Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Wang, Qing , Yang, Chang-an , Xie, Helou , Wang, Xingzhu and Zhang, Hailiang(2010) 'Effect of mesogenic density on liquid-crystalline behaviours of polymethacrylates bearing azobenzene mesogen', Liquid Crystals, 37: 4, 435 — 443

To link to this Article: DOI: 10.1080/02678291003642578

URL: http://dx.doi.org/10.1080/02678291003642578

Liquid Crystals,
Vol. 37, No. 4, April 2010, 435–443

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Effect of mesogenic density on liquid-crystalline behaviours of polymethacrylates bearing azobenzene mesogen

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(Received 28 October 2009; final version received 21 January 2010)

Three sets of novel side-chain liquid-crystalline polymers, poly[3-(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PHABM), poly[3, 5-di(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PDHABM) and poly[3, 4, 5-tri(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PTHABM), with different mesogenic densities were successfully designed and synthesised. The chemical structures of all the monomers were confirmed by ^{1}H nuclear magnetic resonance (NMR), and ^{13}C NMR spectroscopy and elemental analysis, and the characterisation of the polymers was performed by ^{1}H NMR spectroscopy and gel permeation chromatography. Their phase structures and transitions were investigated using differential scanning calorimetry, polarising optical microscopy and single-angle X-ray scattering in order to study the effect of mesogenic density on liquid-crystalline behaviour. Each of the PHABMs exhibited only a glass transition and a smectic phase during the heating and cooling process, while PDHABMs and PTHABMs showed a glass transition and broader temperature range liquid-crystalline behaviour, including both nematic and smectic phases. In addition, the clearing temperatures of the three types of polymers were found to be in the order: PTHABM $>$ PDHABM $>$ PHABM, and the liquid crystal temperature range had the same order.

Keywords: side-chain liquid-crystalline polymers; mesogenic density; phase behaviour; azobenzene mesogen

1. Introduction

The design and synthesis of novel side-chain liquid-crystalline polymers (SCLCPs) have been the focus of much research interest due to their considerable application potential as new materials for advanced information storage, holographic imaging and non-linear optics [1–8]. In addition, the isotropic properties arising from the mesogenic side-groups has meant that the phase transitions and structures at a fundamental level have also been a very significant topic of research [9–15]. The liquid-crystalline properties of SCLCPs, i.e. phase transition temperatures and the nature of the mesophases, depend on the chemical structure of the polymer including the nature of the polymer backbone [16–18], the flexible spacer [19–22] and the mesogenic unit [23–26], as well as the molar mass, polydispersity and tacticity [27–29]. Furthermore, the density of the mesogen along the polymer backbone is a very important factor.

Commonly, many SCLCPs such as poly(siloxane)s, poly(methacrylate)s and polyethylenes contain one mesogen per two atoms in the polymer backbone. The phase behaviour and liquid-crystalline properties of these SCLCPs has been widely reported in previous studies [30–41]. By comparison, SCLCPs containing a larger number of mesogens per two atoms in the polymer backbone have almost been neglected, and this is particularly true for SCLCPs containing three mesogens per two atoms in the polymer backbone. In the literature, several approaches have been described by which to tune mesogen density [42–48]. For example, the coupling of swallow-tailed 1-alkenes containing two mesogens with poly(siloxane)s by hydrosilylation provides an increased mesogenic density in the SCLCPs, and the experimental results show that the temperature width of the mesophase was retained down to low mesogenic contents.

In fact, a comparison of the polymers containing a single mesogenic side-group with those polymers having paired ones reveals a general trend in that both the temperature window of the mesophase and the degree of order in the mesophase are increased with increasing mesogenic density. It is interesting, therefore, to investigate these structure-property relationships when the ratio of the mesogenic units is increased in the polymer backbone. There have been some reports of liquid-crystalline materials having increased mesogenic density, but this work has been ignored in recent years. Therefore, we investigated the difference in thermal behaviour of polymethacrylate derivatives containing one, two or three pendant groups per repeating unit and the difference in phase behaviours of these new

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ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678291003642578
http://www.informaworld.com

SCLCPs compared with conventional monosubstituted materials. In other words, how important is the ratio of mesogenic units to the number of atoms in the polymer backbone in determining the thermotropic behaviour of SCLCPs?

In this work, we report the synthesis and characterisation of three different polymethacrylates bearing one, two or three pendant mesogenic groups per repeating unit, respectively. We report the difference in their thermal behaviour and the effect of mesogenic density on liquid-crystalline behaviour when compared with polymethacrylates bearing a single azobenzene mesogen. A sketch of these polymers with different mesogenic densities is shown in Figure 1. The polymers were obtained by radical polymerisation and the synthetic route is shown in Scheme 1.

