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Mesogenic Homologous Series of Cinnamates with Propoxyethyl Terminal Chain

Sachin Ramchandra Vishe[1], Tarun M. Patel[2], Mikita Shah[3], H N Patel[4], Khusbu. Patel[5], Parasar Modh[6]

[1]Department of Chemistry& Chemical Sciences, Sabarmati University,
[2,3,4]Shree Maneklal M. Patel Institute of Sciences & Research Sector 15/23, Kadi Sarva Vishwavidhyalaya, Gandhinagar, India.
[5]Sir P. T Sciences College Department of Chemistry, Modasa, Shri C.N.P.F. Arts & D.N. Science College – Dabhoi

*Author for correspondence:
Email: hement_2patel@yahoo.co.in
Email: drpatel16185@gmail.com

Article Info

ABSTRACT:

New melogenic homologous series of cinnamates with substituted ethyl tail: Propoxyethyl[4(4-n-alkoxycinnamoyloxy) benzoates] has been synthesized by condensing an appropriate 4-n-alkoxycinnamoylchloride with propoxyethyl 4-hydroxybenzoate. The synthesized compounds were characterized by combination of elemental analysis and standard spectroscopic methods. In the present series all the compounds synthesized exhibit mesomorphism. Methoxy to n-propyloxy derivatives exhibit monotropic nematic mesophase.
n-butyloxy to n-pentyloxy derivatives exhibit both enantiotropic smectic A as well as nematic mesophases. n-hexyloxy to n-hexadecyloxy derivatives exhibit only enantiotropic smectic A mesophase. The mesomorphic properties of the present series were compared with structurally related mesogenic homologous series to evaluate the effect of propoxyethyl tail and cinnamoyloxy central linkage on phase transition.

Keywords: propoxyethyl tail, cinnamoyloxy central linkage, monotropic, enantiotropic, phase transition.

1. Introduction

Terminal groups present in a moiety have their own importance because of their polarity. It has been found that terminally substituted functional group exhibit more stable phase transition than do non-substituted mesogenic compounds. Any terminal functional group, which increases the molecular polarizability, without significantly increasing the molecular breadth, increases the thermal stability of the resulting phase transition. Phase transition behaviour of the liquid crystalline compound is principally dependent on its molecular arrangement, where a slight change in the molecular different shape results in a significant change in its phase transition properties[1] Many mesogenic homologous series with -COO-, -N=N-, -CH=N-,-CH=CH-,-C≡C-,-CH=CH-COO-,-CONH-,etc., as their central linkages , as well as a alkyl and /or alkoxy chains "as terminal groups", have been reported [1-4].In earlier years , cinnamic acid ester (C_6H_5-CH=C-COO-) has extensively integrated into molecular modelling to develop new liquid crystalline derivatives possessing low melting points , high clearing points and suitable phase transition temperature ranges [5-14].Earlier , Jones and Ratto [15] observed that esters of cinnamic acid have low melting point and wide nematic isotropic transition temperature. Zhang et al. [16] have shown cinnamates are photoalignment materials which make them useful in liquid crystal displays. Cinnamate esters have been well known for many years and exhibit extensive literature in liquid crystal area [17-25]. Vora and Rajput [26] reported that binary mixtures of cinnamates esters show a wide range of smectic and nematic phase transition. Sadashiva et al. [27] reported the synthesis , characteristics and phase transition properties of some esters of*trans*-4-n -alkoxycinnamic acid and trans-4-*n*-alkoxy-∝-methylcinnamic acid with branched alky-chain terminals , compounds they prepared showed to exhibit ferroelectric and anti-ferroelectric phases . Kashyap et al. [28] reported a comparative study of two homologous series of benzoate- and cinnamate-linked derivatives. Thaker and Kanojiya [29] reported the phase transition properties of liquid crystalline derivatives with biphenyl moiety containing azo-ester, azo-cinnamate central linkages and different terminal groups. Doshi et al. [30] have reported the synthesis and phase transition properties of *n*-butyl-4-(4'-*n*-alkoxy cinnamoyloxy) cinnamates. Doshi and Patel have [31] reported cis-cinnamate esters, namely, *n*- hexyl-4-(4'*n*-alkoxy cinnmoyloxy) cinnamates. They have also [32] reported cis-cinnamate esters, namely, *n*-hexyl-4-(4'-*n*-alkoxy cinnamoyloxy) cinnamates. Serrano et al. [33] reported synthesis, characterization and photo-reactivity of liquid crystalline cinnamates. The reactivity of photo reactive samples containing these derivatives and a low percentage of a triplet sensitizer were investigated by them at different temperatures and phases. Kawatsuki et al. [34] synthesised and studied the photoreaction of side-chain liquid-crystalline polymers comprising cinnamoyl biphenyl mesogens. Zhang et al [35] reported novel liquid crystal photo alignment layer-by-layer and self-assembled with long chain cinnamate polyelectrolyte. Photo-cross-linking and photosensitive behaviour of cinnamoyl group have imported its use in liquid crystalline materials which can be used in in-plane Switching Mode liquid crystal Display as well as biomaterials [36-39]. Cinnamoly-containing Liquid Crystal with reactive vinyl groups can be used as optical data shortage, photonic devices and liquid crystal polymers actuators [40,41]. Earlier, Prajapati et al. [42] have reported Schiff's base cinnamates comprising naphthalene moiety. Terminal groups, on the other hand, have their own role because of their polarity. It has been found that terminally substituted liquid crystalline compounds exhibit more stable phase transition as compared to un-substituted liquid crystalline compounds. Any terminal group, which increases the molecular polarizability, without significantly increasing the breadth of moiety, increases the thermal stability of resulting phase transition. Our literature study indicated that, compared with mesogenic esters with normal and achiral branched terminal alkyl chains, liquid crystalline esters having chains containing differing kinds of atoms are very few. Chiang et al. [43-44]

