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# A New Series of Two-Ring-Based Side Chain Liquid Crystalline Polymers: Synthesis and Mesophase Characterization

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A new series of side chain liquid crystalline polymers containing a core, a butamethylenoxy spacer, ester groups, and terminal alkoxy groups were synthesised and their structures were confirmed. The core was constructed with two phenyl rings and an ester linking unit. All the polymers were characterised by hot-stage polarising optical microscopy, differential scanning calorimetry, variable temperature X-ray diffraction, thermogravimetric analysis, and gel permeation chromatography. The polymers were found to be liquid crystalline. The nematic and smectic A (S<sub>A</sub>) phases were observed for the homologues with short-terminal chains (C2 and C6), whereas the homologues with longer chains (C8 to C12) exhibited a smectic C phase. The thermal stability of the polymers was found to be in the range of 293 to 326°C and the molecular weights of the polymers were found to vary from  $6 \times 10^3$  to  $1.3 \times 10^4$ .

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## Introduction

Thermotropic side chain liquid crystalline polymers (SCLCP) have become important in view of their interesting material properties.<sup>[1]</sup> The ability to form films, fibres, and sheets, characteristic of synthetic polymers, and their tendency to respond to external stimuli, typical of liquid crystals, are conveniently shared in SCLCP.<sup>[2]</sup> In contrast to main chain liquid crystalline polymers, SCLCP are easy to solubilise in common solvents at room temperature and their mesophase temperatures are relatively low (~ambient).<sup>[3]</sup> Owing to this, SCLCP have attracted a lot of attention from researchers around the world. The pioneering work of Finkelmann, Plate, and others resulted in the formation of SCLCP.<sup>[4–7]</sup> In terms of molecular design, typical SCLCP usually consist of a flexible acrylic/methacrylic backbone with a spacer, a core, and terminal alkyl/alkoxy chains.<sup>[8,9]</sup> Attempts to synthesise SCLCP without spacers have largely been unsuccessful.<sup>[10,11]</sup>

The design and developments related to SCLCP have been thoroughly reviewed<sup>[12,13]</sup> and it is clear that most of the systems investigated make use of either acrylic/methacrylic or siloxane as back bones. Typically, a spacer and back bone (acrylic/methacrylic) are linked through ether (C–O–C) linkages, while the core (mostly two-ring based) is constructed with either ester

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or azomethine linkages.<sup>[14–16]</sup> Earlier studies on two-ring polyacrylates with ether linking units between the spacer and core units, exhibited nematic and smectic A (S<sub>A</sub>) phases that have high isotropic temperatures.<sup>[16–19]</sup> In this context, in the present work, a series of new polymers were synthesised in order to study the structure–property relationship, improve the phase stability, and to reduce the isotropic temperature. Introducing ester linkages between the spacer and the two-ring-based core resulted in nematic, S<sub>A</sub>, and smectic C (S<sub>C</sub>) phases with a wide temperature range, and reduced the isotropic temperature of the polymers, significantly.

# **Results and Discussion**

## Synthesis of Liquid Crystalline Polymers

A series of acrylic acid-based monomers containing a two-ring core, a butamethylenoxy spacer, ester linking units, and various terminal alkoxy groups was synthesised as shown in Scheme 1. The solution polymerisation of these monomers resulted in good yields of the corresponding SCLCP and they were characterised by using standard analytical techniques in order to confirm the chemical structure. The FT-IR spectrum of a representative



A) DMF, SOCl<sub>2</sub>, reflux, 1 h; triethylamine, methyl ethyl ketone, 0°C, 3 h. B) Pd/C, H<sub>2</sub>, THF, room temp., 24 h.
 C) *N*,*N'*-Dicyclohexylcarbodiimide, 4-dimethylaminopyridine, dichloromethane/THF 0°C, 12 h.
 D) Benzoyl peroxide, 1,4-dioxane, 70°C 12 h.

Scheme 1. Synthetic strategy of two-ring monomers and polymers.



**Fig. 1.** FT-IR spectrum of poly-{4-[(acryloyloxybutoxy)carbonyl]phenyl 4-ethoxybenzoate} (4a).

polymer is given in Fig. 1. The C–H stretching absorption of the back bone, spacer, and terminal chain units of the polymer is noticed as a broad peak at 2957 cm<sup>-1</sup>. A very intense absorption centred at  $1737 \text{ cm}^{-1}$  is attributed to the carbonyl ester groups present in the polymer. The intensity of this absorption clearly supports the presence of a large number of carbonyls in the polymer. In addition, the appearance of one absorption signal for three carbonyl esters suggests that their chemical environment is not significantly different. Ring skeletal vibrations (C=C) are

noticed at 1606 and 1510 cm<sup>-1</sup>. The C–H stretching of the methyl and methylene groups are observed at 1451 and 1394 cm<sup>-1</sup>. The C–O–C stretching vibrations of the ester and ether groups (asymmetric and symmetric) are observed at 1268, 1207, and 1164 cm<sup>-1</sup> respectively. These features and the absence of an absorption at 1634 cm<sup>-1</sup>, which is typical for the C=C stretching of an acrylic unit, clearly indicated the formation of polymers.

In Fig. 2, the <sup>1</sup>H NMR spectrum of the polymer shows broad signals due to the highly viscous nature of the sample and geminal and vicinal couplings of protons from neighbouring monomeric units. The peaks that appear at 4.09 and 4.33 ppm are from oxymethylene protons. A peak at 2.31 ppm is assigned to the backbone methine proton, while those that appear at 1.80 and 1.44 ppm are contributed by the methylene protons of the backbone as well as the spacer and terminal methyl protons, respectively. The disappearance of peaks at 5.82, 6.11, and 6.41 ppm, which are characteristic of acrylic  $-CH_2$  and -CH protons present in the monomer, unambiguously supports the formation of polymers.