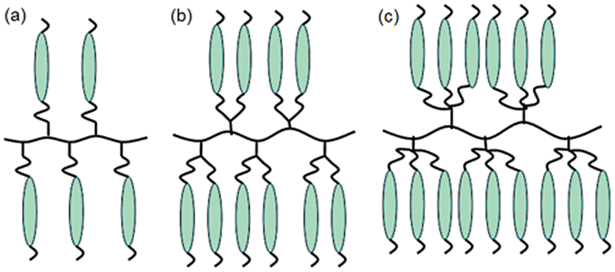
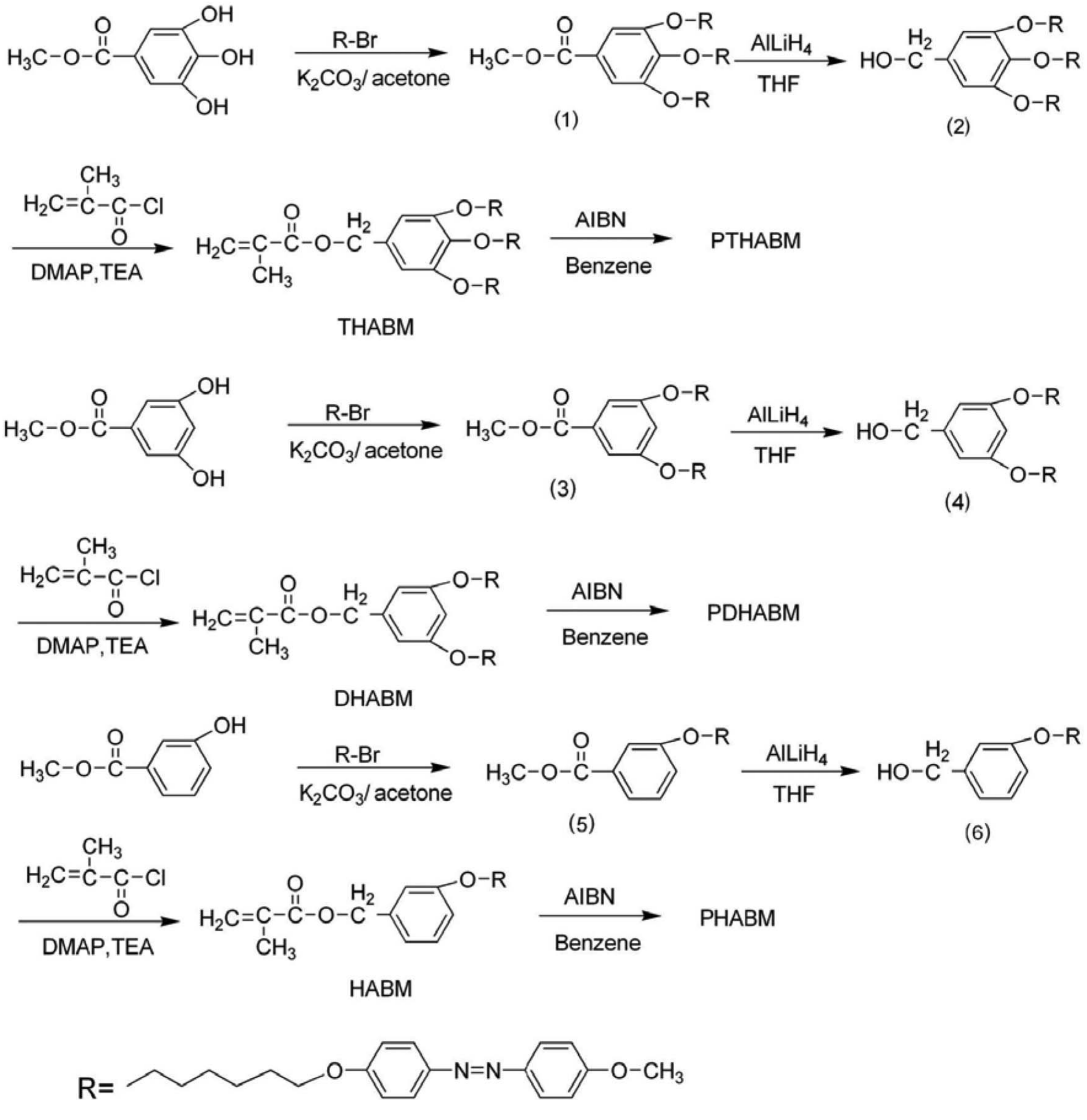


Figure 1. Sketch of the methacrylate polymers with different mesogenic densities. Polymer side-chain bearing: (a) one pendant mesogenic group per repeating unit; (b) two pendant mesogenic groups per repeating unit; (c) three pendant mesogenic groups per repeating unit.



Scheme 1. Synthetic route of the monomers and their polymers.

2. Experimental Details

2.1 *Materials*

Anhydrous tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under argon and used immediately. Benzene, used in the polymerisation reactions, was washed successively with concentrated sulphuric acid and deionised water, dried with anhydrous calcium chloride, and distilled from calcium hydride. Triethylamine (Et_3N) (Shanghai Chemical Reagents Co., AR grade, Shanghai, PR China) was refluxed with potassium hydroxide and distilled. Dichloromethane (CH_2Cl_2) (Shanghai Chemical Reagents, AR grade) was shaken with portions of concentrated sulphuric acid until the acid layer remained colourless and then washed with water, aqueous 5% sodium bicarbonate and with water again, and finally distilled from calcium hydride. 2, 2-azobisisobutyronitrile (AIBN) 98% (Acros Chemical Co.) was freshly recrystallised from methanol. 4-Dimethylaminopyridine (DMAP) was purchased from Aldrich Chemical Co. Anhydrous sodium sulphate was used to dry all organic extracts.