studied the effects of ethoxyethoxyethoxy (EO) and butoxyethoxyethoxy (BO) chains on phase transition. They observed that the BO – containing liquid crystals have greater SmC* phase stability than the corresponding EO-containing materials. Alkoxyethyl as terminal chain has been reported as well in the literature. Wu and Lui [45] reported the synthesis and ferroelectric properties of the new chiral liquid crystal derived from (S) lactic acid with alkoxyethanols. Vora and Prajapati [46-47] have reported methoxyethyl and ethoxyethyl ester of 4-(4'-n-alkoxy-benzoyloxy) benzoic acid and alpha-methyl cinnamate. Prajapati and Pandya have [48-49] have reported four mesogenic homologous series of azo/esters having methoxyethyl and ethoxy ethyl terminal chain. Prajapati et al. [50-51] have also synthesized a mesogenic homologous series of Schiff's base ester containing a methoxyethyl and ethoxy ethyl tail and evaluated the effect of such tail on mesomorphism. Earlier, Prajapati et al have reported [52] mesogenic Schiff's base ester with chloroethyl tail. Prajapati and Patel [53-55] have also reported mesogenic cinnamates with a substituted ethyl terminal chain as well as the dielectric relaxation study of two different mesogenic cinnamates with a substituted ethyl terminal chain.

In continuation of our previous work on cinnamic acid derivatives and substituted ethyl tails respectively, the cinnamoyl central linkage containing propoxy ethyl tail, aiming to investigate the influence of central linkage and the substituted ethyl tail on the mesophase behaviour of the prepared liquid crystalline compounds. The general structural formula for the synthesized new homologous series of compounds in are shown in Scheme 1.
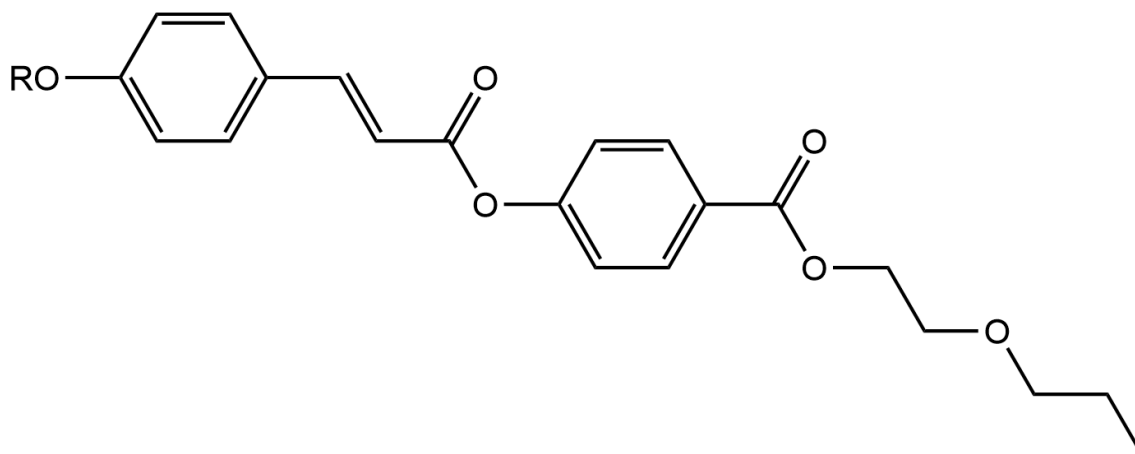
2-propoxyethyl (*E*)-4-((3-(4-*n*-alkoxyphenyl)acryloyl)oxy)benzoate (**I***n*)

