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Supporting Information

Determining Water Sorption and Desorption in Thin Hydrophilic Polymer Films by Thermal Treatment

Yeongun Ko[1], Jason R. Miles[1], Jan Genzer[1,2,*]

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[2] Global Station for Soft Matter, Global Institution for Collaborative Research and Education, Hokkaido University, Sapporo, 060-0808, Japan

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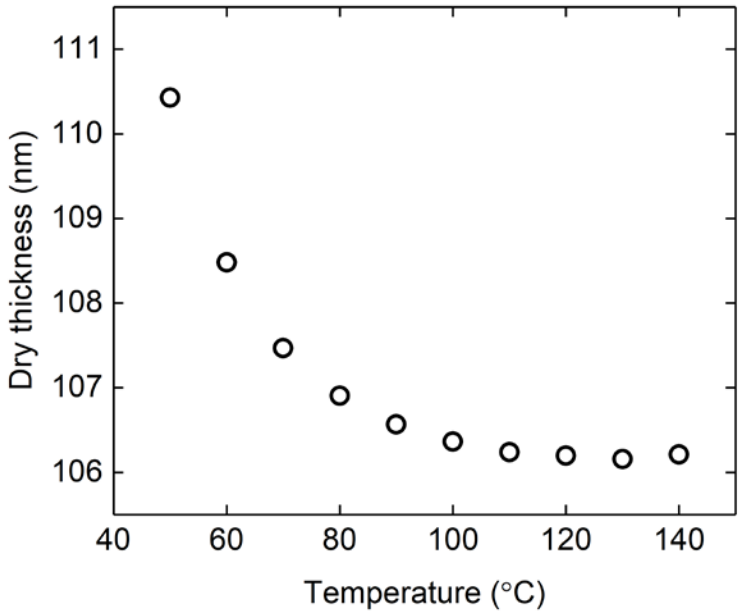


Figure S1. Thickness of qPDMAEMA-DQ 54 polymer brushes on a silicon substrate during cooling from 140°C to 50°C under ~200 kPa of nitrogen flow.

We tested water sorption into quaternized poly(2-(dimethylamino)ethyl methacrylate) brushes with 54 mol % degree of quaternization (qPDMAEMA-DQ 54) under ~200 kPa of nitrogen gas flow. To collect the data, we built a set-up that enables nitrogen gas flowing directly onto the sample surface. Upon cooling, the sample thickness increases with decreasing temperature, which reveals that flowing dry nitrogen gas over the sample does not inhibit water sorption into the polymer.

Figure S2 plots the scattering length density (SLD) profile used to model neutron reflectivity data from poly(2-(dimethylamino)ethyl methacrylate) polymer brushes. The data demonstrate that both as-prepared samples and those measured in vacuum at 50 and 80°C retain absorbed water (D_2O in this case) from moisture for up to at least 16 hrs.

Figure S3 displays the dry thickness (left ordinate) and refractive index (right ordinate) of a thin poly(methyl methacrylate) (PMMA) film resting on a flat silicon wafer subjected to cooling/heating cycles. We detected no change in the dry thickness and refractive index. The break in the slopes for the dry thickness and refractive index occurs at the polymer glass transition temperature (T_g~127°C).

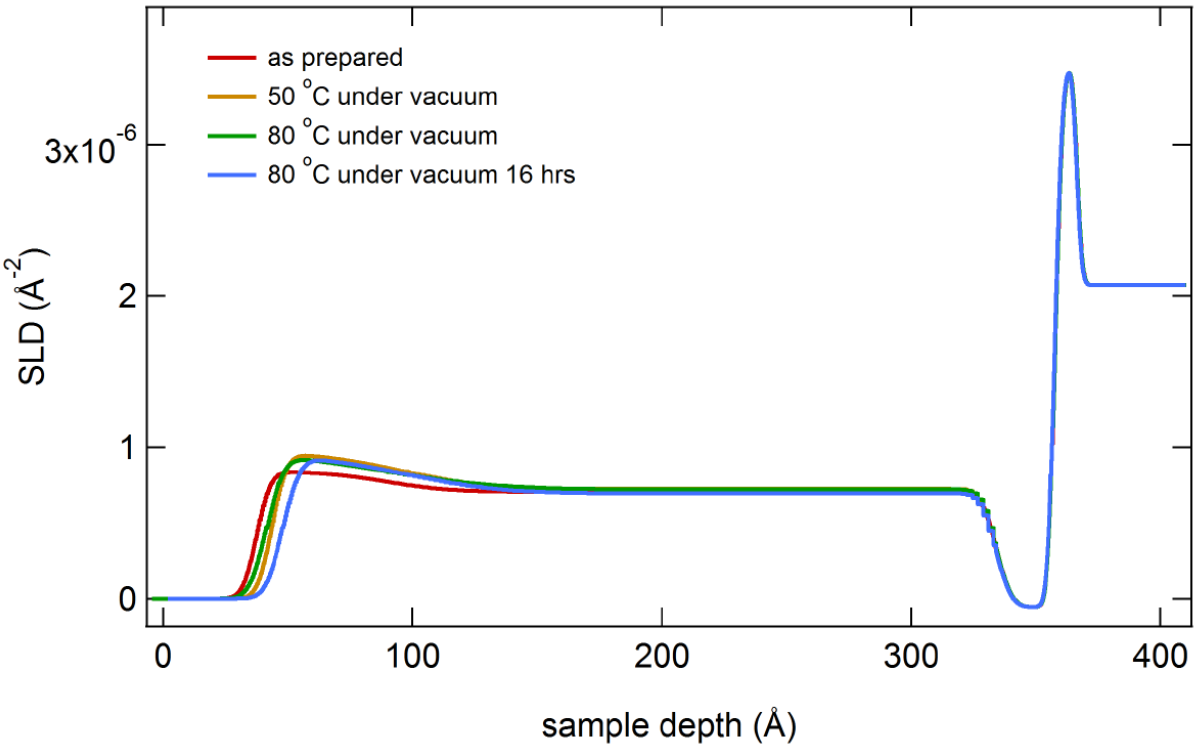


Figure S2. Scattering length density of poly(2-(dimethylamino)ethyl methacrylate) polymer brush measured in as-prepared sample (red), sample annealed at 50°C under vacuum (orange) for 1 hr, and annealed at 80°C under vacuum for 1 hr (green) and 16 hrs (blue).

