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Electronic Supplementary Information

Control of the alignment of liquid crystal molecules on a sequence-polymerized film by surface migration and polarized light irradiation

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Synthesis and characterization of polymers

NMR of the monomers and the copolymer

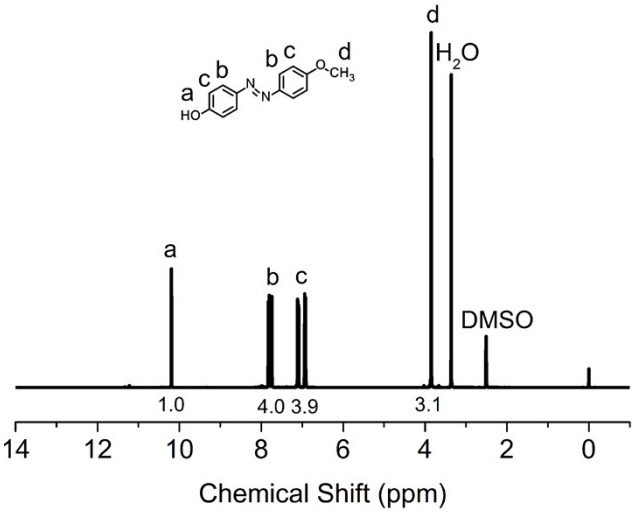

Figure S1. ^{1}H NMR spectrum of MAzOH in DMSO-d6.

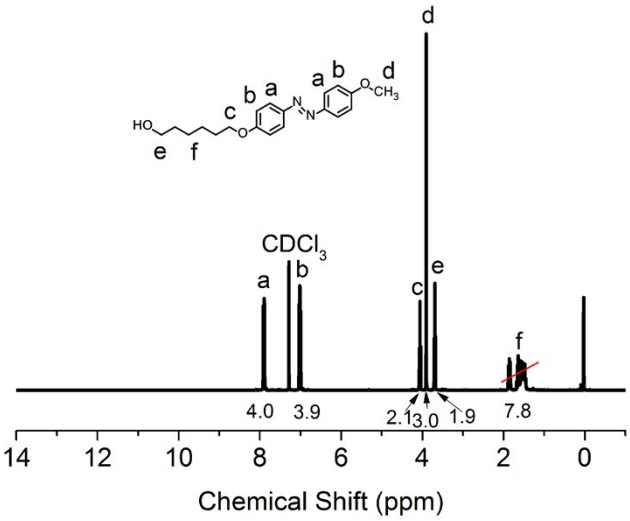

Figure S2. ^{1}H NMR spectrum of MAz6OH in $CDCl_3$.

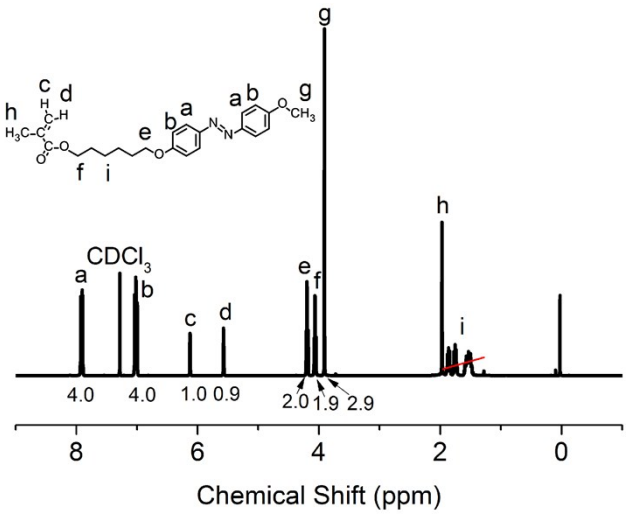

Figure S3. ^{1}H NMR spectrum of MAz6Me in $CDCl_3$.

