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Hu, G., Qian, W., Tang, Y. et al. (2025) Mesomorphic behavior of novel photopolymerizable carbazole liquid crystals and photocuring for 4D printing. *Crystal Growth & Design*, 25 (18). pp. 7669-7683. ISSN: 1528-7483

<https://doi.org/10.1021/acs.cgd.5c00858>

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Mesomorphic Behaviour of Novel Photopolymerisable Carbazole Liquid Crystals and Photo-curing for 4D Printing

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Stephen M. Kelly*

ABSTRACT: Four novel carbazole-based photopolymerisable liquid crystals (PLCs) incorporating diacrylates or non-conjugated dienes, were designed and synthesised to study their mesomorphic behaviour and photo-curing properties, with a focus on future applications in 4D printing. A combined analysis protocol using polarised optical microscopy (POM), differential scanning calorimetry (DSC), small angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) revealed a favourably wide range of nematic phases near room temperature and a slow tendency to crystallise. It should be advantageous in applications requiring good surface-alignment of the reactive mesogen in the nematic phase. This behaviour could be attributed to the effects of polymerisation under prolonged high temperatures for acrylates and the high entropy of long, branched, flexible alkyl chains in dienes. The polymerisation process induces a kinetic competition between LC ordering and network formation. This work establishes protocols for real-time phase monitoring during polymerisation, resolving longstanding ambiguities in LC phase identification under thermal polymerisation. Furthermore, photo-curing tests of the acrylate and diene monomers demonstrated high photopolymerisation efficiency and good thermal stability, particularly for the acrylate monomers.

KEYWORDS: Photopolymerisable liquid crystals; mesomorphic behaviour; nematic phase; 4D printing.

1. INTRODUCTION

Photopolymerisable liquid crystals (PLCs),¹⁻⁵ often also referred to as reactive mesogens (RMs), represent a unique class of functional materials that synergetically combine the anisotropic properties of liquid crystals (LCs) with the structural versatility and functionality of organic mainchain polymers. Their importance stems from their ability to retain molecular alignment, especially on planar device substrates, during polymerisation, enabling the fabrication of highly crosslinked polymer networks as macroscopically aligned, thin solid films, with the desired spectrum of tailored optical, mechanical, physical and optoelectronic responsive properties.⁶⁻¹⁰ Hence, unlike conventional LCs, which exhibit dynamic fluidity, PLCs undergo a transition from a fluidic LC phase to a solid polymer network, thereby "freezing" and "locking in" the orientational order of the fluid reactive mesogens. The liquid crystalline phase of such reactive mesogens (RMs), typically of a nematic or smectic phase, which is susceptible to external stimuli, such as light, heat, electric fields or surface treatments.¹¹⁻¹⁴ These characteristics make them indispensable in advanced applications such as optical-electronic devices,¹⁵⁻¹⁷ sensors, soft robotics, and stimuli-responsive smart materials for 4D printing.¹⁸⁻²⁰ The 4D printing technique builds on 3D printing by using smart materials, that respond to external stimuli, such as light, heat, water, electricity, or magnetic fields, etc., to produce time-dependent changes in structure, shape, and performance, enabling self-deformation, self-repair, and self-assembly of the endproducts.²¹ PLCs are a type of stimuli-responsive polymer that undergo large, reversible, anisotropic shape changes when subjected to stimuli, such as heat or light,

making them ideal smart materials for 4D printing.

However, previous research mainly focused on commercial photopolymerisable phenyl-ester liquid crystal monomers, such as ‘RM82’ and ‘RM257’ for 4D printing.²²⁻²⁴ These monomers exhibit drawbacks in terms of unfavorable mesophase transition temperatures and limited mechanical properties in printing inks, as these commercial reactive mesogens were designed for display applications rather than for 4D printing.¹ Therefore, in this article, we synthesised four novel photopolymerisable liquid crystals specifically designed for optimising their 4D printing properties from the perspective of their molecular structure. These liquid crystalline compounds have rigid, rod-shaped, conjugated aromatic cores incorporating a phenyl-carbazole-phenyl unit, in order to provide an optimal mechanical performance for 4D printing applications. At the same time, the presence of symmetrical flexible photopolymerisable alkyl chains in a terminal position were incorporated in the molecular structure to induce good monomer solubility in printing ink applications and to tune their mesophase transition temperatures to be suitable for shape-memory effects. These novel PLCs show a favourably wide range of nematic phases near room temperature, a slow crystallisation process and high photopolymerisation efficiency in just tens of seconds.

The advantageous slow crystallisation could be attributed to the effects of polymerisation under prolonged high temperatures for acrylates and the high entropy of long, branched, flexible alkyl chains in dienes. Liquid crystalline phases, such as nematic, smectic, or columnar phases, are highly sensitive, in terms of molecular mobility, intermolecular interactions, and external physical and electrooptical stimuli,

for example. Thermal or photochemical polymerisation of polymerisable end-groups, attached, for example, by flexible spacers to highly conjugated aromatic molecular cores, gives rise to highly crosslinked polymer networks as thin solid films, for example, attached to each other *via* a network of covalent bonds. The nature, for example, of the crosslinking density, reaction kinetics and monomer structure can modulate the stability of LC phases, shift phase transition temperatures, or even suppress certain phases entirely. This interplay between polymerisation and phase behaviour complicates the identification of LC phases and the characterisation of transitions, as the reaction itself perturbs the system in real time.²⁵⁻²⁹

Current research on non-polymerisable LCs benefits from well-established theories and experimental protocols for phase identification. Techniques such as polarised optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) reliably correlate thermal transitions, optical textures, and molecular packing. However, studies on PLCs remain limited and fragmented to some degree. Most prior work focused on the properties of the final liquid crystal polymer network,³⁰⁻³⁵ often neglecting systematic analysis of LC phase evolution during, for example, a spontaneous thermally induced polymerisation process of heating cycles. The transient nature of reactive monomers, coupled with overlapping signals from polymerisation exotherms and phase transitions, creates ambiguities in data interpretation. Consequently, the field lacks a unified framework to predict how polymerisation kinetics or monomer chemistry influences LC phase stability, representing a knowledge gap that hinders the rational design of PLC-based materials

and their application in the creation of highly stable, functional polymer networks.

This study addresses these challenges by systematically investigating the phase behaviour of reactive LC monomers under thermal polymerisation conditions, employing a multi-technique approach combining POM, DSC, SAXS, and WAXS. Four novel nematic monomers with different polymerisable groups, i.e., acrylates and non-conjugated dienes, were designed and synthesised to elucidate how chemical functionality impacts liquid crystalline phase transitions. The polymerisation process induces a kinetic competition between LC ordering and network formation. This work establishes protocols for real-time phase monitoring during polymerisation, resolving longstanding ambiguities in LC phase identification under thermal polymerisation. By bridging the gap between polymer science and liquid crystals, this research provides a theoretical foundation for designing PLCs with controlled orientation and functionality.

2. EXPERIMENTAL

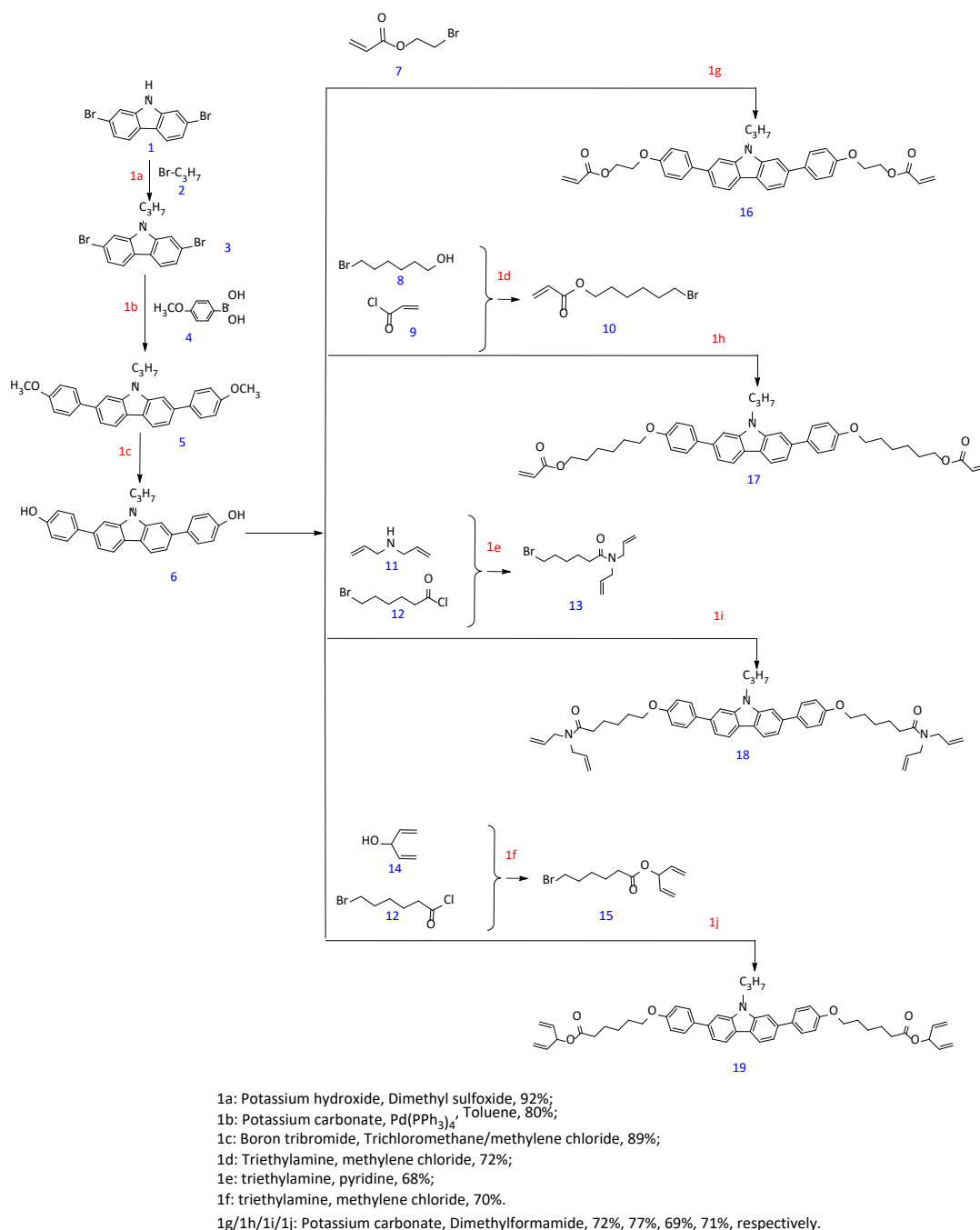
2.1 Materials and methods

The starting materials, reagents and solvents for synthesising the reaction intermediates and final compounds were purchased from commercial companies such as Bide Pharma, Aladdin, Energy Chemical, Crystalltech, Shanghai Macklin Biochemical, Adamas-beta, etc. They were used as provided unless otherwise stated. The chemical structures of the reaction intermediates and final compounds were characterised by using a combination of analytical techniques, i.e., ^1H NMR, ^{13}C NMR and HRMS. The ^1H and ^{13}C NMR spectra were recorded using a Bruker AVANCE NEO spectrometer. High Resolution

Mass spectra (HRMS) were recorded using an Agilent 6545 Q-TOF electrospray ionization mass spectrometer (ESI-MS). The mesogenic types and phase transition temperatures of these polymerizable liquid crystals were identified by using a combination of Polarised Optical Microscopy (POM), Differential Scanning Calorimetry (DSC) and X-ray Diffraction (XRD). The POM was carried out using an England Linkam THMS600 hot/cold platform and a Leica DM2500 polarizing microscope. The powder of sample about 0.1 mg was placed between two glass slides with slight pressure to prepare a thin film for POM measurement with heating/cooling cycles at 5°C/min. DSC curves were recorded by using a Netzsch DSC 214 Polyma with the powder of sample about 5 mg under heating/cooling rates of 5 °C/min. Transmission and Grazing Incidence X-ray Diffraction (XRD) and Synchrotron wide angle X-ray scattering (WAXS) experiments were carried out at station L16 of the Diamond Light Source (DLS) using an X-ray intensity of 14.5 keV. Samples were macroscopically and uniformly aligned using either a magnetic field (0.5 Tesla) or by mechanical shearing on a silicon substrate. The sample was held in a capillary of 1.0 mm in diameter. Diffraction patterns were collected at different temperatures in order to assess the order and mesophase transition temperatures. The d-spacing value is calculated from Bragg equation $d = \lambda / (2 \sin \theta)$, where 2θ is the scattering angle at the position of maximum intensity of the scattering peak. The *In-situ* Infrared (IR) spectra of reactive monomers at different temperatures (RT, 100°C, 150°C, and 200°C) were recorded using Shimadzu IRPrestige-21 with variable-temperature ATR. After initial measurement at room temperature, the sample was heated to the target temperature at

a ramp rate of 5°C/min. The spectrum was collected after equilibrating at the target temperature for 10 minutes. However, *ex-situ* IR spectra of reactive monomers at different temperatures were measured via KBr pelletisation using Bruker Tensor II Fourier transform infrared spectrometer. Samples underwent controlled heating (5°C/min ramp to 100°C, 150°C, 200°C, and 250°C with 10-min isothermal holds) followed by ambient cooling. Their IR spectra via KBr pelletisation were acquired at room temperature. Infrared (IR) spectra of printing inks were measured using Bruker Tensor II Fourier transform infrared spectrometer via ATR method. The condition of heating to 100°C for printing inks refers to heating the printing ink to 100°C first, then cooling it to room temperature for IR test. The IR spectra of inks were also acquired at room temperature.

2.2 Material synthesis



Scheme 1. The reaction pathways used to synthesise the photopolymerisable carbazole liquid crystals (16 & 17 and 18 & 19) with acrylate or diene endgroups, respectively.

2,7-Dibromo-9-propyl-9H-carbazole (3)

Potassium hydroxide (4.3 g, 24.9 mmol) was added in small portions into a stirred mixture of 2,7-dibromo-9H-carbazole (5.0 g, 15.4 mmol) in DMSO (25 cm³). The

resultant mixture was stirred for 1 hour at room temperature, 1-bromopropane (2.46 g, 20.0 mmol) was then added and the resultant reaction mixture was stirred overnight. The reaction mixture was filtered to yield the crude product, which was washed with portions of ethanol (3 x 100 cm³) and dried under vacuum to give the desired product as a white powder (5.20 g, 92%).

¹H NMR (600 MHz, CDCl₃) δ 7.89 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 1.6 Hz, 2H), 7.34 (dd, J = 8.3, 1.7 Hz, 2H), 4.17 (t, J = 7.3 Hz, 2H), 1.89 (h, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H).