Scheme1: General structural formula of series I*n* compounds

Experimental

Synthesis

4-Hydroxybenozic acid, 4-hydroxybenzaldehyde, malonic acid, pyridine, Conc.H_2SO_4, $SOCl_2$, 2- propoxyethanol the appropriate *n*-alkyl halides, and anhydrous K_2CO_3 were used as received. Solvents were dried and distilled before use. Microanalysis of the compounds was performed on Coleman carbon-hydrogen analyser, and the values obtained are in close agreement with those calculated.IR spectra were determined by KBr pellets, using a Shimadzu IR-408 spectrophotometer. ^{1}H NMR spectra were obtained with a Perkin-Elmer R-32 spectrometer using tetramethylsilane (TMS) as terminal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from the reference; $CDCl_3$ was used as solvent for all the compounds. The phase assignments and transition temperatures were determined by thermal polarized light microscopy using a polarizing microscope

(LeitzLaborlux 12 POL) equipped with a heating stage. The enthalpies of transition, reported as Jg^{-1}, were measured on a Mettler TA-4000 systems, at a scanning rate 5°C min^{-1}. The instrument was calibrated using pure indium as a standard.

The synthetic route to compounds of series **I** is illustrated in the scheme **1**.

[Insert Sheme 1 about here]

Propoxyethyl 4-hydrobenzoate (**A**) was synthesized by the esterification of 4-hydroxybenzoic acid with propoxyethanol, respectively as described earlier [56]. 4-*n*-Alkoxybenzaldehydes (**B**) were prepared by the method of Vyas and Shah [57]. Trans-4-*n*-Alkoxycinnamic acids (**C**) were synthesized from the corresponding 4-*n*-alkoxybenzaldehyde and malonic acid following the method reported by Gray and Jones [58]. Trans-4-*n*-Alkoxycinnamoly chlorides (**D**) were prepared by treating corresponding acids with excess of thionyl chloride under reflux for two hours [59].

Synthesis of series – I compounds

Propoxyethyl 4- hydroxy benzoate (0.01 mole) was dissolved in dry pyridine (10ml) and a cold solution of an appropriate trans-4-*n*-alkoxycinnamoly chloride (0.015 moles) in dry pyridine (10 ml) was added slowly to it with constant stirring in an ice bath. The mixture was allowed to stand over night at room temperature. It was acidified with cold aqueous hydrochloric acid (1N). The product obtained was filtered and washed successively with water (2x50ml) and water (2x30ml). Then the crude mass was chromatographed on silica gel (100-200 mesh size) using petroleum ether (60-80˚ C) and ethyl acetate mixture (95:5) as eluent. Removal of solvent from the eluate afforded solid materials, which was crystallized repeatedly from methanol. The purities of all these compounds were checked by thin layer chromatography (Merck kieselgel 60F 254 pre – coated plates

The elemental analysis of all the compounds of the series was found satisfactory in table **2.** The spectral data of the representative members, *n*-pentyloxy, *n*-octyloxy and tetradecyloxy derivatives, of series **I** are given below**.**

 [Insert Table 2 about here]

Spectral Data

Propoxyethyl[4(4-n-pentoxycinnamoyloxy) benzoate]

UV spectrum nm = 299.6 and 319.6

IR spectrum (KBr) Vmax/ Cm^{-1} = 2928,2850,1735 (-COO-),1714,1633(-CH=CH-), 1606,1512, 1462,1252, 1166, 830

^{1}HNMR Spectrum (400 MHz, CDCl$_3$): δ 0.92 (t, 3H, -CH$_3$), 1.36-1.45 (m, 4H, 2X-CH$_2$), 1.70-1.87(m, 5H, Ar-O-C-CH$_2$), And 3H of (-O-C-C-CH$_3$), 3.98-4.02 (m, 6H, 4H of -CH$_2$-O-CH$_2$ and 2H of Ar-O-CH$_2$), 4.3-4.4 (t, 2H, -COOCH$_2$), 6.52(d, 1H, -ArCH=), 6.91 (d, 2H, ArH), 7.25 (d, 2H of ArH), 7.50 (d, 2H, ArH),7.80 (d,1H, =CH-COO), 7.84 (d, 2H, ArH).

