Supporting Information: Random Liquid Crystalline Copolymers Consisting of Prolate and Oblate Liquid Crystal Monomers

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Light transmission of LC polymers

The light transmission of unpolarized light through the LC (co)polymers was measured using a Perkin Elmer Lambda 950 UV–visible spectrophotometer. Representative light transmission spectra for 50 um-thick of homopolymers of LCM1 and LCM3 are shown in Figure S1. The average light transmission of the LC polymers with wavelengths ranging from 450 nm to 550 nm were used in Equation (1) of the main text.
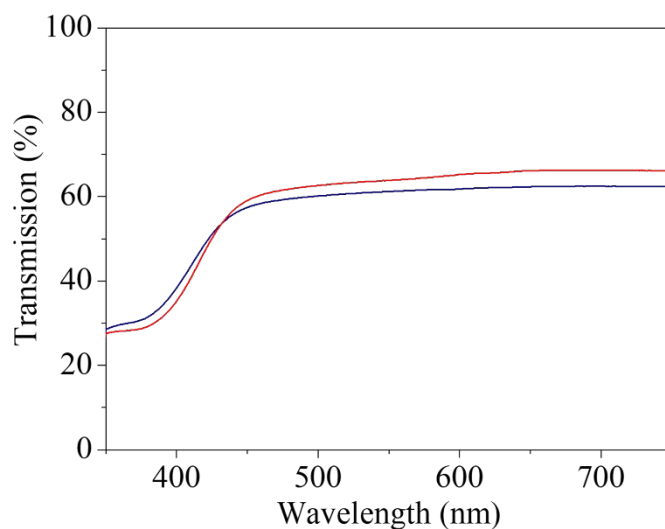

Figure S1. Light transmission spectra for homopolymers of LCM1 (blue) and LCM3 (red). The thickness of the LC polymer samples is ~50 μm.

Effect of crosslinker on T_{LC-I} of LC polymers

Here we investigate the effect of the non-LC crosslinker, HDDA, on the thermal properties of the LC polymers. In our experiments, we synthesized and characterized LCM1 homopolymers with and without HDDA. Inspection of Figure S2 reveals no significant difference in the T_{LC-I} values of LCM1 with 0 and 2.5% by weight of HDDA.
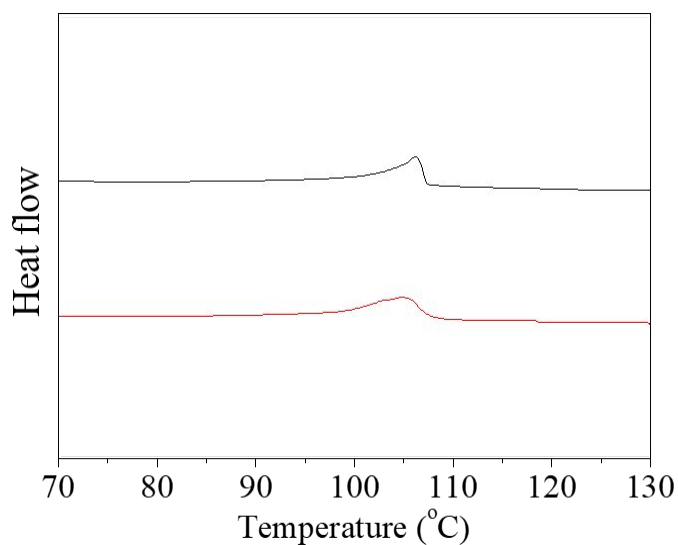

Figure S2. DSC traces of LCM3 homopolymers with (red) and without (black) crosslinker HDDA. The weight fraction of HDDA was 2.5% wt based on the total mass of the homopolymer. Cooling rate: 2 °C/minute.