2,7-*bis*-(4-Methoxyphenyl)-9-propyl-9H-carbazole (**5**)

A 2M aqueous solution of K₂CO₃ (20.7 g, 149.8 mmol, purged with N₂) was added dropwise to a mixture of 2,7-dibromo-9-propyl-9H-carbazole (5.00 g, 13.6 mmol), (4-methoxyphenyl)boronic acid (4.7 g, 30.9 mmol), Pd(PPh₃)₄ (0.79 g, 0.68 mmol) in a degassed mixture of toluene and H₂O (1:1, v/v) (50 cm³). The resultant reaction mixture was heated under reflux at 120 °C for 12h under intensive stirring and then allowed to cool to room temperature. The resultant precipitate was isolated by filtration, washed with ethanol (3 x 100 cm³) and dried under vacuum to give the desired product as a white powder (4.6 g, 80.0%).

¹H NMR (600 MHz, CDCl₃) δ 8.11 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.7 Hz, 4H), 7.53 (s, 2H), 7.43 (d, J = 9.5 Hz, 2H), 7.04 (d, J = 8.7 Hz, 4H), 4.35 (t, J = 7.2 Hz, 2H), 3.89 (s, 6H), 1.98 (h, J = 7.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H).

4,4'-(9-Propyl-9H-carbazole-2,7-diyl)diphenol (**6**)

A cooled (0 °C) solution of boron tribromide (19.9 g, 79.8 mmol) in anhydrous dichloromethane (45 cm³) was added dropwise *via* a syringe to a solution of 2,7-bis-(4-methoxyphenyl)-9-propyl-9H-carbazole (5.6 g, 13.3 mmol) in dichloromethane (50 cm³) in a dried Schlenk tube at -78°C. The resultant reaction mixture was stirred at 0 °C for 1h. The resulting mixture was allowed to warm slowly to room temperature and then stirred overnight. The resulting green solution was poured slowly into ice water (200 cm³), stirred for 1h and then extracted with ethyl acetate (3 x 100 cm³). The combined organic extracts were washed with brine (3 x 50 cm³), dried over MgSO₄, filtered and the solvent removed under reduced pressure. The resultant crude product was purified by flash column chromatography on silica gel using a mixture (3/7, v/v) of ethyl acetate/petroleum ether as eluent to give the desired product as a white solid (4.6 g, 89.0%).

¹H NMR (600 MHz, Acetone-*d*) δ 8.42 (s, 2H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.76 (s, 2H), 7.65 (d, *J* = 8.2 Hz, 4H), 7.45 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.1 Hz, 4H), 4.54 (t, *J* = 7.2 Hz, 2H), 2.02 – 1.98 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

6-Bromohexyl acrylate (**10**)

A solution of acryloyl chloride (11.2 g, 123.7 mmol) in DCM (80 cm³) was added dropwise to a solution of 6-bromohexan-1-ol (18.6 g, 103.1 mmol) and triethylamine (10.4 g, 103.1 mmol) in DCM (150 cm³) at 0 °C. The resultant reaction mixture was stirred at 0 °C for 2h. The resulting mixture was allowed to warm slowly to room

temperature and then stirred overnight. The white precipitate was filtered off and the filtrate was concentrated under reduced pressure. Purification was carried out via column chromatography [silica gel, PE] to yield a yellow oil (17.3 g, 72%).

^1H NMR (600 MHz, CDCl_3) δ 6.40 (dd, $J = 17.4, 1.5$ Hz, 1H), 6.12 (dd, $J = 17.3, 10.5$ Hz, 1H), 5.82 (dd, $J = 10.4, 1.4$ Hz, 1H), 4.16 (t, $J = 6.6$ Hz, 2H), 3.41 (t, $J = 6.8$ Hz, 2H), 1.91 – 1.84 (m, 2H), 1.73 – 1.65 (m, 2H), 1.53 – 1.45 (m, 2H), 1.45 – 1.37 (m, 2H).

N,N-diallyl-6-Bromohexanamide (**13**)

A solution of 6-bromohexanoyl chloride (21.97 g, 102.92 mmol) in pyridine (80 cm^3) was added dropwise to a mixture of diallylamine (5.00 g, 51.46 mmol) and triethylamine (15.62 g, 154.38 mmol). The resultant reaction mixture was stirred at 0 °C for 2h. The resulting mixture was slowly warmed to room temperature and stirred overnight. The white precipitate was filtered off and the filtrate was concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, PE:DCM = 10:1~3:1, v/v] to yield a yellow oil (9.59 g, 68%).

^1H NMR (400 MHz, CDCl_3) δ 5.82-5.66 (m, 1H), 5.23-5.05 (m, 2H), 3.99-3.95 (m, 1H), 3.88-3.83 (m, 1H), 3.52 (t, $J = 6.7$ Hz, 1H), 2.33-2.28 (m, 1H), 1.82-1.73 (m, 1H), 1.70-1.61 (m, 1H), 1.50-1.40 (m, 1H).

Penta-1,4-dien-3-yl 6-bromohexanoate (**15**)

A solution of 6-bromohexanoyl chloride (5.00 g, 23.41 mmol) in DCM (30 cm^3)

was carefully added to a solution of penta-1,4-dien-3-ol (2.16 g, 25.76 mmol) and triethylamine (2.36 g, 23.41 mmol) in DCM (50 cm³) at 0°C. The reaction mixture was stirred at 0°C for 2h. The resulting mixture was slowly warmed to room temperature and stirred overnight. The white precipitate was filtered off and the filtrate was concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, PE:DCM = 15:1~5:1, v/v] to yield a yellow oil (4.28 g, 70%).

¹H NMR (600 MHz, CDCl₃) δ 5.85 – 5.78 (m, 2H), 5.69 (t, *J* = 6.2 Hz, 1H), 5.28 (d, *J* = 17.2 Hz, 2H), 5.21 (d, *J* = 10.5 Hz, 2H), 3.38 (t, *J* = 6.8 Hz, H), 2.34 (t, *J* = 7.5 Hz, H), 1.90 – 1.82 (m, 2H), 1.70 – 1.61 (m, 2H), 1.50 – 1.43 (m, 2H).

((9-Propyl-9H-carbazole-2,7-diyl)-*bis*-(4,1-phenylene))bis(oxy))bis(ethane-2,1-diyl) diacrylate (**16**)

A mixture of 4,4'-(9-propyl-9H-carbazole-2,7-diyl)diphenol (0.50 g, 1.2 mmol), K₂CO₃ (0.49 g, 3.5 mmol) and DMF (10 cm³) was heated (100 °C) and stirred overnight. 2-Bromoethyl acrylate (0.84 g, 3.6 mmol) was added to the reaction mixture, which was then stirred for a further 24h. The cooled reaction mixture was poured into water (50 cm³) and then the crude product was extracted into DCM (3 x 100 cm³). The combined organic extracts were washed with brine (3 x 100 cm³), dried (MgSO₄), filtered, and concentrated under reduced pressure. Purification of the crude product was carried out *via* column chromatography [silica gel, PE:DCM = 1:10~1:3, v/v] and recrystallization from PE/DCM to yield a white crystalline solid (0.68 g, 78 %).

^1H NMR (600 MHz, CDCl_3) δ 8.11 (d, J = 8.0 Hz, 2H), 7.66 (d, J = 8.6 Hz, 4H), 7.53 (s, 2H), 7.43 (dd, J = 8.0, 1.5 Hz, 2H), 7.05 (d, J = 8.7 Hz, 4H), 6.48 (dd, J = 17.3, 1.4 Hz, 2H), 6.20 (dd, J = 17.3, 10.4 Hz, 2H), 5.88 (dd, J = 10.5, 1.4 Hz, 2H), 4.59-4.54 (m, 4H), 4.35 (t, J = 7.2 Hz, 2H), 4.31-4.28 (m, 4H), 1.97 (h, J = 7.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 166.17, 157.96, 141.60, 138.58, 135.40, 131.44, 128.67, 128.11, 121.59, 120.52, 118.43, 114.99, 106.83, 66.09, 64.84, 62.97, 44.63, 22.39, 11.94.

HRMS (ESI) calcd for $\text{C}_{37}\text{H}_{35}\text{NO}_6$ (M^+H^+): 590.2543, found: 590.2541.

(((9-Propyl-9H-carbazole-2,7-diyl)bis(4,1-phenylene))bis(oxy))bis(hexane-6,1-diyl) diacrylate (**17**)

A mixture of 4,4'-(9-propyl-9H-carbazole-2,7-diyl)diphenol (3.00 g, 7.62 mmol), K_2CO_3 (2.95 g, 21.34 mmol) and DMF (30 cm^3) was heated (100 $^\circ\text{C}$) and stirred overnight. 6-Bromohexyl acrylate (5.01 g, 21.34 mmol) was added to the reaction mixture, which was then stirred for a further 24h. The cooled reaction mixture was poured into water (50 cm^3) and then the crude product was extracted into DCM (3 x 100 cm^3). The combined organic extracts were washed with brine (3 x 100 cm^3), dried (MgSO_4), filtered, and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, PE:DCM = 1:10~1:2, v/v] and recrystallization from PE/DCM to yield the desired product as a white crystalline solid (4.12 g, 77 %).

^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.1$ Hz, 2H), 7.65 (d, $J = 8.8$ Hz, 4H), 7.53 (d, $J = 1.5$ Hz, 1H), 7.43 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 4H), 6.41 (dd, $J = 17.3, 1.5$ Hz, 2H), 6.13 (dd, $J = 17.3, 10.4$ Hz, 2H), 5.82 (dd, $J = 10.4, 1.5$ Hz, 2H), 4.35 (t, $J = 7.2$ Hz, 3H), 4.19 (t, $J = 6.6$ Hz, 4H), 4.04 (t, $J = 6.4$ Hz, 4H), 2.02-1.93 (m, 2H), 1.89-1.81 (m, 4H), 1.78-1.69 (m, 4H), 1.54-1.44 (m, 8H), 1.02 (t, $J = 7.4$ Hz, 3H).
 ^{13}C NMR (151 MHz, CDCl_3) δ 166.36, 158.52, 141.58, 138.70, 134.71, 130.57, 128.59, 128.55, 121.49, 120.43, 118.38, 114.80, 106.75, 67.90, 64.55, 44.60, 29.21, 28.58, 25.80, 25.78, 22.37, 11.91.

HRMS (ESI) calcd for $\text{C}_{45}\text{H}_{51}\text{NO}_6$ (M^+H^+): 702.3795, found: 702.3796.

6,6'-(((9-Propyl-9H-carbazole-2,7-diyl)bis(4,1-phenylene))bis(oxy))bis(N,N-diallylhexanamide) (**18**)

A mixture of 4,4'-(9-propyl-9H-carbazole-2,7-diyl)diphenol (0.50 g, 1.27 mmol), K_2CO_3 (0.49 g, 3.55 mmol) and DMF (10 cm^3) was heated (100 $^\circ\text{C}$) and stirred overnight. *N,N*-diallyl-6-bromohexanamide (5.01g, 21.34mmol) was added to the reaction mixture, which was then was stirred for a further 24h. The cooled reaction mixture was poured into water (50 cm^3) and then the crude product was extracted into DCM (3 x 100 cm^3). The combined organic extracts were washed with brine (3 x 100 cm^3), dried (MgSO_4), filtered, and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, PE:DCM = 1:5~2:1, v/v] and recrystallization from PE/DCM to yield a white crystalline solid (0.68 g, 69 %).

^1H NMR (600 MHz, $\text{DMSO}-d$) δ 8.15 (d, $J = 8.1$ Hz, 2H), 7.80 (s, 2H), 7.74 (d, $J = 8.7$

Hz, 4H), 7.44 (d, $J = 1.5$ Hz, 2H), 7.04 (d, $J = 8.7$ Hz, 4H), 5.88 – 5.79 (m, 2H), 5.76 – 5.68 (m, 2H), 5.19 – 5.07 (m, 8H), 4.49 (t, $J = 7.2$ Hz, 2H), 4.01 (t, $J = 6.4$ Hz, 4H), 3.88 (t, 8H), 2.33 (t, $J = 7.3$ Hz, 4H), 1.89-1.82 (m, 2H), 1.78-1.70 (m, 4H), 1.63-1.55 (m, 4H), 1.49-1.40 (m, 4H), 0.93 (t, $J = 7.3$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 172.92, 158.54, 141.60, 138.72, 134.70, 133.45, 132.98, 128.56, 121.50, 120.44, 118.39, 117.18, 116.58, 114.82, 106.77, 67.88, 49.18, 47.93, 44.62, 32.92, 29.22, 25.98, 25.08, 22.39, 11.94.

HRMS (ESI) calcd for $\text{C}_{51}\text{H}_{61}\text{N}_3\text{O}_4$ (M^+H^+): 780.4740, found: 780.4745.

Di(penta-1,4-dien-3-yl) 6,6'-(((9-propyl-9H-carbazole-2,7-diyl)-*bis*-(4,1-phenylene))-*bis*-(oxy))dihexanoate (**19**)

A mixture of 4,4'-(9-propyl-9H-carbazole-2,7-diyl)diphenol (1.00 g, 2.54 mmol), K_2CO_3 (0.98 g, 7.11 mmol) and DMF (50 cm^3) was heated (100 $^\circ\text{C}$) and stirred overnight. Penta-1,4-dien-3-yl 6-bromohexanoate (1.85g, 7.11mmol) was added to the reaction mixture, , which was then stirred for a further 24h. The cooled reaction mixture was poured into water (50 cm^3) and then the crude product was extracted into DCM (3 x 100 cm^3). The combined organic extracts were washed with brine (3 x 100 cm^3), dried (MgSO_4), filtered, and concentrated under reduced pressure. Purification was carried out *via* column chromatography [silica gel, PE:DCM = 1: 8~1:2, v/v] and recrystallization from PE/DCM at 0 $^\circ\text{C}$ to yield a white solid (1.36 g, 71 %).

^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 8.1$ Hz, 2H), 7.64 (d, $J = 8.7$ Hz, 4H), 7.53 (d, $J = 1.5$ Hz, 2H), 7.43 (dd, $J = 8.1, 1.5$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 4H), 5.90-5.80

(m, 4H), 5.77-5.69 (m, 2H), 5.33 (t, $J = 1.3$ Hz, 2H), 5.29 (t, $J = 1.3$ Hz, 2H), 5.25 (t, $J = 1.2$ Hz, 2H), 5.23 (t, $J = 1.2$ Hz, 2H), 4.35 (t, $J = 7.2$ Hz, 2H), 4.03 (t, $J = 6.4$ Hz, 4H), 2.41 (t, $J = 7.5$ Hz, 4H), 2.03-1.92 (m, 2H), 1.90-1.81 (m, 4H), 1.80-1.71 (m, 4H), 1.36-1.19 (m, 4H), 1.02 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 172.65, 158.60, 141.70, 138.82, 135.26, 134.85, 128.67, 121.61, 120.55, 118.50, 117.58, 114.91, 106.88, 75.02, 67.87, 44.72, 34.56, 29.12, 25.80, 24.85, 22.49, 12.04.