Propoxyethyl[4(4-n-Octyloxycinnamoyloxy) benzoate]

UV spectrum nm = 299.6 and 318.9

IR spectrum (KBr) Vmax/ Cm^{-1} = 3349.86, 2922.11 ,1724 (-COO-),1624 (-CH=CH-), 1511, 1467.9, 1255.14, 1107.1, 833.6

^{1}HNMR Spectrum (400 MHz, CDCl$_3$): δ 0.88 (t, 3H, -CH$_3$), 1.26-1.37 (m, 10H, 5X-CH$_2$), 1.59-1.66(m, 5H,2H, of Ar-O-C-CH$_2$& 3H of (-O-C-C-CH$_3$), 3.47-3.78m (m, 4H of -CH$_2$-O-CH$_2$), 3.99.0 (t, 2H of Ar-O-CH$_2$), 4.47 (t, 2H, -COOCH$_2$), 6.47(d, 1H, -ArCH=), 6.92 (d, 2H, ArH),

7.24-7.33 (m, 2H or ArH), 7.53-7.55 (d, 2H, ArH),7.82-7.86 (d,1H, =CH-COO), 8.13 (d, 2H, ArH)

Propoxyethyl[4(4-n-dodecyloxycinnamoyloxy) benzoate]
UV spectrum nm = 298.8 and 318.4
IR spectrum (KBr) Vmax/ Cm^{-1} = 3182.3, 2923.9, 1733.9 (-COO-), 1666 (-CH=CH-), 1514, 1461.9, 1259.4, 1122, 823.5
^{1}HNMR Spectrum (400 MHz, CDCl$_3$): δ 0.87 (t, 3H, -CH$_3$), 1.46-1.58 (m, 10H, 5X-CH$_2$), 1.61-1.82(m, 5H,2H, of Ar-O-C-CH$_2$& 3H of (-O-C-C-CH$_3$), 3.47-3.78m (m, 4H of -CH$_2$-O-CH$_2$), 3.99.0 (t, 2H of Ar-O-CH$_2$), 4.47 (t, 2H, -COOCH$_2$), 6.47(d, 1H, -ArCH=), 6.92 (d, 2H, ArH), 7.24-7.33 (m, 2H or ArH), 7.53-7.55 (d, 2H, ArH),7.82-7.86 (d,1H, =CH-COO), 8.13 (d, 2H, ArH)

2. Result and Discussion

Optical microscopy studies
As a preliminary investigation, the mesophases exhibited by compounds of series **I**   were concluded by the optical microscopic studies.
On cooling, isotropic liquids of series **I,** *n*-methoxy to *n*-propyloxy derivatives exhibit monotropic small droplets that coalesced to the classical schileren texture of the nematic phase. On further cooling *n*-butyloxy to *n*-hexadecyloxy derivatives also gave focal conic texture characteristic of smectic A mesophase. (figure **3**).

[Insert Figure 3 about here]

Mesomorphic behavior
Series I: Propoxyethyl[4(4-*n*-alkoxycinnamoyloxy) benzoates]
Twelve compounds have been synthesized in series **I**. Methoxy to *n*-propyloxy derivatives exhibit monotropic nematic mesophase. *n*-butyloxy to *n*-pentyloxy derivatives exhibit both enantiotropic smectic A as well as nematic mesophases. *n*-hexyloxy to *n*-hexadecyloxy derivatives exhibit only enantiotropic smectic A mesophase.

 The transition temperatures are recorded in table **1**. The plot of transition temperatures against the number of carbon atoms in the alkyl chain for the series **I** is given in figure **1**. It can be noticed that crystal-isotropic transition temperatures decrease sharply with an initial increase in the length of terminal alkoxy tail except for the last two homologues. The SmA-N and N-I transition temperatures exhibited rising tendency.

[Insert Table 1 about here]
[Insert Figure 1 about here]
Calorimetric studies:
Calorimetry is a valuable method for the detection of phase transitions. It yields quantitative results; therefore, we may draw conclusions concerning the nature of the phases which occur during the transitions. In present study, enthalpies of derivative of series **I** (*n*=4) were measured by differential scanning calorimetry. Data are recorded in table **3.** Thermograms are given in figure **2.**
[Insert Figure 2 about here]
[Insert Table 3 about here]

Table **4** summarizes comparison of smectic mesophase range, transition temperature and molecular structure of representative compound **10** (*n*=12) of the present series I as well as compare with structurally related other compounds **A** (54), **B** (54), **C** (46), **D** (53), **E** (60), and **F** (46)

The smectic mesophase range and SmA-I transition temperature of the compound **10** is lower by 11°C and 22°C, respectively as compared to that of compound **A**. The molecular structure of compound **10** differs from compound **A** only at the one terminus. The compound **10** have Propoxyethyl tail whereas compound A have methoxy ethyl tail at the same end. Gray (61) has explained that extension of methylene spacer beyond certain number lowers the transition temperatures in many esters.