The <sup>13</sup>C NMR spectra of the monomer and respective polymer are shown in Fig. 3. The spectra show two kinds of peaks, i.e. intense and sharp peaks and low intensity and broad peaks. These contrasting features indicate not only the difference in the chemical environment, but also their location in the polymer. A group of low intensity and broad signals centred at 174.55 and 172.82 ppm are assigned to the carbonyl ester of the acrylic unit. In the monomer spectrum, the signal pertaining to the carbonyl ester of the acrylic unit is noticed as a sharp and moderately intense line at 166.33 ppm. The increase in the chemical shift values in the polymer and broadening of the line for the carbonyl ester clearly suggest that these carbons are sensitive to configurational heterogeneity. The spectrum also shows medium intensity peaks in the region of 160–165 ppm, which arises from the quaternary carbons of the phenyl ring present in the core. Four



Fig. 3. <sup>13</sup>C NMR spectra of monomer **3a** and polymer **4a**.

sharp lines in the region between 113 and 133 ppm are contributed by the methine carbons of two phenyl rings. The spectrum shows three peaks at 64.06, 64.27, and 63.91 ppm, arising from the oxymethylene carbons. Among them, the one seen at 64.27 ppm is of low intensity and broad, while the other two are sharp, which suggests that the centre line arises from the  $O-CH_2$  carbon that is in the proximity to the carbonyl ester of the acrylic backbone. In the 30–45 ppm region, two low intensity peaks are noticed at

42.62 and 31.61 ppm and are assigned to the back bone of methine as well as the methylene carbons. These peaks are contributed by many lines arising from the stereochemically different monomeric units in the polymeric chain. Two sharp peaks at 25.41 and 14.76 ppm are assigned to the centre methylenes of the spacer and the methyl carbons of the terminal chain, respectively. The FT-IR, <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra unambiguously confirmed the formation of polymer.

## Polarising Optical Microscopy (POM)

The polymers synthesised were subjected to POM experiments in order to find their mesophase characteristics and the results are listed in Table 1. The results revealed that all the polymers were enantiotropic. On cooling the sample of 4a from an isotropic melt, its POM image exhibited a threaded texture, which is typical of a nematic phase, and focal conic fans of a SA phase (Fig. 4). On continuous cooling to room temperature, the fan texture was retained. The immobility of the sample, when pressing the coverslips, indicates the formation of a frozen liquid crystal glass, which is a feature commonly observed in SCLCP.<sup>[20]</sup> In the case of 4b, the next higher homologue of the series, a similar observation with varying temperatures was obtained. The POM investigation of 4c, 4d, and 4e revealed the formation of a  $S_{C}$ phase (Fig. 4). However, a broken fan texture without homeotropy was observed for 4c, whereas the texture consists of schlieren and broken fans with homeotropic domains for 4d. In the case of 4e, the observation of a homogeneous schileren texture across the field confirmed the S<sub>C</sub> phase.

Since all the samples retain liquid crystalline textures even at room temperature, identification of solidification was difficult unlike for the low-molecular-weight liquid crystals. In order to identify the fluidity, the coverslip was sheared at regular intervals on cooling, and the sample mobility was observed. To establish the enantiotropic nature of the mesophase, the samples were reheated where mobility, typical of a liquid crystal phase, was found at different temperatures for different polymers. It is quite interesting to note that the smectic mesomorphism dominated over the nematic phase. The appearance of the  $S_C$  phase in higher homologues is attributed to the lengthy

Table 1. Differential scanning calorimetry (DSC) and hot optical<br/>polarising microscopy (HOPM) data of polymers $T_g$ , glass transition temperature;  $\Delta H$ , change in enthalpy

Sample code	Т <sub>g</sub> [°С]	Transitions observed by DSC <sup>A</sup>	Transition temperatures [°C]	$\Delta H$ [kJ mol <sup>-1</sup> ]	Phases observed by HOPM <sup>A</sup>
4a	14	I–N, N–S <sub>A</sub>	108, 106	16.94	N, S <sub>A</sub>
4b	11	I–N, I–S <sub>A</sub>	117, 80	1.22, 0.73	N, S <sub>A</sub>
4c	10	I-S <sub>C</sub>	104	3.98	$S_C$
4d	18	I-S <sub>C</sub>	94	3.81	$S_C$
4e	$32.0^{\mathrm{B}}$	I–S <sub>C</sub>	92	3.68	$S_C$

<sup>A</sup>I: isotropic, N: nematic,  $S_A$ : smectic A,  $S_C$ : smectic C. <sup>B</sup>The melting temperature.



**Fig. 4.** The hot stage optical polarising microscopy photographs of (a) the focal conic fan texture of the smectic A ( $S_A$ ) phase of **4a** at 104°C, (b) the  $S_A$  phase of **4b** at 122°C, (c) the focal conic smectic C ( $S_C$ ) phase of **4c** at 93°C, and (d) the schilerene texture of the  $S_C$  phase of **4d** at 69°C.



Fig. 5. Differential scanning calorimetry thermograms of polymers 4a-4e on heating. I, isotropic; N, nematic;  $S_A$ , smectic A;  $S_C$ , smectic C; Cr, crystallization.

terminal chain. The ester linking units of the polymers favour the conjugation that enhances the molecular polarisability, which contributes to lateral interactions rather than terminal interactions, which are responsible for the smectic phase.

#### Differential Scanning Calorimetry (DSC) Studies

To corroborate the POM observations, the polymer samples were subjected to DSC analysis. Each polymer sample was subjected to two heating and cooling cycles. The results obtained from the second heating and cooling are considered for discussion. DSC traces of the polymers are given in Fig. 5 and Fig. 6. Phase transitions temperatures and the associated enthalpy values determined from DSC are listed in Table 1. A good agreement was noticed in terms of transition temperatures and the mesophases observed by hot stage optical polarising microscopy (HOPM). For instance, the DSC thermogram of 4b showed two transitions (at 80°C and 117°C), which correspond to S<sub>A</sub> to nematic and nematic to isotropic phases, respectively, whereas a single broad peak at 108°C, due to the merging of two transitions, which correspond to SA to nematic and nematic to isotropic phases were observed for 4a. In the case of 4c, 4d, and 4e, only a single transition was observed in the DSC for the S<sub>C</sub> phase. In addition to the transitions that are related to mesophases, glass transition phenomena were also observed for all the polymers except 4e.