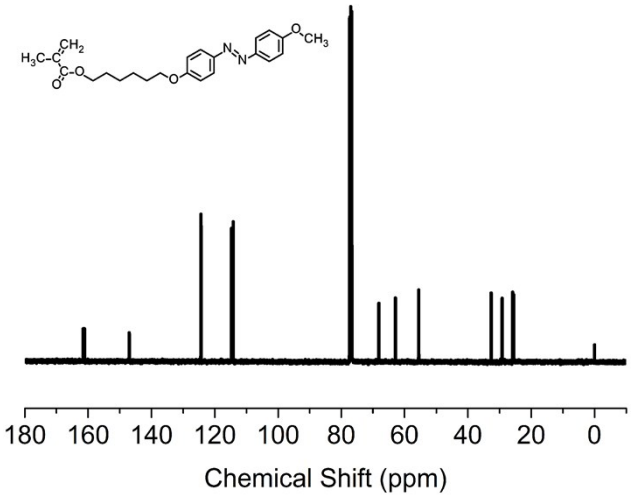

Figure S4. ^{13}C NMR spectrum of MAz6Me in $CDCl_3$.

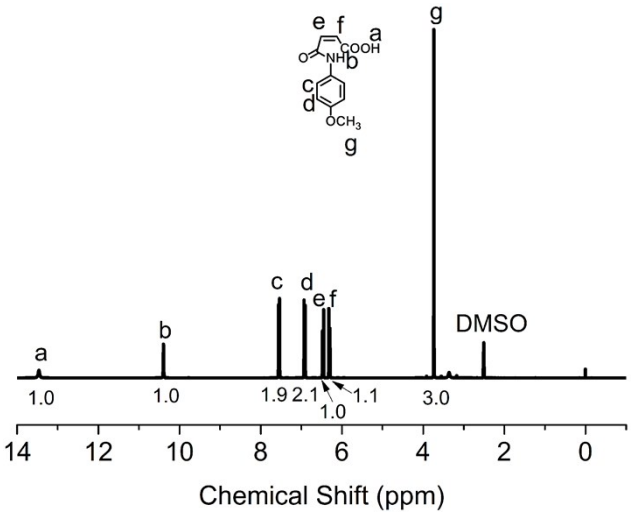

Figure S5. ^{1}H NMR spectrum of AMA in DMSO-d6.

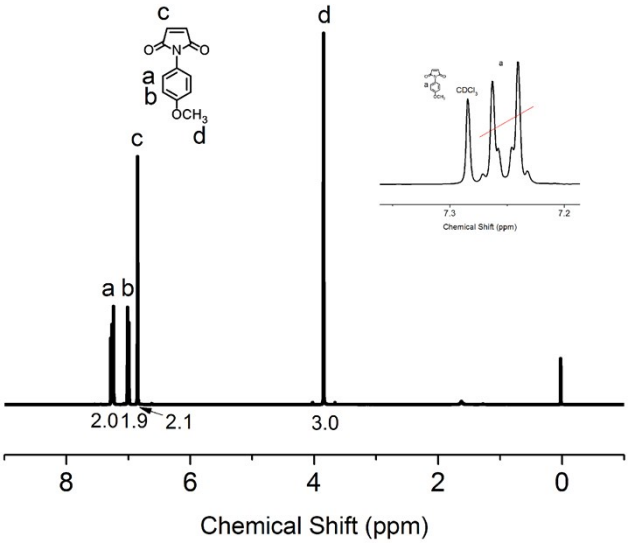

Figure S6. ^{1}H NMR spectrum of NPAMI in $CDCl_3$.

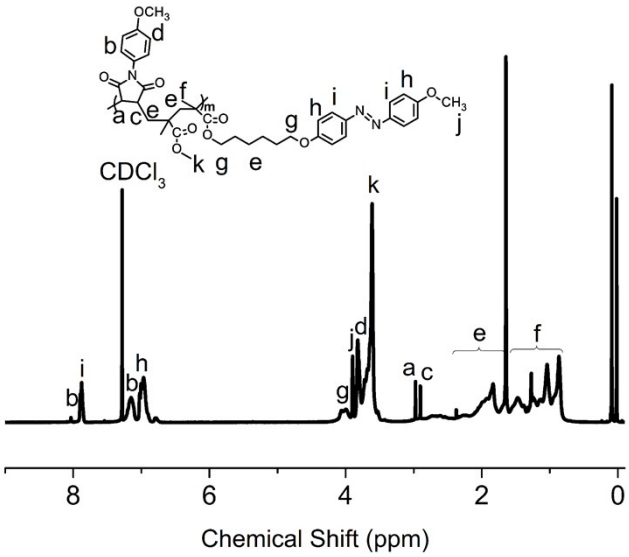

Figure S7. ^{1}H NMR spectrum of the copolymer **P11** in $CDCl_3$.

