

Supporting Information

Initiator-dependent kinetics of lyotropic liquid crystal-templated thermal polymerization

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Gap dependency test for rheological measurements

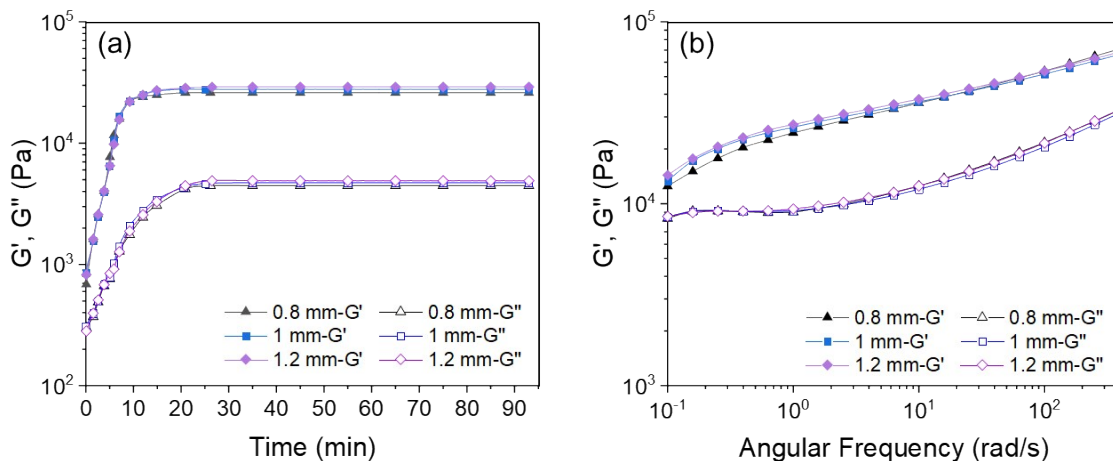


Fig. S1. Confirming the absence of wall slip during rheological measurements: typical rheological behavior of the sample with lamellar LLC structure (a) during polymerization by APS and (b) after polymerization under different gaps between the measuring plates.

Typical raw data for DSC analysis

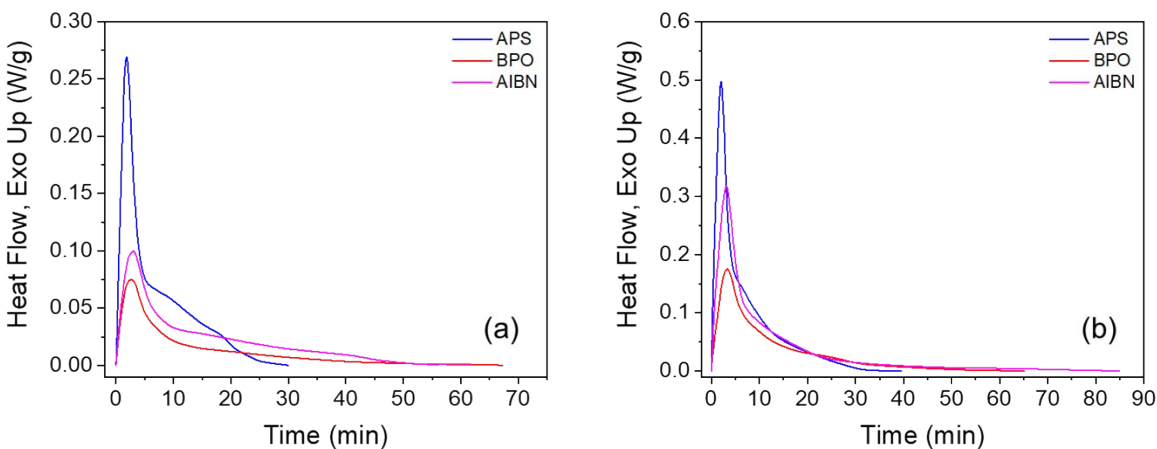


Fig. S2. Typical raw DSC data for the polymerization in (a) lamellar and (b) hexagonal structures using different initiators. The heat flow has been normalized to the total weight of the mesophase used for the analysis (not total monomer content).