Glass transition temperatures ( $T_g$ s) of the polymers were found to be either lower or close to room temperature, due to the presence of the spacer, thereby allowing the samples to appear to be rubbery in nature. Generally, SCLCP exhibit two kinds of transitions, i.e. glass to rubbery transitions (at the  $T_g$ ) and mesophase transitions.<sup>[9,21]</sup> The transition enthalpy associated with mesophase transitions is high, since they are first order thermodynamic transitions, whereas those associated with  $T_g$ are too low to be identified because they are second-order transitions. On heating, all the polymers showed typical second-order transitions, followed by a first-order transition; the



Fig. 6. Differential scanning calorimetry thermograms of polymers 4a-4e on cooling. I, isotropic; N, nematic;  $S_A$ , smectic A;  $S_C$ , smectic C; Cr, crystallization.



Fig. 7. X-Ray diffraction patterns of homopolymers at  $80^{\circ}C$  (4c) and  $85^{\circ}C$  (4e).

former was assigned to  $T_{\rm g}$ , while the later was attributed to isotropisation. Similarly, on cooling, isotropic to mesophase and mesophase to glass transitions were observed.

#### Variable-Temperature X-Ray Diffraction (VT-XRD) Studies

The existence of a S<sub>C</sub> phase in the polymers was also confirmed by using VT-XRD measurements. The X-ray diffraction profiles measured at 80°C for **4c** and 85°C for **4e** are given in Fig. 7. The figure shows the sharp and intense reflections at  $2\theta = 2.77^{\circ}$  (**4c**) and at  $2\theta = 2.88^{\circ}$  (**4e**) in the small angle region and the broad humps in the wide angle region. The appearance of sharp reflections in the small angle region, which is typical for layerlike ordering,<sup>[22–24]</sup> confirmed the S<sub>C</sub> phases in the polymers, as observed by POM and DSC. The broad hump observed in the wide angle region is due to the liquid-like order which arises from the terminal octyl and dodecyl chains. The calculated *d*-spacing values for the sharp reflections were found to be 30.0 and 30.2 Å, respectively, which suggest interdigitation of the molecules in the smectic layers.

### Thermogravimetric Analysis (TGA)

The thermal stability of all the polymers was determined by TGA and TGA traces are given in Fig. 8. Accordingly, the initial and final degradation temperatures (IDT and FDT) and decomposition temperature at 50% weight loss were calculated and listed in Table 2. The IDT for all the samples is around 300°C, while the FDT are found to be in the range between 450 and 495°C. The temperature at which 50% weight loss of the polymers was found to be  $\sim$ 400°C. These values suggest that the thermal stability of the polymers is reasonably good.

# Molecular Weight Determination

All the polymers synthesised were analysed by gel permeation chromatography (GPC) in order to determine the molecular weight. The weight average molecular weight  $\langle M_{\rm w} \rangle$ , number average molecular weight  $\langle M_{\rm n} \rangle$ , and polydispersity (PDI)



Fig. 8. Thermogravimetric analysis curves of polymers 4a–4e.

Table 2. The initial and final degradation temperatures (IDT andFDT) and decomposition temperature at 50 % weight loss (50 %) of the<br/>polymers

Sample code	IDT [°C]	50 % [°C]	FDT [°C]
4a	303	391	478
4b	321	398	457
4c	326	413	488
4d	311	403	495
4e	293	395	456

values are listed in Table 3. Since monomers were polymerised by a free radical addition mechanism, the PDI values were found to be more than 1.5 for low-molecular-weight polymers. The  $<M_w>$  of the polymers are in the range 6000–13000, whereas the monomer weights are in the range of 400–550 g mol<sup>-1</sup>. Thus the degree of polymerisation (DP) was found to be between 16 and 23. The lower homologue polymers showed low molecular weights, while the higher homologue polymers, i.e. decyl and dodecyl polymers (**4d** and **4e**), showed a substantial increase in their molecular weight. Similarly, the PD values also showed an increasing tendency for decyl and dodecyl polymers.

#### Conclusions

In summary, a new series of polymers were synthesised in order to establish their structure–property relationships. Although some of the monomers failed to show liquid crystalline property, all the polymers synthesised enantiotropically exhibited nematic and smectic phases. The  $S_C$  phase of the representative samples was confirmed by XRD analysis. Disappearance of the nematic and  $S_A$  phases from the C8–C12 homologues and stabilisation of the  $S_C$  phase at C8 was observed along the series. The introduction of an ester group between the spacer and core reduced the isotropic temperatures and stabilised the  $S_C$  phase when compared with the ether analogues. In addition, increasing the aspect ratio of the monomers increases the possibility of a more ordered phase ( $S_C$ ). DSC and TGA analysis of the polymers revealed their good thermal stability.

## Experimental

# Materials

Benzyl-4-hydroxy benzoate, 4-ethoxy benzoic acid, 4-hexyloxy benzoic acid, 4-octyloxy benzoic acid, 4-decyloxy benzoic acid, 4-dodecyloxy benzoic acid, 4-hydroxybutyl acrylate, palladium on charcoal (Pd/C, 10%), N,N'-dicyclohexylcarbodiimide (DCC), and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich, USA and used without further purification. N,N'-Dimethylformamide, tetrahydrofuran (THF), ethanol, and methanol (SD Fine, Mumbai, India) were used as received. Dichloromethane (DCM), methyl ethyl ketone (MEK), ethyl acetate, diethyl ether, n-hexane, acetone, acetonitrile, isopropyl alcohol, potassium hydroxide (pellets), Celite-540, anhydrous potassium carbonate, anhydrous sodium sulphate, and silica gel (100–200 mesh) were obtained from Merck-India, Mumbai and used as received.