In **Figure S4**, we plot the thickness of three different hydrophilic polymer thin films: (a) poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA), (b) poly(2-vinylpyridine) (P2VP), and (c) poly(4-vinylpyridine) (P4VP) as a function of temperature (measured upon cooling). P2VP and P4VP spuncast films of comparable thicknesses are examined. The P2VP and P4VP films annealed initially to elevated temperatures exhibit a linear decrease in thickness upon cooling up to their T_g (95.0°C and 151.5°C for P2VP and P4VP, respectively[1,2]) followed by another linear decease in thickness (with a lower slope in thickness *vs.* temperature due to lower CTE in the glassy state) down to a certain temperature, at which the thickness starts to increase due to water uptake. This is quite remarkable given that the temperature at which the thickness increases for P2VP and P4VP is below the T_g of the two materials.

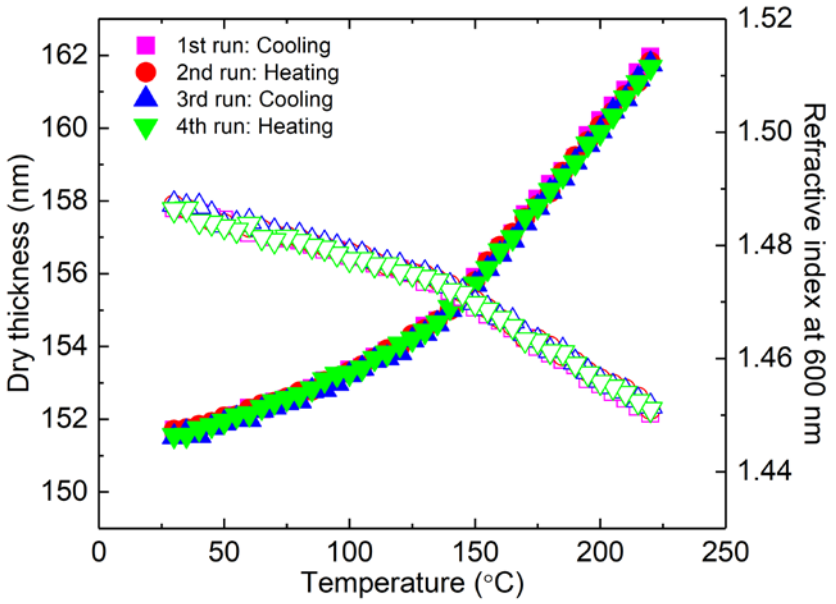


Figure S3. Dry thickness (solid symbols. left ordinate) and refractive index (open symbols. right ordinate) of PMMA thin film on a silicon wafer with temperature. Heating/cooling rate is 0.5°C/min.

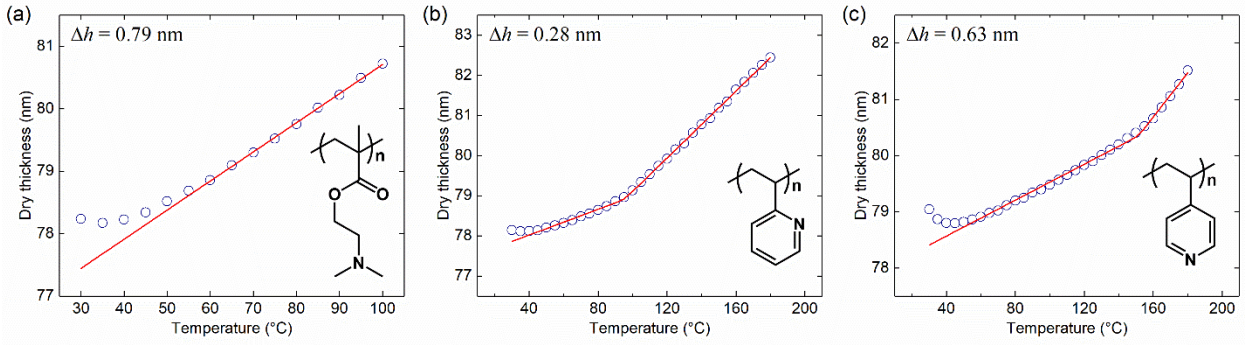


Figure S4. Measured dry thickness of (a) PDMAEMA brushes, spin-coated (b) P2VP and (c) P4VP film on a silicon substrate with temperature (open mark) and extrapolated dry thickness from **Equation 1** in the main text (red line). Δh denotes the difference between the film thickness measured at ambient conditions and the "true" thickness extrapolated from the data collected at 100°C.

PDMAEMA absorbs the largest amount of water, *i.e.*, Δh, among the three specimens studied followed by P4VP and P2VP spin-coated films. At 30°C the PDMAEMA chains are in the rubbery state, which facilitates higher sorption of water due to relatively high free volume of PDMAEMA.[3] We note that the aliphatic tertiary amine in PDMAEMA possesses more degrees of freedom than nitrogen atoms in the heterocycles of P4VP or P2VP. P4VP contains more

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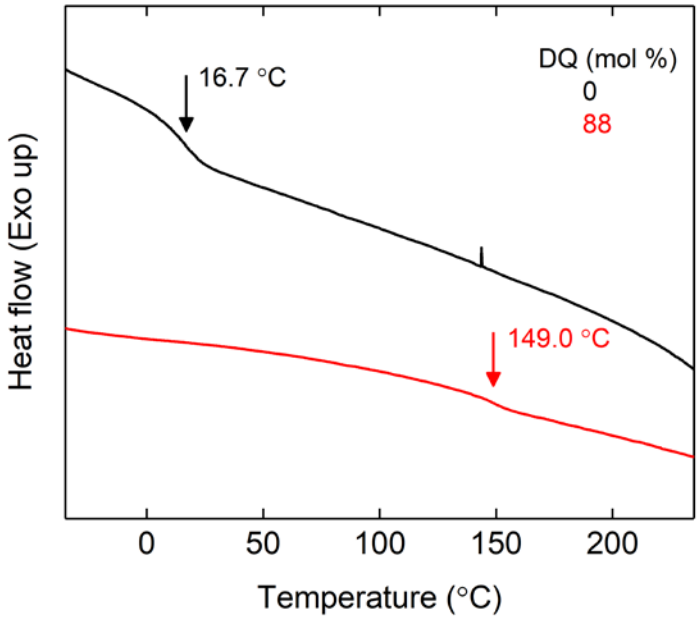


Figure S5. DSC heat flow curves for bulk qPDMAEMA-DQ 0 and qPDMAEMA-DQ 88 with a heating rate of 10°C/min. The colored arrows indicate the glass transition temperatures for corresponding polymers.