HRMS (ESI) calcd for $\text{C}_{49}\text{H}_{55}\text{NO}_6$ (M^+H^+): 754.4108, found: 754.4107.

3. RESULTS AND DISCUSSION

3.1 Mesomorphic behaviour of photopolymerisable liquid crystals

Four novel photopolymerisable liquid crystals (**16-19**), including two acrylate monomers with different length of alkyl chains (**16** & **17**) and two dienes with amide (**18**) or ester linking groups (**19**), were synthesised. A combination of POM, DSC and XRD was used to study their liquid crystalline behaviour in terms of mesomorphism and transition temperatures. The compounds (**16-19**) were found to exhibit a nematic liquid crystalline phase over a wide temperature range with a high degree of supercooling below the melting with a low recrystallisation temperature near room temperature. This a very slow crystallisation process is advantageous for controlling the macroscopic molecular alignment of thin, homogeneous layers of these novel polymerizable liquid crystals, so-called reactive mesogens (RMs) on a planar device substrate with a high order. This behaviour is particularly favourable in the fabrication

of high-quality thin films in a variety of optoelectronic devices utilising liquid crystals. Furthermore, a precise control of liquid crystalline orientation will also promote the rapid development of 4D printing shape-memory structures.

3.1.1 Acrylate monomer (16)

Photopolymerisable acrylate liquid crystals may spontaneously cross-link at high temperatures, sometimes making it more difficult to identify mesogenic textures and transition temperatures using a combination of POM and DSC analytical techniques. The flexible, terminal alkyl chains with a photopolymerizable group at the end of the chain in the acrylate monomer (**16**) appears to induce a slow molecular re-arrangement and a slow crystallization upon cooling from the liquid crystalline state.

[Figure 1](#) contains optical images of the acrylate (**16**) upon heating and cooling at different temperatures observed using POM. The characteristic nematic Schlieren texture, with disclination lines and thread-like points and brushes, was observed below the clearing point (N-I = 130 °C) as shown in [Figure 1a](#). The birefringent Schlieren texture reappears from the optically black isotropic state upon cooling just below the clearing point (I-N), see [Figures 1b and 1c](#). The thread-like texture appears somewhat blurry on further cooling (98 °C) as shown in [Figure 1d](#). The sample recrystallizes spontaneously, but very slowly, on further cooling (64 °C), see [Figure 1e](#), where large crystalline domains (top right corner) are observed. The large crystalline domains (right side) continue to grow as the temperature is further reduced, as shown in [Figure 1f and 1g](#), where darker domains of low birefringence can still be observed. No obvious

changes in the POM images are observed on further cooling, e.g., from 56 °C to 10 °C, as shown in [Figure 1h](#).

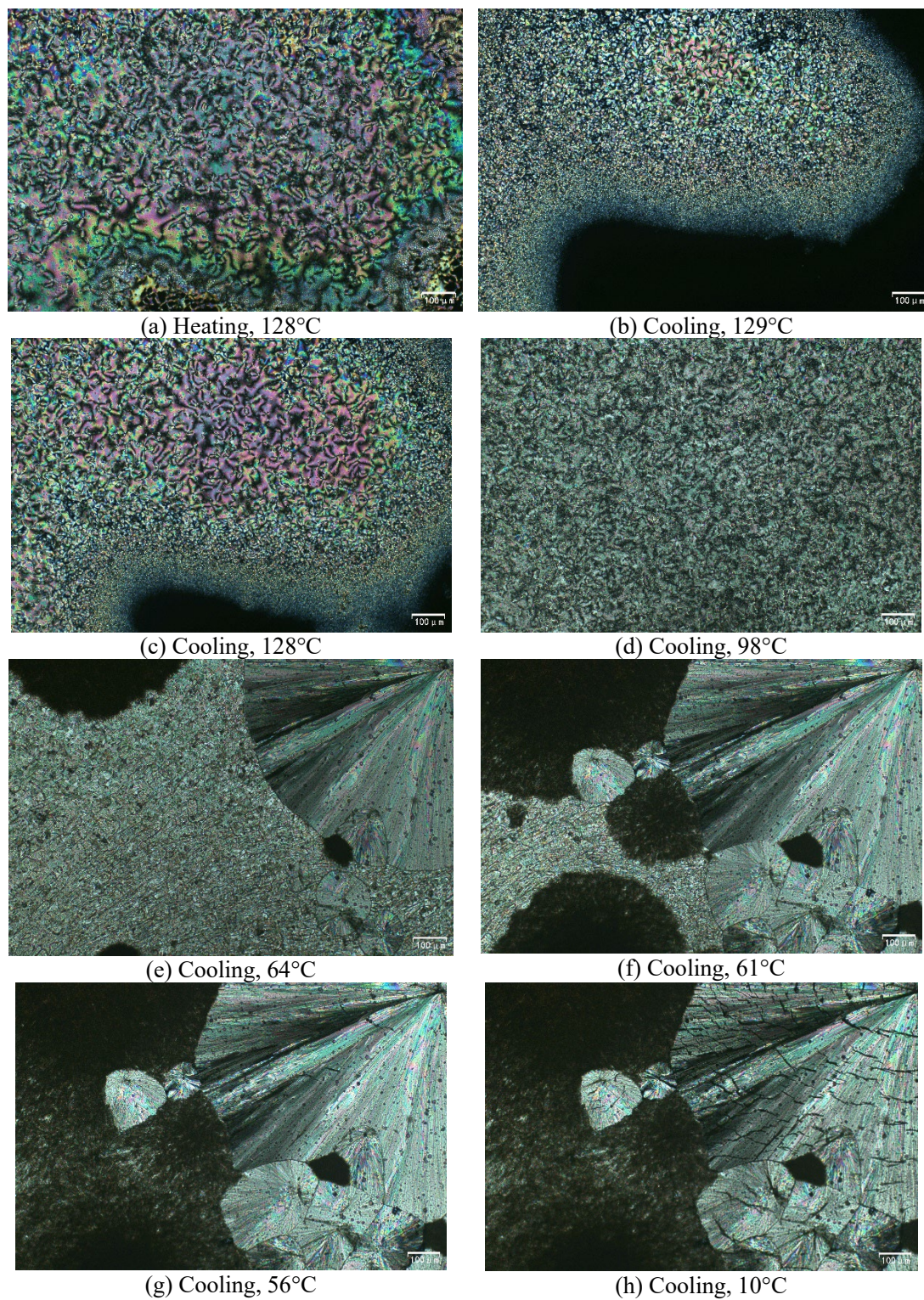


Figure 1. The POM images of compound (16) upon heating (a) and cooling (b-h) at different temperatures.

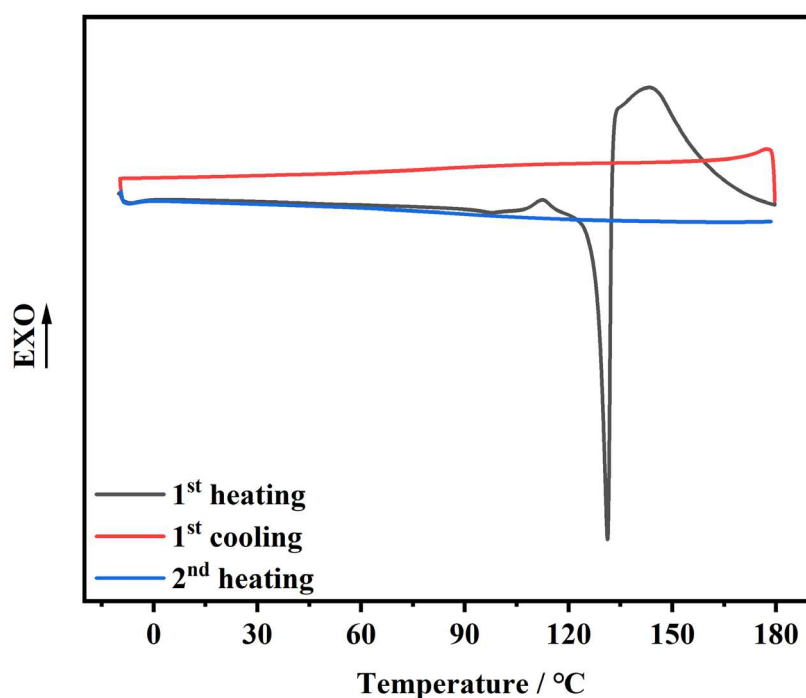


Figure 2. The heating and cooling cycles of the DSC trace as a function of temperature (-10 °C to 180 °C) for compound (16).

DSC analysis was used to further confirm the mesophases and transition temperatures of the new materials (16-19). Figure 2 shows the DSC curves on heating and cooling for compound (16). The DSC heating curve on the first heating cycle shows a small recrystallisation exotherm, i.e., a crystal-crystal transition, at about 110 °C and an endotherm at approximately 130 °C consistent with the clearing point (N-I) determined using POM. However, a large, wide exothermic peak at about 140 °C was observed on further heating, suggesting spontaneous thermally-induced polymerisation and crosslinking processes. Hence, when this sample was cooled to below 0 °C and heated again to 180 °C, no transition peaks could be observed, which is consistent with the formation of a highly crosslinked polymer network on the first heating cycle.

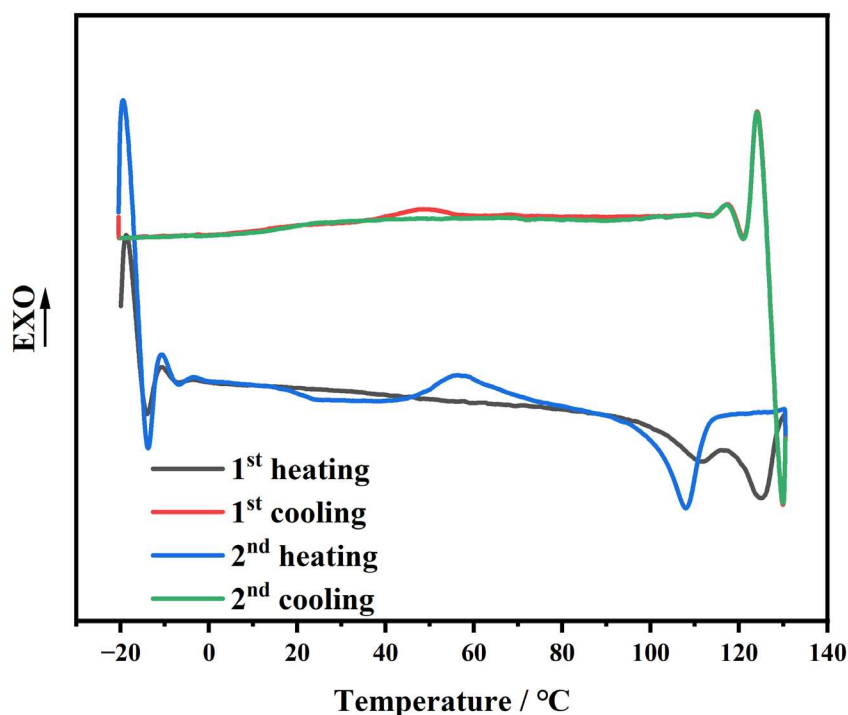


Figure 3. The heating and cooling cycles of the DSC trace as a function of temperature (-20 °C to 130 °C) for compound (16).

In order to eliminate any polymerisation, the DSC sample was heated into the isotropic state just above the clearing point (N-I) of 130 °C and then rapidly cooled to -20°C. The DSC curves for two heating/cooling cycles are recorded as shown in [Figure 3](#). The first heating curve shows two consecutive endothermic peaks close to 130°C corresponding to the melting point of compound (16). On cooling to about 60 °C in the first DSC cycle, an exothermic peak, corresponding to the nematic to crystalline transition, i.e., recrystallisation (N-Cr), is observed. On heating to about 60 °C on the second DSC cycle, an exothermic peak, corresponding to a crystal-to-crystal transition (Cr1-Cr2), is observed. The melting point (Cr-N) is observed at about 120 °C, which is slightly lower than that measured on the first DSC cycle, perhaps due to the presence of a different crystal form (Cr2) formed in the recrystallisation process (Cr1-Cr2) on

heating. However, no transition peak was observed at the second cooling curve. The inconsistency between the two heating and cooling cycles indicates that the sample underwent significant changes, probably polymerisation, during the heating and cooling processes with long-time heating, though to a lesser extent than when heated to 180 °C, as a significant exothermic peak associated with polymerisation was not observed. The presence of partial birefringent areas of solid material due to the presence of some polymerized material also created difficulties in identifying a sharp and clear transition between the nematic and crystalline phases using POM.

Transmission and Grazing Incidence XRD experiments were carried out and the diffraction patterns were collected at different temperatures to assess the order and phase transition temperatures of the reactive mesogens (**16-19**). The transmission XRD data show no orientation of a sample of compound (**16**) at any temperature despite application of a significant magnetic field (0.5 Tesla). Mechanical shearing of a sample of compound (**16**) on a silicon substrate led to crystallisation at room temperature (Figure 4a), as shown by grazing incidence X-ray scattering. Heating of the sample led it to melt at about 120 °C and then form an isotropic liquid at 140°C. Upon cooling from isotropic state to 120 °C, the sample shows nematic character as evidenced by an enhanced intensity of the wide-angle scattering peak in the vertical direction. The orientational order improves on further cooling and a nematic phase is observed at temperatures down to 30 °C as shown in Figures 4b and 4c. The d-spacing of the broad wide-angle scattering is found to be approximately 4.4 Å, corresponding to the average lateral distance between the adjacent molecules aligned parallel to the substrate surface.

This behaviour is consistent with the results observed using POM. Furthermore, the exhibition of nematic character on cooling to 30°C, as shown by these XRD studies, is representative of a slow crystalline process and the co-existence of a nematic phase and crystalline elements present due to the occurrence of polymerisation.