The smectic mesophase range and SmA-I transition temperature of the compound **10** is lower by 19°C and 14°C, respectively as compared to that of compound **A**. Again the difference between the molecular structure of compound **10** and **B** lies at the one terminus only of the compound **10** have propoxyethyl tail whereas compound **B** has polar chloro ethyl tail at the same end. the compound has more polar chloro terminal group where's compound **10** have comparatively less polar propoxy terminal group. The presence of more polar terminal chloro group increase is the overall polarizability of compound **B** as compared to compound **10** which is responsible for the higher smectic range & SmA-I transition temperature of compound **B**.

The smectic mesophase and SmA-I transition temperature of compound **10** is higher by 20°C and 41°C respectively as compared to that at compound **C**. the molecule of compound **10** and compound **C** differ only at the central linkages. The molecule of compound **10** have cinnamoyloxy (-CH=CH-COO-) central linkages, while compound **C** have ester (-COO-) central linkages. Gray (61) has explain that the addition of double bond in the system increases the length and over all polarizability of the rod like molecules.

The smetic mesophase range and SmA-I transition temperature of the compound **10** is lower by 3°C and 6°C, respectively as compared to that of compound **D**. the molecule structure of compound 10 differ from compound **D** only at the one terminus. The compound **10** have propoxy ethyl tail whereas compound **D** have ethoxyethyl tail at same end. Gray (61) has explained that extension of methylene spacer beyond certain number lowers the transition temperatures in many esters.

The smetic mesophase range and SmA-I transition temperature of the compound **10** is lower by 1°C and 24°C, respectively as compared to that of compound **E**. The molecular structure of **10** differ from compound **E** only at the one terminus. The compound **10** have propoxy ethyl tail whereas compound **E** have butoxy ethyl tail at the same end. Gray (61) has explained that extension of methylene spacer beyond certain number lowers the transition temperatures in many esters.

The smectic mesophase and SmA-I transition temperature of compound **10** is higher by 10°C and 44° C, respectively as compared to that of compound **F**. The molecule of compound **10** and compound **F** differ only at the central linkages. The molecule of compound **10** have cinnamoyloxy (-CH=CH-COO-) central linkage, while compound **F** have ester central linkage. Gray (61) has explained that the addition of double bond in the system increases the length and polarizability of the rod like molecule.
[Insert Table 4 about here]

3. Conclusion

In this article we have presented the synthesis and characterization of new mesogenic homologous series of cinnamates with propoxyethyl tail. The present series with propoxyethyl tail are thermally less stable compared to the structurally related other mesogenic homologous series having ethoxyethyl, butoxyethyl, chloroethyl and methoxyethyl tail. The present series with cinnamoyloxy central linkage are thermally more stable as compared to the structurally related series containing ester central linkage due to the greater molecular length and polarizability of the molecular resulting from additional -CH=CH- units in the central linkage.