Differential scanning calorimetry (DSC, Q2000, TA instruments) analysis was used to measure glass transition temperatures of bulk qPDMAEMA. Each sample of 7-9 mg was heated to 250°C followed by cooling down to -50°C at a rate of 10°C/min to remove thermal history. The heat flow curves are obtained in the second heating process at a rate of 10°C/min. The glass transition temperature (T_g) was clearly obtained for qPDMAEMA-DQ 0 and DQ 88 as shown in **Figure S5**. The heat flow curves for the other samples show uncertain results due to the broad melting peak. We tabulated the T_g in **Table S1**.

Table S1. Glass transition temperatures of qPDMAEMA from DSC analysis.

DQ (mol %)	T_g (°C)
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64	148.8†
88	149.0

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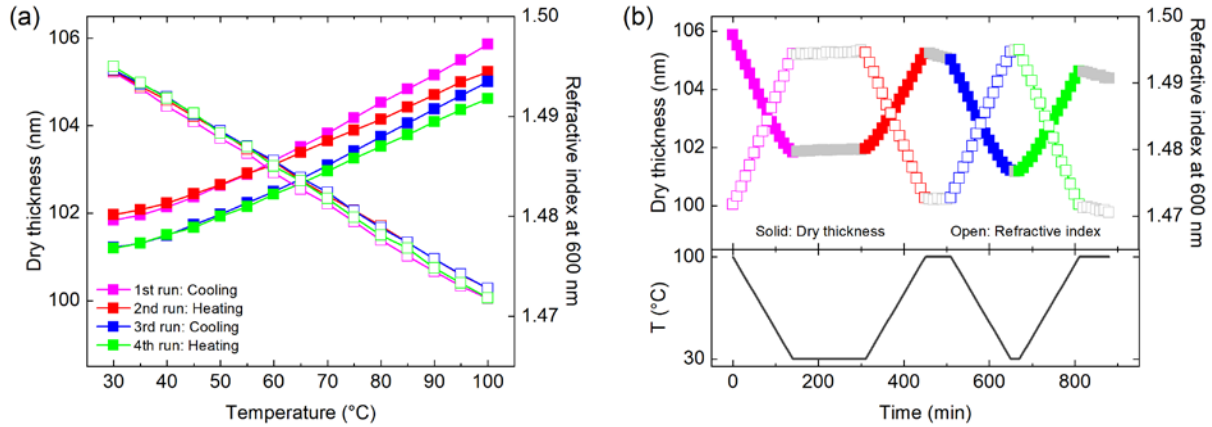


Figure S6. (a) Dry thickness (solid symbols, left ordinate) and refractive index at 600 nm (open symbols, right ordinate) of PDMAEMA brushes with cooling/heating temperature at the rate of 0.5°C/min. (b) (upper panel) Dry thickness (solid symbols, left ordinate) and refractive index (open symbols, right ordinate) of PDMAEMA brushes with time. (lower panel) Corresponding temperature profile (grey line). The colors in the upper panel in part (b) match to those in part (a).

We performed ellipsometry measurements on PDMAEMA brushes during subsequent cooling/heating cycles. The results are plotted in **Figure S6**. In contrast to similar experiments on qPDMAEMA grafts that exhibit a large hysteresis in thickness due to water desorption (heating) and absorption (cooling) (*cf.* **Figure 7**) we detect minimal differences in the dry thickness and refractive index in PDMAEMA specimens. A small decrease in the dry thicknesses during thermal heating suggests minimal degradation of PDMAEMA at elevated temperatures.

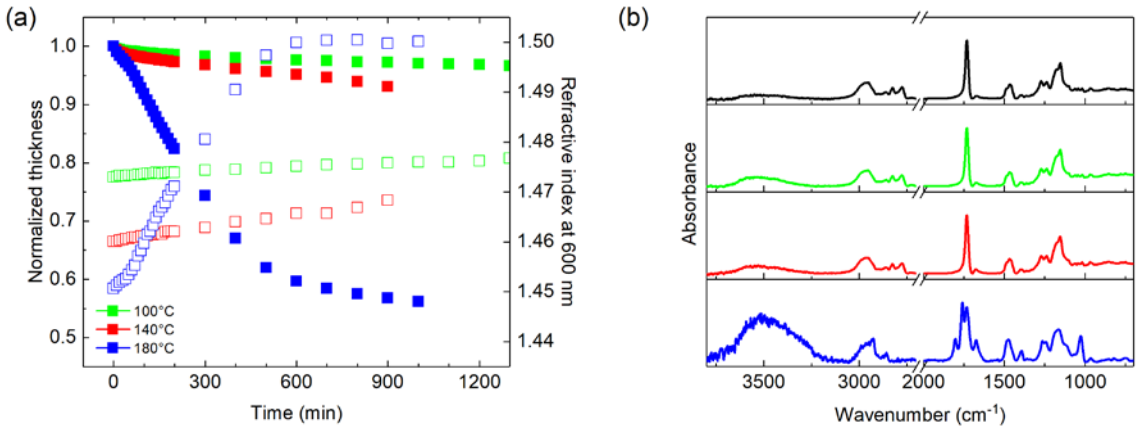


Figure S7. (a) Normalized dry thickness (solid symbols. left ordinate) and refractive index at 600 nm (open symbols. right ordinate) of PDMAEMA brushes annealed at 100°C (green, thickness 92 nm), 140°C (red, thickness 93 nm), and 180°C (blue, thickness 97 nm) as a function of annealing time. (b) FTIR-ATR spectra of parent PDMAEMA brushes (black) and PDMAEMA brushes after annealing (2200 mins at 100°C, 900 min at 140°C, and 1000 mins at 180°C). The color scheme in (b) follows that in (a). correlating samples with (a): 100 °C (green, 88 nm thickness), 140 °C (red, 87 nm dry thickness) and 180 °C (blue, 54 nm dry thickness). All thicknesses were measured at quoted temperatures.