Theoretical concentration of the free radicals generated by different initiators over time

The theoretical cumulative concentration of free radicals generated through the decomposition of initiators was calculated by the following equation:¹

$$[R] = 2f[I]_0(1 - e^{-k_d t})$$

Where $[R]$, f , $[I]_0$, k_d and t are the cumulative concentration of free radicals, the initiator efficiency, initial concentration of the initiator, decomposition rate constant of the initiator, and time, respectively. The average value of 0.5 is commonly used for f in the case of AIBN.² However, there is not a firm average value reported in the literature for BPO³ and APS.⁴ Therefore, to cancel out the effect of f , we normalized $[R]$ to f , resulting in the following equation:

$$\frac{[R]}{f} = 2[I]_0(1 - e^{-k_d t})$$

It should be noted that this calculation was made just to have a comparison among different initiators in terms of difference in the rate of free radical generation over time. So, the presented concentrations do not reflect the actual free radical concentration during LLC templating.

The calculation was made for the monomer content used in the formulation of lamellar structure (the calculation itself does not depend on the LLC structure) at three different temperatures. To do so, the values shown in Table S1 was used for k_d of different initiators. To calculate the k_d values, the activation energy, pre-exponential factor, and k_d at the reference temperature were obtained from the literature for different initiators.^{2,4-7} k_d was then calculated at the desired temperature using Arrhenius equation. The initial concentration for all of the initiators was 0.33 M with respect to the total monomer content.

Table S1. Decomposition rate constant of different initiators at different temperatures.^{2,4-7}

Initiator	T (°C)	k_d (s ⁻¹)
APS	55	2.54×10^{-6}
	65	1.09×10^{-5}
	75	4.36×10^{-5}
AIBN	55	6.18×10^{-6}
	65	2.53×10^{-5}
	75	9.57×10^{-5}
BPO	55	2.04×10^{-6}
	65	7.85×10^{-6}
	75	2.79×10^{-5}

To make similar calculations for the systems in which the combination of two initiators with total concentration of 5 mol% is used (2.5 mol% APS + 2.5 mol% AIBN or 2.5 mol% APS + 2.5 mol% BPO), the following equation was used. In these samples, the initial concentration for each initiator was 0.165 M.

$$\frac{[R]}{f} = \frac{[R]_{APS}}{f_{APS}} + \frac{[R]_{AIBN \text{ or } BPO}}{f_{AIBN \text{ or } BPO}}$$