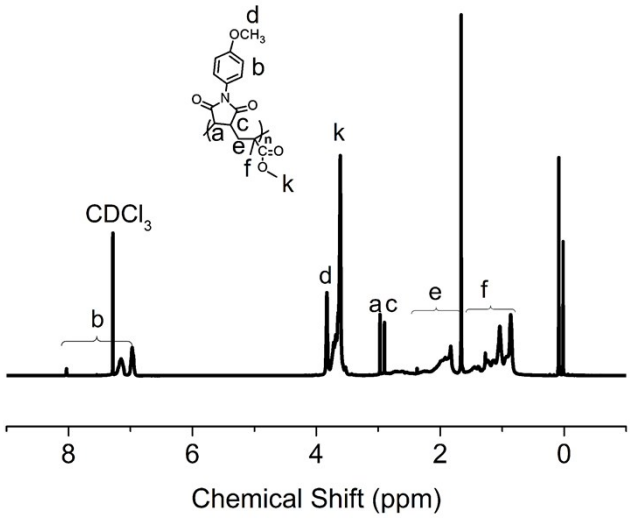

Figure S8. ^{1}H NMR spectrum of the crude product from the polymerization of MMA and NPAMI for 21 h in $CDCl_3$.

GPC spectra of the copolymers

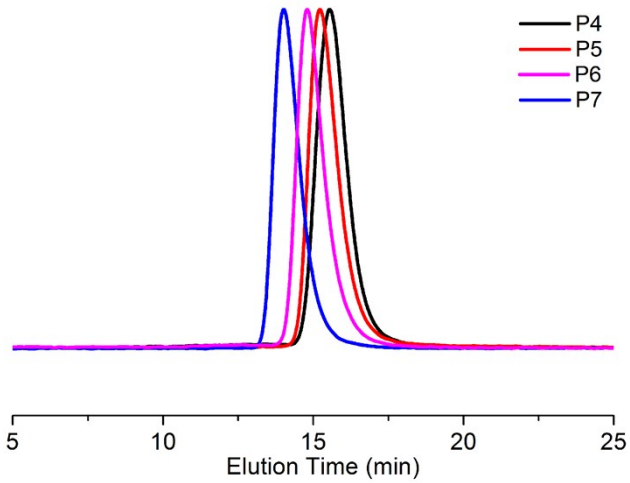

Figure S9. GPC spectra of copolymers **P4**-**P7** with feeding ratio of NPAMI of 10 mol %.