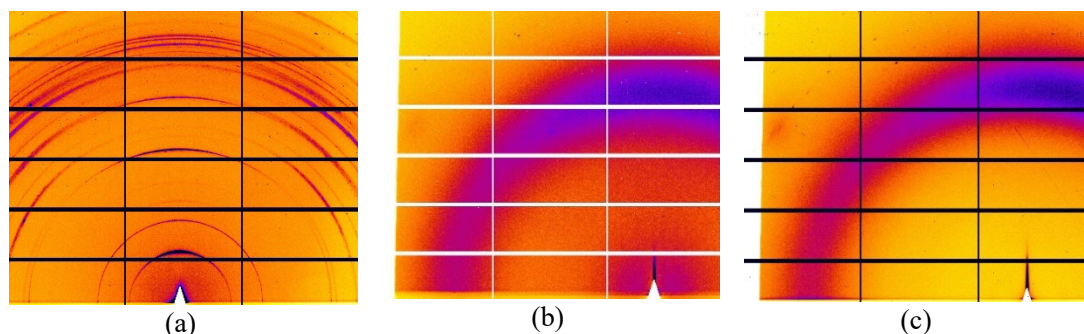
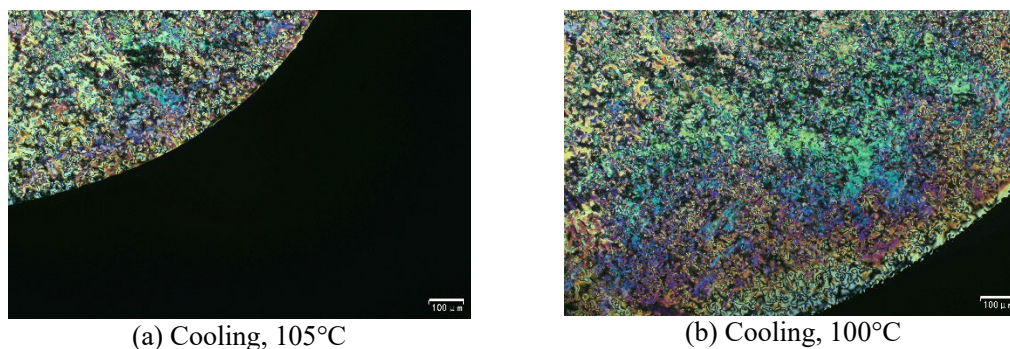


Figure 4. Grazing Incidence X-ray Diffraction (GIXRD) patterns collected on thin films on silicon substrate, oriented by mechanical shearing. (a) Crystal at room temperature; (b) Nematic shown by oriented wide angle scattering at 100°C on cooling; (c) Nematic at 30°C with better orientational order.

3.1.2 Acrylate monomer (17)

The compound (17) possesses longer terminal acrylate alkyl chains than those of the analogous compound (16) and its mesomorphic behaviour was also investigated by a combination of the complementary POM, DSC and XRD analytical techniques.



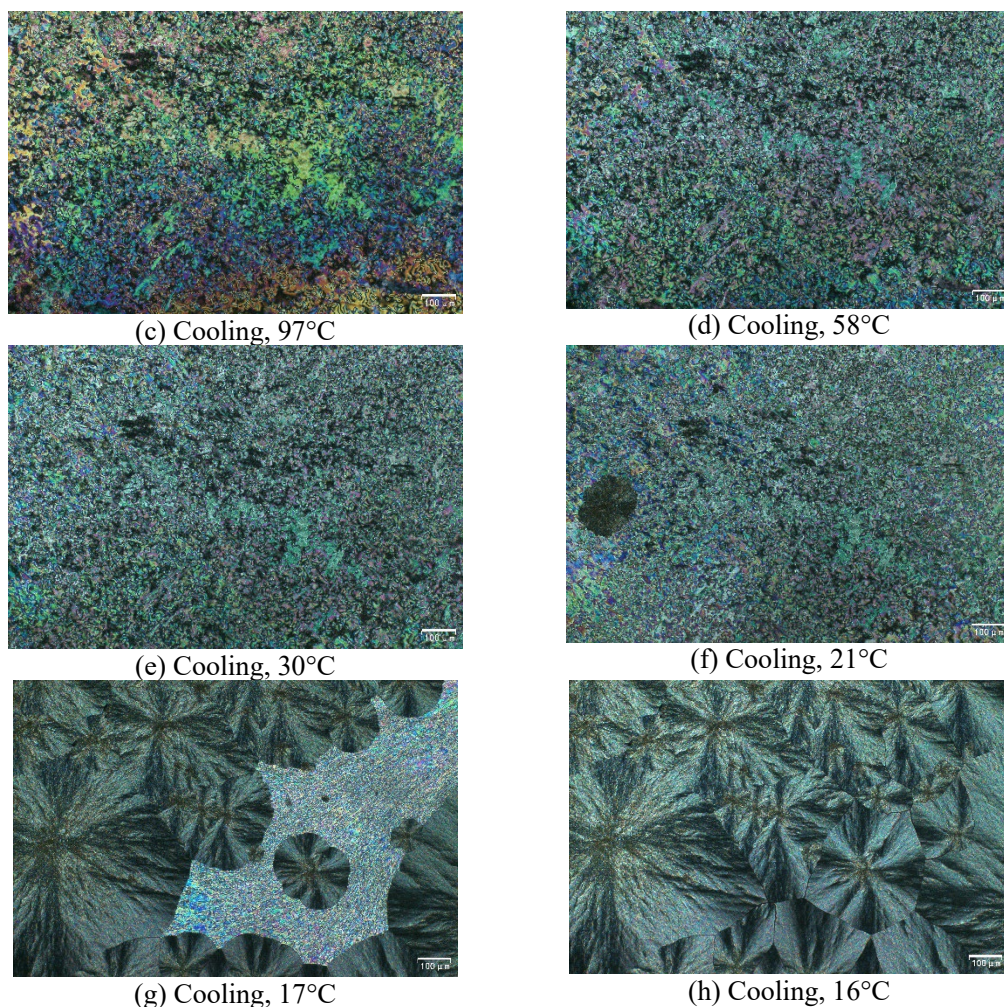


Figure 5. The POM images of compound (17) on cooling at different temperatures.

Figure 5 shows POM images of thin films of compound (17) on a planar substrate upon cooling from isotropic state. When the sample was cooled to 105 °C, a typical nematic marble texture appears as shown in Figure 5a. On further cooling, the marble texture is observed to spread to cover the isotropic black background. Figures 5b and 5c show the marble texture upon cooling to 100 °C and 97 °C, respectively. At lower temperatures, the morphological characteristics of the marble texture show no obvious change. However, the sample changes colour due to an increasing order, as shown in Figures 5d and 5e on to cooling to 58 °C and 30 °C, respectively. However, when the sample was cooled to 21 °C, a small ‘black’ crystal region appears as shown in Figure

5f. Upon further cooling, large crystalline domains form progressively, see Figure 5g, until the POM image reveals a completely crystalline texture see Figure 5h.

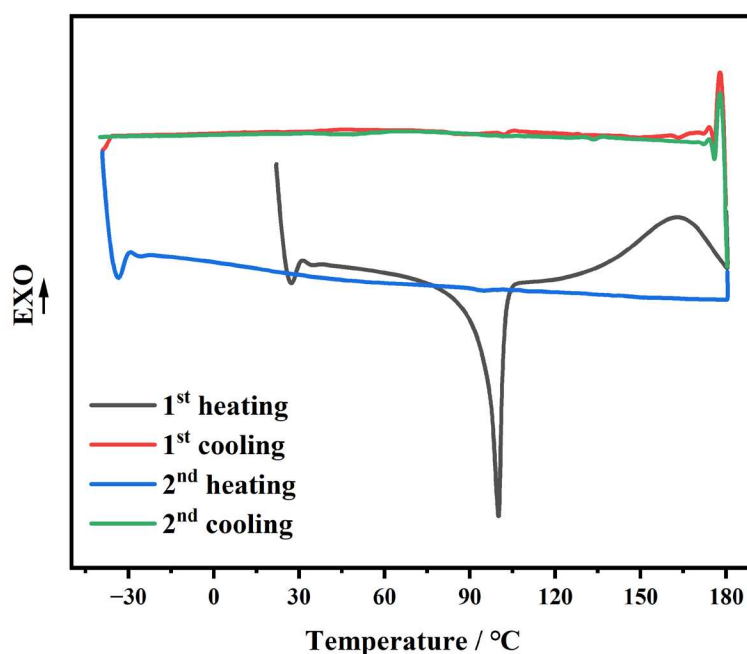


Figure 6. The heating and cooling cycles of the DSC trace as a function of temperature (-30 °C to 180 °C) for compound (17).

DSC analysis of compound (17) was used to confirm its mesogenic transition temperatures, see Figure 6. When the sample is heated, the DSC curve shows a significant melting endothermic peak with the endset temperature at about 105°C, consistent with the melting point determined by using POM. On further heating, a typical broad polymerisation exothermic peak is observed with the peak temperature at 160 °C. However, when the sample was cooled and the heated for the second time, no obvious peak was observed due to spontaneous polymerisation of the sample on heating. A DSC measurement with an endset temperature of 140 °C was carried out in order to eliminate polymerisation, see Figure 7. As expected, the first heating curve only shows a melting peak with the endset temperature at approximately 108 °C, without a

characteristic polymerisation exotherm. The second heating curve shows a small recrystallisation exotherm at about 20 °C and a small endothermic peak at about 60 °C. The second cooling curves do not contain any peaks for mesophase transitions due to a combination of spontaneous polymerisation and a slow crystalline process.

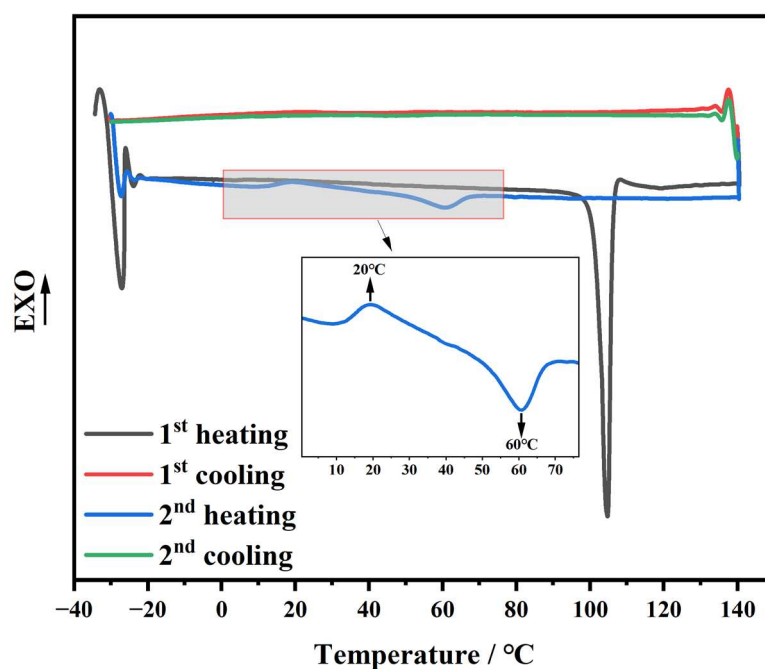


Figure 7. The heating and cooling cycles of the DSC trace as a function of temperature (-30 °C to 140 °C) for compound (17).

XRD analysis supports the results obtained from POM and DSC analyses. For example, the XRD data of compound (17) confirms the presence of a crystalline phase at room temperature, see Figure 8a. The sample melts at about 110 °C to form an enantiotropic nematic phase, as shown in figure 8b. The wide-angle d-spacing was determined to be about 4.4 Å, also see Figure 8b. At the same time, a peak in the small angle region corresponding to the longitudinal length of the molecule was also found with a d-spacing of 34.6 Å, see Figure 8c, while the theoretical longitudinal length was calculated as about 44.6 Å, see Figure 9. This 10 Å discrepancy, suggests the presence

of an interdigitated structure. As the sample is heated to 135 °C, XRD data still indicates the presence of nematic character, see Figure 8d, but not the isotropic state, which is indicative of the occurrence of spontaneous polymerisation.

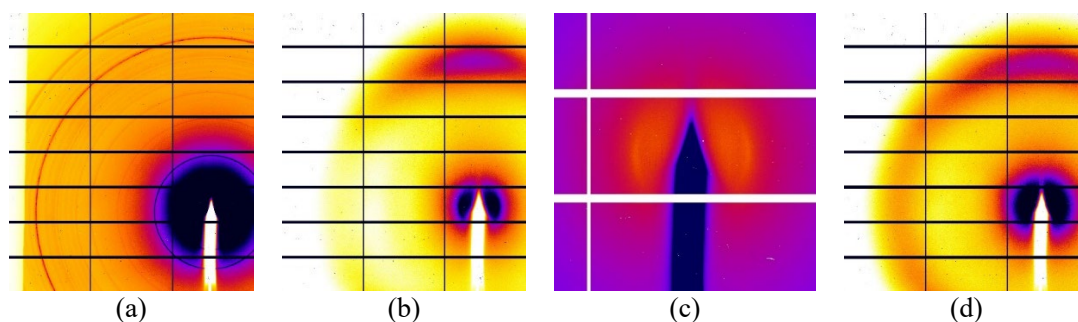


Figure 8. Transmission XRD in a horizontal 0.5 Tesla magnetic field. (a) Crystal at room temperature; (b) oriented wide angle scattering peak observed for nematic at 95 °C; (c) oriented small angle scattering peak due to longitudinal packing of molecules in the nematic phase; (d) oriented wide angle scattering peak for nematic at 135 °C.

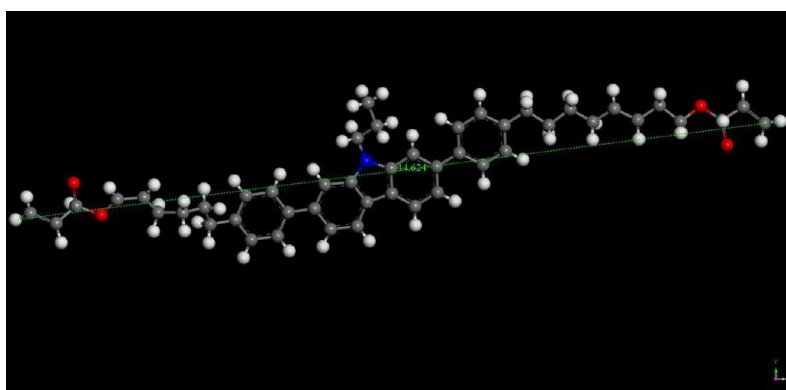


Figure 9. Molecular model of compound (17) *via* Materials Studio, showing a molecular length of about 44.6 Å.

3.1.3 Diene monomer (18)

Two non-conjugated diene monomers, with either an amide or an ester group (18 & 19, respectively) as a linking unit between the rigid aromatic core and the flexible aliphatic chain attached in a terminal position to the aromatic core, were prepared in order to compare their mesomorphic behaviour with that of their acrylate analogues (16 and 17).

