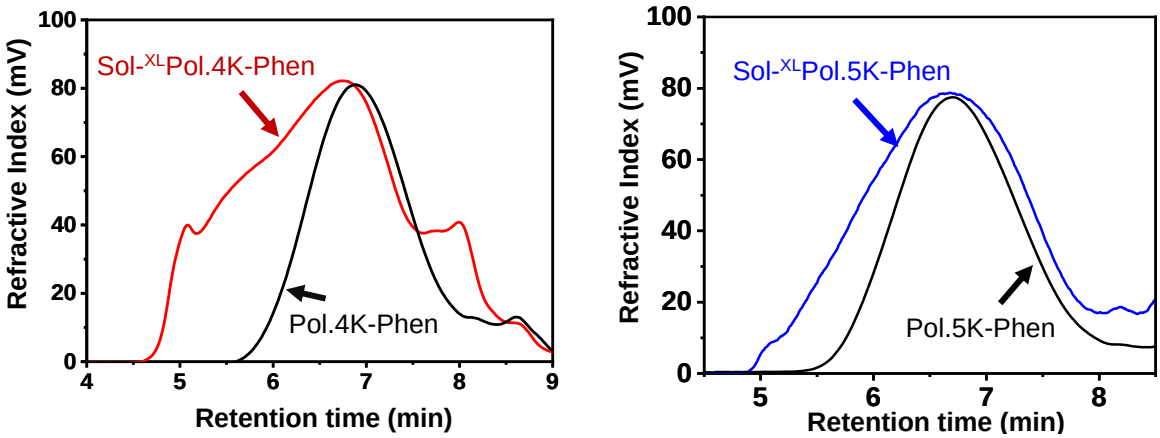


Figure S3. GPC RI traces of (A) Pol.4K-Phen (black) and the sol fraction of the ^{XL}Pol.4K-Phen (red) and (B) Pol.5K-Phen (black) and the sol fraction of the ^{XL}Pol.5K-Phen (blue). The GPC solvent was THF + salts (Tetra-n-butylammonium bromide) and the concentration of the samples was 1 mg mL^{-1}.

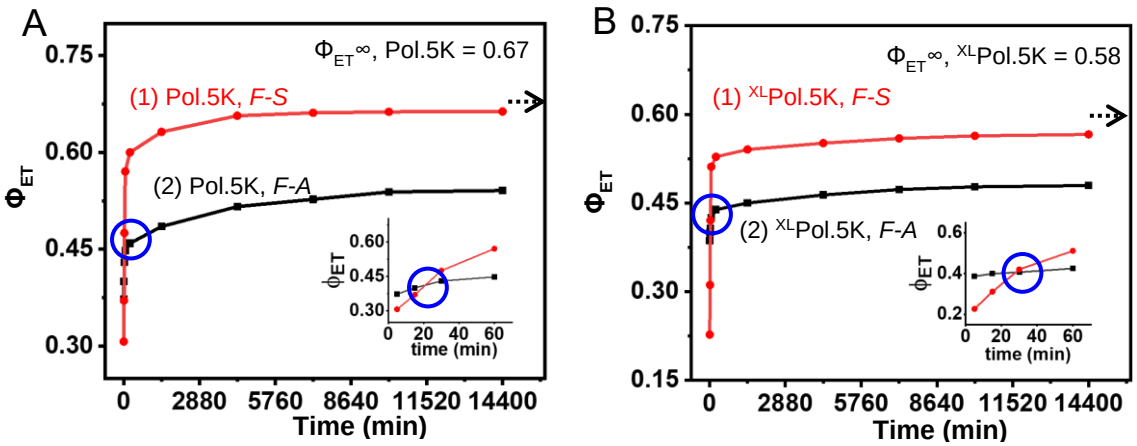


Figure S4. (A) The evolution of the efficiency of energy transfer Φ_{ET} of films upon annealing 80°C for Pol.5K from (1) the F-S interface and (2) the F-A interface; (B) Φ_{ET} of films upon annealing 80°C for ^{XL}Pol.5K from (1) the F-S interface and (2) the F-A interface.