2.2 *Instruments and measurements*

^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on a Bruker ARX400 spectrometer at room temperature using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane as the internal standard. Gel permeation chromatographic (GPC) measurements were carried out at 35°C on a Waters 2410 instrument equipped with three Waters μ-Styragel columns (10^3, 10^4 and 10^5 Å) in series, using THF as the eluent at a flow rate of 1.0 ml min^{-1}. All the GPC data were calibrated with polystyrene standards. Differential scanning calorimetry (DSC) (Perkin-Elmer Pyris I with a mechanical refrigerator) was utilised to study the phase transitions of the monomers and polymers. A typical DSC sample size was 5.0 mg. The samples were encapsulated in hermetically sealed aluminium pans, and the pan weights were kept constant. The temperature and heat flow scale at different cooling and heating rates were calibrated using standard materials such as indium and benzoic acid. The thermogravimetric analysis (TGA) was performed on a TA-SDT 2960 instrument at a heating rate of 10°C min^{-1} in nitrogen atmosphere. Elemental analysis was carried out with an Elementar Vario EL instrument. To observe the liquid-crystalline textures of the samples, polarising optical microscopy (POM) experiments were carried out on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage. The POM samples were obtained using small amounts of the polymers, which were melt-pressed between two cover glasses. Small-angle X-ray scattering (SAXS) experiments were performed with a high-flux small-angle X-ray scattering instrument (SAXSess, Anton Paar) equipped with Kratky blockcollimation system and a Philips PW3830 sealed-tube X-ray generator (Cu Kα). The one-dimensional (1D) diffraction patterns were recorded on an imaging plate with a pixel size of 42.3 × 42.3 μm^2 which extends to the high-angle range (the q range covered by the imaging plate is from 0.06 to 29 nm^{-1}, i.e., the 2q from 0.08 to 42° with the X-ray wavelength λ of 0.1542 nm).

2.3 *Monomer synthesis*

2.3.1 *4-(6-Bromohexyloxy)-4′-methoxy azobenzene (R-Br)*

R-Br was prepared according to the literature [49]. ^{1}H NMR (400 HMz, $CDCl_3$, ∂, ppm): 1.55–1.51 (m, 4H, —CH_2—), 1.93–1.82 (m, 4H, —CH_2—), 3.45–3.42 (m, 2H, —CH_2Br), 3.89 (s, 3H, —OCH_3), 4.06–4.02 (m, 2H, —CH_2—), 7.01–6.97 (m, 4H, Ar-H), 7.89–7.86 (m, 4H, Ar-H).

2.3.2 *3, 4, 5- Tri (4′-methoxy-4-oxy hexyloxy azobenzene) benzyl formate (1)*

A mixture of methyl 3, 4, 5-trihydroxybenzoate (75 mmol), R-Br (300 mmol), potassium carbonate (350 mmol) and dry acetone (360 ml) was refluxed with stirring for 24 h under nitrogen. After the mixture cooled to room temperature it was filtered and washed with acetone to remove R-Br. The precipitate was dissolved in CH_2C1_2, then, the potassium salt was filtered off. The solvent was distilled off under reduced pressure. The yellow solid was dried in a vacuum oven at 60°C for 12 h. Yield: 56%. ^{1}H NMR (in $CDCl_3$, δ, ppm): 1.57–1.85 (m, 24H, –CH_2), 3.88 (s, 12H, –OCH_3), 3.96–4.02 (m, 12H, –OCH_2), 6.82 (s, 2H, Ar-H ortho to COO), 6.89–6.99 (m, 12H, Ar-H ortho to –OCH_2), 7.86–7.89 (m, 12H, Ar-H ortho to –N=N—).

2.3.3 *3, 4, 5-Tri (4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methanol (2)*

3, 4, 5-Tri (4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methanol 2 was prepared by the reduction of 1 with lithium aluminium hydride ($LiAlH_4$). 1 (20 mmol) was added slowly to a suspension of $LiAlH_4$ (20 mmol) in dry THF (160 ml) at 0°C under a flow of nitrogen. After the addition was complete, the mixture was reacted for a further 2 h at room temperature. The reaction was found to be complete by thin-layer chromatography and ^{1}H

NMR analyses. Water was then added slowly with vigorous stirring to terminate the reaction and diluted hydrochloric acid was used to adjust the pH of the mixture to 7. The product was extracted with CH_2Cl_2. The extracts were dried over magnesium sulphate and condensed to give a yellow solid. Afterwards, the crude product dissolved in CH_2Cl_2 was purified by column chromatography. The solvent was removed by vacuum distillation and 2 was obtained. Yield: 78%. ^{1}H NMR (400 HMz, $CDCl_3$, δ ppm): 1.57–1.85 (m, 24H, –CH_2), 3.88 (s, 9H, –OCH_3), 3.99–4.05 (m, 12H, –OCH_2), 4.61 (s, 2H, –CH_2 ortho to —OH), 6.57 (s, 2H, Ar-H ortho ro CH_2OH), 6.89–6.99 (m, 12H, Ar-H ortho to –OCH_2), 7.84–7.88 (m, 12H, Ar-H ortho to –N=N—).