UV/Vis spectra of the copolymers

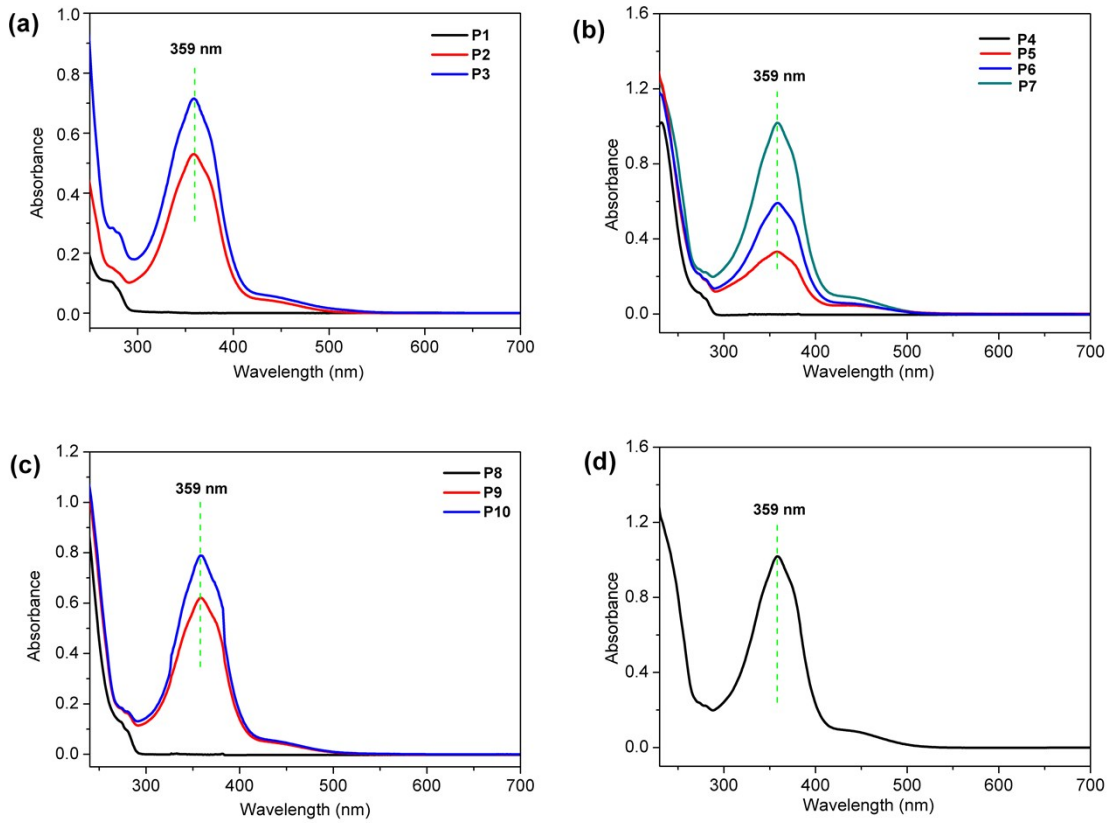

Figure S10. UV/Vis spectra of copolymers **P1-P10** with feeding ratio of NPAMI of 5 mol % (a), 10 mol % (b), 15 mol % (c) and **P11** (d).

The thermal properties of the copolymer P11

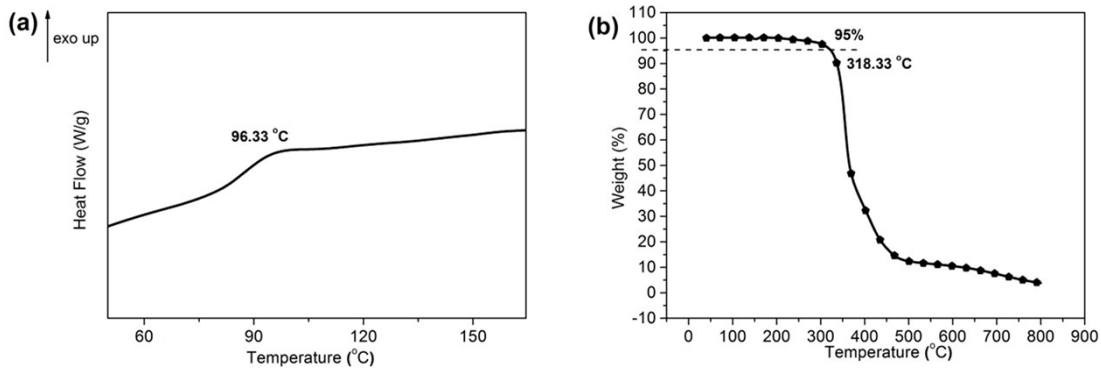

Figure S11. The DSC (a) and TGA curves (b) of the copolymer **P11**.

Calculation methods

Hardware. The hardware used for molecular modeling was the "Sun Hybrid System" based at the center for High Performance Computing in Cape Town, South Africa.

Software. The computational result in this study was calculated using the DMol[3] density functional theory (DFT) code [1–3] as implemented in Accelrys Materials Studio (Version 2016). The nonlocal generalized gradient approximation (GGA) exchange–correlation functional was employed in all geometry optimizations, viz., the PW91 functional of Perdew and Wang[4]. An all-electron polarized split valence basis set, termed double numeric polarized (DNP), was used. All

geometry optimizations employed highly efficient delocalized internal coordinates[5]. The tolerance for convergence of the self-consistent field density was set to 1×10^{-5} hartrees, while the tolerance for energy convergence was set to 1×10^{-6} hartrees. Additional convergence criteria included the tolerance for converged gradient (0.002 hartree $Å^{-1}$) and the tolerance for converged atom displacement (0.005 Å). The thermal smearing option in Materials Studio makes use of a fractional electron occupancy scheme at the Fermi level according to a finite-temperature Fermi function[6].