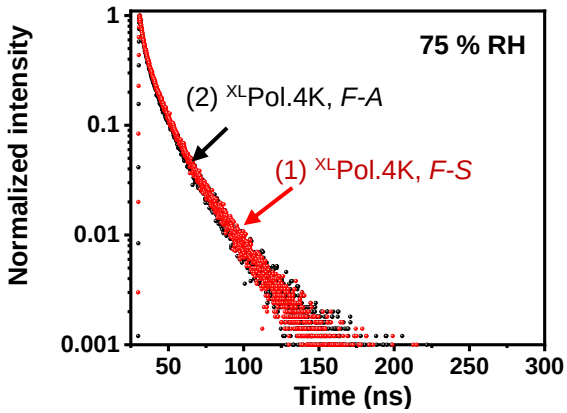


Figure S5. A) Normalized donor fluorescence decay profiles (I_D(t)) of films annealed at 80°C under 75% relative humidity for 30 min cast from the dispersion at 30 wt % solids (1:1 wt ratio of mixed Phen- and DNP-labeled nanoparticles) of ^{XL}Pol.4K

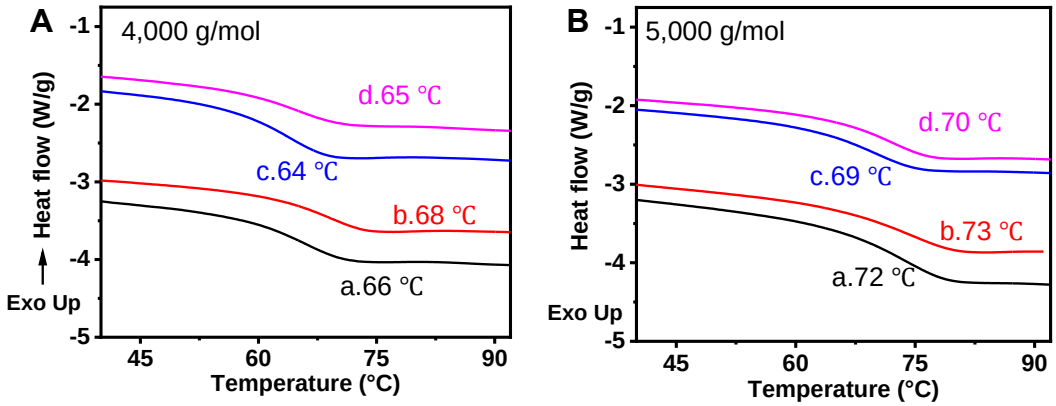
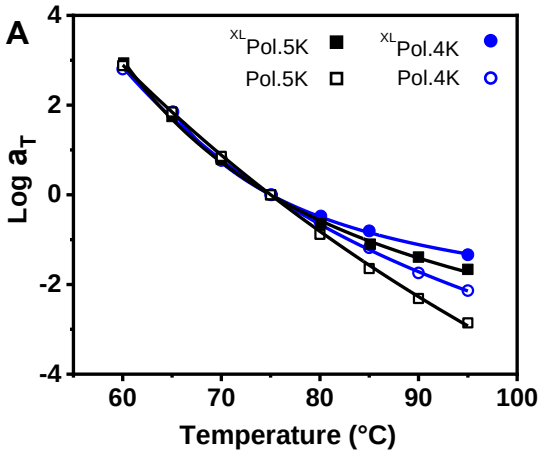


Figure S6. DSC curves of cross-linked polymer reacted with NGDE only. The fully dried samples were equilibrated at 120 °C and then scanned over a temperature range of -60 to 120 °C at a ramp of 10 °C /min for 2 complete cycles. T_g was determined as the inflection point of the second DSC heating curve at 10 °C min^{-1}. In each graph, curve a and b refer to Pol-Phen and Pol-DNP and curve c and d refers to ^{XL}Pol-Phen and ^{XL}Pol-DNP, respectively.



B

Samples	C_1	C_2	E_{av} (kcal/mol)
^{XL}Pol.4K	3.3	27.1	47
Pol.4K	8.6	60.5	69
^{XL}Pol.5K	5.3	41.5	56
Pol.5K	22.2	124.6	90

Figure S7. (A) Plot of log(a_T) against temperature ranging from 60 to 95 °C. The dot lines represent the experiment data and the solid lines are the WLF fitting. From the curve, we obtained the values of C_1 and C_2, which are presented in Table (B), at T_0 = 75 °C. We calculated the average value of activation energy (E_{av}) of different samples in the range of temperatures from 60 to 80 °C by plotting ln(a_T) in Arrhenius fashion against the inverse of the absolute temperature.

REFERENCES

(1) Gonzalez-Alvarez, M. J.; Paternoga, J.; Breul, K.; Cho, H. J.; Roshandel, M. Z.; Soleimani, M.; Winnik, M. A. Understanding particle formation in surfactant-free waterborne coatings prepared by emulsification of pre-formed polymers. *Polym. Chem.* **2017,** 8 (19), 2931-2941.

(2) Liu, Y.; Tran, K.; Zhou, H.; Heck, A.; Breul, K.; Emsermann, J.; Gonzalez-Alvarez, M. J.; Hoof, L.; Lu, Y.; Soleimani, M.; Winnik, M. A. Investigating Molecular Exchange between Partially Cross-Linked Polymer Particles Prepared by a Secondary Dispersion Process. *Macromolecules* **2019,** 52 (14), 5245-5254.