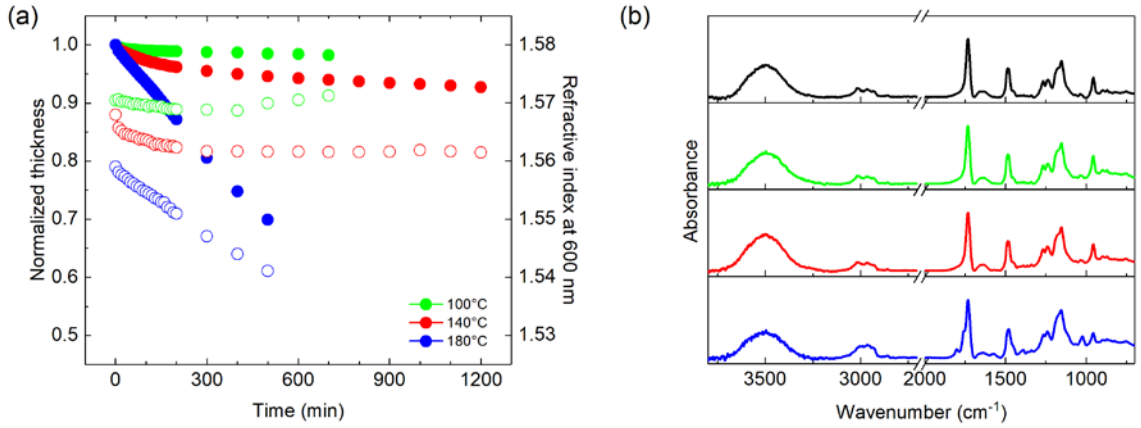


Figure S8. (a) Normalized dry thickness (solid symbols. left ordinate) and refractive index at 600 nm (open symbols. right ordinate) of qPDMAEMA-(DQ 78) annealed at 100°C (green, thickness 127 nm), 140°C (red, thickness 123 nm), and 180°C (blue, thickness 125 nm) as a function of annealing time. (b) FTIR-ATR spectra of parent qPDMAEMA brushes (black, dry thickness 125 nm) and qPDMAEMA brushes after annealing (700 mins at 100°C, 1200 min at 140°C, and 500 mins at 180°C). The color scheme in (b) follows that in (a). correlating samples with (a): 100 °C (green, 124 nm dry thickness), 140 °C (red, 115 nm dry thickness) and 180 °C (blue, 88 nm dry thickness).

PMMA thin films remain stable during the heating/cooling cycles (upper annealing temperature 220 °C). PDMAEMA and qPDMAEMA brushes exhibit some degradation when heated to elevated temperatures, as deduced from ellipsometry and FTIR-ATR measurements performed

at 100, 140 and 180°C. **Figure S7a**, **S8a** display the dry thickness (and refractive index) variations with time at each temperature. While at 100°C both PDMAEMA and qPDMAEMA are stable, annealing the samples to 140 and 180°C causes some thermal degradation (**Figure S7b**). Interestingly, qPDMAEMA appears to be more stable than PDMAEMA, as deduced from the thickness data and the corresponding FTIR measurements (**Figure S8b**). The FTIR spectra indicate chemical changes near ~1733 cm^{-1} (carbonyl group) likely due to decomposition at 180°C.[4,5]

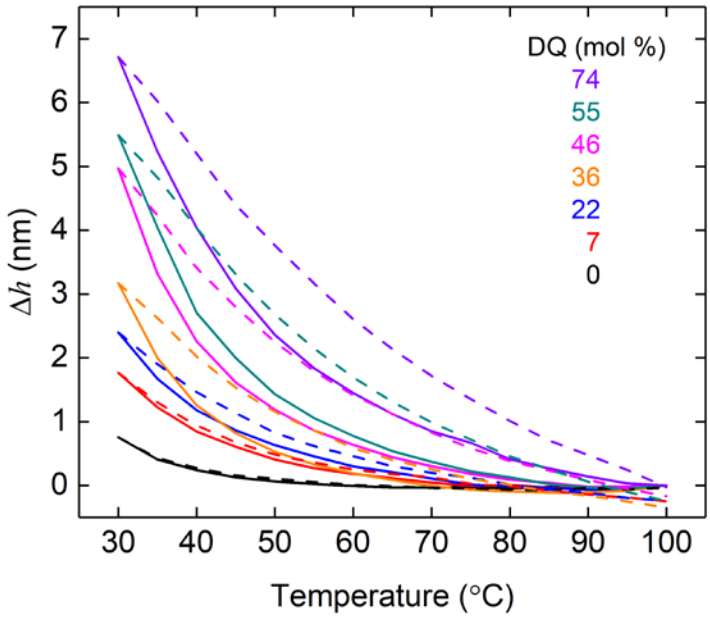


Figure S9. The difference between the film thickness measured and the thickness extrapolated from the data collected at 100°C as a function of temperature. Solid curves are in cooling process and dashed curves are in heating process.

In **Figure S9** we plot the amount of water trapped inside qPDMAEMA for various DQ, Δh. the values were obtained by subtracting the thickness of the dry film (obtained by extrapolation as explained earlier) from the total thickness measured upon cooling and heating. As noted earlier, the amount of water absorbed from air increases, leading to an increase in Δh, with decreasing the cooling temperature and reaches a certain maximum value at room temperature, Δh_{RT}. The Δh_{RT} increases with increasing DQ (**Figure 6**). Upon heating, water is liberated from the film, which leads to a decrease in Δh. For small DQ (<10 mol%) the cooling and heating temperatures that produce the same Δh are nearly identical. However, with increasing DQ (>30 mol%), the heating temperature needed to produce the same Δh is higher than the cooling temperature.

Thus, with increasing DQ it becomes increasingly more challenging to remove water from the polymer layer and higher temperatures are needed to drive the water away from the films.