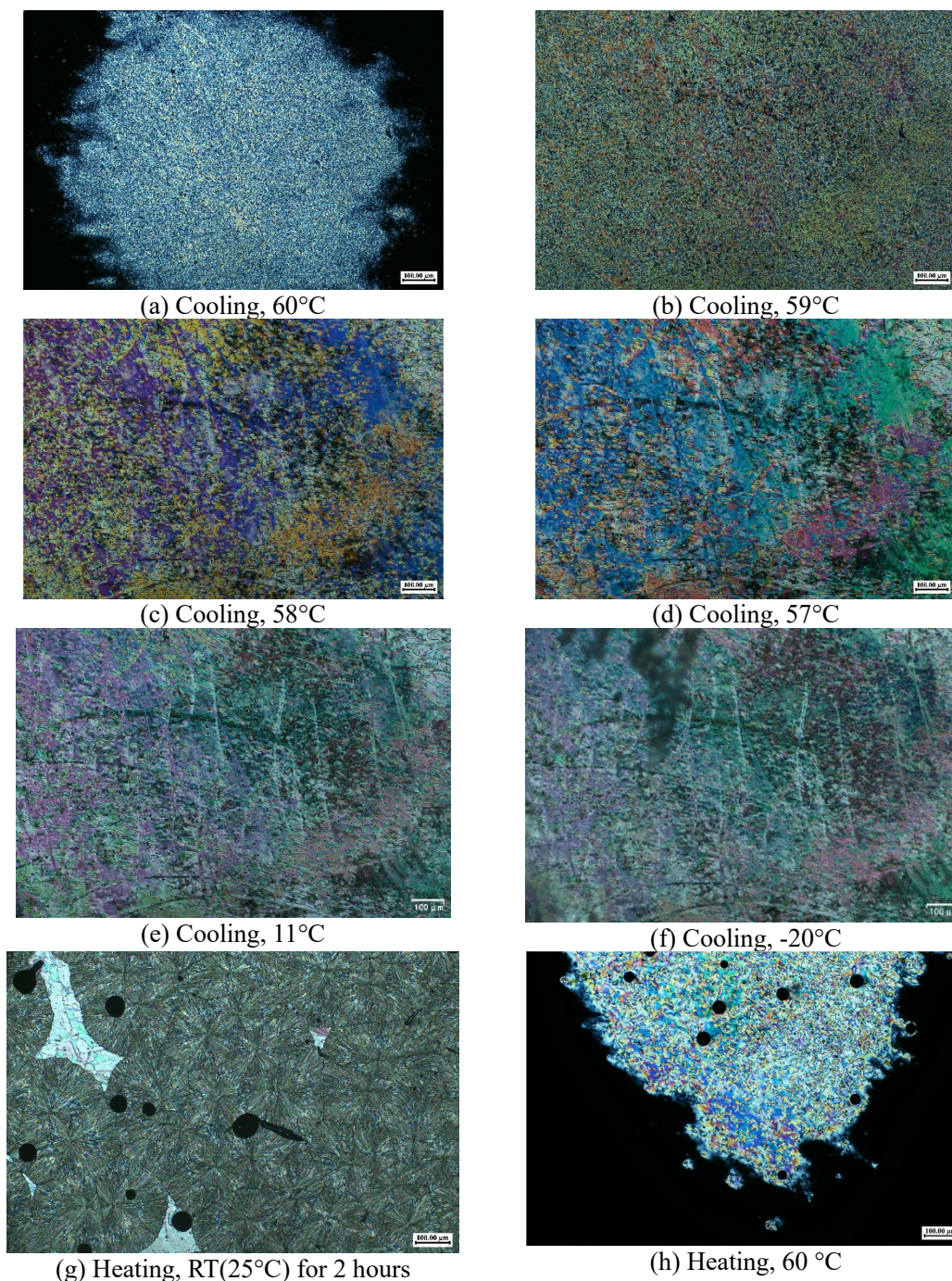


Figure 10. The POM images of compound (18) on cooling and heating at different temperatures.

The POM images upon cooling and heating at different temperatures of compound (18) are shown in Figure 10. Compound (18) exhibits a clearing point from the nematic phase to the isotropic phase (N-I) at 115°C. However, the isotropic black background is retained, probably due to a homeotropic (perpendicular) alignment of the nematic

phase, until about 60 °C when a birefringent texture becomes apparent, as shown in [Figure 10a](#). On further cooling, a characteristic nematic marble texture is observed down to -20 °C, as shown in [Figures 10b-10f](#) on cooling to 59 °C, 58 °C, 57 °C, 11 °C and -20 °C, respectively. However, when the sample was allowed to reattain room temperature (about 25°C), large crystalline domains were formed over a period of 2 hours, which is indicative of a very slow crystalline process, as shown in [Figure 10g](#). An isotropic texture then appears at about 60°C on heating the marble texture. [Figure 10h](#) shows the typical nematic thread-like texture on heating from the marble texture to 60 °C just before it forms the isotropic state.

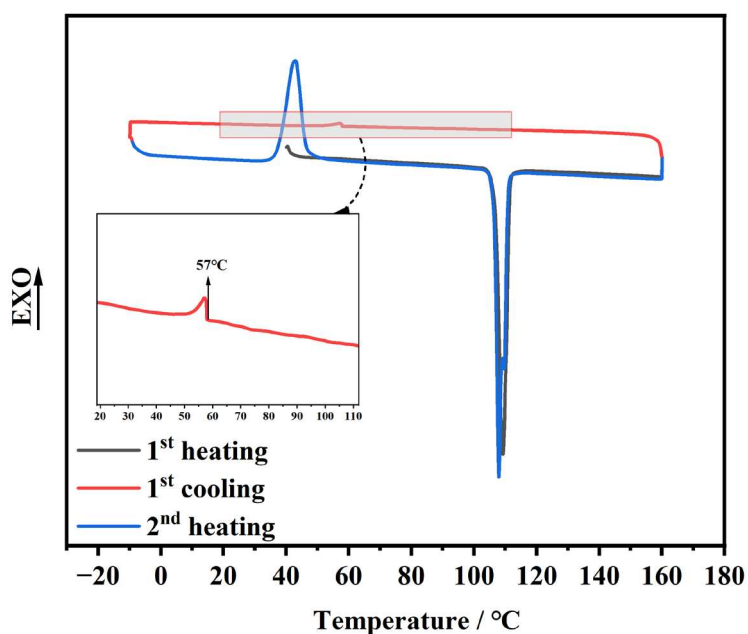


Figure 11. The heating and cooling cycles of the DSC trace as a function of temperature (-10 °C to 160 °C) for compound (**18**).

The DSC curve of compound (**18**), see [Figure 11](#), is consistent with the POM observations. The two heating curves exhibit similar endothermic peaks corresponding to melting with both onset temperatures of about 115°C, implying that the diene

monomer does not spontaneously polymerise. On cooling, a small exothermic peak appears at about 60 °C, which is consistent with the appearance of the marble texture observed during the POM studies, corresponding to the transition from the isotropic to the nematic phase. However, a peak corresponding to crystallisation is not observed on cooling. When the sample was heated again, a recrystallisation endotherm was observed at about 40 °C. The DSC curve confirms the expected thermal stability of the diene compound (**18**) with respect to spontaneous polarization on heating. However, the material (**18**) still shows a very slow crystalline process.

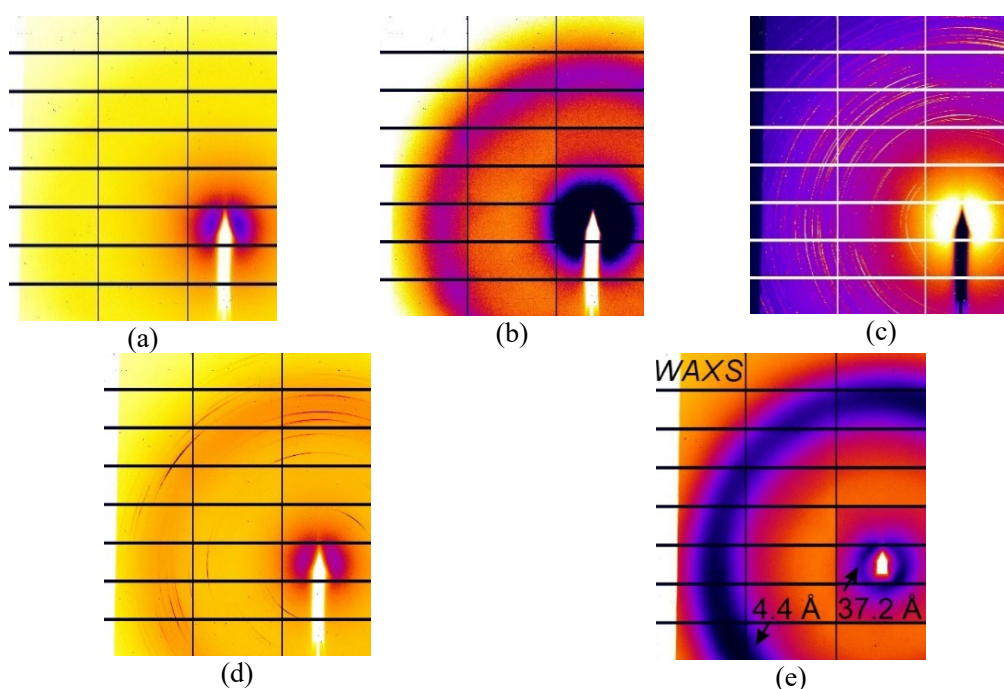
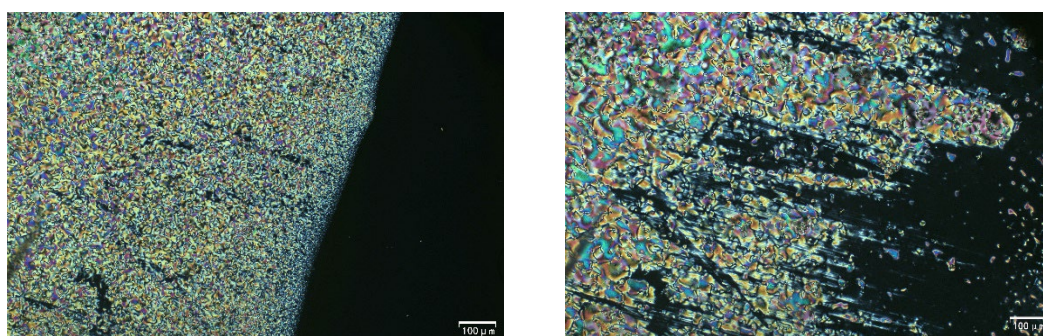


Figure 12. (a) amorphous structure at room temperature; (b) isotropic melt at 120 °C; (c) crystallisation at 100°C; (d) crystallisation at 50 °C; (e) WAXS pattern of the nematic phase formed by the compound (**18**), recorded on quenched sample and the peak in the SAXS region is shown clearly on a different intensity scale. The d-spacings are indicated on the SAXS and WAXS peaks, respectively.

The XRD spectra of samples of compound (**18**) do not show the presence of nematic phase using magnetic alignment. As shown in Figure 12, the sample of

compound (**18**) shows an amorphous phase at room temperature with any nonuniform orientation, see [Figure 12a](#). The diffraction pattern does not change in a material way on heating up to 120 °C, see [Figure 12b](#). The diffraction patterns obtained on cooling the sample, shows a crystalline state at 100 °C and 50 °C, as shown in [Figures 12c and 12d](#), respectively. However, a quenched and sheared sample of compound (**18**) shows a nematic phase at room temperature, see [Figure 12e](#). A diffuse, but oriented *WAXS* peak with a d-spacing centred around 4.4 Å was also observed. This confirms the presence of a nematic phase for compound (**18**). A diffuse *SAXS* peak was also observed, with its intensity maximum being concentrated in a perpendicular direction to the *WAXS* peak. The d-spacing of this *SAXS* peak is centred at 37.2 Å, and close to its longitudinal molecular length of ~45 Å. This diffuse nature of the *SAXS* peak indicates that the layer-like packing of molecules of compound (**18**) are only local without any long range order, as expected from a nematic phase. It appears that the applied magnetic field is not strong enough to induce a uniform, macroscopic orientation in the nematic phase of the compound (**18**) due to the high viscosity of the sample.

3.1.4 Diene monomer (**19**)



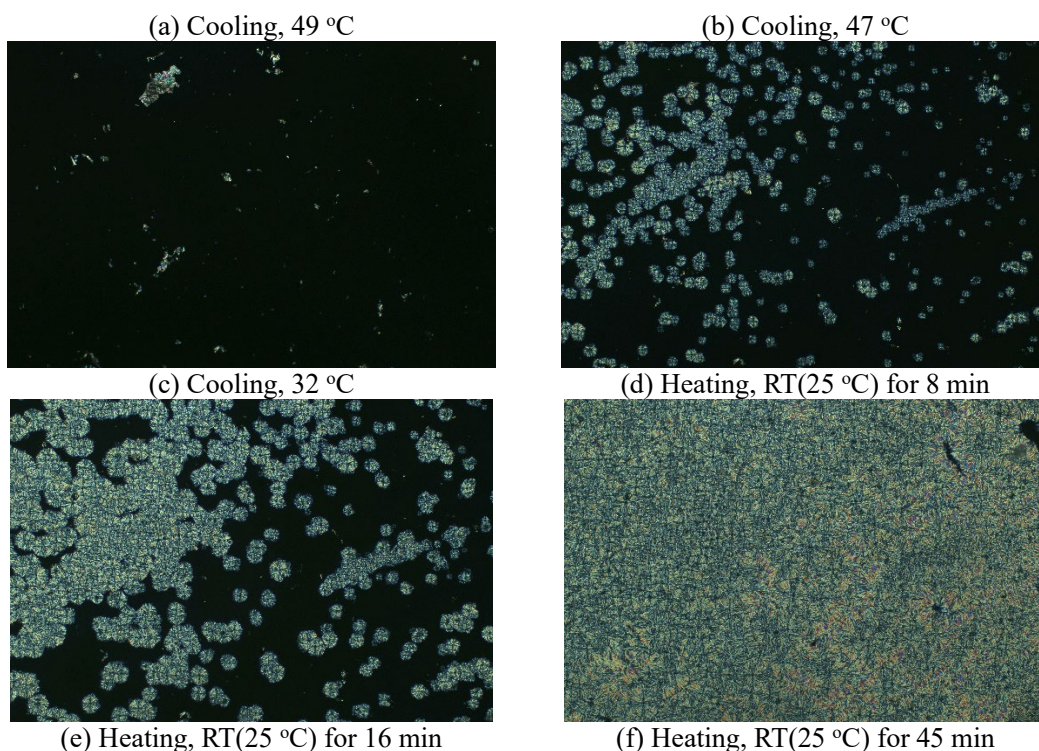


Figure 13. The POM images of compound (19) on cooling from isotropic state.

The diene monomer (19) with an ester moiety instead of an amide function as the polymerizable group attached to the terminal aliphatic chains was also synthesised in order to investigate its mesomorphic behaviour. Figure 13 shows the POM images of a thin, uniform sample of compound (19) upon cooling from the isotropic state. A characteristic nematic thread-like texture appears at 50 °C and spreads rapidly as shown in Figure 13a. On further cooling, the thread-like texture first becomes isotropic and remains so on cooling to 15 °C. However, when the sample was allowed to warm to room temperature(RT, about 25 °C), the sample crystallises slowly, see Figures 13b-13f.

