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Electronic Supplementary Information (ESI)

pH-Responsive liquid crystal double emulsion droplets prepared using microfluidics

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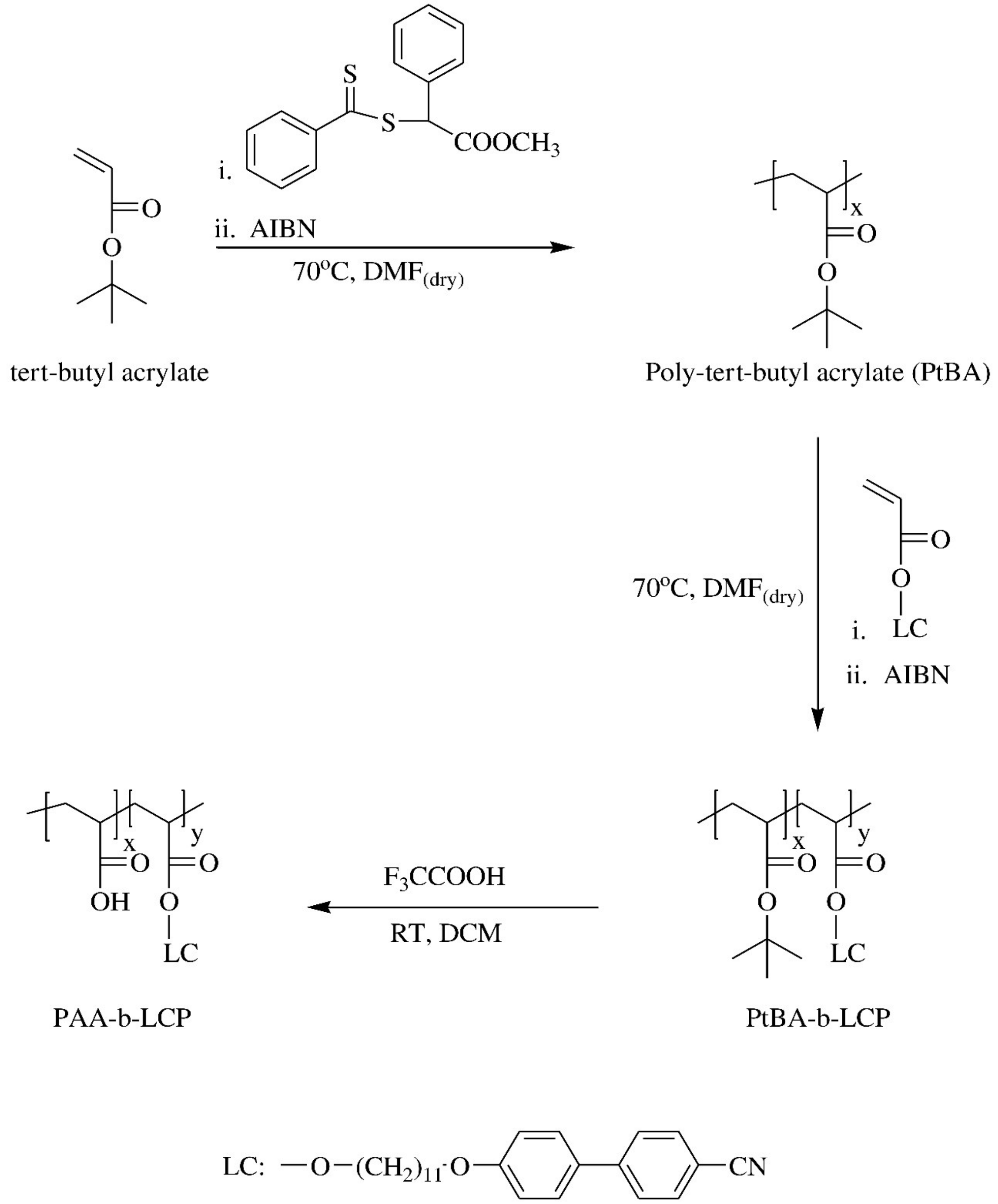
Experimental details