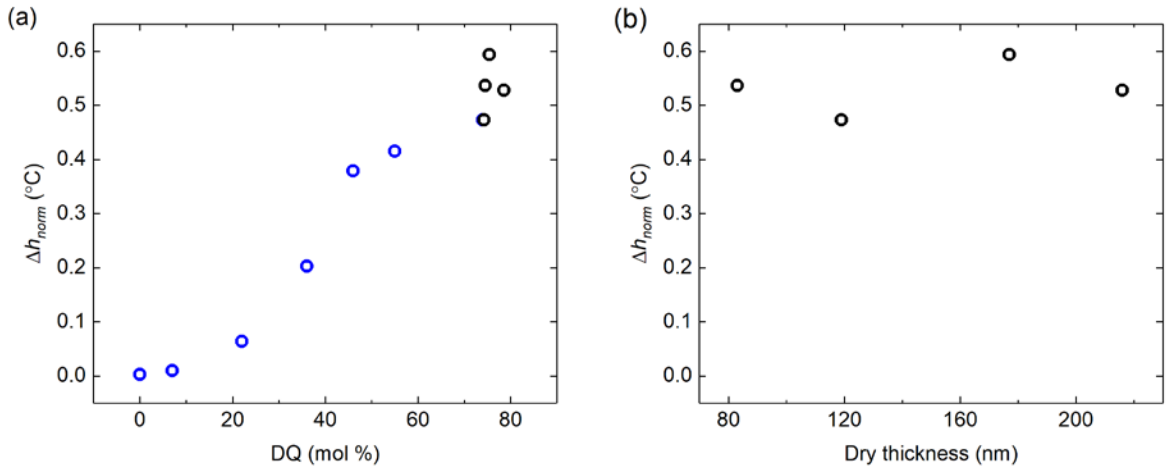


Figure S10. (a) Area between normalized thicknesses (by 100°C) of heating and cooling processes with (a) different DQ with PDMAEMA dry thickness ~100 nm (blue open symbols) and (b) different dry thicknesses (black open symbols) with DQ ~76 mol %.

To obtain a measure of the ability of the polymer layer to retain water, we integrated the area between the solid and dashed curves and normalize the value by the film thickness measured at 100°C (Δh_{norm}). In **Figure S10a** we plot Δh_{norm} as a function of DQ. In **Figure S10b** we plot Δh_{norm} for samples with DQ~81 mol % and different thickness. DQ has a strong effect on the hysteresis since qPDMAEMA polymer films with higher DQ will more likely form dense "surface skin" layer than those with lower DQ (**Figure S10a**). The existence of this "skin layer" was proposed and discussed by Unger et al. in the past.[6]

We do not currently have a direct evidence of the presence of this "skin layer". However, the data plotted in **Figure S10b**, which reveal that Δh_{norm} is independent of the layer thickness and thus the total amount of water trapped inside the film, suggest the presence of such a "skin layer". More work would have to be done to study this phenomenon in more detail further.

References

(1) Glor, E. C.; Angrand, G. V; Fakhraai, Z. Exploring the Broadening and the Existence of Two Glass Transitions Due to Competing Interfacial Effects in Thin, Supported Polymer Films. *J. Chem. Phys.* **2017**, *146* (20), 203330.

(2) Kuo, S.-W.; Wu, C.-H.; Chang, F.-C. Thermal Properties, Interactions, Morphologies, and Conductivity Behavior in Blends of Poly(Vinylpyridine)s and Zinc Perchlorate. *Macromolecules* **2004**, *37* (1), 192–200.

(3) White, R. P.; Lipson, J. E. G. Polymer Free Volume and Its Connection to the Glass Transition. *Macromolecules* **2016**, *49* (11), 3987–4007.

(4) Holland, B. J.; Hay, J. N. The Kinetics and Mechanisms of the Thermal Degradation of Poly(Methyl Methacrylate) Studied by Thermal Analysis-Fourier Transform Infrared Spectroscopy. *Polymer* **2001**, *42* (11), 4825–4835.

(5) Roy, S. G.; Bauri, K.; Pal, S.; Goswami, A.; Madras, G.; De, P. Synthesis, Characterization and Thermal Degradation of Dual Temperature- and PH-Sensitive RAFT-Made Copolymers of N,N-(Dimethylamino)Ethyl Methacrylate and Methyl Methacrylate. *Polym. Int.* **2013**, *62* (3), 463–473.

(6) Unger, K.; Resel, R.; Coclite, A. M. Dynamic Studies on the Response to Humidity of Poly (2-Hydroxyethyl Methacrylate) Hydrogels Produced by Initiated Chemical Vapor Deposition. *Macromol. Chem. Phys.* **2016**, *217* (21), 2372–2379.

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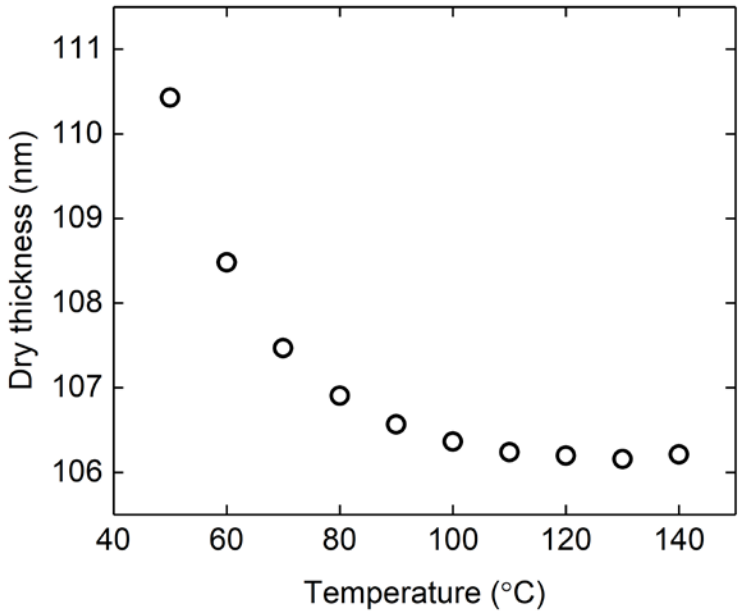