4. Refrences

1. Vill V Liquid Crystal 2.0, Database of Liquid Crystalline Compounds for Personal Computers, Fijitsu Kyushu system (FQS) Ltd Fukuoka LCI Hamburg 1996.
2. Demus D, Goodby JW, Gray G.W.et al.*in* Handbook of Liquid Crystals. Wiley-VCH Verlag: 1998; Volume 1.
3. Demus D. One hundred years of liquid-crystal chemistry: thermotropic liquid crystals with conventional and unconventional molecular structure. Liq Cryst. 1989;5(1):75-110. DOI 10.1080/02678298908026353.
4. Pal SK, Kumar S. Liquid crystal dimers. Cambridge (UK): Cambridge university press; 2017.
5. Yelamaggad CV, Shanker G. Synthesis and characterization of non-symmetric chiral dimers. Liq Cryst. 2007;34(9);1045-1057. DOI 10.1080/02678290701616280.
6. Bobrovsky A, Shibaev V, Hamplová V, et al. Photoinduced phase transitions and helix untwisting in the SmC* phase of a novel cinnamoyl-based liquid crystal. Liq Cryst. 2009; 36(9):989-997. DOI 10.1080/02678290903171696.
7. Enz E, Findeisen-Tandel S, Dabrowski R, et al. On the balance between syn- and anticlinicity in smectic phases formed by achiral hockey-stick mesogens with and without chiral dopants. J Mater Chem. 2009;19(19):2950–2957. DOI 10.1039/B820717H.
8. Li X, Cui J, Zhang W, et al. Controllable photo-switching of cinnamate-based photonic films with remarkable stability. J Mater Chem. 2011;21(44):17953-17959. DOI 10.1039/C1JM11708D.
9. Chakraborty A, Das B, Das MK, et al. New hockey stick compounds with a lateral methyl group showing nematic, synclinic and anticlinic smectic C phases. Liq Cryst. 2011; 38(9):1085-1097. DOI 10.1080/02678292.2011.596227.
10. Tokita M, Itoh M, Marumo K, et al. Macrocyclised phenyl cinnamate dimer utilisable as photo responsive chiral dopant for nematic liquid crystals. Liq Cryst. 2013;40(7):900-905. DOI 10.1080/02678292.2013.790094.
11. Tandel RC, Patel NK. Synthesis and mesomorphic properties of chiral nematic liquid crystals based on cholesterol. Liq Cryst. 2014;41(4):514-521. DOI 10.1080/02678292.2013.861031.
12. Selvarasu C, Kannan P. Synthesis, characterization of azobenzene and cinnamate ester based calamitic liquid crystalline compounds and their photoresponsive properties, J. Mol. Stru., 2015;1092:176-186. DOI 10.1016/j.molstruc.2015.03.026.
13. da Rosa RR., TariqM, WeberCSB, et al. Hybrid liquid crystals tetrazolyl and isoxazolyl cinnamates. Liq. Cryst. 2016;43(11),1659-1670. DOI 10.1080/02678292.2016.1193908.
14. Selvarasu C, Kannan P. Alkyloxy azo-cinnamate ester based thermotropic liquid crystals and their photo physical investigations. Mol. Cryst. Liq. Cryst. 2017;648(1): 77-87. DOI 10.1080/15421406.2017.1301859.
15. Jones FB, Ratto JJ. Liquid Crystals II. Liquid Crystalline Properties of Transcinnamic

Acid Esters. In: Johnson JF, Porter RS. (eds) Liquid Crystals and Ordered Fluids. Springer, Boston, MA, 1974.p723-731

16. Cui L, Xie P, Zhang R, et al. Photo-driven liquid crystal cell with high sensitivity. Liq Cryst. 1999;26(10):1541-1546. DOI 10.1080/026782999203878.

17. Gray GW, Harrison KJ. The Liquid Crystalline Properties of Alkyl, Aryl and Arylalkyl-4- *p*-substituted benzylideneamino-cinnamates and α-methylcinnamates. Mol Cryst Liq Cryst. 1971;13(1):37–60. DOI 10.1080/15421407108083536.

18. Jones F, Ratto J. Liquid crystalline properties in some alkyl and alkoxycinnamic acid esters. J Chem Soc Chem Commun. 1973; (21):841-842. DOI 10.1039/C3973000841B.

19. Dave JS, Vora RA. Mesomorphic behaviour of biphenyl esters-1. Biphenyl-4-*trans-p-n*-Alkoxycinnamates. Mol Cryst Liq Cryst. 1974;28(3-4):269-273. DOI 10.1080/15421407408082824.

20. Sadashiva BK. Mesomorphic properties of some α-methyl cinnamic acids and their esters. Mol Cryst Liq Cryst. 1976;35(3-4):205-210. DOI 10.1080/15421407608083670.

21. Lohar JM, Dave JS. Synthesis and study of new mesogens 2. *p*-(*p'*-n-alkoxy cinnamoyloxy) benzylidene p"-anisidines (1) and *p*-(*p'-n*-alkoxycinnamoyloxy) benzylidene anilines (2). Mol Cryst Liq Cryst. 1981;70(1-4): 279-287. DOI 10.1080/00268948108073594.

22. Lohar JM, Patel GH. Mesomorphic characteristics of thermotropic mesogens *p-p'*-disubstituted phenyl cinnamates i: *p*-(*p'*-n-alkoxycinnamoyloxy)-acetophenones. Mol Cryst Liq Cryst. 1981;74(1-4):19–24. DOI 10.1080/00268948108073691.

23. Lohar JM, Mahsru U. Study of Anisotropic Phase Transitions of Some New Mesogenic Esters: Methyl p-(p'-n-Alkoxycinnamoyloxy) benzoates. Indian J Chem -Section A. 1981; 20(02):125-128.

24. Urs MSR, Sadashiva BK. New Compounds with re-entrant nematic phases. Mol Cryst Liq Cryst. 1982;72(7-8):227-231. DOI 10.1080/01406568208084684

25. Arai K, Satoh H. Liquid crystalline phase- formation behavior of cellulose cinnamate. J. Appl. Polym. Sci. 1992;45(3):387-390. DOI 10.1002/app.1992.070450302.