2.3.4 3, 4, 5-Tri (4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate (THABM)

Methacryloyl chloride (20 mmol) was added dropwise at 0–5°C to a mixture of 2 (10 mmol), Et_3N (15 mmol) and DMAP (15 mmol) in THF (50 ml). Then, the mixture was stirred at 25°C for 12 h. After extraction with CH_2Cl_2 and water three times, the combined organic layer was dried over magnesium sulphate. The mixture was filtered, then the filtered solvent was removed by vacuum distillation and a yellow solid was obtained. The crude product was purified by column chromatography on silica gel with CH_2Cl_2 as the eluent. The solvent were removed by vacuum distillation, and the monomer HABM was obtained. Yield: 92%. ^{1}H NMR (400 HMz, $CDCl_3$, δ, ppm): 1.57–1.85 (m, 24H, –CH_2), 1.97 (s, 3H, –CH_3 ortho to C=C), 3.88 (s, 9H, –OCH_3), 3.97–4.02 (m, 12H, –OCH_2), 5.12 (s, 2H, –CH_2 ortho to —COO), 5.55 (s, 1H, *cis* CH=), 6.12 (s, 1H, *trans* CH=), 6.58 (s, 2H, Ar-H ortho to CH_2OCO), 6.95–7.00 (m, 12H, Ar-H ortho to –OCH_2), 7.83–7.88 (m, 12H, Ar-H ortho to –N=N—). ^{13}C NMR (100 HMz, $CDCl_3$, δ ppm): 18.55 (—CH_3), 25.78, 26.01, 26.10, 26.15, 29.38, 29.46, 29.52, 30.44 (—CH_2—), 55.66 (-OCH_3), 66.81, 68.10, 68.40, 69.14 (—OCH_2—), 73.37 107.05, 114.32, 114.82, 124.49, 124.51, 131.44, 138.29, 147.10, 147.28, 153.30, 161.30, 161.70 (Ar), 125.90 (CH_2=) 136.48 (=C—), 167.34 (C=O). Anal. calcd for $C_{68}H_{78}O_{11}N_6$ (M_w = 1154.6): C, 70.72; N, 7.21; H, 6.76; found: C, 70.69; N, 7.27; H, 6.80.

2.3.5 3, 5-Di (4′-methoxy-4-oxy hexyloxy azobenzene)benzyl formate (3)

3 was synthesised from methyl 3, 5-dihydroxybenzoate in the same manner as 1. Yield: 71%. ^{1}H NMR (400 HMz, $CDCl_3$, δ ppm): 1.57–1.85 (m 16H, –CH_2), 3.88 (s, 9H, –OCH_3), 3.97–4.02 (m, 8H, –OCH_2), 6.89–6.99 (m, 11H, Ar-H), 7.86–7.89 (m, 8H, Ar-H ortho to –N=N—).

2.3.6 3, 5-Di (4′-methoxy-4-oxy hexyloxy azobenzene)benzyl methanol (4)

4 was synthesised from 3 in the same manner as 2. Yield: 71%. ^{1}H NMR (400 HMz, $CDCl_3$, δ ppm): 1.57–1.85 (m, 16H, –CH_2), 3.88 (s, 6H, –OCH_3), 3.98–4.02 (m, 8H, –OCH_2), 4.66 (s, 2H, –CH_2 ortho to —OH), 6.89–6.99 (m, 11H, Ar-H), 7.86–7.88 (m, 8H, Ar-H ortho to –N=N—).

2.3.7 3, 5-Di (4′-methoxy-4-oxy hexyloxy azobenzene)benzyl methacrylate (DHABM)

The monomer DHABM was synthesised from 4 in the same manner as the monomer THABM. Yield: 89.0%. ^{1}H NMR (400 HMz, $CDCl_3$, δ ppm): 1.57–1.85 (m, 16H, –CH_2), 2.06 (s, 3H, –CH_3 ortho to C=C), 3.88 (s, 6H, –OCH_3), 3.97–4.02 (m, 8H, –OCH_2), 5.12 (s, 2H, –CH_2 ortho to —COO), 5.55 (s, 1H, cis CH=), 6.12 (s, 1H, trans CH=), 6.89–6.99 (m, 11H, Ar-H), 7.86–7.88 (m, 8H, Ar-H ortho to –N=N—). ^{13}C NMR (100 HMz, $CDCl_3$, δ ppm): 18.52 (-CH_3), 25.98, 26.02, 29.29, 29.31 (—CH_2—), 55.66 (—OCH_3), 66.47 (—OCH_2—), 68.00, 68.27 (—OCH_2—), 101.07, 106.43, 114.30, 114.81, 124.45, 124.49, 138.42, 147.08, 147.23, 160.53, 161.29, 161.69 (Ar) 125.99 (CH_2=), 136.36 (=C—), 167.24 (C=O). Anal. calcd for $C_{49}H_{56}O_8N_4$ (M_w = 828.4): C, 70.96; N, 6.74; H, 6.77; found: C, 70.99; N, 6.76; H, 6.81.

