Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Interfacial and Volumetric Sensitivity of the Dry Sintering Process of Polymer Colloidal Crystals: A Thermal Transport and Photonic Bandgap Study

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Stages of latex film formation

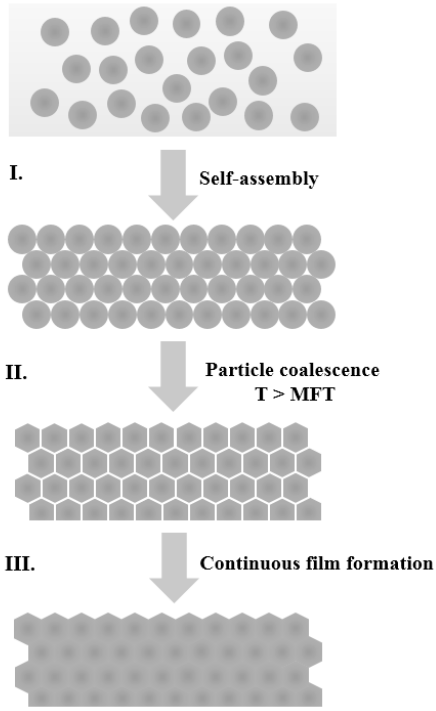

Figure S 1**:** Schematic view on the three stages of the colloidal film formation process. (I.) Self-assembly of the particles; (II.) particle coalescence by exceeding the particles minimum film formation temperature (MFT); (III.) continuous film formation due to interpenetration of the polymer chains across the particle-particle interfaces.

Details on laser flash analysis

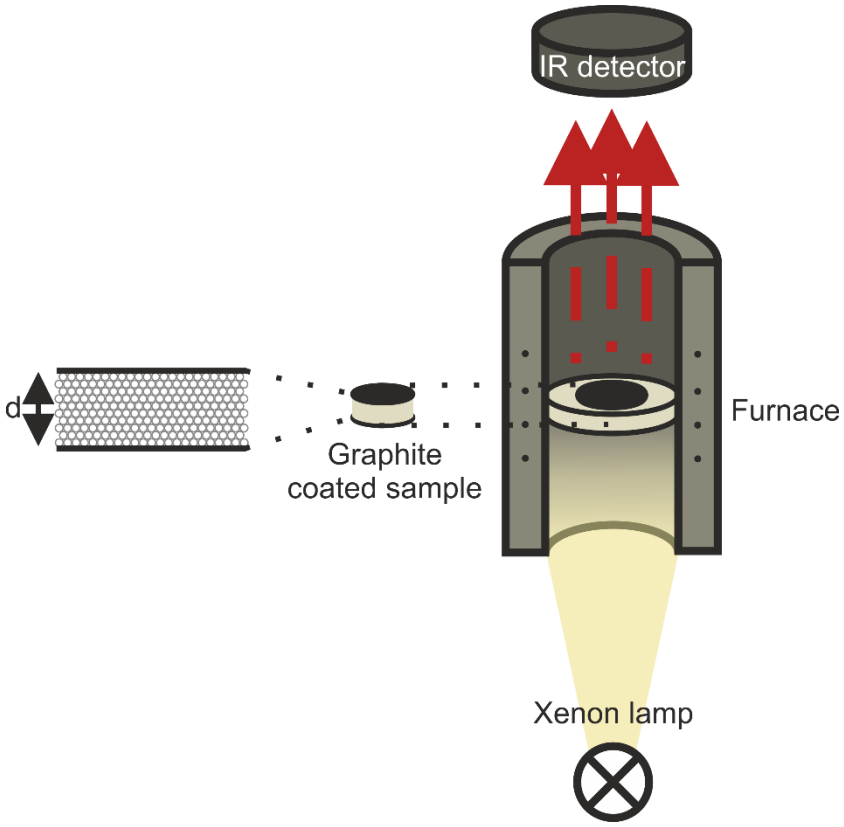

Figure S 2: Schematic setup of a Laser flash apparatus.