Synthesis of PAA-*b*-LCP: The chain transfer agent (CTA) *S*-methoxycarbonylphenylmethyl dithiobenzoate (MCPDB) and the liquid crystal (LC) monomer 4-cyanobiphenyl-4′-oxyundecylacrylate (LC11) were synthesized using our previously reported methods.[1] Scheme S1 shows the reversible addition–fragmentation chain transfer (RAFT) polymerization scheme for the synthesis of the macroinitiator PtBA-*b*-MCPDB. MCPDB (19 mg, 0.06 mmol), *tert*-butyl acrylate (tBA) (1.28 g, 10 mmol), and DMF (1.5 mL) were added to a graduated vial, and nitrogen gas was bubbled through the mixture for 60 min. A Schlenk flask containing AIBN (5 mg, 0.02 mmol) was maintained under vacuum for 60 min, and the previously prepared solution of tBA and CTA in DMF was introduced into the flask using a syringe needle previously purged with N_2. The flask was then placed in an oil bath at 70 °C for 15 h to allow the RAFT reaction to take place. Subsequently, the resulting macroinitiator, PtBA-b-MCPDB, was precipitated in a mixture of methanol/water (1:1, v/v). Scheme S1 shows the overall reaction scheme for the synthesis of PtBA-*b*-LCP. To prepare PtBA-*b*-LCP via the RAFT method, AIBN (0.5 mg, 0.003 mmol), LC11 (84 mg, 0.2 mmol), and PtBA-b-MCPDB (110 mg, 0.004 mmol) were added to a Schlenk flask. The Schlenk flask was kept under vacuum for 60 min, and DMF was introduced into the flask using a syringe needle previously purged with N_2. The flask was then placed in an oil bath at 80 °C for 15 h. After the reaction had reached completion, the product was precipitated in a mixture of methanol/water (1:1, v/v). Volatile materials were removed in a vacuum oven at 40 °C to yield the product PtBA-*b*-LCP as a powder. The resulting PtBA-*b*-LCP (0.1 g) was dissolved in dichloromethane (DCM, 5 mL); subsequently, trifluoroacetic acid (TFA, 1 ml) was added at 20 °C with stirring for 24 h to promote hydrolysis. PAA-*b*-LCP was then obtained upon removal of the by-products using a rotatory evaporator, followed by drying in a vacuum oven at 40 °C for 24 h. The obtained PAA-b-LCP had a molecular weight of PAA(22k)-b-LCP(6k), where the numbers in parenthesis represent the number-averaged molecular weight, which was measured using gel permeation chromatography (GPC, Acme9000, Young Lin Instrument Co., Ltd). Detailed NMR and FT-IR data for PAA(22k)-b-LCP(6k) were presented in our previous publication.[1]



RT: Room temperature

Scheme S1. RAFT polymerization of PtBA-b-MCPDB and PAA-b-LCP.[1]

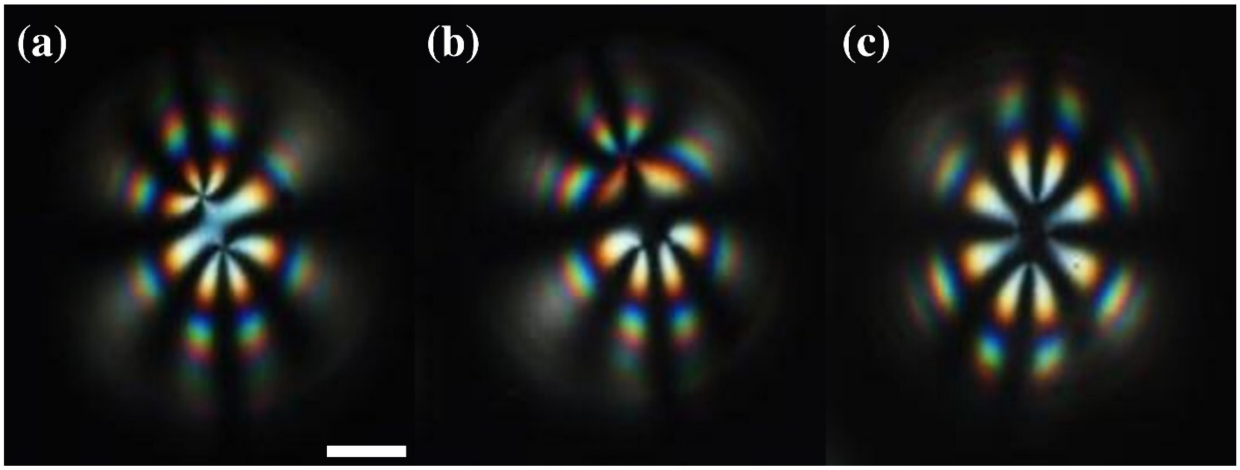


Figure S1. Defect structures of an NLC DED with (a) two (two +1), (b) three (one +1 and two +1/2), and (c) four (four +1/2) defects when both the inner and outer fluids were 1 wt% aqueous PVA solution. The scale bar is 50 µm.