2.3.8 3-(4′-Methoxy-4-oxy hexyloxy azobenzene) benzyl formate (5)

5 was synthesised from methyl 3-hydroxybenzoate in the same manner as 1. Yield: 78%. ^{1}H NMR (400 HMz, $CDCl_3$, δ ppm): 1.57–1.85 (m, 8H, –CH_2), 3.88 (s, 6H, –OCH_3), 4.02–4.07 (m, 4H, –OCH_2), 6.89–7.92 (m, 8H, Ar-H), 7.86–7.89 (m, 4H, Ar-H ortho to –N=N—).

2.3.9 3-(4′-Methoxy-4-oxy hexyloxy azobenzene) benzyl methanol (6)

6 was synthesised from 5 in the same manner as 2. Yield: 71%. ^{1}H NMR (400 HMz, $CDCl_3$, δ ppm): 1.57–1.85 (m, 8H, –CH_2), 3.88 (s, 3H, –OCH_3), 3.98–4.06 (m, 4H, –OCH_2), 4.66 (s, 2H, –CH_2 ortho to —OH), 6.89–6.99 (m, 8H, Ar-H), 7.86–7.88 (m, 4H, Ar-H ortho to –N=N—).

2.3.10 3-(4′-Methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate (HABM)

The monomer HABM was synthesised from 6 in the same manner as the monomer THABM. Yield: 91%. ^{1}H NMR (400 HMz, $CDCl_3$, δ ppm): 1.57–1.85 (m, 8H, —CH_2), 2.06 (s, 3H, —CH_3 ortho to C=C), 3.88 (s, 3H, —OCH_3), 3.97–4.07 (m, 4H, –OCH_2), 5.12 (s, 2H, —CH_2 ortho to —COO), 5.55 (s, 1H, cis CH=), 6.12 (s, 1H, trans CH=), 6.89–6.99 (m, 8H, Ar-H), 7.88–7.91 (m, 4H, Ar-H ortho to —N=N—). ^{13}C NMR (100 HMz, $CDCl_3$, δ ppm): 18.49 (—CH_3), 26.00, 26.03, 29.30, 29.34 (—CH_2—), 55.66 (—OCH_3), 66.40 (—OCH_2—), 67.92, 68.27 (—OCH_2—), 114.25, 114.27, 114.30, 114.80, 120.19, 124.46, 124.48, 129.71, 137.77, 147.10, 147.25, 159.39 161.28, 161.68 (Ar), 125.95 (CH_2=), 136.37 (=C—), 167.32 (C=O). Anal. calcd for $C_{30}H_{34}O_5N_2$ (M_w = 502.2): C, 71.65; N, 5.63; H, 6.74; found: C, 71.69; N, 5.57; H, 6.82.

2.4 Synthesis of polymers

All the polymers were obtained by conventional solution radical polymerisation. Typical polymerisation was carried out as follows. The monomer THABM (1.0 mmol), AIBN (0.01 mmol) and benzene (1.50 ml) were transferred into a polymerisation tube. After three freeze-pump-thaw cycles, the tube was sealed off under a vacuum. Polymerisation was carried out at 60°C for 24 h. The sample was diluted in THF and precipitated in a large volume of hot acetone. The sample was purified by reprecipitating three times from THF to hot acetone and dried at room temperature overnight in a vacuum oven.

3. Results and discussion

3.1 Synthesis and characterisation of the monomers and polymers

As shown in Scheme 1, each of the monomers (HABM, DHABM and THABM) was synthesised in three steps and the preparation and characterisation of the materials, 4-(6-bromohexyloxy)-4′-methoxy azobenzene, has been described elsewhere [49]. First, 3, 4, 5-tri (4′-methoxy-4-oxy hexyloxy azobenzene) benzyl formate was prepared by the reaction of methyl 3, 4, 5-trihydroxybenzoate and 4-(6-bromohexyloxy)-4′-methoxy azobenzene in a hot potassium salt solution of acetone. Then 3, 4, 5-tri (4′-methoxy-4-oxy hexyloxy azobenzene) benzyl formate was reduced using $LiAlH_4$ in THF to give 3, 4, 5-tri (4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methanol. The last step was completed by the esterification of methacryloyl chloride and 3, 4, 5-tri (4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methanol in THF at 0–5°C. The structures of the monomers and the polymers were confirmed by ^{1}H NMR spectroscopy and representative structures are provided in the supporting material. ^{1}H NMR spectroscopy, shown in Figure S-1 in the supplementary material which is available via the multimedia link on the online article webpage, was used to confirm the monomer THABM and corresponding polymer PTHABM. The characteristic resonance peaks of the vinyl substituent of the monomer are seen at 6.12 and 5.55 ppm. After polymerisation, these signals disappeared completely, and the peaks in the polymer's spectra were quite broad because of the lower mobility of the protons, consistent with the expected polymer structure. The monomers and polymers were completely soluble in the common organic solvents such as chloroform, THF, chlorobenzene, 1, 2-dichlorobenzene, and so on. GPC analysis was performed to determine the apparent M_n and molecular weight distributions of the polymers. The molecular characterisations of the polymers are summarised in Table 1.

Table 1. Gel permeation chromatograpy, differential scanning calorimetry and thermogravimetric analysis results and thermotropic properties of polymers.