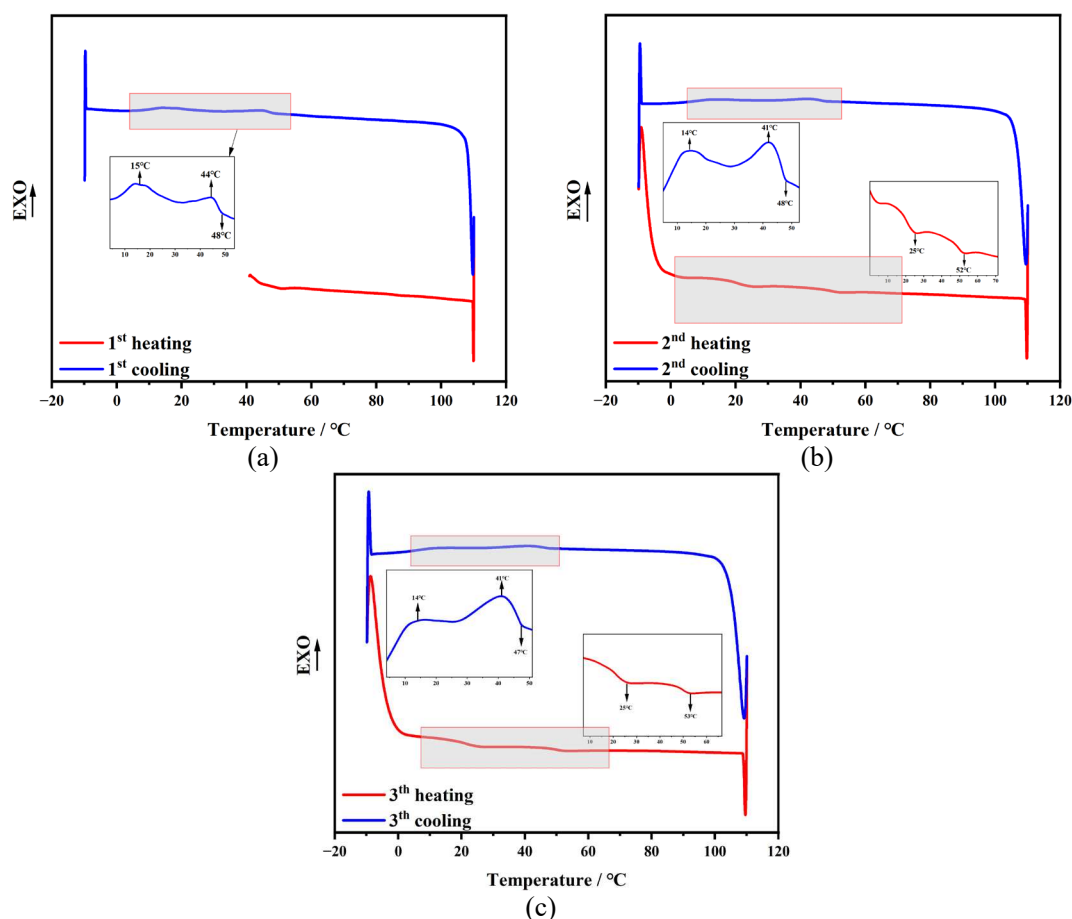


Figure 14. The heating and cooling cycles of the DSC trace as a function of temperature (-10°C to 110°C) for compound (19).

The DSC curves of compound (19), see Figure 14, support the POM observations. As shown in Figure 14a, when the sample was cooled from the isotropic state to -10°C, the curve shows two exothermic peaks at about 45 °C and 15 °C. The peak at 45 °C (onset about 50 °C) corresponds to the isotropic to nematic transition, while the peak at 15 °C (onset about 30 °C) indicates a nematic to crystalline transition. The transition temperatures are consistent with the POM results. When the sample was heated to isotropic state and then cooled for the second cycle, as shown in Figure 14b, two exothermic peaks appear on cooling. Two corresponding endothermic peaks on heating were observed due to the reversible nature of this phase transition. The transition

temperatures on cooling for the 2nd and 3rd cycles show a good agreement with the 1st cooling cycle, see Figure 14c. These endotherms on heating are slightly shifted along the x axis from their corresponding exotherms on cooling due to hysteresis. Heating and cooling cycles were performed sequentially with increasing rates, 5 °C min⁻¹, see Figure 14a, 10 °C min⁻¹, see Figure 14b and 15 °C min⁻¹, see Figure 14c, respectively. Compound (19) with diene ester linking groups exhibits good stability without spontaneous polymerisation on heating up to the nematic clearing point. Compound (19) exhibits weak, broad transition peaks with small enthalpy values. These characteristics suggest that compound (19) should be particularly suitable for design photo-curing 3D printing inks which require a combination of good solubility, stability and photo-induced cross-linking ability.

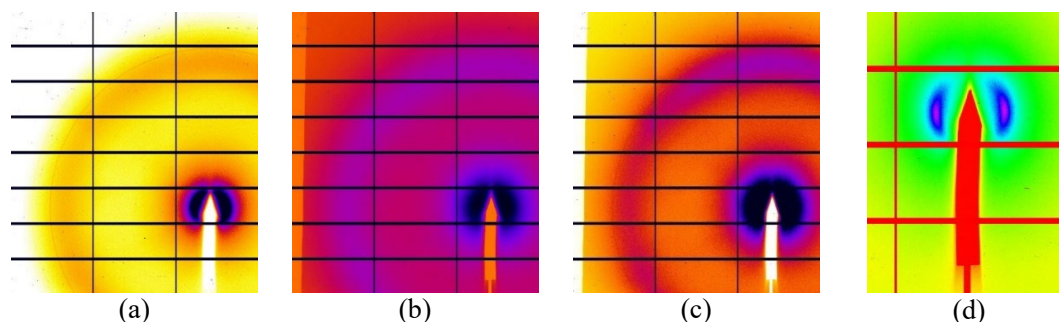


Figure 15. (a) crystal at room temperature; (b) isotropic at 60 °C; (c) nematic-crystalline at 35 °C; (d) small angle diffraction pattern.

XRD data of compound (19), see Figure 15, confirms the conclusions above. Figure 15a shows crystalline character with small angle orientation at room temperature, which becomes isotropic at about 60 °C, see Figure 15b. This sample shows both nematic and crystalline phases below 37 °C, see Figure 15c. The wide-angle d-spacing was determined as being about 4.1 Å, for the nematic phase, see Figure 15c. A small

angle d-spacing of 39 Å, see [Figure 15d](#), corresponds to the molecular length of about 40 Å, see [Figure 16](#).

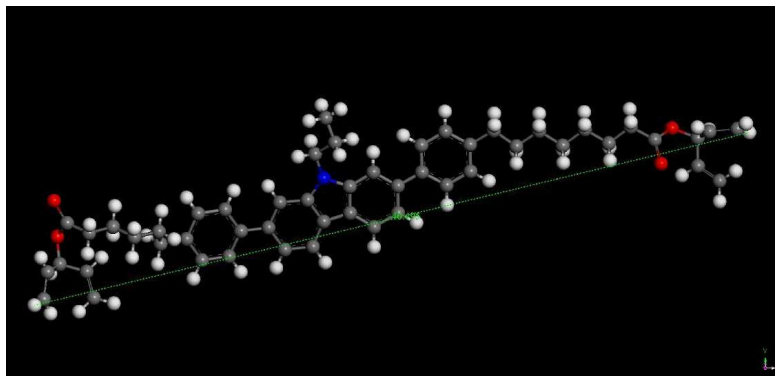


Figure 16. Molecular model of compound (19) *via* Materials Studio, showing a molecular length of about 40Å.

3.2 Infrared spectra of diacrylate and diene monomers

In addition to determinative POM, DSC and XRD, Infrared spectra of these reactive monomers were also measured at different temperatures using both *in-situ* variable-temperature ATR and *ex-situ* KBr pelletisation methods to provide complementary information on thermal polymerisation of diacrylate and diene monomers.

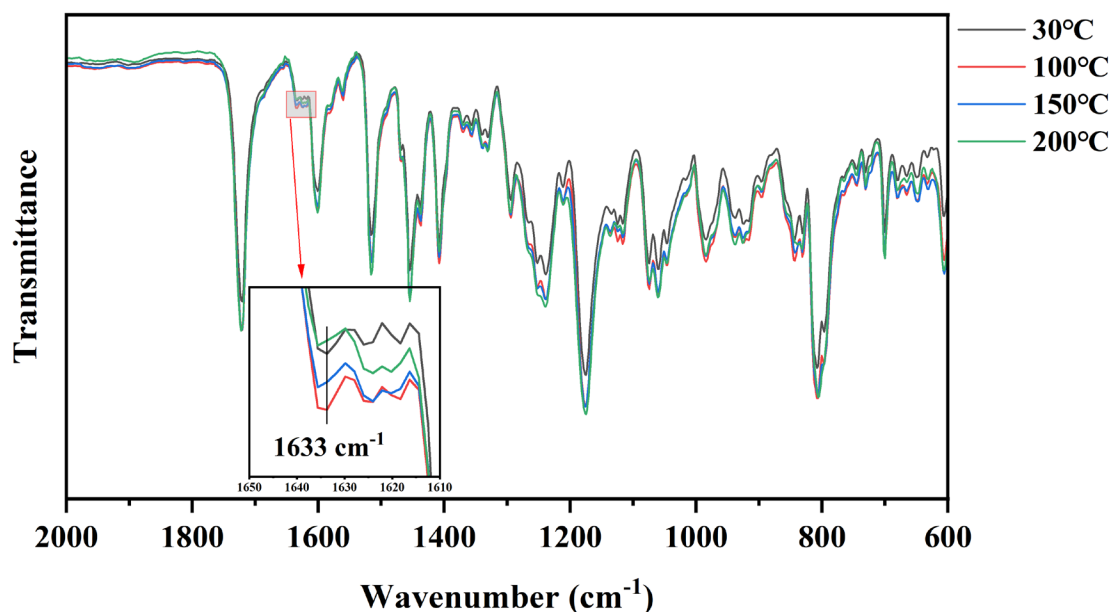


Figure 17. IR spectra of diacrylate monomer (**16**) at different temperatures (RT, 100°C, 150°C, and 200°C) via *in-situ* variable-temperature ATR method.

The *In-situ* Infrared (IR) spectra of reactive monomers at different temperatures (room temperature (RT, ~25°C), 100°C, 150°C, and 200°C) were recorded using Shimadzu IRPrestige-21 with variable-temperature ATR. After initial measurement at room temperature, the sample was heated to the target temperature at a ramp rate of 5°C/min. The spectrum was collected after equilibrating at the target temperature for 10 minutes. [Figure 17](#) compares the IR spectra of diacrylate monomer (**16**) at different temperatures (RT, 100°C, 150°C, and 200°C) measured by *in-situ* variable-temperature ATR method. The characteristic absorption peaks of carbon-carbon double bonds (C=C, non-aromatic) generally appear between 1600-1680 cm⁻¹, depending on their chemical environment. This characteristic stretching vibration peak is usually found between 1630-1640 cm⁻¹ for acrylates. The IR spectra in [Figure 17](#) reveal the characteristic C=C stretching vibration peaks of the acrylate moiety at approximately 1633 cm⁻¹, exhibiting

changes in peak shape with increasing temperature. Concurrently, the intensity of the peaks at 150°C and 200°C also weakens relative to their intensity at 100°C. This intensity attenuation and shape change of the C=C peak at higher temperatures could be due to the polymerisation of double bonds. The result is consistent with its DSC curve shown in Figure 2 which gives a large, wide exothermic peak at about 140°C on the 1st heating, suggesting spontaneous thermally-induced polymerisation. Interestingly, the initial peak intensity at room temperature is observed to be lower than at higher temperature. This apparent anomaly is likely attributable to the *in-situ* high-temperature IR measurement methodology itself. Elevated temperature increases molecular motion, thus leading to an enhanced C=C stretching vibration. But as the temperature increases, polymerisation gradually becomes dominant and the characteristic C=C peak intensity decreased.

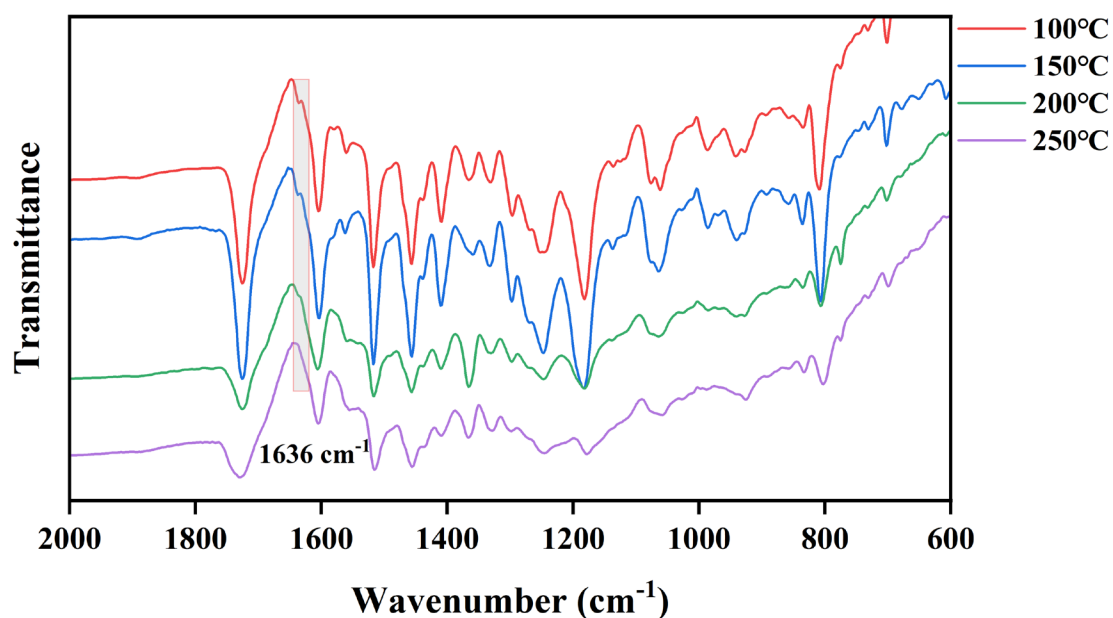


Figure 18. IR spectra of diacrylate monomer (**16**) at *ex-situ* high temperatures (100°C, 150°C, 200°C, and 250°C) via KBr pelletisation method

While *in-situ* variable-temperature ATR provides real-time monitoring capability, its inherent limitation as a point-contact surface technique must be acknowledged: the diamond crystal interrogates only a microscopic sample area (typically 100-500 μm diameter), resulting in attenuated peak intensities due to shallow penetration depth ($<2\ \mu\text{m}$). This surface-biased sampling could also renders subtle spectral changes. Particularly the minor C=C bond consumption at low polymerisation conversion is difficult to resolve above noise thresholds. High-temperature *in-situ* measurement also adds significant complexity and affect inherently IR spectra. Therefore, we also performed added measurement of diacrylate monomer (**16**) at *ex-situ* high temperature via KBr pelletisation method. KBr pelletisation achieves bulk volumetric averaging by homogenously dispersing the sample throughout the halide matrix, yielding stronger absorptions with enhanced signal-to-noise ratios. Samples underwent controlled heating (5°C/min ramp to 100°C, 150°C, 200°C, and 250°C with 10-min isothermal holds) followed by ambient cooling. Their IR spectra were acquired at room temperature, as shown in [Figure 18](#). It could be seen that the characteristic peak intensity for C=C bonds in acrylates at approximately 1636 cm^{-1} decreased with the increase of the test temperature from 100°C, 150°C to 200°C, until disappeared at 250°C, manifesting a high degree of polymerisation of acrylates.