In all cases optimized geometries were subjected to full frequency analyses at the same GGA/PW91/DNP level of theory to verify the nature of the stationary points. Equilibrium geometry was characterized by the absence of imaginary frequencies. The reported relative Gibbs free energies refer to Gibbs free energy corrections to the total electronic energies at 298.15 K and 1 atm.

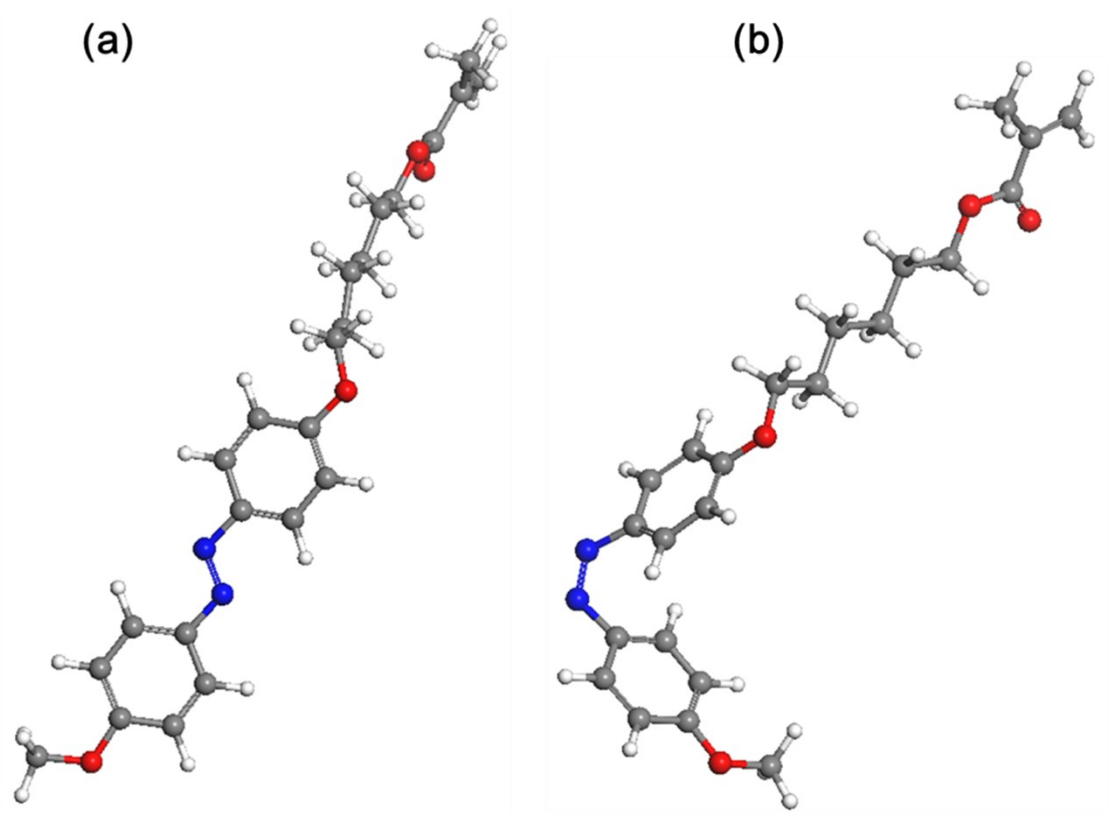

Figure S12. The geometrical structures of trans (a) and cis (b) isomers of MAz6Me.