Sample	M_n ($\times10^{-4}$)^a	M_w/M_n^{a}	Transition temperature (°C) and corresponding enthalpy changes (J mol^{-1})^b under cooling	T_d (°C)^c
PHABM-1	2.39	2.05	g78 S135(16.15) I	387
PHABM-2	5.80	2.79	g78 S136(15.95) I	387
PHABM-3	14.11	2.86	g79 S136(15.81) I	388
PDHABM-1	1.31	2.07	g55 S93(0.14) N145(3.56) I	386
PDHABM-2	6.64	2.84	g57 S95(0.12) N152(3.45) I	384
PDHABM-3	22.15	2.61	g58 S95(0.12) N153(3.36) I	387
PTHABM-1	2.93	1.89	g65 S110(0.69) N173(1.00) I	377
PTHABM-2	5.31	2.43	g66 S117(0.43) N176(0.73) I	379
PTHABM-3	8.35	2.64	g67 S127(0.28) N180(0.56) I	382

Notes: [a]Based on gel permeation chromatograpy measurements. [b]Obtained from the second heating differential scanning calorimetry experiments; heating rates were 10°C min^{-1}. [c]The decomposition temperature at 5.00% weight loss of the sample was obtained from thermogravimetric analysis under nitrogen atmosphere.

3.2 Phase transitions and phase structures

The thermal and liquid-crystalline behaviours of the polymers were examined using DSC and POM. All the polymers exhibited thermotropic liquid-crystalline properties. Their transition temperatures and associated enthalpy changes are summarised in Table 1. Before investigating the mesomorphic properties of the polymers, their thermal stabilities were first examined using TGA under nitrogen atmosphere. The results shown in Table 1 indicated that all the polymers were quite stable with the temperatures at 5% weight loss above 370°C in nitrogen. The liquid-crystalline phase transitions of the polymers were studied by DSC. To eliminate the effect of thermal history, we heated all the samples from 30 to 230°C at a rate of 10°C min^{-1} and then kept them at 230°C for 5 min. The DSC thermal traces were recorded at 10°C min^{-1} during the second heating and these are shown in Figure 2. From Figure 2, it can be observed that each of the polymers of poly[3-(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PHABMs) showed a glass transition and a liquid-crystalline phase transition, while each of the polymers of poly[3, 5-di(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PDHABMs) and poly[3, 4, 5-tri(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PTHABMs) showed a glass transition and two liquid-crystalline phase transitions during the heating and cooling process. From Table 1 and Figure 2, we found that the molecular weight dependence of the transition temperature was very slight in accordance with the behaviour described by Imrie *et al.* [50].

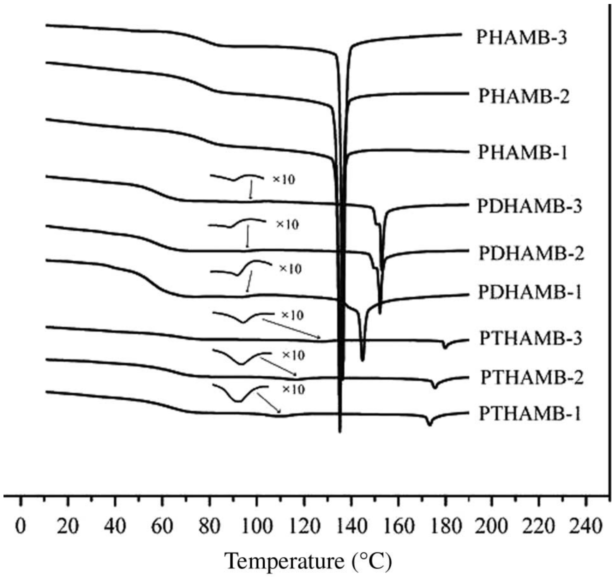


Figure 2. The differential scanning calorimetry curves of polymers during the second heating at a rate of 10°C min^{-1}.

The optical textures shown by the polymers were observed with POM for samples cast from THF solution and slowly dried at room temperature. Here, we use the samples (PTHABM-1, PDHABM-1 and PHABM-1) as representative examples. Figure 3(a) and (b) show the POM textures of PTHABM-1 and were obtained at 90°C and 150°C, respectively. Figure 3(a) is an example of a typical focal-conic fan texture, which is characteristic of a smectic phase. Figure 3(b) shows a schlieren texture and is characteristic of a nematic phase. For PDHABM-1, a characteristic focal-conic fan texture did not appear until the glass transition temperature (Figure 3(c)), and on subsequent heating the fan texture turned into a typical schlieren texture above 93°C (Figure 3(d)); all textures disappeared above 145°C, indicating the isotropic phase was formed. When the temperature reached glass transition temperature, for PHABM-1, an obvious focal-conic fan texture appeared and on subsequent heating the fan texture remained (Figure 3(e)), but all textures disappeared above 135°C, indicating the presence of only a smectic phase in agreement with the DSC result.