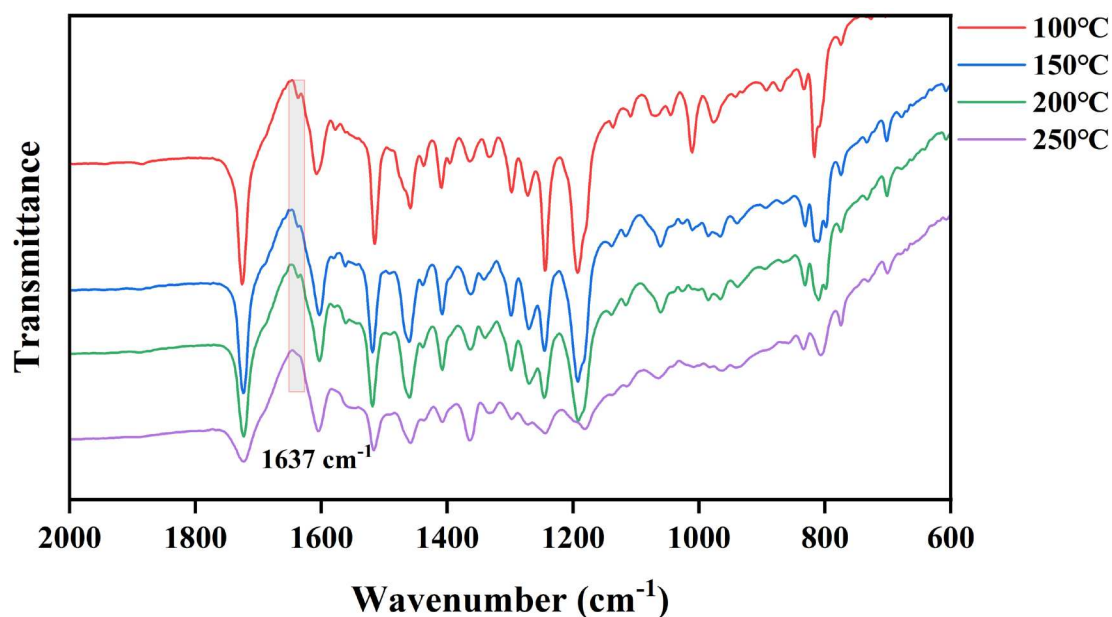


Figure 19. IR spectra of diacrylate monomer (**17**) at *ex-situ* high temperatures (100°C, 150°C, 200°C, and 250°C) via KBr pelletisation method.

A similar result was observed in the IR spectra of diacrylate monomer (**17**) measured by KBr pelletisation, as shown in [Figure 19](#). The characteristic peak intensity for C=C bonds in acrylates at approximately 1637 cm^{-1} showed a decreased trend with the increase of the test temperature from 100°C, 150°C, 200°C to 250°C. We also performed IR measurement for diacrylate monomer (**17**) via *in-situ* variable-temperature ATR, see [Figure 20](#). The IR spectra of diacrylate monomer (**17**) at RT, 100°C, 150°C, and 200°C reveal the characteristic C=C stretching vibration peaks at approximately 1635 cm^{-1} . The nearly identical peak intensity and shape at both 100°C and 150°C were observed during *in-situ* ATR measurements, while a attenuation in peak intensity and a change in shape was found upon heating to 200°C. It suggests the occurrence of polymerisation at 200°C, a conclusion well-supported by the DSC data ([Figure 6](#)) which shows a large, broad polymerisation exotherm with a peak value at

above 160°C. However, a slight decrease (Figure 19) of the characteristic peak intensity from 100°C to 150°C measured by KBr pelletisation may mean a low degree of polymerisation.

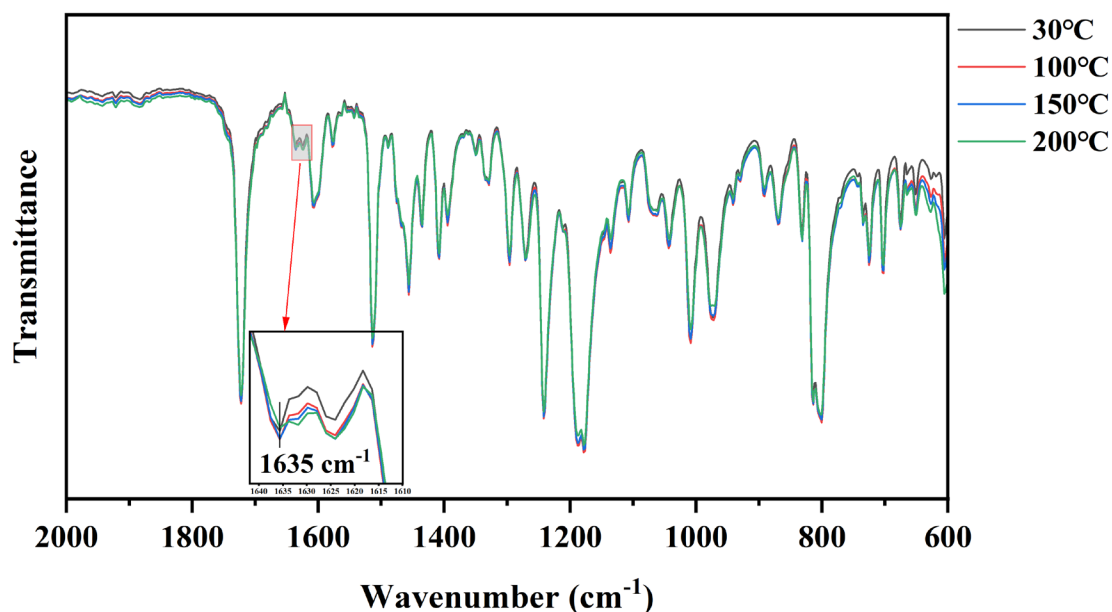


Figure 20. IR spectra of diacrylate monomer (**17**) at different temperatures (RT, 100°C, 150°C, and 200°C) via *in-situ* variable-temperature ATR method.

The IR spectra of diene monomer (**18**) at different temperatures (RT, 100°C, 150°C, and 200°C) were measured via *in-situ* variable-temperature ATR method and shown in Figure 21. The IR result shows the characteristic C=C stretching vibration peak of diene monomer (**18**) at approximately 1637 cm⁻¹ and maintains stable peak shape and shift at different temperatures. However, the intensity of the characteristic C=C stretching peak in the diene monomer **18** exhibits a progressive increase with rising temperature from RT, 100°C, 150°C, to 200°C. This behaviour is likely attributable to the dominant effect of the *in-situ* high-temperature testing methodology itself. As discussed above, Elevated temperature increases molecular motion, thus leading to an enhanced C=C stretching

vibration and intensifying the IR absorption peak. However, a counteracting decrease in peak intensity for diacrylate monomers (**16**) and (**17**) was observed because polymerisation gradually becomes dominant with the increase of temperature. Therefore, for diene monomer (**18**), the absence of a counteracting decrease in peak intensity suggests significantly less, or potentially no, polymerisation occurred across this temperature range. This interpretation aligns directly with the DSC data (Figure 11), which shows no observable exothermic polymerisation peak, confirming the lack of substantial thermal polymerisation for the diene monomer (**18**) under these conditions.

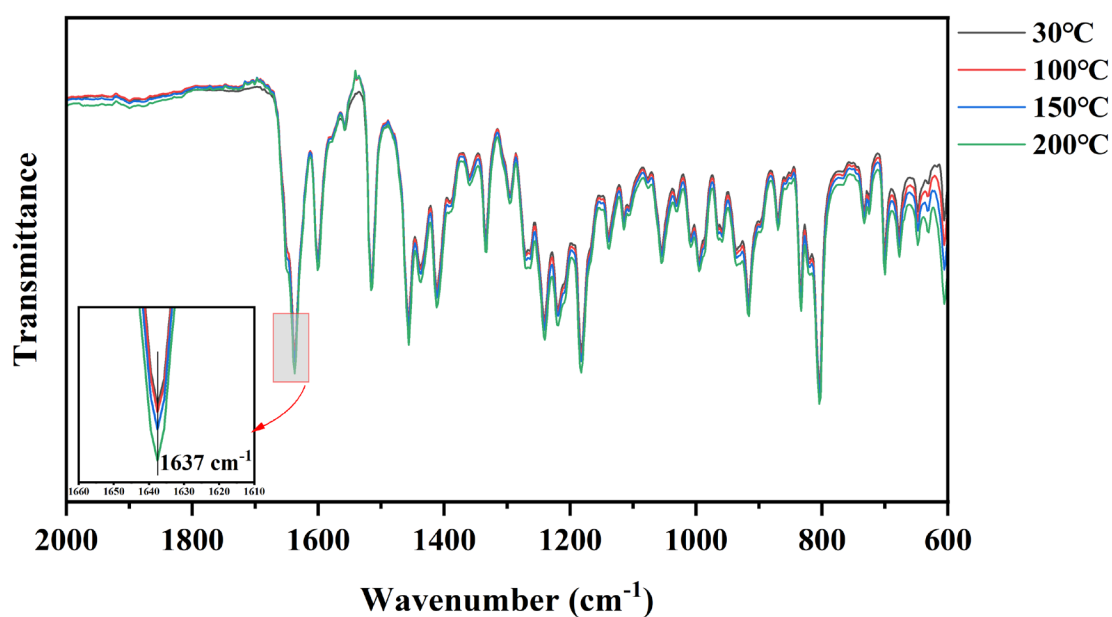


Figure 21. IR spectra of diene monomer (**18**) at different temperatures (RT, 100°C, 150°C, and 200°C) via *in-situ* variable-temperature ATR method.

The IR spectra of diene monomer (**18**) measured via KBr pelletisation at high temperatures also further prove the conclusion above. It can be seen from Figure 22 that the characteristic peak of double bonds in dienes at approximately 1638 cm⁻¹ show

an increased intensity as the temperature rises. The characteristic peak of double bonds for compound (18) was observed clearly even at 250°C, suggesting a high thermal stability of diene monomers. It can also be well-supported by the DSC results of diene monomers (18) and (19) in Figures 11 and 14, respectively, which shows undetectable thermal polymerisation exotherm.

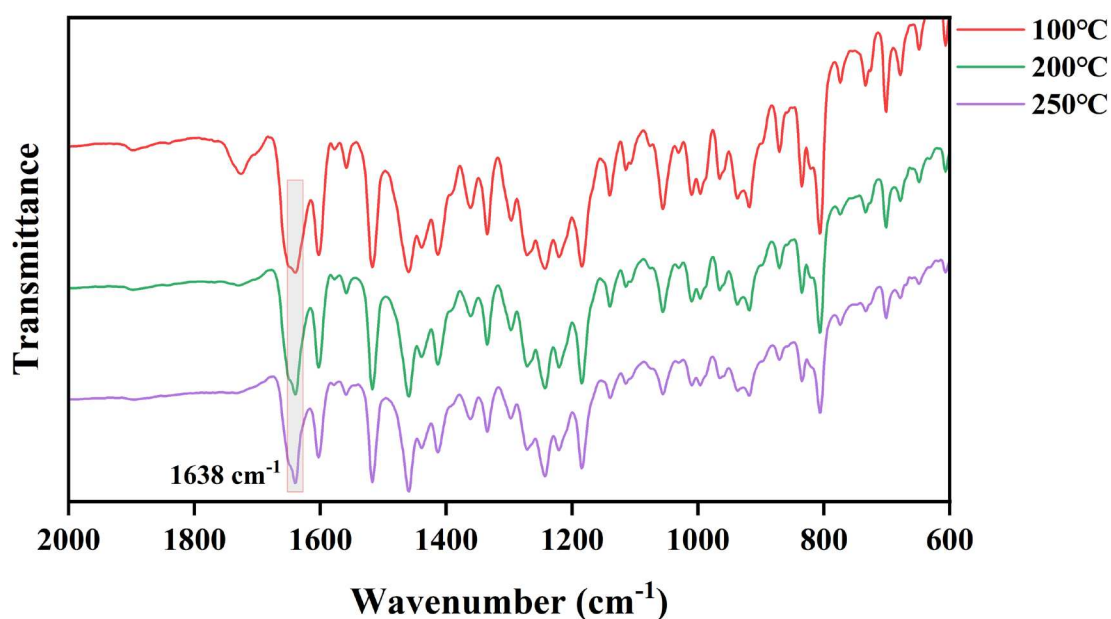


Figure 22. IR spectra of diene monomer (18) at *ex-situ* high temperatures (100°C, 200°C, and 250°C) via KBr pelletisation method.

Overall, IR spectroscopy measures the absorption of specific wavelengths of IR light corresponding to the vibrational frequencies of specific chemical bonds (e.g., C=C stretch at ~1630-1640 cm^{-1} for acrylates and dienes). The intensity of an absorption peak is proportional to the concentration of the bond type responsible for that vibration. The disappearance of a C=C bond due to polymerisation reduces the concentration of C=C bonds in the sample. However, for a small extent of polymerisation (low conversion), the change in concentration of C=C bonds is relatively small. The IR

absorption peak intensity decreases linearly with concentration, but the absolute change in absorbance for a small concentration change might be within the noise level or baseline drift of the spectrometer. Overlapping peaks (common in complex liquid crystal molecules with aromatic rings, polar groups, etc.), and path length variations could also easily obscure the subtle change for less polymerisation.