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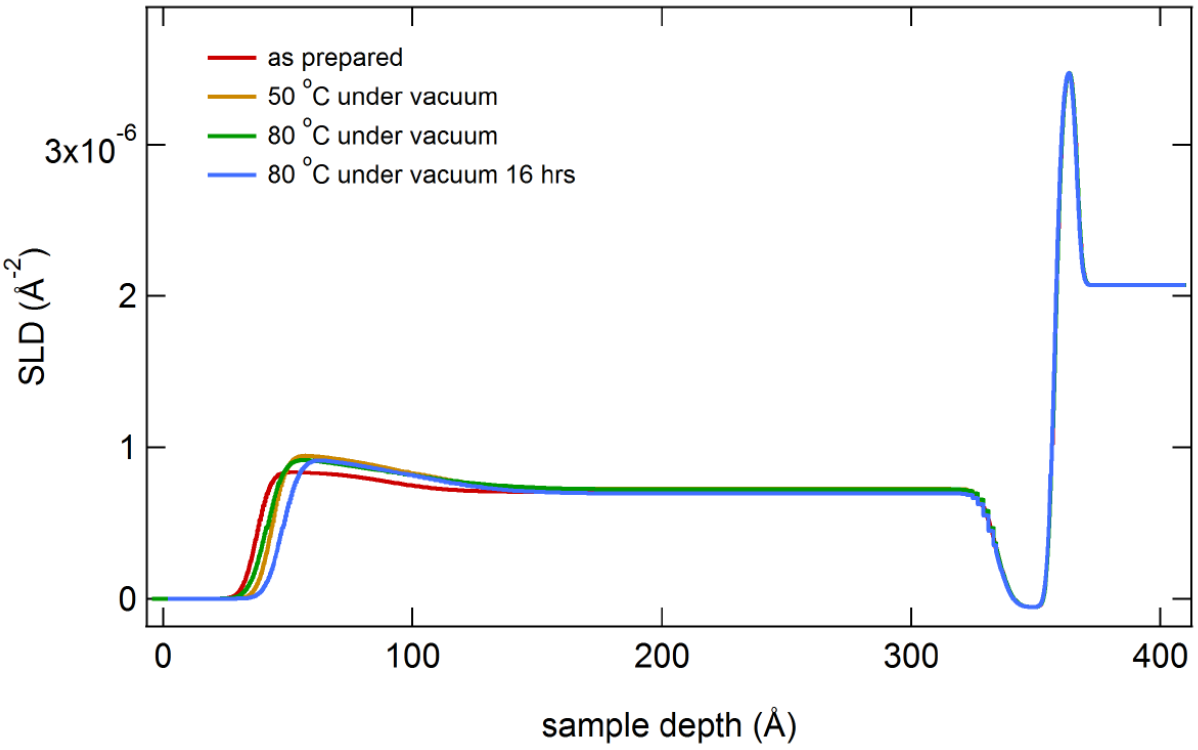


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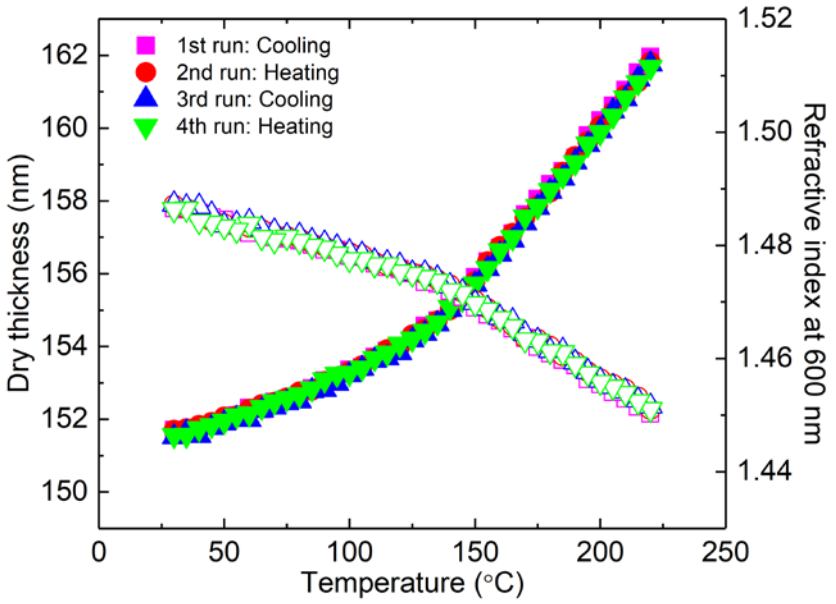


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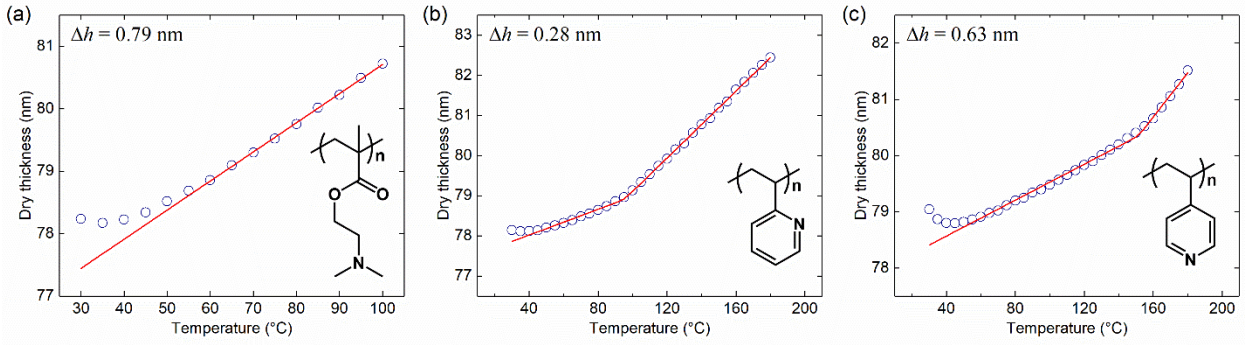


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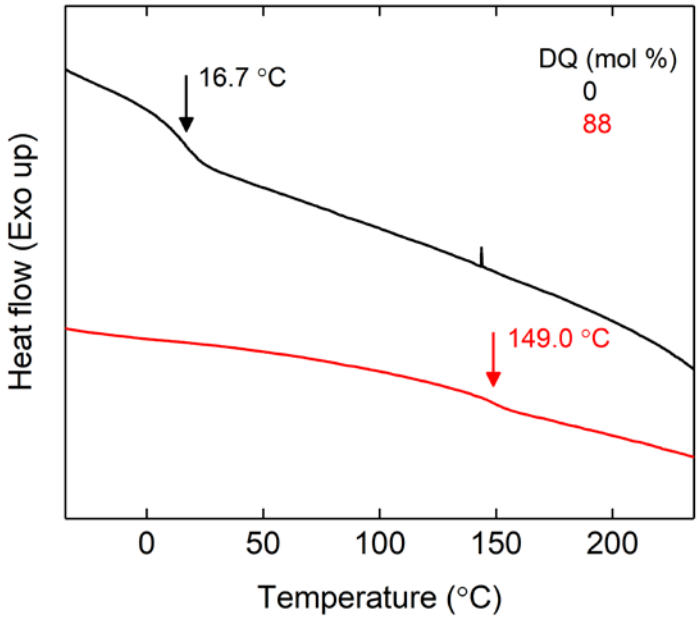