The preparation of liquid crystal (LC) cells

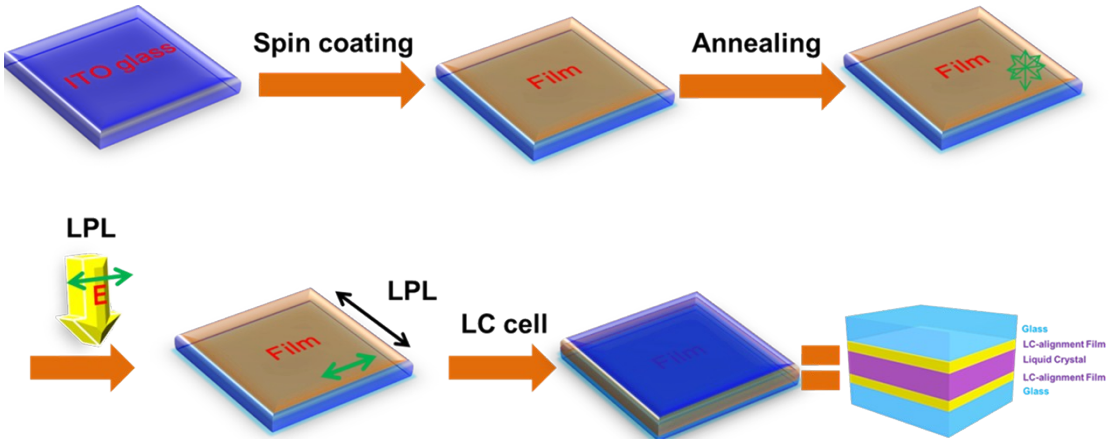

Figure S13. Schematic illustration of the procedure for the preparation of LC cells.

The transparency of the LC cell

UV/vis transmission spectroscopic measurements were employed to characterized the transparency of films. The UV-vis transmittance spectroscopies of fresh **P7** and annealed **P7** films in the range of 300-800 nm are shown in Figure S14a. The LC-aligning films were first subjected to annealing treatment before being vertically irradiated with LPL (365 nm, 5.0 J cm^{-2} dose at room temperature). The combination of thermal annealing and LPL irradiation of LC alignment films generated LC cells. The 5CB LC cell with the LC alignment layers prepared through sequence-controlled polymerization is seen in Figure S14b. From the photograph, the transparency of this LC cell can be easily seen. This good transparency is very conducive to application in LC displays.

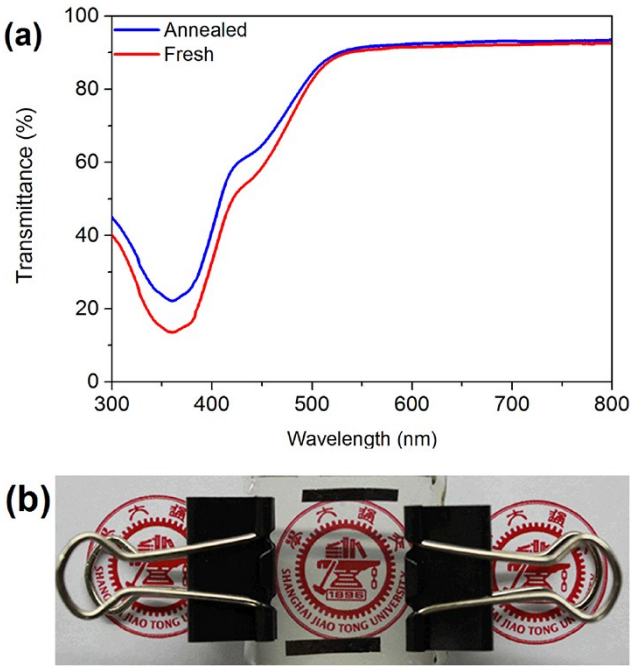

Figure S14. (a) UV-vis transmittance spectroscopies of fresh **P7** and annealed **P7** films. (b) LC cell prepared by **P7** films.

The pretilt angles for LC cells

Table S1. The thermal properties of the sequence-controlled copolymers and the pretilt angles for LC cells.

	P1	**P2**	**P3**	**P4**	**P5**	**P6**	**P7**	**P8**	**P9**	**P10**
Tg(°C)	125.47	115.46	108.07	133.50	123.24	118.93	94.66	135.09	125.39	119.46
Pretilt angle(°)	0.3	2.1	2.4	0.4	1.9	2.8	4.1	0.3	1.7	3.7

Supporting References

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6. M. Weinert and J. W. Davenport, *Physical Review B Condensed Matter*, 1992, **45**, 13709-13712.