#### Measurements

The FT-IR spectra of samples were recorded by the KBr pellet method on a Thermo Mattson FT-IR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra of the compounds were recorded using a JEOL ECA 500 NMR spectrometer; the samples were dissolved in CDCl<sub>3</sub> and TMS was used as an internal standard. The electron

Table 3.	Molecular	weights	(g mole <sup>-1</sup>	) of the polymers
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Sample code	Weight-average molecular weight $(M_w)$	Number-average molecular weight $(M_n)$	Polydispersity
4a	6861	3666	1.87
4b	6096	3979	1.53
4c	7138	4661	1.53
4d	11004	5466	2.01
4e	13165	6840	1.92

impact (EI) mass spectra were recorded using a JEOL DX-303 spectrometer. Elemental analyses were recorded using an Elemental Analyzer for CHNS, Model-Euro EA 3000, Euro Vector S.P.A. The molecular weights of polymers were determined using a WATERS GPC model BREEZE Million-3 fitted with a DRI detector. THF was used as the mobile phase at a flow rate of  $1 \text{ mL min}^{-1}$  at 30°C. The weight-average molecular weights were calculated from the calibration curve that was plotted using linear polystyrene standards (1000–60000).

The mesophase behaviour and phase stability was investigated using an Olympus BX50 POM equipped with a Linkam THMS heating stage and TMS 94 temperature programmer with a C 7070 digital camera. The samples were placed between two 12 mm coverslips and were heated with a programmed heating rate. DSC scans were performed using a TA Instruments Q-10 series. The experiments were carried out in a nitrogen atmosphere at a heating rate of 5°C min<sup>-1</sup>. Each sample was subjected to two heating and cooling cycles and data obtained from the second heating and cooling cycle were considered for discussion. All the samples were crimpled in aluminium pans to ensure good thermal contact between the sample and the pan. TGA thermograms of the polymer samples were recorded on a Q-10 series instrument in a nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup> in the temperature range of 30–800°C.

Small-angle X-ray scattering peaks were measured with an evacuated high performance SAXS instrument 'SAXSess' (Anton Paar KG, Graz, Austria). The 'SAXSess' was attached to a conventional X-ray generator (Philips, Holland) equipped with a sealed X-ray tube (Cu anode target type, producing  $Cu_{K\alpha}$ X-rays with a wavelength of 0.154 nm), operating at 40 kV and 50 mA. The samples were measured using the paste cell method. The scattered X-ray intensities were detected with a 2D-imaging plate detection system Cyclone (Packard, A Packard Bioscience Co.) with a spatial resolution of  $50 \times 50 \,\mu\text{m}^2$  per pixel at a sample to detector distance of 265 mm. Scattering data read from the imaging plate were first corrected for the absorption of the X-rays in the sample and transformed to the q scale ( $q = 4\pi/$  $\lambda \cdot \sin \theta/2$ ; program SAXS Quant; Anton Paar KG, Graz, Austria). The SAXS measurements were further corrected with the empty cell measurements.

## *Synthesis of 4-[(Benzyloxy)carbonyl]phenyl 4-Ethoxybenzoate (1a)*

In a representative experiment, 30.6 g (81 mmol) of 4-ethoxy benzoic acid was placed in a 250 mL round bottom flask. To this, 14.27 g (250 mmol) of thionyl chloride was added and refluxed for 1 h. The excess thionyl chloride was removed and the product was dissolved with 150 mL of MEK and added dropwise to a mixture of 22.8 g (100 mmol) of benzyl 4-hydroxybenzoate and 18.36 g (120 mmol) of triethylamine in 300 mL of MEK at 0°C over 1 h. The reaction mixture was then stirred for 3 h at room temperature. The triethylamine salt obtained was filtered off and the solvent was evaporated. The crystalline solid thus obtained was washed with 5% aqueous sodium hydroxide and twice with distilled water. It was purified by recrystallising from isopropyl alcohol.

Yield: 75%, mp 109–111°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3069 (aromatic C–H<sub>str</sub>), 2978, 2935 (C–H<sub>str</sub>), 1726 (C=O<sub>str</sub>), 1604 and 1506 (C=C<sub>str</sub> aromatic), 1441 (C–H<sub>ben</sub>), 1276, 1255, 1214, and 1159 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.14 (t, *J* 8.39, 4H, Ar-H), 7.46 (d, *J* 7.05, 2H, Ar-H), 7.40 (t, *J* 7.04, 2H, Ar-H), 7.35 (t, *J* 6.71, 1H, Ar-H), 7.30 (d, *J* 8.79, 2H, Ar-H), 6.98 (d, *J* 9.12, 2H, Ar-H), 5.38 (s, 2H),

4.12 (q, J 6.95, 2H, O–CH<sub>2</sub>), 1.46 (t, J 6.88, 3H, CH<sub>3</sub>).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 165.84, 164.46, 163.65, 155.01, 136.08, 132.51, 131.40, 128.73, 128.39, 128.29, 127.62, 121.98, 121.16, 114.46, 66.90, 63.96, 14.77. *m*/*z* (EI) 376.4 (M<sup>+</sup>). Anal. Calc. for C<sub>23</sub>H<sub>20</sub>O<sub>5</sub>: C 73.39, H 5.35. Found: C 73.12, H 5.21 %.

# 4-[(Benzyloxy)carbonyl]phenyl 4-Hexyloxybenzoate (1b)

Yield: 73 %, mp 69.2°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3068 (aromatic C–H<sub>str</sub>), 2944, 2868 (C–H<sub>str</sub>), 1722 (C=O<sub>str</sub>), 1602 and 1506 (C=C<sub>str</sub> aromatic), 1468 (C–H<sub>ben</sub>), 1261, 1202, and 1160 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.15 (t, *J* 8.93, 4H, Ar-H), 7.47 (d, *J* 7.30, 2H, Ar-H), 7.42 (t, *J* 7.25, 2H, Ar-H), 7.35 (t, *J* 7.20, 1H, Ar-H), 7.29 (d, *J* 8.45, 2H, Ar-H), 6.99 (d, *J* 8.78, 2H, Ar-H), 5.38 (s, 2H), 4.05 (t, *J* 6.29, 2H, O–CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 1.49 (m, 2H, CH<sub>2</sub>), 1.36 (m, 4H, CH<sub>2</sub>), 0.95 (t, *J* 6.68, 3H, CH<sub>3</sub>).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 165.82, 164.46, 163.88, 155.03, 136.11, 132.49, 131.40, 128.73, 128.39, 128.29, 127.62, 121.99, 121.11, 114.49, 68.47, 66.89, 31.66, 29.16, 25.77, 22.72, 14.17. *m*/z (EI) 432.5 (M<sup>+</sup>). Anal. Calc. for C<sub>27</sub>H<sub>28</sub>O<sub>5</sub>: C 74.97, H 6.52. Found: C 74.42, H 6.24%.