X-ray scattering of LC polymers

We performed wide angle x-ray scattering (WAXS) to confirm the alignment of the LC director along the z-axis in homopolymers of LCM1 and LCM3. Inspection of Figure S3 reveals that the LC functional groups of the LC homopolymers are aligned parallel with the direction of the applied magnetic field.
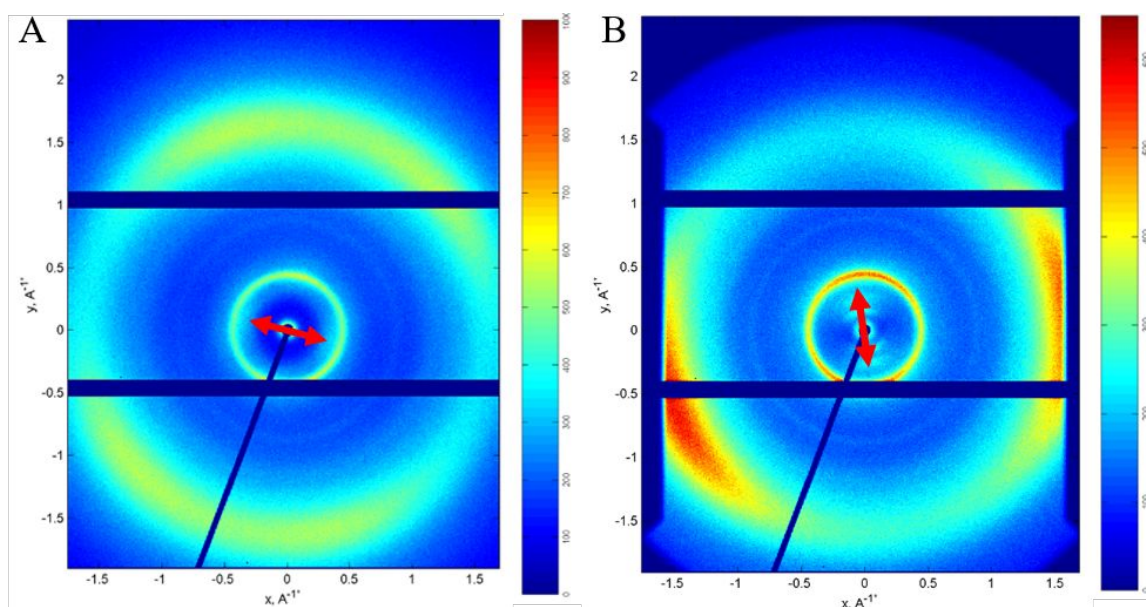

Figure S3. 2D x-ray scattering as a function of azimuthal angle and momentum transfer corresponding to (A) LCM3 and (B) LCM1 homopolymers. Red, double-headed arrows indicate the magnetic field orientation during LC homopolymer synthesis.

To provide further insights into the effect of the random polymer structure, we estimated the scalar order parameter of the LC polymers using x-ray analysis according to Reference 1.[1] Specifically, the scalar order parameter can be calculated by:

$$\text{Scalar order parameter} = \frac{1}{2}\left(3\langle\cos^2\beta\rangle - 1\right) \tag{S1}$$

where β is the angle between a LC molecular symmetry axis and the director of the LC functional groups in LC polymers. $\langle\cos^2\beta\rangle$ can be calculated by:

$$\langle\cos^2\beta\rangle = \left.\sum_{n=0}^{5}\frac{f_{2n}}{2n+3}\middle/\sum_{n=0}^{5}\frac{f_{2n}}{2n+1}\right. \tag{S2}$$

$$I(\theta) = f_0 + \frac{2}{3}f_2\cos^2\theta + \frac{8}{15}f_4\cos^4\theta + \frac{16}{35}f_6\cos^6\theta + \frac{128}{315}f_8\cos^8\theta + \frac{256}{693}f_{10}\cos^{10}\theta \tag{S3}$$

in which I and θ are the normalized scattering intensity and scattering angle, respectively. We estimated the scalar order parameter of the homopolymers of LCM1 and LCM3 and the random copolymer of LCM1–LCM2 and LCM1–LCM3 to be ~ 0.250, ~ 0.275, ~ 0.278 and ~ 0.102, respectively. The LCM1 composition of the random copolymers is 40% by weight.