Measurements were carried out under helium atmosphere to enable a good heat transfer from the oven to the sample. Before the measurement, the top and bottom of the samples were metalized with a 100-200 nm gold or silver layer, which serves as blocking layer for the light pulse. Additionally, both sides were coated with a thin layer of graphite (<20 μm), to ensure a high absorbance of the light pulse at the bottom side and a high IR emission at the top side. The generated heat of the light pulse at the bottom side is transported through the sample and emitted as IR radiation at the top side of the sample. The intensity of the IR signal is then recorded in dependence of time. The raw data is fitted using a radiation fit model provided from Linseis. From laser flash analysis, the sample's thermal diffusivity α is calculated according to equation 1.

$$\alpha = \frac{1.38 \cdot d^2}{t_{1/2}} \quad (1)$$

where d represents the thickness of the sample and $t_{1/2}$ is the time needed to reach half of the maximum temperature rise. The thermal conductivity κ can then be calculated as follows:

$$\kappa(T) = \alpha(T) \cdot c_p(T) \cdot \rho(T) \quad (2)$$

C_p is the specific heat capacity of the sample, which is determined by DSC. ϱ representing the density of the sample. The density of the colloidal crystals and the molten colloidal films is determined by 3D macroscopy and a buoyancy balance, respectively.

The thickness and the density of the crystal will undergo significant changes during film formation (thickness decreases, density increases). However, it is not possible to follow these changes during the laser flash experiment in-situ. Therefore, a step-function behavior was assumed at T_g for the thickness and the density of the crystal by determining both quantities before and after the laser flash experiment.

For time-dependent laser flash analysis the changes in sample thickness have to be considered more precisely. Since it is not possible to follow the decrease in thickness during laser flash analysis *in-situ*, we determined the time-dependent behaviour of the sample thickness at 70, 75, and 80°C separately (Figure S 3A). The crystal thickness was found to follow a single-exponential function. By measuring the sample thickness before and after the experiment it is possible to incorporate this behaviour into the calculations of α according to equation 1 assuming the same exponential behaviour between the measurable initial and final sample thickness within the laser flash experiment.

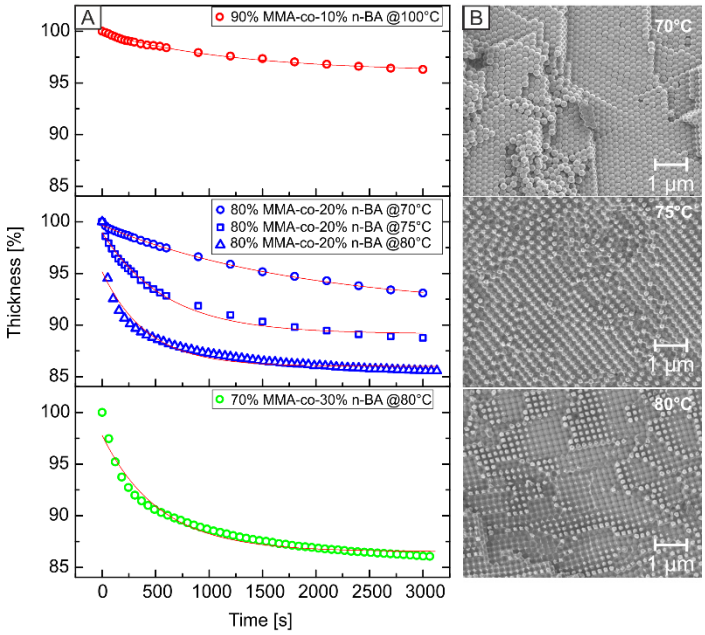

Figure S 3**:** a) Time-dependent decay of the thickness of different colloidal crystals: the thickness reduction can be described by an exponential decay. b) SEM side-view micrographs of 80% MMA-co-20% nBA colloidal crystals annealed for 50 min at the denoted temperature:

The crystal thickness behaves similarly for every temperature under investigation. The thickness decreases faster with increasing temperature due to a higher mobility of the polymer chains at higher temperatures. This leads to a faster softening of the particles, resulting in a faster loss of porosity and thus, to a faster decrease in height of the crystal.