# 4-[(Benzyloxy)carbonyl]phenyl 4-Octyloxybenzoate (1c)

Yield: 73 %, mp 66.8°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3068 (aromatic C–H<sub>str</sub>), 2924, 2859 (C–H<sub>str</sub>), 1731 (C=O<sub>str</sub>), 1604 and 1507 (C=C<sub>str</sub> aromatic), 1473 (C–H<sub>ben</sub>), 1258, 1202, and 1162 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.14 (t, *J* 8.90, 4H, Ar-H), 7.44 (d, *J* 7.47, 2H, Ar-H), 7.39 (t, *J* 7.20, 2H, Ar-H), 7.33 (t, *J* 7.04, 1H, Ar-H), 7.28 (d, *J* 8.55, 2H, Ar-H), 6.96 (d, *J* 8.65, 2H, Ar-H), 5.39 (s, 2H), 4.02 (t, *J* 6.64, 2H, O–CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 1.45 (m, 2H, CH<sub>2</sub>), 1.30 (m, 8H, CH<sub>2</sub>), 0.88 (t, *J* 6.79, 3H, CH<sub>3</sub>).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 165.81, 164.44, 163.88, 155.04, 136.12, 132.49, 131.41, 128.73, 128.40, 128.28, 127.62, 121.99, 121.11, 114.49, 68.47, 66.89, 31.93, 29.46, 29.36, 29.21, 26.11, 22.79, 14.25. *m/z* (EI) 460.5 (M<sup>+</sup>). Anal. Calc. for C<sub>29</sub>H<sub>32</sub>O<sub>5</sub>: C 75.62, H 7.00. Found: C 75.31, H 7.15 %.

#### 4-[(Benzyloxy)carbonyl]phenyl 4-Decyloxybenzoate (1d)

Yield: 75 %, mp 68°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3032 (aromatic C–H<sub>str</sub>), 2923, 2852 (C–H<sub>str</sub>), 1721 (C=O<sub>str</sub>), 1604 and 1507 (C=C<sub>str</sub> aromatic), 1456 (C–H<sub>ben</sub>), 1264, 1208, and 1160 (C–O–C<sub>asym &</sub> symstr of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.15 (t, J 9.17, 4H, Ar-H), 7.45 (d, 7.48, 2H, Ar-H), 7.40 (t, J 6.88, 2H, Ar-H), 7.34 (t, J 7.09, 1H, Ar-H), 7.29 (d, J 8.37, 2H, Ar-H), 6.97 (d, J 8.88, 2H, Ar-H), 5.37 (s, 2H), 4.04 (t, J 6.54, 2H, O–CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 1.48 (m, 2H, CH<sub>2</sub>), 1.34 (m, 12H, CH<sub>2</sub>), 0.88 (t, J 6.89, 3H, CH<sub>3</sub>).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 165.84, 164.47, 163.87, 155.01, 136.08, 132.48, 131.40, 128.72, 128.38, 128.28, 127.61, 121.98, 121.09, 114.49, 68.47, 66.89, 32.00, 29.66, 29.46, 29.42, 29.18, 26.07, 22.79, 14.23. *m*/z (EI) 488.6 (M<sup>+</sup>). Anal. Calc. for C<sub>31</sub>H<sub>36</sub>O<sub>5</sub>: C 76.20, H 7.42. Found: C 76.44, H 7.21 %.

## 4-[(Benzyloxy)carbonyl]phenyl 4-Dodecyloxybenzoate (1e)

Yield: 75 %, mp 67°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3057 (aromatic C–H<sub>str</sub>), 2917, 2850 (C–H<sub>str</sub>), 1726 (C=O<sub>str</sub>), 1604 and 1507 (C=C<sub>str</sub> aromatic), 1470 (C–H<sub>ben</sub>), 1290, 1253, 1214, and 1166 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.15 (t, J 9.13, 4H, Ar-H), 7.45 (d, J 7.66, 2H, Ar-H), 7.40 (t, J 7.19, 2H, Ar-H), 7.34 (t, J 7.05, 1H, Ar-H), 7.29 (d, J 8.41, 2H, Ar-H), 6.97 (d, J 8.59, 2H, Ar-H), 5.36 (s, 2H), 4.03 (t, J 6.92, 2H, O–CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 1.48 (m, 2H, CH<sub>2</sub>), 1.31 (m, 16H, CH<sub>2</sub>), 0.88 (t, J 6.75, 3H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 165.82, 164.46, 163.87, 155.02, 136.09, 132.48, 131.40, 128.72, 128.38, 128.28, 127.61,

121.98, 121.10, 114.48, 68.46, 66.89, 32.02, 29.75, 29.70, 29.67, 29.47, 29.18, 26.08, 22.80, 14.25. m/z (EI) 516.6 (M<sup>+</sup>). Anal. Calc. for  $C_{33}H_{40}O_5$ : C 76.71, H 7.42. Found: 76.45, H 7.56 %.

## Synthesis of 4-[(4-Ethoxybenzoyl)oxy] Benzoic Acid (2a)

In a typical experiment, 19.52 g (52.5 mmol) of **1a** was placed in a 500 mL three necked round bottom flask and 100 mL of THF was added. A 1.9 g portion of 10 % Pd/C was added to the solution and it was purged with hydrogen gas at room temperature for 48 h in order to obtain the acid.<sup>[25,26]</sup> The Pd/C catalyst was then removed by filtering the reaction mixture through Celite-540 and upon evaporation of the solvent yielded the white solid which was recrystallised from propan-1-ol.