NMR characterization of LC polymers

Here we performed NMR characterization to confirm the full conversion of the LC monomers during photopolymerization. The LC polymers were dissolved in deuterated chloroform, and the NMR measurement was conducted on a 400 MHz Avance NEO ^{1}H NMR. As evidenced in Figure S4, the disappearance of the peaks between 5.5–6.5 ppm in the ^{1}H NMR measurements, which corresponds to the non-aromatic C=C double bonds, indicates a full conversion of the reactive LC monomers during photopolymerization. In addition, the weak peaks around 7.5–8.0 ppm can be attributed to the aromatic ring in 2-hydroxy-2-methylpropiophenone, which is the remaining photoinitiator.[2]
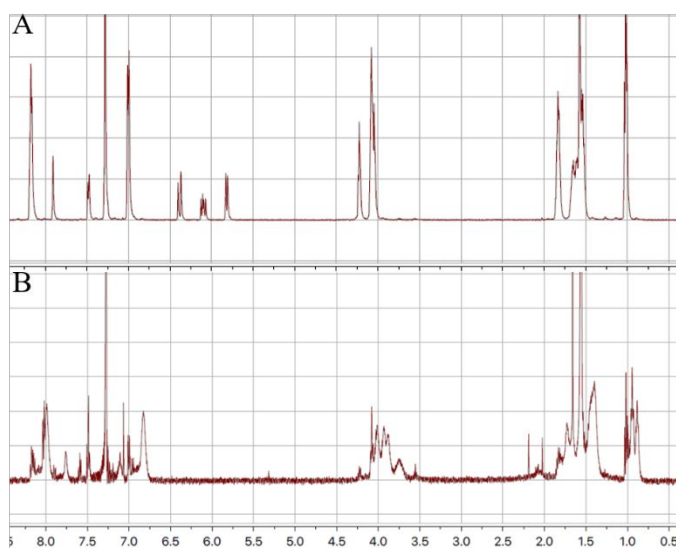
Figure S4. ^{1}H NMR spectrum of LCM1 monomer (A) before and (B) after polymerization.

Molecular weight and polydispersity of LC (co)polymers

Here we performed GPC measurements to characterize the number-average molecular weight (M_n), weight-average molecular weight (M_w), and PDI (M_w/M_n) of the LC (co)polymers synthesized in this work. The measurement results are summarized in Table S1.

Table S1. Molecular weight and polydispersity of LC (co)polymers.

(Co)polymer composition			M_n	M_w	PDI
LCM1 (wt%)	LCM2 (wt%)	LCM3 (wt%)	(g/mol)	(g/mol)	
100	0	0	18020	28395	1.58
0	100	0	23641	40871	1.73
0	0	100	23158	43875	1.89
80	20	0	18459	31116	1.69
60	40	0	18806	33865	1.80
40	60	0	21357	48853	2.29
20	80	0	18037	27417	1.52
80	0	20	18573	29742	1.60
60	0	40	16838	28170	1.67
40	0	60	17640	32707	1.85

20	0	80	20050	48556	2.42
0	80	20	19338	31772	1.64
0	60	40	16039	34294	2.14
0	40	60	17421	31177	1.79
0	20	80	20817	45819	2.20

DSC measurement of random LC copolymers

Here we performed DSC characterization to determine the T_{LC-I} of the random LC copolymers. As evidenced in Figure S5, the T_{LC-I}s of the LCM1–LCM2 random copolymers lie between the T_{LC-I}s of the respective homopolymers, whereas the T_{LC-I}s of the LCM1–LCM3 random copolymers lie below the T_{LC-I}s of the respective homopolymers.
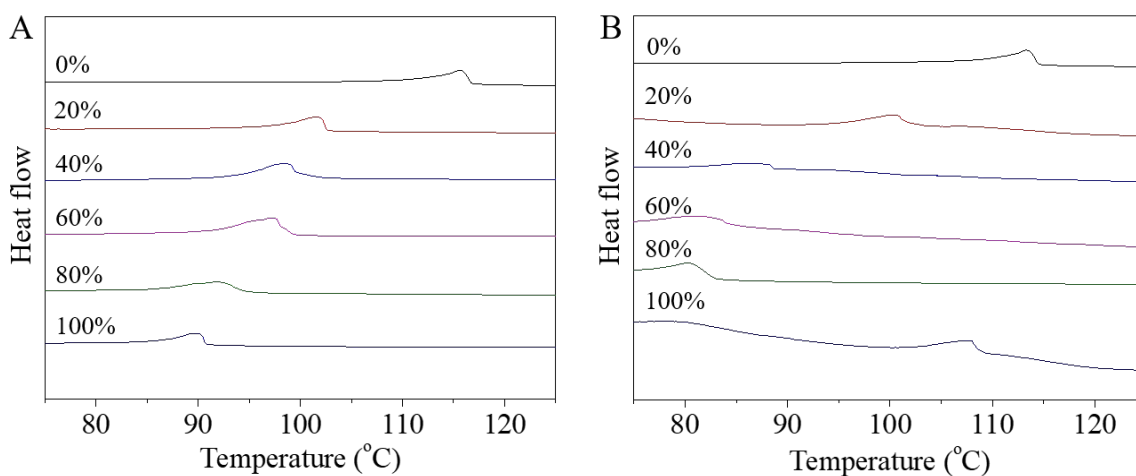