To elucidate further the phase structures, SAXS experiments were performed at different temperatures. Figure 4 shows the SAXS intensity profiles of PTHABM-1 during the cooling scan. On cooling the PTHABM-1 sample from 200 to 140°C, only an intense broad peak in the higher q region (11–18 nm^{-1}) was seen, which indicated that only a short-range order exists in the molecular lateral packing. Based on the SAXS profiles shown in Figure 4, we confirmed that the phase was a nematic phase. When PTHABM-1 was cooled to 90°C, three higher order reflections were seen at 2.06, 4.11 and 6.26 nm^{-1} (d-spacing was 3.05, 1.53 and 1.01 nm). The scattering vector ratio of the diffractions in the low q region followed 1:2:3, indicating a typical smectic phase structure. On the basis of the results of DSC, POM and SAXS, it is proposed that for each of the PTHABMs, the two phase transitions seen are from the isotropic to nematic phase transition at higher temperature and from the nematic to smectic phase at lower temperature, respectively. From Figure 2, Figure 3(c) and (d) and SAXS (annotation: the SAXS patterns of PDHABM-1 were similar to those of PTHABM-1), it is proposed that the phase transitions and phase structures of PDHABMs are the same as those of PTHABMs. From Figure 2, Figure 3(e) and SAXS (the SAXS patterns of PHABM-1 only displayed the same SAXS pattern as PTHABM-1 at 90°C), it is proposed that the phase transition seen for the PHABMs is from the isotropic to smectic phase.

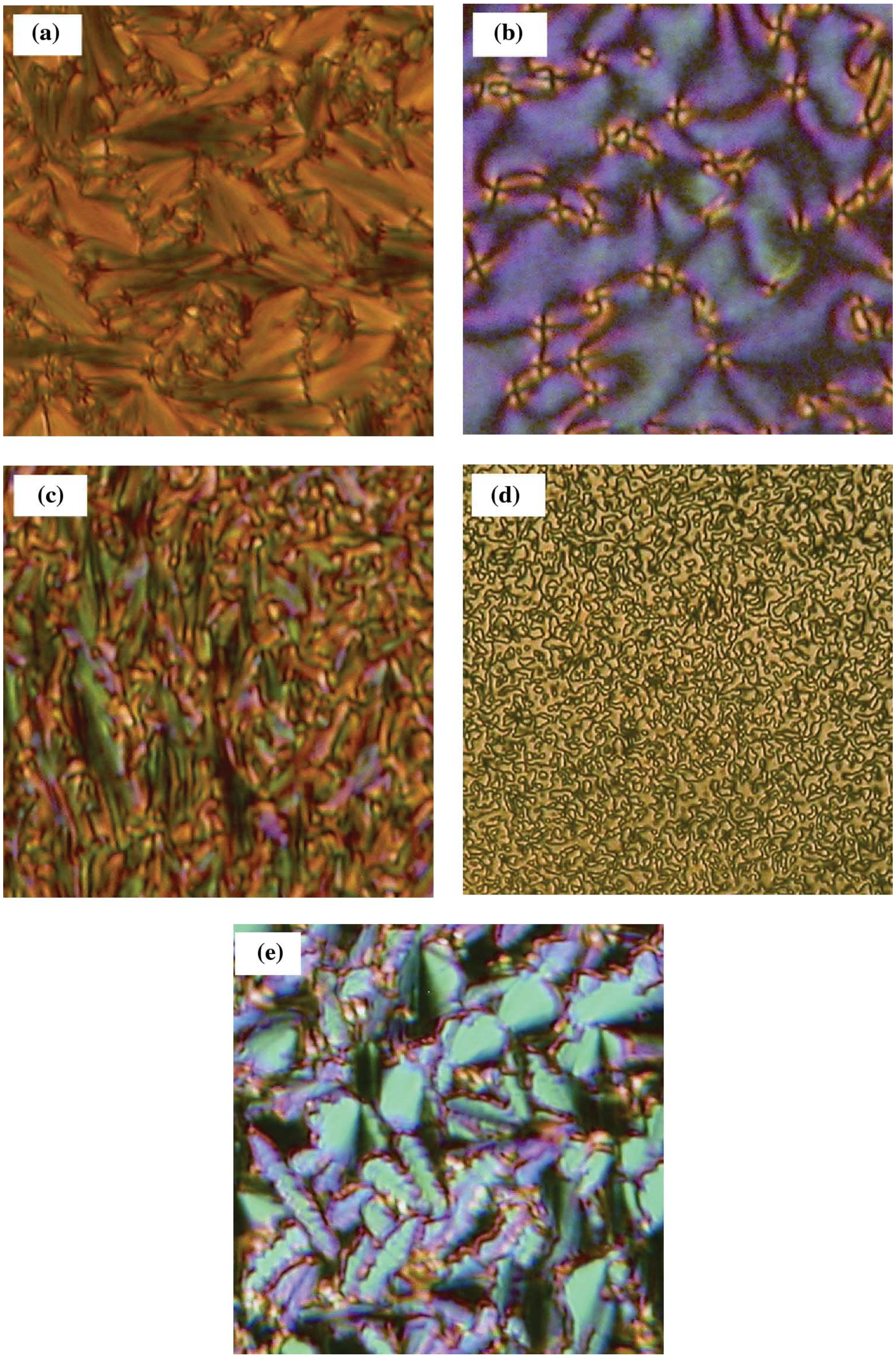


Figure 3. Polarising optical microscopy images: (a) poly[3, 4, 5-tri(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PTHABM-1) at 90°C; (b) PTHABM-1 at 150°C; (c) poly[3, 5-di(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PDHABM-1) at 80°C keeping for 16 h; (d) PDHABM-1 at 130°C; (e) poly[3-(4′-methoxy-4-oxy hexyloxy azobenzene) benzyl methacrylate] (PHAMB-1) at 120°C.