Yield: 90 %, mp nematic, 227–273°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3049 (aromatic C–H<sub>str</sub>), 2996, 2946 (C–H<sub>str</sub>), 2668, 2549 (O–H<sub>str</sub> of carboxylic acid) 1746 (C=O<sub>str</sub>), 1685 (C=O<sub>str</sub> of carboxylic acid), 1603 and 1510 (C=C<sub>str</sub> aromatic), 1425 (C–H<sub>ben</sub>), 1260, 1211, and 1158 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (acetone- $d_6$ ) 8.10 (d, J 8.49, 4H, Ar-H), 7.40 (d, J 8.92, 2H, Ar-H), 7.09 (d, J 9.13, 2H, Ar-H), 4.17 (q, J 6.80, 2H, O–CH<sub>2</sub>), 1.39 (t, J 6.9, 3H, CH<sub>3</sub>).  $\delta_{\rm C}$  (acetone- $d_6$ ) 165.90, 163.94, 163.78, 155.07, 132.24, 131.16, 128.01, 122.18, 121.18, 114.56, 63.84, 13.47. *m/z* (EI) 286.2 (M<sup>+</sup>). Anal. Calc. for C<sub>16</sub>H<sub>20</sub>O<sub>5</sub>: C 67.12, H 4.92. Found: C 67.03, H 5.01 %.

# 4-[(4-Hexyloxybenzoyl)oxy] Benzoic Acid (2b)

Yield: 90 %, mp nematic, 169–245°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3073 (aromatic C–H<sub>str</sub>), 2936, 2864 (C–H<sub>str</sub>), 2664, 2546 (O–H<sub>str</sub> of carboxylic acid) 1739 (C=O<sub>str</sub>), 1686 (C=O<sub>str</sub> of carboxylic acid), 1603 and 1509 (C=C<sub>str</sub> aromatic), 1470 (C–H<sub>ben</sub>), 1250, 1208, and 1162 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (acetone- $d_6$ ) 8.12 (d, J 8.88, 2H, Ar-H), 8.10 (d, J 9.17, 2H, Ar-H), 7.40 (d, J 8.14, 2H, Ar-H), 7.10 (d, J 9.05, 2H, Ar-H), 4.11 (t, J 6.84, 2H, O-CH<sub>2</sub>), 1.79 (m, 2H, CH<sub>2</sub>), 1.49 (m, 2H, CH<sub>2</sub>), 1.33 (m, 4H, CH<sub>2</sub>), 0.88 (t, J 6.89, 3H, CH<sub>3</sub>).  $\delta_{\rm C}$ (acetone- $d_6$ ) 166.07, 163.95, 155.07, 132.23, 131.17, 128.01, 122.17, 121.16, 114.60, 68.27, 31.46, 25.54, 22.45, 13.47. *m/z* (EI) 342.3 (M<sup>+</sup>). Anal. Calc. for C<sub>20</sub>H<sub>22</sub>O<sub>5</sub>: C 70.15, H 7.91, N 6.47. Found: C 70.01, H 6.23 %.

## 4-[(4-Octyloxybenzoyl)oxy] Benzoic Acid (2c)

Yield: 90 %, mp nematic, smectic, 147–239°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3079 (aromatic C–H<sub>str</sub>), 2922, 2853 (C–H<sub>str</sub>), 2653, 2534 (O–H<sub>str</sub> of carboxylic acid) 1734 (C=O<sub>str</sub>), 1683 (C=O<sub>str</sub> of carboxylic acid), 1600 and 1508 (C=C<sub>str</sub> aromatic), 1470 (C–H<sub>ben</sub>), 1253, 1208, and 1161 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.20 (d, *J* 8.39, 2H, Ar-H), 8.15 (d, *J* 8.67, 2H, Ar-H), 7.34 (d, *J* 8.43, 2H, Ar-H), 6.99 (d, *J* 9.05, 2H, Ar-H), 4.05 (t, *J* 6.16, 2H, O–CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 1.48 (m, 2H, CH<sub>2</sub>), 1.32 (m, 8H, CH<sub>2</sub>), 0.88 (t, *J* 6.93, 3H, CH<sub>3</sub>).  $\delta_{\rm C}$ (CDCl<sub>3</sub>) 165.9, 164.46, 163.90, 155.61, 132.52, 132.00, 126.72, 122.12, 120.99, 114.49, 68.48, 31.95, 29.43, 29.34, 29.17, 26.08, 22.76, 14.23. *m/z* (EI) 370.4 (M<sup>+</sup>). Anal. Calc. for C<sub>22</sub>H<sub>26</sub>O<sub>5</sub>: C 71.33, H 7.07. Found: C 71.05, H 7.19 %.

#### 4-[(4-Decyloxybenzoyl)oxy] Benzoic Acid (2d)

Yield: 90 %, mp nematic, smectic, 132–233°C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3073 (aromatic C–H<sub>str</sub>), 2921, 2853 (C–H<sub>str</sub>), 2670, 2552 (O–H<sub>str</sub> of carboxylic acid) 1736 (C=O<sub>str</sub>), 1690 (C=O<sub>str</sub> of carboxylic acid), 1603 and 1510 (C=C<sub>str</sub> aromatic), 1425 (C–H<sub>ben</sub>), 1260, 1205, and 1163 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.14 (m, *J* 8.05, 4H, Ar-H), 7.30 (d, *J* 9.07, 2H, Ar-H), 6.98 (d, *J* 9.04, 2H, Ar-H), 4.05 (t, *J* 6.39, 2H, O–CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 1.49 (m, 2H, CH<sub>2</sub>), 1.31 (m, 12H, CH<sub>2</sub>), 0.88 (t, *J* 6.38, 3H, O–CH<sub>2</sub>). $\delta_{\rm C}$  (CDCl<sub>3</sub>) 168.90, 164.53, 163.83, 154.96, 132.46, 131.64, 127.87, 121.87, 121.08, 114.46, 68.44, 31.97, 29.63, 29.43, 29.37, 29.14, 26.04, 22.76, 14.22. *m/z* (EI) 399.4 ([M + H]<sup>+</sup>). Anal. Calc. for C<sub>24</sub>H<sub>30</sub>O<sub>5</sub>: C 72.33, H 7.58. Found: C 72.56, H 7.45 %.