Figure S5. Representative DSC traces for random copolymers of (A) LCM1–LCM2 and (B) LCM1–LCM3 as a function of chemical composition. The percentage indicates the composition of (A) LCM2 and (B) LCM3 in the LC copolymers. Cooling rate: 2 °C/minute.

DSC measurement of LC homopolymer mixtures

To provide insights into the LC monomer configuration-dependent T_{LC-I} of the random

LC copolymers, we measured the thermal properties of mixtures of LC homopolymers. In

contrast to the random LC copolymers which exhibit a single T_{LC-I}, the homopolymer

mixture shows two individual T_{LC-I}s corresponding to each homopolymer, as shown in

Figure S6. We hypothesize that the existence of two T_{LC-I}s is due to incomplete mixing of
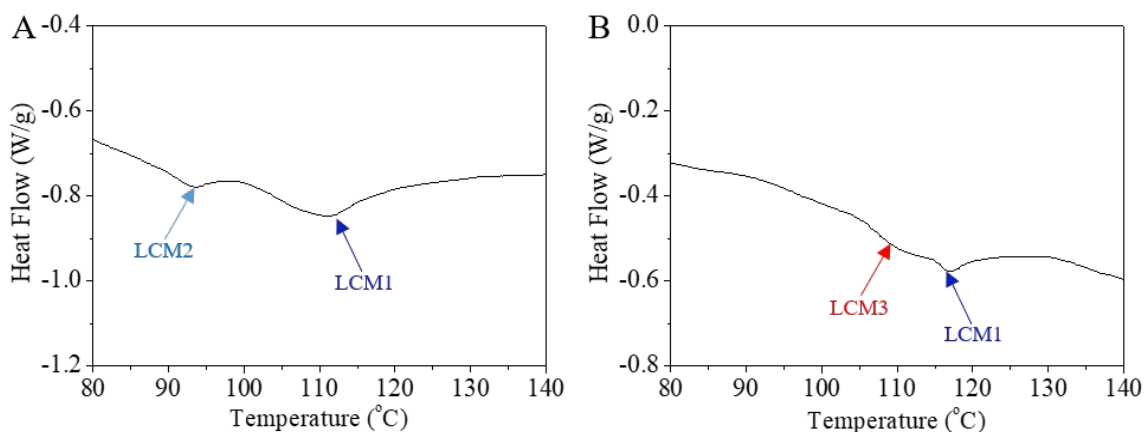
two different LC homopolymers.

Figure S6. DSC traces of homopolymer mixtures of (A) LCM1–LCM2 and (B) LCM1–

LCM3. The weight fraction of LCM1 homopolymers is 60% by weight based on the total

mass of the homopolymer mixture. Heating rate: 2 °C/minute.

Thermal behavior of LCM2–LCM3 random copolymer

Here we characterized the thermal properties of the other pair of random copolymers

consisting of different configurations of LC monomers (e.g., LCM2 and LCM3). As shown

in Figure S7A, the T_{LC-I}s of the LCM2–LCM3 random copolymers lie below the T_{LC-I}s of

the respective homopolymers (90 °C and 107 °C for LCM2 and LCM3 homopolymers,

respectively). In addition, Figure S7B shows that the T_{LC-I}s of the unpolymerized mixtures

lie between the T_{LC-I}s of the respective monomers. The characteristic behaviors of the