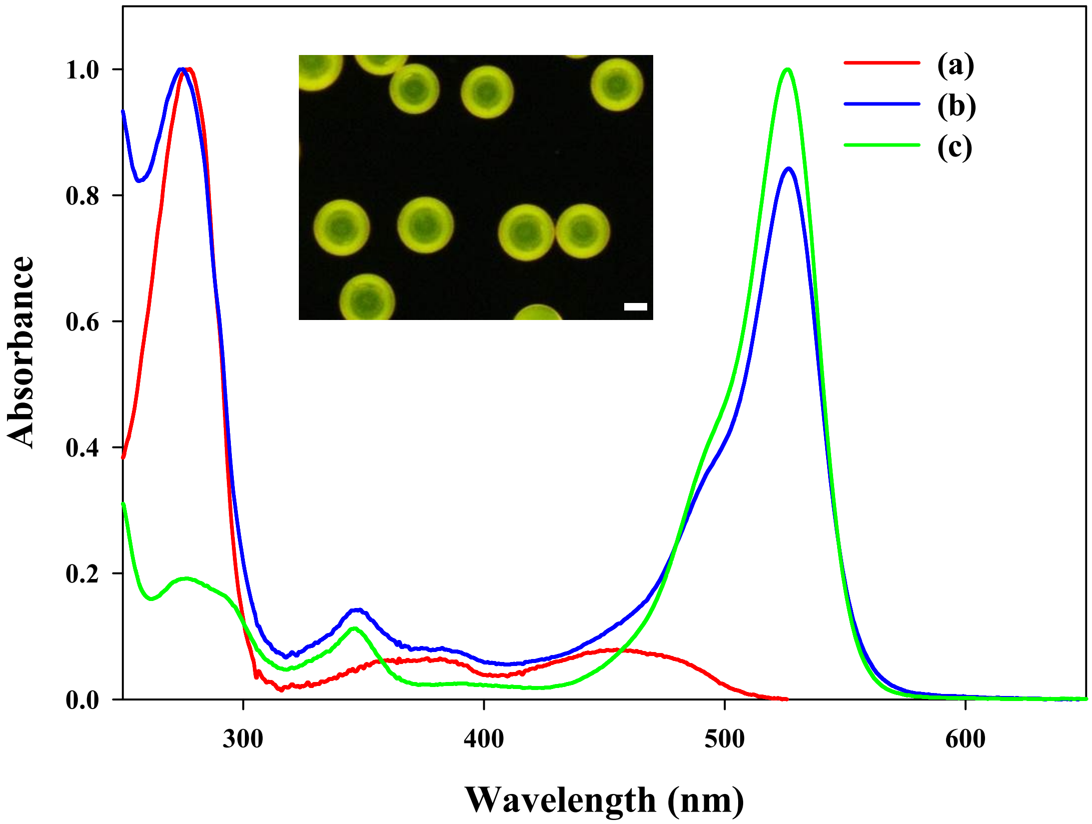


Figure S2. UV-Vis absorption spectra of (a) GOx, (b) GOx-$_{\mathrm{rhd}}$, and (c) rhodamine 6G. The inset shows a fluorescent image of NLC DED$_{\mathrm{PAA\text{-}GOx}}$ at pH = 7. The scale bar is 100 µm.

Video S1. Video recorded during production of the NLC DEDs using a capillary microfluidic device that combines co-flow and flow focusing geometries.

Reference

1. D.-Y. Lee, J.-M. Seo, W. Khan, J. A. Kornfield, Z. Kurji and S.-Y. Park, *Soft Matter*, 2010, **6**, 1964-1970.