26. Vora RA, Rajput SJ. Binary mesogenic systems comprised of ester mesogens and non-mesogens. Mol Cryst Liq Cryst. 1991;209(1):265-277. DOI 10.1080/00268949108036201.

27. Kasthuraiah N, Sadashiva BK, Krishnaprasad S, et al. Synthesis and mesomorphic properties of some esters of *trans*-4-n-alkoxycinnamic and *trans*-4-n-alkoxy-α-methylcinnamic acids exhibiting ferroelectric and antiferroelectric phases. Liq Cryst. 1998;24(5):639–45. DOI 10.1080/026782998206740.

28. Kashyap D, Patel S, Prajapati V, et al. Effect of the linking unit on the calamitic-shaped liquid crystal: a comparative study of two homologous series of benzoate and cinnamate linked compounds. Mol Cryst Liq Cryst. 2019;681(1):58-70. DOI 10.1080/15421406.2019.1652009

29. Thaker BT, Kanojiya JB. Mesomorphic properties of liquid crystalline compounds with biphenyl moiety containing azo-ester, azo-cinnamate central linkages and different terminal group. Liq Cryst. 2011;38(8):1035-1055. DOI 10.1080/02678292.2011.594525.

30. Patel RB, Chauhan ML, Doshi AV. Synthesis and Study of New Homologous Series of Mesogens: *n*-Butyl-*p*-(*p'-n*-alkoxy cinnamoyloxy) Cinnamates. Der Pharma Chemica. 2010;2(6): 157-164

31. Patel RB, Doshi AV. Synthesis and study of a new homologous series of Cis Cinnamate Esters of Mesogens: *n*-Hexyl-*p*- (*p'-n*-alkoxy cinnamoyloxy) Cinnamates, Der Pharma Chemica. 2011;3(1): 338-348.

32.   Patel HB, Doshi AV. Synthesis and mesomorphic properties of a novel ester homologous series: 4-(4'-*n*-Alkoxybenzoyloxy) benzyl cinnamates. Mol Cryst Liq Cryst. 2015;606(1): 56-65. DOI 10.1080/15421406.2014.915627.

33.   Oriol L, Piñol M, Serrano JL, et al.Synthesis, characterization and photoreactivity of liquid crystalline cinnamates, J. Photochem. Photobiol. A 2003;155(1-3):37-45. DOI 10.1016/S1010-6030(02)00367-2.

34.   Kawatsuki N, SakashitaS, Takatani K, et al.Synthesis, characterization and photoreaction of side- chain liquid- crystalline polymers comprising cinnamoyl biphenyl mesogen, Macromolecular Chemistry and Physics. 1996;197(6):1919-1935. DOI 10.1002/macp.1996.021970612.

35.   Zhang L, Sun X, Peng Z, et al. A novel liquid crystals photoalignment layer-by-layer self-assembled film fabricated with long side-chain cinnamate polyelectrolyte. Liq Cryst. 2011;38(8):989-994. DOI 10.1080/02678292.2011.589538.

36.   Wei P, Wang YP, Xia YM, He Y, Wang YM. Synthesis and properties of novel photocrosslinkable aromatic-aliphatic liquid crystal copolyesters based on poly (ethylene glycol) and cinnamic acid. Liquid Crystals. 2019;46(2):176-84. DOI 10.1080/02678292.2018.1482507.

37.   Dmochowska E, Bombalska A, Kula P. Synthesis and mesomorphic properties of four ring, rod-like fluorene derivatives - the influence of the lateral substitution on mesomorphic properties of 2,7-bis(4-alkylphenyl)-fluorenes. Liquid Crystals. 2020;47(1):17-27. DOI 10.1080/02678292.2019.1622047.

38.   Zhu G, Wang F, Liu WJ, Gong XJ, Geng PF, Gao ZW, Wang YH. Synthesis of photosensitive polyimide for liquid crystal alignment under non-polarised UV ageing lamp irradiation and a study on the possible mechanism of alignment. Liquid Crystals. 2020;47(4):489-99. DOI 10.1080/02678292.2019.1658816.

39.   Yu HL, Zhu G, Wang YH. Preparation of polyimide alignment films with high photosensitivity and low solid content. Liquid Crystals. 2021. DOI10.1080/02678292.2020.1799446.

40.   Bubnov A, Cigl M, Sedlackova N, Pociecha D, Bohmova Z, Hamplova V. Self-assembling behaviour of new functional photosensitive cinnamoyl-based reactive mesogens. Liquid Crystals, 2021. DOI 10.1080/02678292.2020.1783586.