#### 4-[(4-Dodecyloxybenzoyl)oxy] Benzoic Acid (2e)

Yield: 90 %, mp nematic, smectic,  $125-223^{\circ}$ C,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3073 (aromatic C–H<sub>str</sub>), 2922, 2851 (C–H<sub>str</sub>), 2670, 2549 (O–H<sub>str</sub> of carboxylic acid) 1733 (C=O<sub>str</sub>), 1689 (C=O<sub>str</sub> of carboxylic acid), 1603 and 1510 (C=C<sub>str</sub> aromatic), 1468 (C–H<sub>ben</sub>), 1261, 1214, and 1163 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.20 (d, *J* 8.87, 2H, Ar-H), 8.15 (d, *J* 8.43, 2H, Ar-H), 7.34 (d, *J* 8.87, 2H, Ar-H), 6.99 (d, *J* 8.97, 2H, Ar-H), 4.06 (t, *J* 6.55, 2H, O–CH<sub>2</sub>), 1.82 (m, 2H, CH<sub>2</sub>), 1.47 (m, 2H, CH<sub>2</sub>), 1.35 (m, 17H, CH<sub>2</sub>), 0.88 (t, *J* 6.52, 3H, CH<sub>3</sub>).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 170.92, 164.43, 163.89, 155.61, 132.51, 131.97, 126.76, 122.15, 121.01, 114.46, 68.46, 32.01, 29.75, 29.73, 29.68, 29.65, 29.45, 29.16, 26.06, 22.79, 14.23. *m*/*z* (EI) 426.5 (M<sup>+</sup>). Anal. Calc. for C<sub>26</sub>H<sub>34</sub>O<sub>5</sub>: C 73.21, H 8.03. Found: C 73.09, H 7.93 %.

#### Synthesis of Monomers

# 4-[(Acryloyloxybutoxy)carbonyl]phenyl 4-Ethoxybenzoate (**3a**)

In a typical experiment, 7.15 g (25 mmol) of 4-[(4ethoxybenzoyl)oxy] benzoic acid and 3.6 g (25 mmol) of 4-hydroxybutylacrylate were placed in a conical flask and dissolved in 100 mL of THF. To this stirred solution, 6.18 g (30 mmol) of DCC dissolved in 50 mL of DCM was added, followed by the addition of DMAP (2.5 mmol) and stirring was continued overnight at room temperature. Filtration of solid dicyclohexyl urea and subsequent evaporation of the solvent yielded a semi solid which was purified by column chromatography using a 1 : 4 mixture of ethyl acetate and hexane as eluent in order to obtain a white solid.

Yield: 60 %,  $v_{max}$  (KBr)/cm<sup>-1</sup> 3075 (aromatic C–H<sub>str</sub>), 2979, 2958 (C–H<sub>str</sub>), 1722 (C=O<sub>str</sub>), 1634 (C=C<sub>str</sub>) 1603, 1578, 1509 (C=C<sub>str</sub> aromatic), 1473 (C–H<sub>ben</sub>), 1260, 1203, and 1164 (C–O– C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.12 (d, J 8.79, 2H, Ar-H), 8.10 (d, J 8.53, 2H) 7.26 (d, J 8.45, 2H, Ar-H), 6.95 (d, J 8.92, 2H, Ar-H), 6.41 (d, J 16.4, 1H), 6.11 (dd, J 10.1 1H), 5.82 (d, J 10.5, 1H), 4.37, (t, J 5.95, 2H), 4.18 (t, J 5.99 2H), 4.10 (m, 2H), 1.85 (br s, 4H), 1.43 (q, 3H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 166.31, 165.93, 164.46, 163.64, 154.91, 132.47, 131.21130.88, 128.49, 127.72, 121.94, 121.15, 114.45, 64.62, 64.11, 63.94, 25.55, 25.49, 14.73. *m/z* (EI) 412.4 (M<sup>+</sup>). Anal. Calc. for C<sub>23</sub>H<sub>24</sub>O<sub>7</sub>: C 66.97 H 5.86. Found: C 66.85, H 5.72 %.

## 4-[(Acryloyloxybutoxy)carbonyl]phenyl 4-Hexyloxybenzoate (**3b**)

Yield: 60 %,  $v_{max}$  (KBr)/cm<sup>-1</sup> 2952, 2865 (C–H<sub>str</sub>), 1726 (C=O<sub>str</sub>), 1636 (C=C<sub>str</sub>), 1604, 1509 (C=C<sub>str</sub> aromatic), 1464 (C–H<sub>ben</sub>), 1262, 1202, and 1164 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.09 (m, 4H), 7.26 (d, *J* 8.5, 2H), 6.94 (d, *J* 8.7, 2H), 6.39 (d, *J* 16.78, 1H), 6.10 (dd, *J* 9.99, 1H), 5.79 (d, *J* 11.53, 1H), 4.34, (t, 2H), 4.21 (t, 2H), 3.99 (t, 2H), 1.77 (m, 6H), 1.43 (m, 2H), 1.31 (m, 4H), 0.88 (t, 3H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 166.23, 165.86, 164.39, 163.84, 154.91, 132.43, 131.19, 130.83, 128.49, 127.69, 121.93, 121.05, 114.45, 68.40, 64.58, 64.08, 31.61, 29.11, 25.72, 25.53, 25.47, 22.66,

14.11. m/z (EI) 468.5 (M<sup>+</sup>). Anal. Calc. for C<sub>27</sub>H<sub>32</sub>O<sub>7</sub>: C 69.21, H 6.88. Found: C 68.95, H 7.01 %.