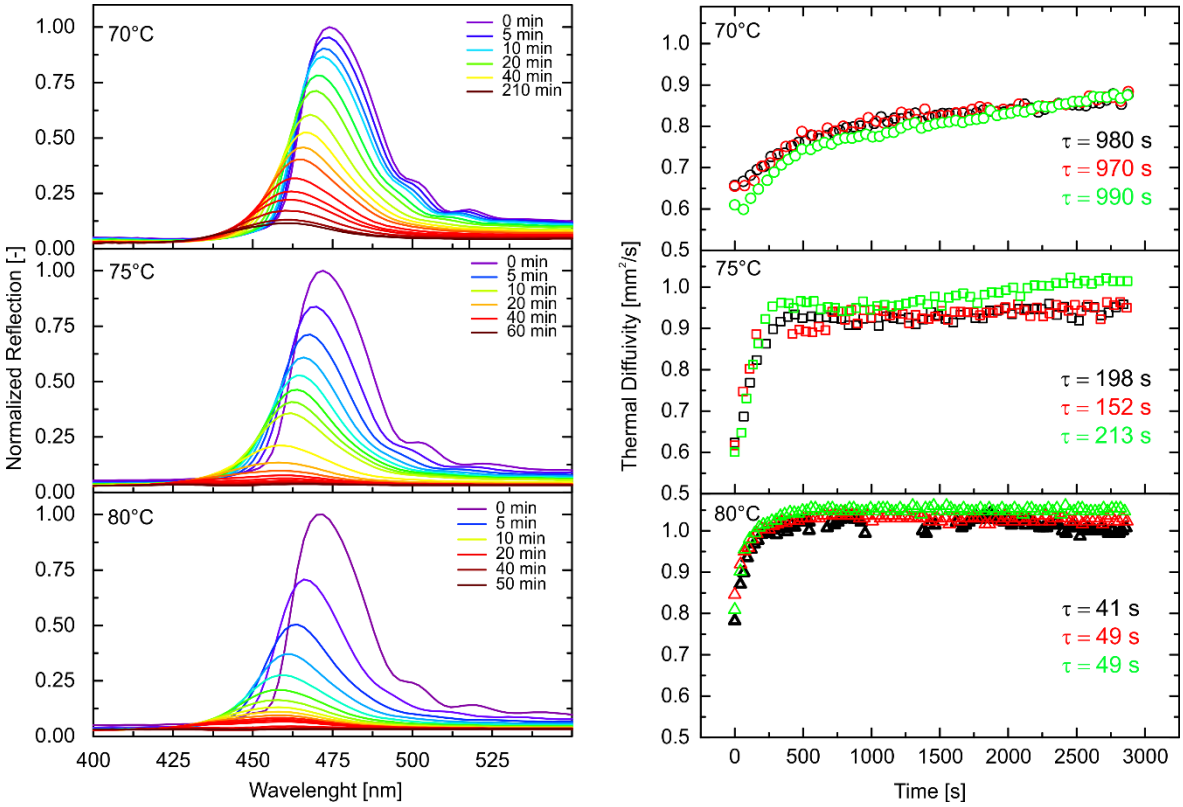

Figure S 4: left) Time-dependent UV-Vis of an 80% MMA-co- 20%-nBA colloidal crystal at 70, 75 and 80°C, respectively. right) Time-dependent laser flash analysis of three individual samples at the specified temperatures.

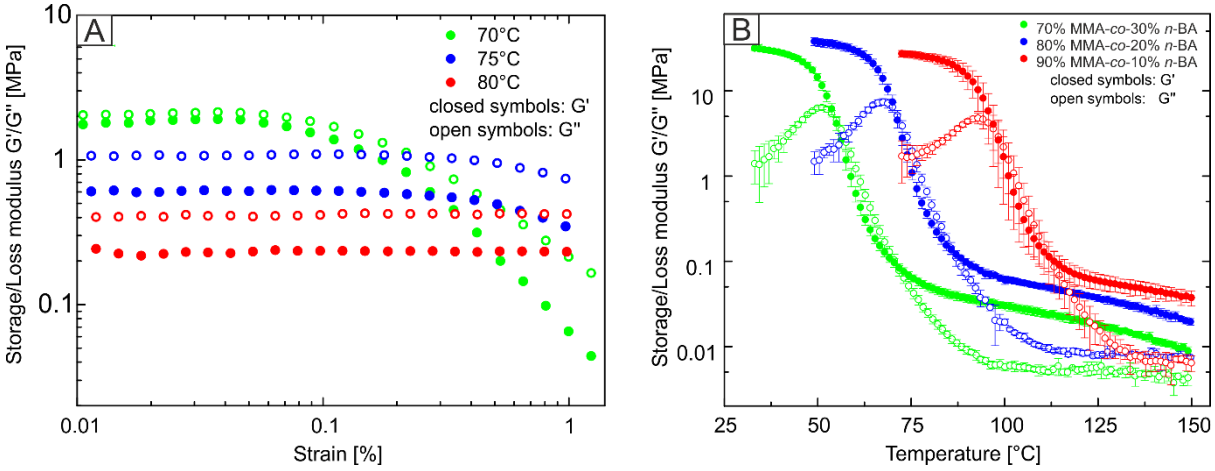

Figure S 5: a) strain sweep for 80% MMA-co- 20%-nBA polymer at 70, 75 and 80°C to determine the viscoelastic regime. b) Temperature-dependent storage/loss modulus of the three different polymers.