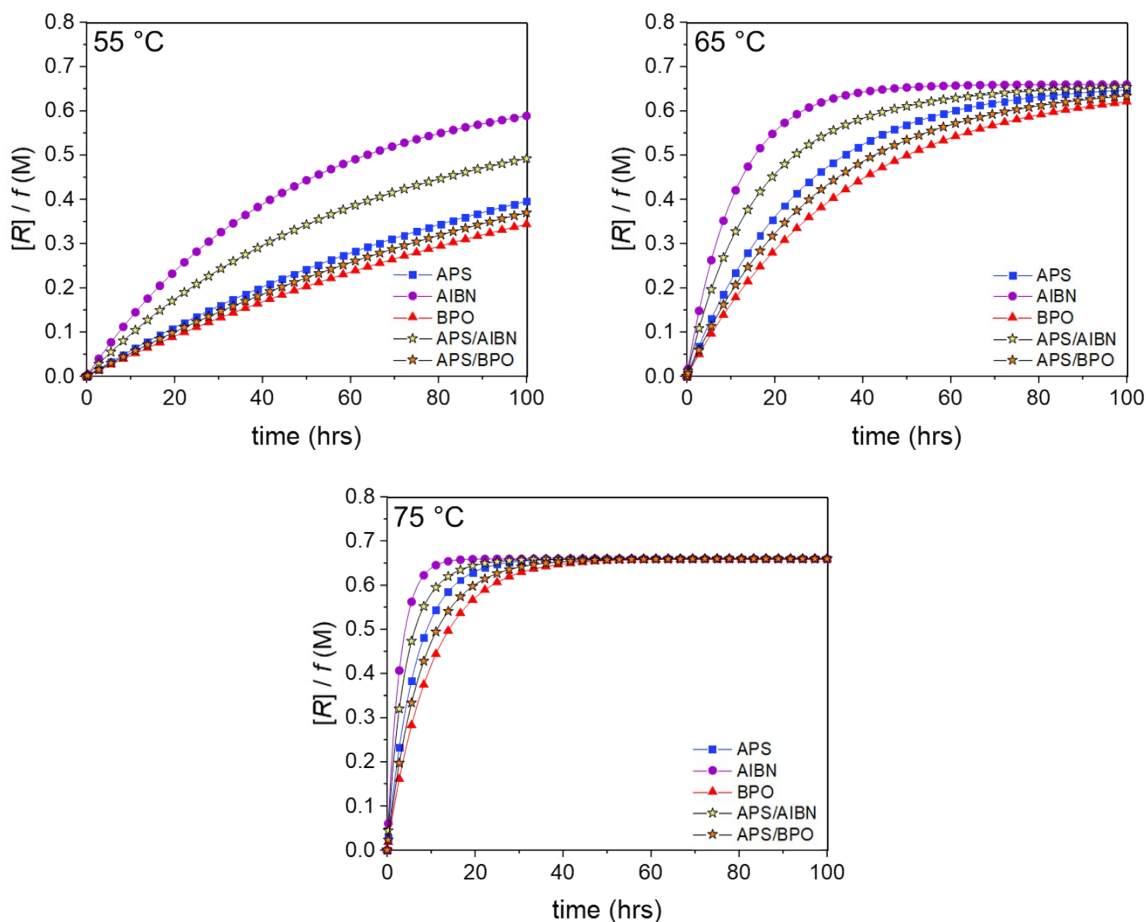


Fig. S3. Normalized theoretical concentration of the free radicals generated by different initiators over time at three different temperatures.