# 4-[(Acryloyloxybutoxy)carbonyl]phenyl 4-Octyloxybenzoate (**3c**)

Yield: 60 %, mp 49°C,  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 2929, 2857 (C–H<sub>str</sub>), 1728 (C=O<sub>str</sub>), 1636 (C=C), 1605, 1510 (C=C<sub>str</sub> aromatic), 1468 (C–H<sub>ben</sub>), 1263, 1202, and 1163 (C–O–C<sub>asym & symstr</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.13 (d, *J* 8.50, 2H), 8.09 (d, *J* 8.36, 2H) 7.27 (d, *J* 9.16, 2H), 6.95 (d, *J* 8.45, 2H), 6.38 (dd, *J* 16.83, 1H), 6.12 (dd, *J* 10.72, 1H), 5.82 (dd, *J* 9.64, 1H), 4.37, (t, *J* 6.1, 2H), 4.23 (t, *J* 6.44, 2H), 4.03 (t, *J* 6.15, 2H), 1.86 (m, 6H), 1.44 (m, 2H), 1.30 (m, 8H), 0.88 (t, *J* 6.47, 3H).  $\delta_{\rm H}$ (CDCl<sub>3</sub>) 166.29, 165.92, 164.46, 163.85, 154.93, 132.46, 131.22, 130.86, 128.50, 127.72, 121.95, 121.08, 114.46, 68.45, 64.61, 64.11, 31.88, 29.41, 29.31, 29.16, 26.06, 25.56, 25.50, 22.74, 14.20. *m/z* (EI) 496.5 (M<sup>+</sup>). Anal. Calc. for C<sub>29</sub>H<sub>36</sub>O<sub>7</sub>: C 70.14, H 7.30. Found: C 70. 37, H 7.18 %.

# 4-[(Acryloyloxybutoxy)carbonyl]phenyl 4-Decyloxybenzoate (**3d**)

Yield: 60 %, mp 42°C,  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 2924, 2853 (C–H<sub>str</sub>), 1726 (C=O<sub>str</sub>), 1636 (C=C<sub>str</sub>), 1606, 1510 (C=C<sub>str</sub> aromatic), 1469 (C–H<sub>ben</sub>), 1274 and 1167 (C–O–C<sub>str</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.13 (d, *J* 9.1, 2H, Ar-H), 8.11 (d, *J* 9.17, 2H, Ar-H) 7.27 (d, *J* 8.41, 2H, Ar-H), 6.95 (d, *J* 9.15, 2H, Ar-H), 6.42 (dd, *J* 16.08, 1H), 6.14 (dd, *J* 9.91, 1H), 5.81 (dd, *J* 9.21, 1H), 4.36, (t, *J* 5.72, 2H), 4.23 (t, *J* 6.14, 2H), 4.03 (t, *J* 6.36, 2H), 1.85 (m, 6H), 1.48 (m, 2H), 1.34 (m, 12H), 0.87 (t, *J* 6.52, 3H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 166.30, 165.94, 164.47, 163.85, 154.92, 132.46, 131.22, 130.88, 128.50, 127.72, 121.95, 121.08, 114.46, 68.45, 64.62, 64.12, 31.98, 29.64, 29.45, 29.40, 29.16, 26.06, 25.56, 25.50, 22.77, 14.22. *m/z* (EI) 524.6 (M<sup>+</sup>). Anal. Calc. for C<sub>31</sub>H<sub>40</sub>O<sub>7</sub>: C 70.96, H 7.68. Found: C 71.05, H 7.59%.

# 4-[(Acryloyloxybutoxy)carbonyl]phenyl 4-Dodecyloxybenzoate (**3e**)

Yield: 60 %, mp 57°C,  $\nu_{max}$  (KBr)/cm<sup>-1</sup> 2921, 2852 (C–H<sub>str</sub>), 1723 (C=O<sub>str</sub>), 1634 (C=C<sub>str</sub>), 1607, 1510 (C=C<sub>str</sub> aromatic), 1470 (C–H<sub>ben</sub>), 1278, 1208, and 1168 (C–O–C<sub>str</sub> of ester and ether, respectively).  $\delta_{\rm H}$  (CDCl<sub>3</sub>) 8.13 (d, J 8.95, 2H, Ar-H), 8.10 (d, J 8.70, 2H, Ar-H), 7.28 (d, J 9.08, 2H, Ar-H), 6.97 (d, J 9.10, 2H, Ar-H), 6.38 (dd, J 16.07, 1H), 6.11 (dd, J 9.98, 1H), 5.81 (dd, J 9.81 1H), 4.37, (t, J 5.91, 2H), 4.23 (t, J 6.02, 2H), 4.03 (t, J 6.42, 2H), 1.82 (m, 6H), 1.46 (m, 2H), 1.33 (m, 16H), 0.87 (t, J 6.65, 3H).  $\delta_{\rm C}$  (CDCl<sub>3</sub>) 166.29, 165.93, 164.46, 163.85, 154.93, 132.45, 131.21, 130.85, 128.50, 127.72, 121.94, 121.09, 114.46, 68.45, 64.61, 64.11, 32.00, 29.74, 29.72, 29.67, 29.64, 29.44, 29.16, 26.05, 25.56, 25.50, 22.77, 14.21. *m/z* (EI) 553.7 ([M + H]<sup>+</sup>). Anal. Calc. for C<sub>33</sub>H<sub>44</sub>O<sub>7</sub>: C 71.71, H 8.02. Found: C 71.89, H 7.92 %.

#### Preparation of Polymers

In a typical experiment, 1 g of **2a** was placed in a polymerisation tube and 1,4-dioxane (30 mL) and 0.01 g of benzoyl peroxide were added. The solution was flushed with nitrogen gas for a few minutes, tightly closed, and kept in a thermostated water bath at  $70 \pm 1^{\circ}$ C. The polymerisation was continued for 24 h, and the viscous polymer thus formed was precipitated by pouring into methanol. The white polymer solid obtained was further purified by redissolving it in chloroform and precipitating it in methanol. Yield: 72 %.

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675