However, a low degree of polymerisation can significantly affect liquid crystalline optical texture and DSC curves. Polymerisation, even involving only a small fraction of double bonds, creates covalent crosslinks or oligomeric segments within this delicate ordered matrix. A single crosslink acts as a pinning site, distorting the director field (local average molecular orientation) over a relatively large volume around it to minimise elastic energy. This disrupts the uniformity of domains. Crosslinks drastically reduce molecular mobility. This can prevent the material from achieving its equilibrium mesophase structure upon cooling or stabilise a metastable structure. Phase transitions are highly cooperative processes and even minor polymerisation can significantly shift transition temperatures or suppress phases entirely. The optical texture observed under POM is a macroscopic manifestation of the director field and domain structure. Small distortions or domain boundary shifts caused by sparse polymerisation sites are amplified into visible changes in birefringence patterns, like schlieren textures domains.

DSC measures the heat flow and its signal (heat flow peak area) is directly proportional to the total enthalpy change (ΔH) occurring during the reaction. Polymerisation itself is exothermic and DSC integrates the heat flow from all reacting bonds. The cumulative heat release from even a small number of double bonds reacting

is substantial and easily detectable as a distinct exotherm. Furthermore, liquid crystal phase transitions involve significant enthalpy changes due to the breakdown of order. Polymerisation, even minimal, stabilises the existing structure through crosslinks, increasing the energy required for subsequent phase transitions. This manifests as a measurable shift in transition temperatures to higher values or broadening/reduction of the transition peak enthalpy. Therefore, both the perturbation of phase transition thermodynamics and the direct heat release from polymerisation make DSC highly sensitive to low conversion. Therefore, this study prioritises POM and DSC analysis as the primary diagnostic tools for evaluating polymerisation-induced mesophase transitions.

3.3 Photo-curing of DLP-printed inks containing these reactive mesogens

In this section, the photo-curing efficiency of DLP-printed inks containing the liquid crystalline monomers (**16**, **18** or **19**) is studied in detail, respectively. The compounds (**16**, **18** and **19**) differ in the nature of the polymerisable group, i.e., acrylate, diene amide or diene ester functions, attached to the end of the alkyl chains attached in a terminal position to the rigid aromatic cores of these compounds. The liquid crystal monomers were formulated into printing inks, and their photopolymerisation efficiency was compared by observing the changes in the infrared characteristic peaks of the photopolymerizable groups at different exposure times. The printing inks containing reactive liquid crystal monomer (**16**, **18** or **19**) (3wt%), *N*-acryloylsemicarbazide (45wt%) as hydrogel monomer, diphenyl (2,4,6-trimethylbenzoyl) phosphine oxide

(TPO) (1wt%) as initiator, 6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl acrylate (24wt%) and acrylic acid (27wt%). Dimethyl sulfoxide (DMSO) was chosen as solvent (65wt% in inks) due to its excellent solubility for these monomers. UV light (wavelength 365 nm, light intensity 9 mW cm^{-2}) was chosen for photo-curing of inks. The infrared spectra of printing inks were measured at room temperature. The condition of heating to 100°C in Figures 23-25 refers to heating the printing ink to 100°C first, then cooling it to room temperature for test. The purpose of heating to 100°C was to observe whether the double bonds in the ink monomers possess thermal stability at 100°C . If thermal stability is absent and crosslinking occurs, the characteristic peaks of the corresponding double bonds will change in the infrared spectrum.

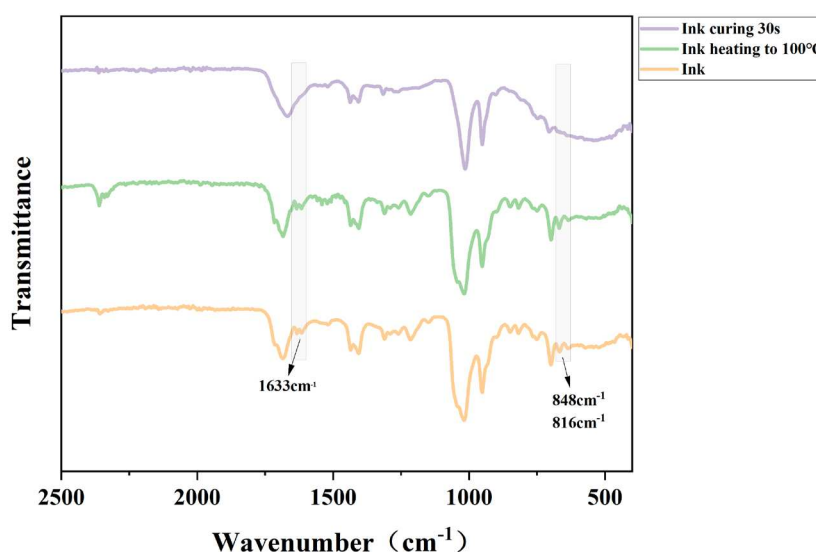


Figure 23. FTIR of photo-curing 3D printing ink containing acrylate monomer (16).

Figure 23 compares the infrared spectra of 4D printing ink containing compound (16) at different curing times, i.e., 0 s (no exposure) and 30 s or with additional heating at 100°C . Figure 23 reveals that before exposure, a distinct stretching vibration peak

for the carbon-carbon double bond in acrylates can be observed around 1633 cm^{-1} . After 30 seconds of UV exposure, this characteristic peak disappears, indicating that the photopolymerisable acrylate (**16**) exhibits a high photopolymerisation efficiency, requiring only tens of seconds of curing exposure even under low-intensity UV light. However, when heated to $100\text{ }^{\circ}\text{C}$ without exposure to light, the acrylate characteristic peaks remained present, without obvious changes in the infrared spectrum. It indicates a relative thermal stability of the acrylate liquid crystal monomer (**16**) on heating to $100\text{ }^{\circ}\text{C}$. It should be noted that the DSC investigation of compound (**16**) shows a high degree of spontaneous polymerisation at about $140\text{ }^{\circ}\text{C}$, as discussed above.

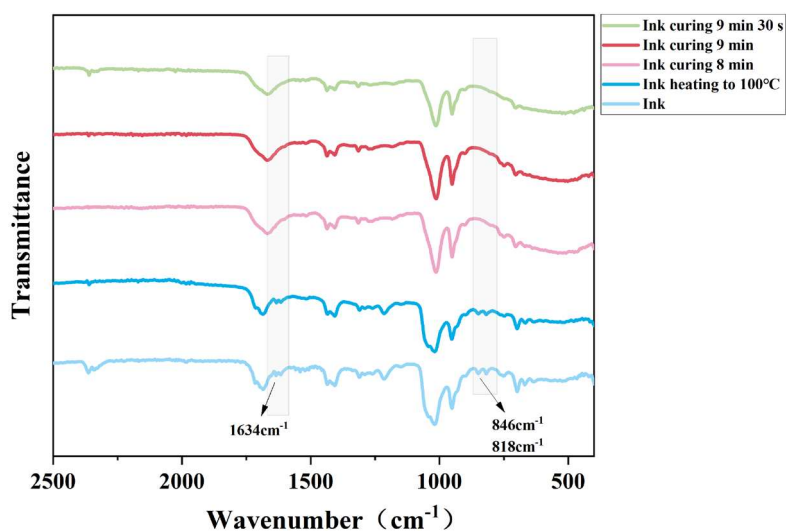


Figure 24. FTIR spectra taken at different times during the photo-curing of the 3D-printing ink containing the diene amide monomer (**18**).

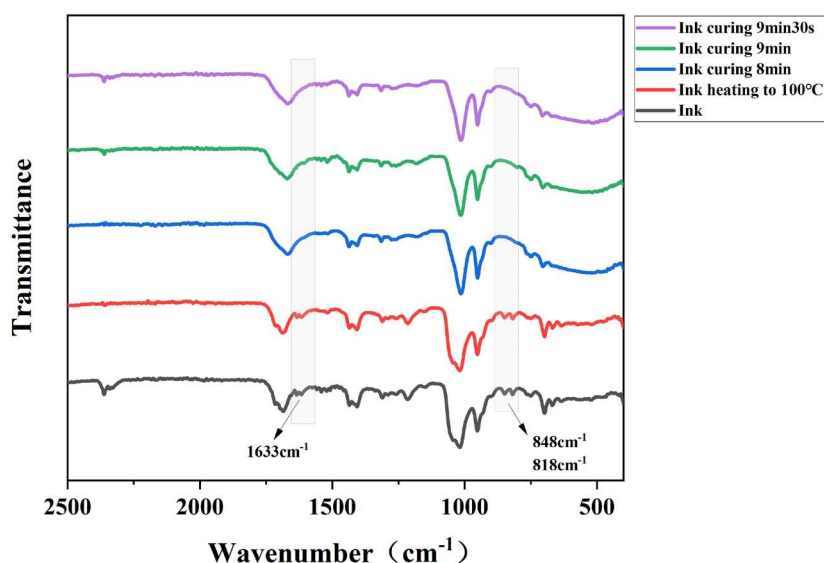


Figure 25. FTIR spectra taken at different times during the photo-curing of the 3D-printing ink containing the diene ester monomer **(19)**.

The infrared spectra of the polymerisable liquid crystal compounds **(18)** and **(19)** taken at different curing times are shown in [Figures 24 and 25](#), respectively. Before exposure, distinct stretching vibration peaks of carbon-carbon double bonds for dienes (approximately 1634 cm^{-1}) and twisting peaks (around 820 cm^{-1}) are observed. However, the diene compounds **(18)** and **(19)** required longer exposure times compared to the acrylates **(16)** and **(17)** to achieve complete curing of the ink. Infrared spectra were obtained at 8 minutes, 9 minutes, and 9 minutes 30 seconds of exposure, clearly showing that the characteristic peaks of carbon-carbon double bonds had disappeared. The 8-minute time was established as the maximum curing time, although the actual photopolymerisation may have occurred earlier while the ink had not yet visibly solidified. Given that 8 minutes is an acceptable curing time, no further optimization for shorter curing times was pursued. As expected, based on previous results, the acrylates **(16)** and **(17)** exhibit significantly higher photopolymerisation efficiency than that exhibited by the corresponding non-conjugated dienes **(18)** and **(19)** under the same

conditions. Additionally, the effect of temperature on triggering polymerisation on the non-conjugated dienes (**18**) and (**19**) was also investigated. Figures 24 and 25 show that heating to 100 °C without light exposure resulted in no obvious polymerisation of compounds dienes (**18**) and (**19**), as indicated by the minimal change in the characteristic peaks of the carbon-carbon double bonds. This result is consistent with the result observed from DSC and POM as discussed above. This suggests that the photopolymerisable groups studied in this investigation are relatively stable to heating within a certain range, such as below 100 °C, which is beneficial for the storage and transportation of these liquid crystal materials. Overall, these photopolymerisable acrylates and dienes were found to exhibit good thermal stability and advantageously high photopolymerisation efficiency upon illumination with appropriate wavelengths of UV light at a relatively low intensity. The good solubility of the compounds (**16-19**) in common organic solvents commonly used to deposit uniform, thin films on planar device substrates by spin coating, for example, is also beneficial for optimising such inks for photo-curing 4D printing technology, such as highly precise DLP 4D printing. Finally, a DLP-printed structure (Figure S1) containing acrylate liquid crystal monomer compound **17** were also demonstrated in the Support Information as an example to highlight the printability of inks containing these reactive mesogens.

4. CONCLUSIONS

A series of novel photopolymerisable carbazole liquid crystals with symmetrical reactive acrylate or diene groups at the end of flexible alkyl chains attached in a terminal

position to a rigid aromatic core was designed, synthesized, characterized and studied as potential photopolymerisable monomers (reactive mesogens) in terms of 4D-printing applications. Their mesomorphic behaviour was studied using a combination of POM, DSC and XRD. These photopolymerisable monomers exhibit a slow crystallisation process of the supercooled nematic phase at room temperature, which is of significant technical advantage for practical applications. Advantageous slow crystallisation could be attributed to the effects of polymerisation under prolonged high temperatures for acrylates and the high entropy of long, branched, flexible alkyl chains in dienes. The polymerisation process induces a kinetic competition between LC ordering and network formation. This work establishes protocols for real-time phase monitoring during polymerisation, resolving longstanding ambiguities in LC phase identification under thermal polymerisation. Furthermore, the acrylate liquid crystal monomers (**16**) and (**17**) photopolymerise readily under appropriate conditions of UV illumination. They also polymerise spontaneously at relatively high temperatures, whereas the non-conjugated diene monomers (**18**) and (**19**) are much more thermally stable.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available.

Demonstration of a DLP-printed structure and its related discussion.

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G.H. conceived the project, led the experiments, and drafted the initial manuscript.

G.H., X.Z., B.Z. and S.M.K. supervised the whole project, analysed the data and edited the manuscript. W.Q., Y.T. and T.K. carried out detailed experimental work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support from the National Natural Science Foundation of China (No. 62204093), International Exchanges 2023 Cost Share from the Royal Society (IEC\NSFC\233501), Natural Science Basic Research Program of Shaanxi (No. 2025JC-YBMS-358), Guangdong Basic and Applied Basic Research Foundation (No. 2021A1515111166), The Natural Science Foundation of Jiangsu Higher Education Institutions of China (No. 22KJB510014), Huai'An Talent Funding for Outstanding Doctors in Universities (No. Z302J22518), Natural Science Foundation of Huai'An City (No. HAB202149), and Research Start-up Fund of Huaiyin Institute of Technology (No. Z301B19582).

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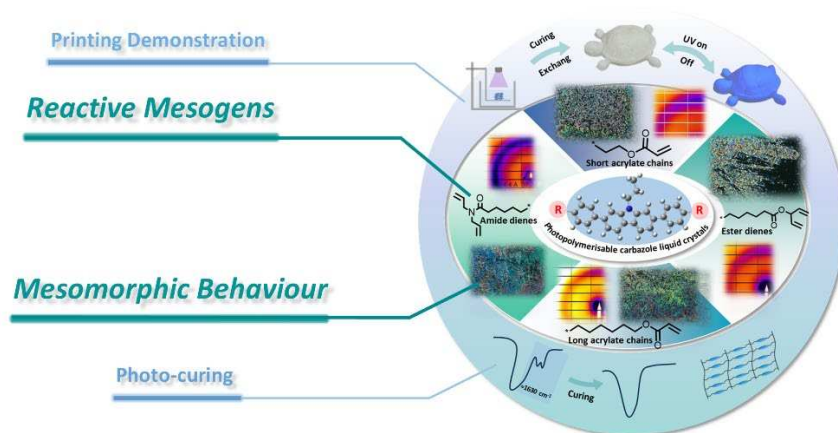
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Mesomorphic Behaviour of Novel Photopolymerisable Carbazole Liquid Crystals and Photo-curing for 4D Printing

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Graphic abstract



Novel carbazole-based photopolymerisable liquid crystals were designed and synthesised to study their mesomorphic behaviour and photo-curing for potential application in 4D printing. The results show a wide range of stable nematic phases near room temperature, a slow crystallisation process and high photopolymerisation efficiency. The work establishes protocols for the liquid crystal phase identification under thermal polymerisation.