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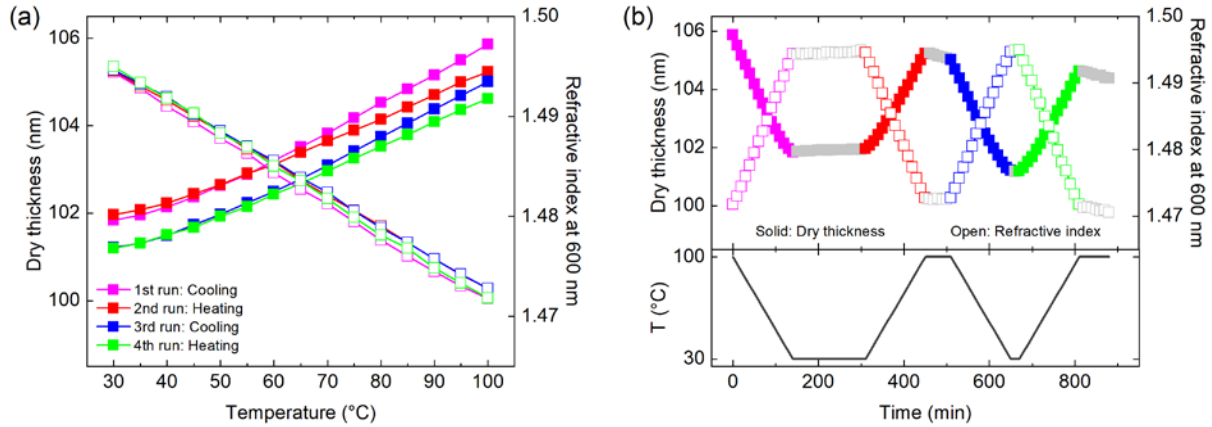


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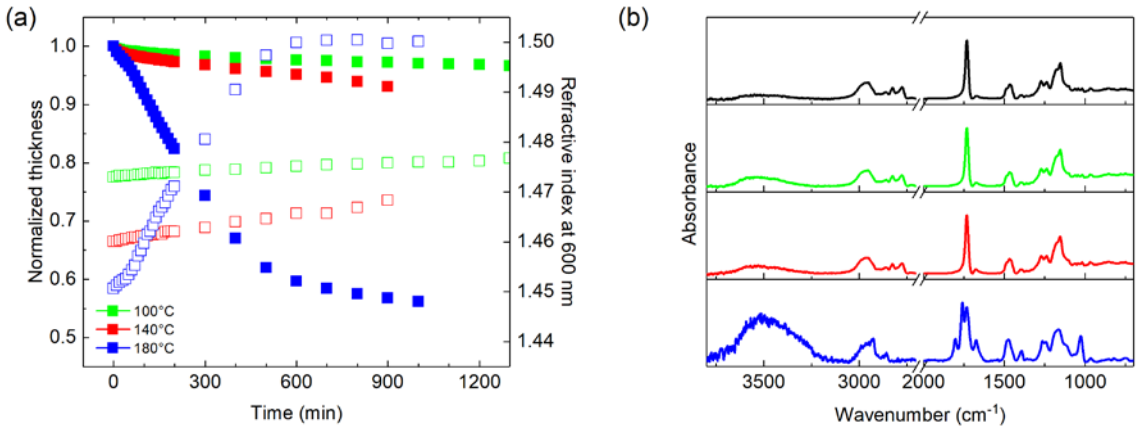


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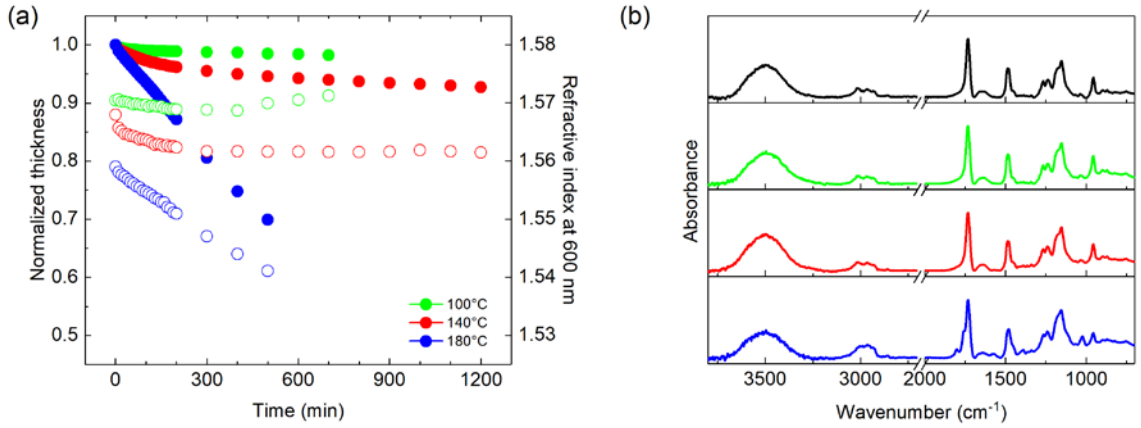


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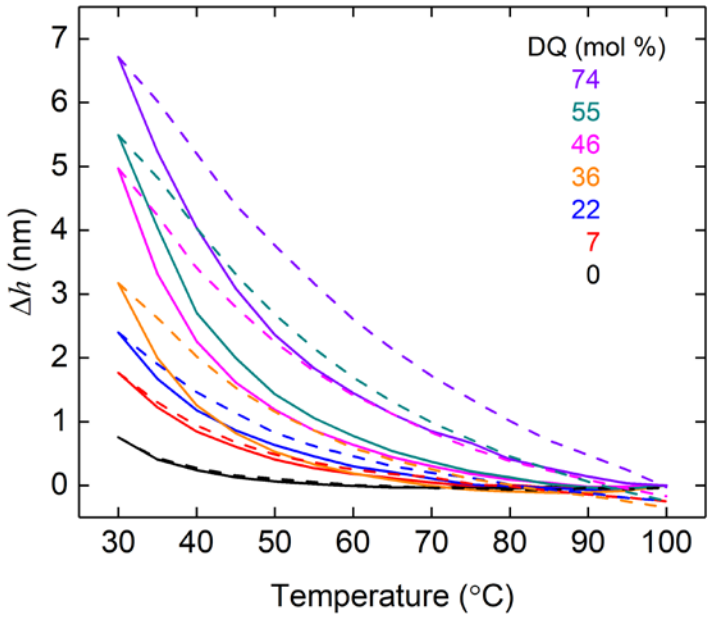


Figure S9. The difference between the film thickness measured and the thickness extrapolated from the data collected at 100°C as a function of temperature. Solid curves are in cooling process and dashed curves are in heating process.

