Supplementary Information

Directing block copolymer self-assembly with permanent magnets: photopatterning microdomain alignment and generating oriented nanopores

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Grain size determination

The orientation distribution coefficient, or orientational order parameter $P_2$, \textbf{Eq. 1}, is determined experimentally from Gaussian fits to the azimuthal intensity distribution.

The dependence of the magnetostatic energy $E_m$ (\textbf{Eq. 2}) on field strength, grain size and $\Delta \chi$ facilitates measurement of grain size, if $\Delta \chi$ is known, and if $P_2$ is measured as a function of field strength. Specifically, the probability of observing a grain at an angle $\varphi$ relative to the field is governed by a Boltzmann factor involving the magnetostatic energy, $|\Delta E_m| = |\Delta \varepsilon_m| V_g$.

The integration of this probability (\textbf{Eq. 3}) yields an orientation distribution coefficient that is a function of the field strength. A least-squares fit of the experimentally measured $P_2(B)$ thereby provides an estimate for the characteristic grain size $\xi$, where the grain volume $V_g = \xi^3$.

\begin{align*}
P_2 &= \left\langle \frac{1}{2} (3 \cos^2 \varphi - 1) \right\rangle \\
E_m &= -\left( \frac{B^2}{2\mu_0} \right) \Delta \chi \xi^3 \cos^2 \varphi
\end{align*}

\textbf{Eq. 1} \hspace{1cm} \textbf{Eq. 2}
\[
P_2 = \frac{\int_0^\pi \frac{1}{2}(3\cos^2 \varphi - 1)e^{-E_m/k_B T} \sin \varphi \, d\varphi}{\int_0^\pi e^{-E_m/k_B T} \sin \varphi \, d\varphi}
\]

(3)
Figure S1: Temperature dependent scattering (a) and the corresponding scattering peak intensity plots of the BCP microstructure and the LC mesophase (b) from the neat block copolymer material. System shows a $T_{odt}$ ($\approx 215 ^\circ C$) well separated from the LC clearing transition ($\approx 80 ^\circ C$).

Figure S2: a) DSC data of the neat and blend materials measured during cooling at 2 °C /min. The neat system displays a transition near 80 °C that is attributed to the formation of a SmA phase directly from an isotropic state. $R=0.75$ displays 3 distinct transitions: Isotropic-Nematic transition, $T_{N-I}\approx 83$ °C, Nematic-SmA transition $T_{N-SmA}\approx 72$ °C, and crystallization at $T_x\approx 47$ °C. For $R=1.5$, $T_{N-SmA}$ is not readily discernible in DSC, while $T_x\approx 55$ °C and $T_{N-I}\approx 89$ °C. b) N-SmA transition for $R=1.5$ is identified from the temperature dependent scattering from the LC mesophase (blue data points) during cooling. The line shows a linear fit to the data from which the onset of N-SmA transition is identified at $\approx 70$ °C.
Figure S3. Temperature dependent polarized optical microscopy experiments conducted on (top to bottom) R=1.5, R=0.75 and R=0 (neat) samples. Left and right insets show POM images at 65 ºC and in the isotropic state, respectively.
Figure S4. Field strength dependence of alignment of $NBCB_{12}$-$b$-$NBPLA3$ material with crosslinkable LC (RM257) at a stoichiometry of $R=1.5$; Full width at half maximum (fwhm) of the microdomain scattering vs. $B^2$. The sample shows saturation of the alignment (fwhm~20 deg) at a field strength of ~0.5 T. The cooling rate chosen for these experiments was 0.5 ºC/min. The line is a visual guide.

Figure S5: Cooling rate dependence of alignment of the blend material ($R=1.5$) at 1 T. The system aligns rapidly and the alignment quality is insensitive to cooling rates lower than ~1ºC/min.
Figure S6: Field dependent alignment quality of R=1.2 sample measured by SAXS at 55 °C with a cooling rate of 0.25 °C/min. Left) Full-width at half maximum (fwhm) of the BCP scattering peak as a function of field strength. The red dotted line is a visual guide. Right) Field dependent orientation distribution coefficient, or orientational order parameters, $P_2$, determined by Gaussian fits of the azimuthal intensity distribution. The solid line is a fit of the data using the field and grain-size dependent magnetostatic energy as a Boltzmann factor in the integration of the orientation probability that yields $P_2$. From the fit the characteristic grain size is 925 nm.

Figure S7: Scheme showing synthesis of the $NBCB_{12}$-$b$-$NBPLA3$ LC BCP by sequential ring
opening metathesis polymerization (ROMP) of side chain functionalized (a) NBCB\textsubscript{12}\textsuperscript{1} and (b) NBPLA\textsubscript{3}\textsuperscript{1} monomers. NBCB\textsubscript{12} volume fraction is \(\sim 73\%\).

Figure S8: Chemical structure and \(^1\text{H}\) NMR spectrum of \textit{NBCB}_{12}-b-\textit{NBPLA3} polymer sample in CDCl\textsubscript{3} at room temperature. Detailed NMR investigation of the monomers can be found in the published data\textsuperscript{1}.

REFERENCES