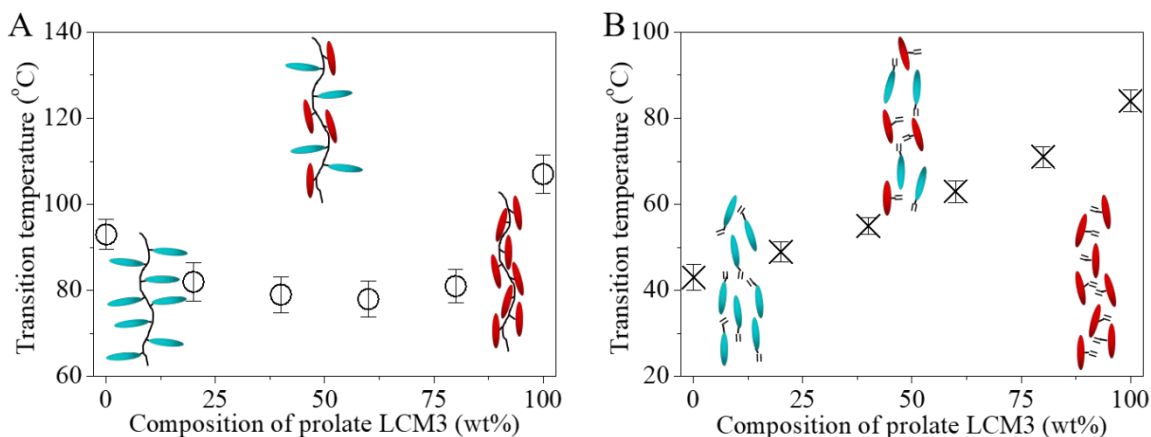LCM2–LCM3 random copolymer is similar to the LCM1–LCM3 random copolymer.

Figure S7. T_{LC-I}s of (A) random copolymers and (B) unpolymerized mixtures consisting of

different configurations of LC monomers (LCM2–LCM3) as a function of monomer

composition.

T_{LC-I}s of LC polymers synthesized by RAFT Polymerization

To provide further insights into the origin of the LC monomer configuration-dependent T_{LC-I}s of the LC copolymers, we used RAFT solution polymerization to synthesize statistically random LC copolymers. As shown in Figure S8, no measurable difference in the T_{LC-I} was observed between LC copolymers synthesized with and without RAFT agents. These results show that the influence of reactivity ratios of different LC monomers on the composition-dependent T_{LC-I}s of the random LC copolymers is negligible.
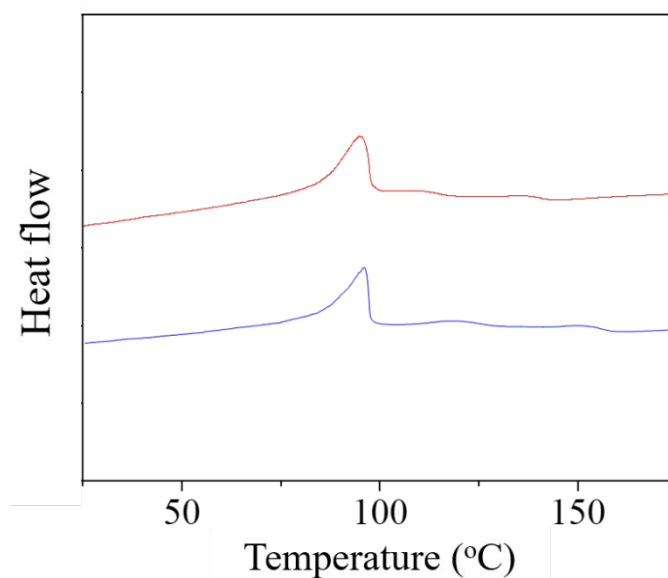

Figure S8. T_{LC-I}s of LCM1–LCM3 random copolymers synthesized with (red) and without (blue) RAFT agent. The composition of LCM1 is 60% by weight based on the total mass

of the random copolymer. [RAFT]:[DMPAP]:[LC monomer] = 1:1:100. Cooling rate: 2

°C/minute.

REFERENCES

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(2)   Arai, T.; Sato, T.; Kanoh, H.; Kaneko, K.; Oguma, K.; Yanagisawa, A. Organic-Inorganic Hybrid Polymer-Encapsulated Magnetic Nanobead Catalysts. *Chem. Eur. J.* **2008**, *14* (3), 882–885. https://doi.org/10.1002/chem.200701371.