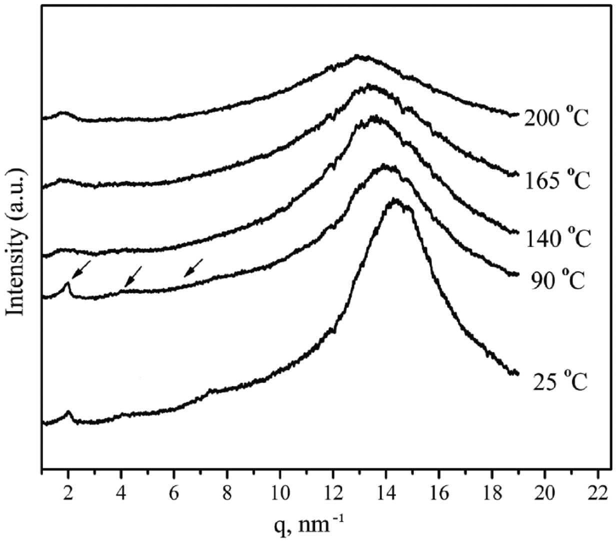


Figure 4. Poly[3, 4, 5-tri(4′-methoxy-4-oxy hexyloxyazo benzene) benzyl methacrylate] (PTHABM-1) single-angle X-ray scattering intensity profiles during cooling at different temperatures.

3.3 Effect of mesogenic density

From the combined experimental results, we found that each of the PHABMs only exhibited a smectic phase on heating and cooling, while each of the PDHABMs and PTHABMs exhibited a smectic phase at lower temperature and a nematic phase at higher temperature. The general features of our findings are summarised in Figure 5. From Figure 5 and Table 1, we observe that the isotropic temperatures T_i of the PHABMs, PDHABMs and PTHABMs are approximatively 135, 150 and 175°C, respectively, and that the temperature range of the liquid-crystalline phases ΔT (from T_i to T_g) of the PHABMs, PDHABMs and PTHABMs are approximatively 57, 95 and 110°C, respectively. Thus the T_i and ΔT of the polymers are found to be in the following order: PTHABMs > PDHABMs > PHABMs, i.e., the polymers possessed higher values of T_i and ΔT on increasing mesogenic density in the side-chain. This may be explained in terms of the concentration of mesogenic groups along the main chain, such that higher density of mesogenic groups favours lateral interactions between successive pendant groups. It is known that the distance between successive pendent mesogenic groups along the polymer backbone plays an important role in mesophase formation in alternating mesogenic polymers.

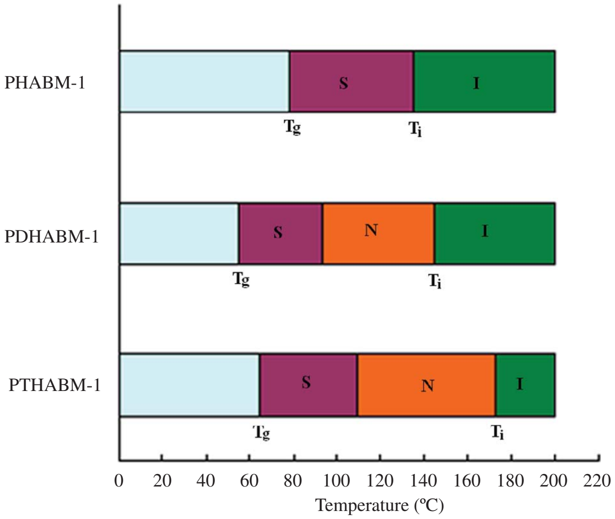


Figure 5. Mesophase behaviour of methacrylate polymers with different mesogenic density.

4. Conclusions

We successfully synthesised three novel monomers HABM, DHABM and THABM with different mesogenic densities, and synthesised the corresponding polymers with different molecular weights via free-radical polymerisation. The chemical structures of the monomers were confirmed by ^{1}H NMR and ^{13}C NMR spectroscopy and elemental analysis. The characterisation of the polymers was performed using ^{1}H NMR spectroscopy and GPC. DSC, POM and SAXS measurements were employed to study the phase structures and transitional behaviour of the polymers. All the polymers showed liquid-crystalline behaviour. Each of the PHABMs exhibited a smectic phase on heating and cooling, while each of the PDHABMs and PTHABMs exhibited both a smectic phase at lower temperature and a nematic phase at higher temperature. In addition, the T_i and ΔT of the polymers were found to be in the order: PTHABMs > PDHABMs > PHABMs, i.e., the polymers possess higher T_i and ΔT on increasing the mesogenic density in the side-chain. This means that increased mesogenic density stabilises the mesophases. The broadening of the temperature range of the mesophase and the variation of liquid-crystalline phases offer some new possibilities in the technological applications of these new materials.

Acknowledgements

This research was financially supported by the National Nature Science Foundation of China (20874082), the Postgraduate Innovation Fund of Hunan Province (S2008yjscx10), the Scientific Research Fund of Hunan Provincial Education Department (06A068), the Key Project of the Chinese Ministry of Education for Science and Technology (No. 207075) and the New Century Excellent Talents in University (NCET-05-0707).

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