In **Figure S9** we plot the amount of water trapped inside qPDMAEMA for various DQ, Δh. the values were obtained by subtracting the thickness of the dry film (obtained by extrapolation as explained earlier) from the total thickness measured upon cooling and heating. As noted earlier, the amount of water absorbed from air increases, leading to an increase in Δh, with decreasing the cooling temperature and reaches a certain maximum value at room temperature, Δh_{RT}. The Δh_{RT} increases with increasing DQ (**Figure 6**). Upon heating, water is liberated from the film, which leads to a decrease in Δh. For small DQ (<10 mol%) the cooling and heating temperatures that produce the same Δh are nearly identical. However, with increasing DQ (>30 mol%), the heating temperature needed to produce the same Δh is higher than the cooling temperature.

Thus, with increasing DQ it becomes increasingly more challenging to remove water from the polymer layer and higher temperatures are needed to drive the water away from the films.

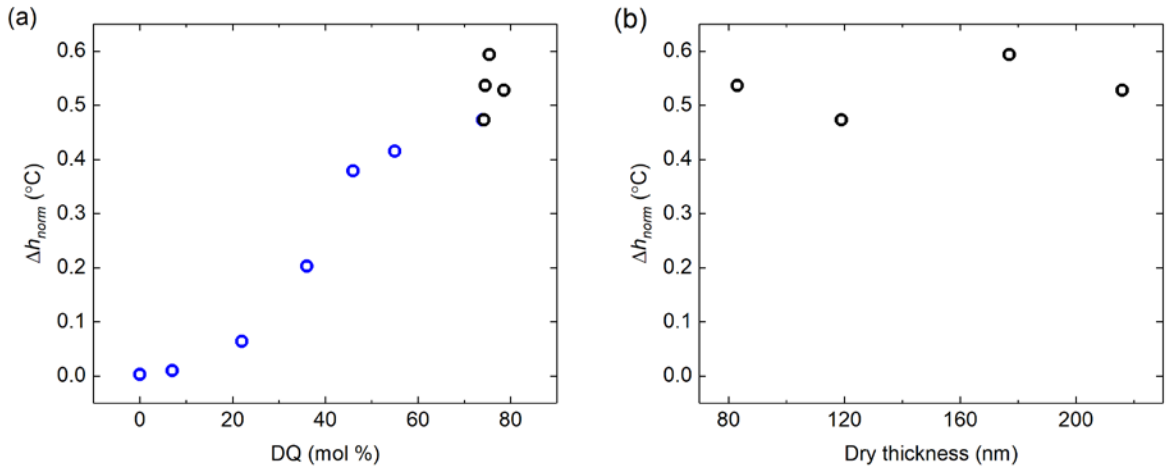


Figure S10. (a) Area between normalized thicknesses (by 100°C) of heating and cooling processes with (a) different DQ with PDMAEMA dry thickness ~100 nm (blue open symbols) and (b) different dry thicknesses (black open symbols) with DQ ~76 mol %.

To obtain a measure of the ability of the polymer layer to retain water, we integrated the area between the solid and dashed curves and normalize the value by the film thickness measured at 100°C (Δh_{norm}). In **Figure S10a** we plot Δh_{norm} as a function of DQ. In **Figure S10b** we plot Δh_{norm} for samples with DQ~81 mol % and different thickness. DQ has a strong effect on the hysteresis since qPDMAEMA polymer films with higher DQ will more likely form dense "surface skin" layer than those with lower DQ (**Figure S10a**). The existence of this "skin layer" was proposed and discussed by Unger et al. in the past.[6]

We do not currently have a direct evidence of the presence of this "skin layer". However, the data plotted in **Figure S10b**, which reveal that Δh_{norm} is independent of the layer thickness and thus the total amount of water trapped inside the film, suggest the presence of such a "skin layer". More work would have to be done to study this phenomenon in more detail further.

References

(1) Glor, E. C.; Angrand, G. V; Fakhraai, Z. Exploring the Broadening and the Existence of Two Glass Transitions Due to Competing Interfacial Effects in Thin, Supported Polymer Films. *J. Chem. Phys.* **2017**, *146* (20), 203330.

(2) Kuo, S.-W.; Wu, C.-H.; Chang, F.-C. Thermal Properties, Interactions, Morphologies, and Conductivity Behavior in Blends of Poly(Vinylpyridine)s and Zinc Perchlorate. *Macromolecules* **2004**, *37* (1), 192–200.

(3) White, R. P.; Lipson, J. E. G. Polymer Free Volume and Its Connection to the Glass Transition. *Macromolecules* **2016**, *49* (11), 3987–4007.

(4) Holland, B. J.; Hay, J. N. The Kinetics and Mechanisms of the Thermal Degradation of Poly(Methyl Methacrylate) Studied by Thermal Analysis-Fourier Transform Infrared Spectroscopy. *Polymer* **2001**, *42* (11), 4825–4835.

(5) Roy, S. G.; Bauri, K.; Pal, S.; Goswami, A.; Madras, G.; De, P. Synthesis, Characterization and Thermal Degradation of Dual Temperature- and PH-Sensitive RAFT-Made Copolymers of N,N-(Dimethylamino)Ethyl Methacrylate and Methyl Methacrylate. *Polym. Int.* **2013**, *62* (3), 463–473.

(6) Unger, K.; Resel, R.; Coclite, A. M. Dynamic Studies on the Response to Humidity of Poly (2-Hydroxyethyl Methacrylate) Hydrogels Produced by Initiated Chemical Vapor Deposition. *Macromol. Chem. Phys.* **2016**, *217* (21), 2372–2379.