Scaling of maximum polymerization rate with initiator concentration

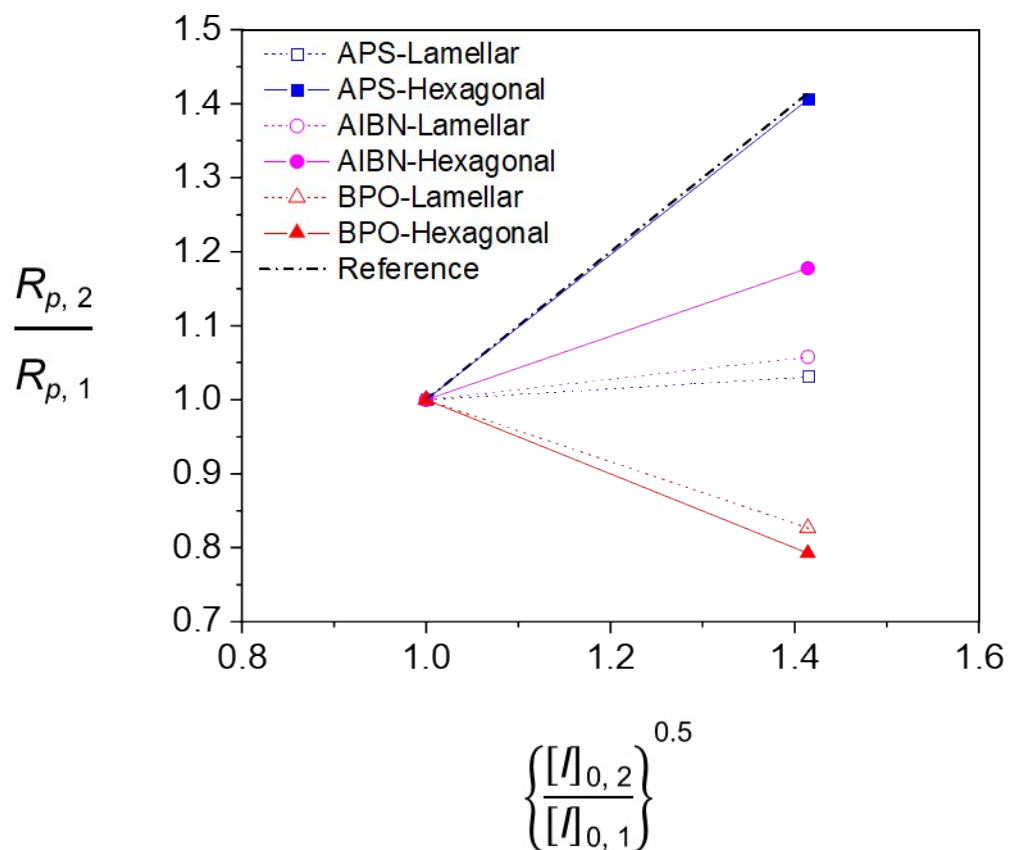


Fig. S4. Change in maximum polymerization rate in lamellar and hexagonal structures with a change in the content of different initiators. $R_{p,1}$ and $R_{p,2}$ are the maximum polymerization rate when initial initiator content of $[I]_{0,1}$ and $[I]_{0,2}$ are used respectively. For different polymerization systems, $[I]_{0,1}$ and $[I]_{0,2}$ are initiator content of 2.5 and 5 mol% with respect to the total monomer content, respectively. In this figure, “Reference” represents the relation of reaction rate with the square root of initial initiator concentration, $R_p \propto ([I]_0)^{0.5}$. The lines connecting the data point are added as a guide for the eye.

Change of overall kinetics rate coefficient with temperature

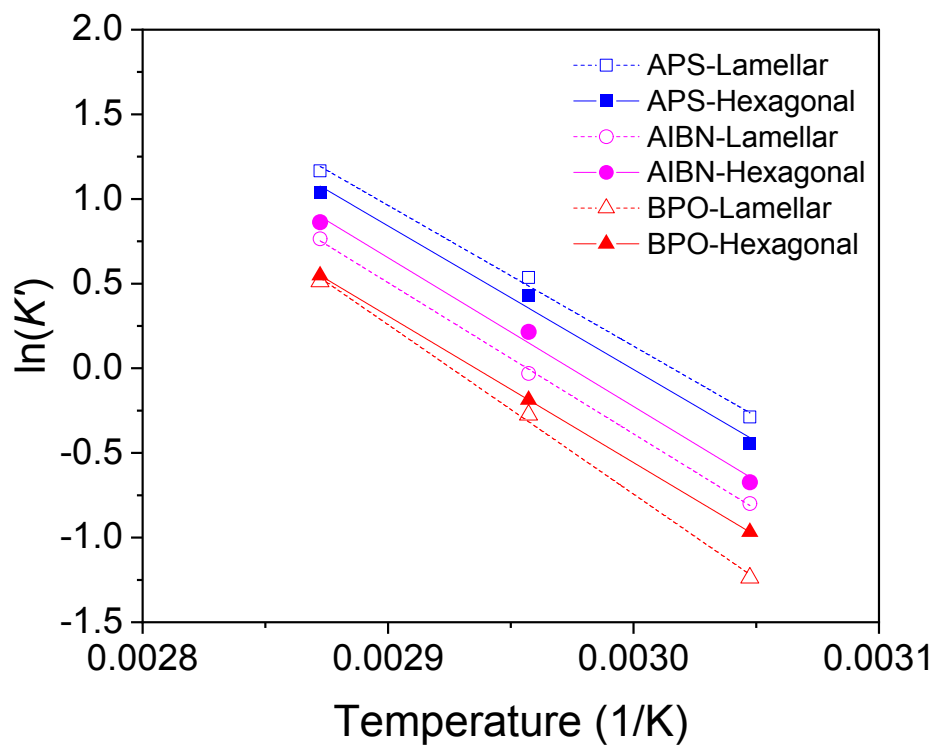


Fig. S5. Overall kinetics rate coefficient vs temperature in lamellar and hexagonal structures using different initiators. Lines are linear fits to data. For APS-initiated system, K' are bigger in lamellar structure compared to hexagonal one in all of the temperatures. The opposite trend is observed for the reactions initiated by AIBN and BPO.

References

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