41.   Hung YH, Liu CY, Chen WC, Liu JH. Thermal and optical properties of amphitropic liquid crystals derived from cholesterol and cinnamic acid. Liquid Crystals 2021. DOI 10.1080/02678292.2020.1795737.

42.   Prajapati AK, Thakkar V, Bonde N. New mesogenic homologous series of Schiff base cinnamates comprising naphthalene moiety. Mol Cryst Liq Cryst. 2003;393(1):41–8. DOI 10.1080/10587250307066.

43.   Chiang YH, Ames AE, Gaudiana RA, et al. Study of tails in smectic liquid crystals. I. The effect of fluorocarbon/hydrocarbon ether tails on phenyl ester biphenyl cores. Mol Cryst Liq Cryst. 1991;208(1):85-98. DOI 10.1080/00268949108233946.

44.   Chiang YH, Ames AE, Nieman A. Studies of tails in smectic liquid crystals. II. The effect of a butoxyethoxyethoxy tail [1]. Mol Cryst Liq Cryst Sci Technol Sect a Mol Cryst Liq Cryst. 1998;312(1):95-99. DOI 10.1080/10587259808042433.

45.   Wu SL, Lai FS. Synthesis and ferroelectric properties of new chiral liquid crystals derived from (S)-lactic acid with alkoxyethanols. Liq Cryst. 2005;32(10):1243-1249. DOI 10.1080/02678290500139799.

46.   Vora RA, Prajapati AK. Low melting smectogenic esters. J. Mys. Univ. Secn. B. 1994;33A:61-68.

47.   Vora RA, Prajapati AK. New mesogenic homologous series of α-methylcinnamates. Proc Indian Acad Sci Chem Sci. 2001;113(2):95-102.

48.   Prajapati AK, Pandya HM. Azomesogens containing an ethoxyethyl terminal chain: Synthesis and characterization. Liq Cryst. 2004;31(6):889-894. DOI 10.1080/02678290410001697558.

49.   Prajapati AK, Pandya HM. Azomesogens with methoxyethyl tail: Synthesis and characterization. J Chem Sci. 2005;117(3):255-261.

50.   Prajapati AK, Bonde N. L. Mesogenic Schiff's Base Esters with a Methoxyethyl Tail, Mol Cryst Liq Cryst. 2007; 461: 15-28. DOI 10.1080/15421400600914882.

51.   Prajapati A. K., Sharma H. C., Chudgar N. K., Synthesis of new mesogenic homologous series with broken alkoxy chain. Mol Cryst Liq Cryst.2001;364:815-823. DOI 10.1080/10587250108025053.

52.   Prajapati AK, Bonde NL, Patel HN. Mesogenic Schiff's base ester with chloroethyl tail. Phase Transitions. 2005;78(6):507-513. DOI 10.1080/01411590500188876.

53.   Prajapati AK, Patel HN. Mesogenic cinnamate with ethoxyethyl tail. my science. 2006;1(6):105-114.

54.   Prajapati AK, Patel HN. Mesogenic cinnamates with a substituted ethyl terminal chain. Liq Cryst. 2007;34(8):903-910. DOI 10.1080/02678290701243846.

55.   Manohar R, Gupta S, Prajapati A K, et al. Dielectric relaxation study of two different mesogenic cinnamates with a substituted ethyl terminal chain. Mol Cryst Liq Cryst. 2011;548(1):86-95. DOI 10.1080/15421406.2011.590370.

56.   Vogel AI, Furniss BS. Vogel's Textbook of Practical Organic Chemistry. 5th ed. London: Longman Scientific & Technical; 1989.

57.   Vyas GN, Shah NM. Organic Synthesis Collective, Vol. IV, revised edn., John Wiley and Sons, New York, 1963; 39: p836

58.   Gray GW, Jones JB. Mesomorphism and chemical constitution. Part II. The trans-p-n-alkoxycinnamic acids. J. Chem. Soc. 1954;1467-1470. DOI 10.1039/JR9540001467.

59.   Dave JS, Vora RA. Mesomorphic behaviour of the cholesteryl esters-i: p-n-alkoxybenzoates of cholesterol, Liquid Crystals and Ordered Fluids. Edited by J. F. Johnson and R. S. Porter, Plenum Press; New York (NY): 1970; p 477-487.

60.   Koshti R, Vyas A, Patel HN, Prajapati AK. Mesogenic homologous series with a butoxyethyl terminal chain. Liq. Cryst. 2021. DOI 10.1080/02678292.2021.1902580

61.   Gray GW. Molecular structure and properties of liquid crystals. London and New York (NY): Academic Press; 1962.
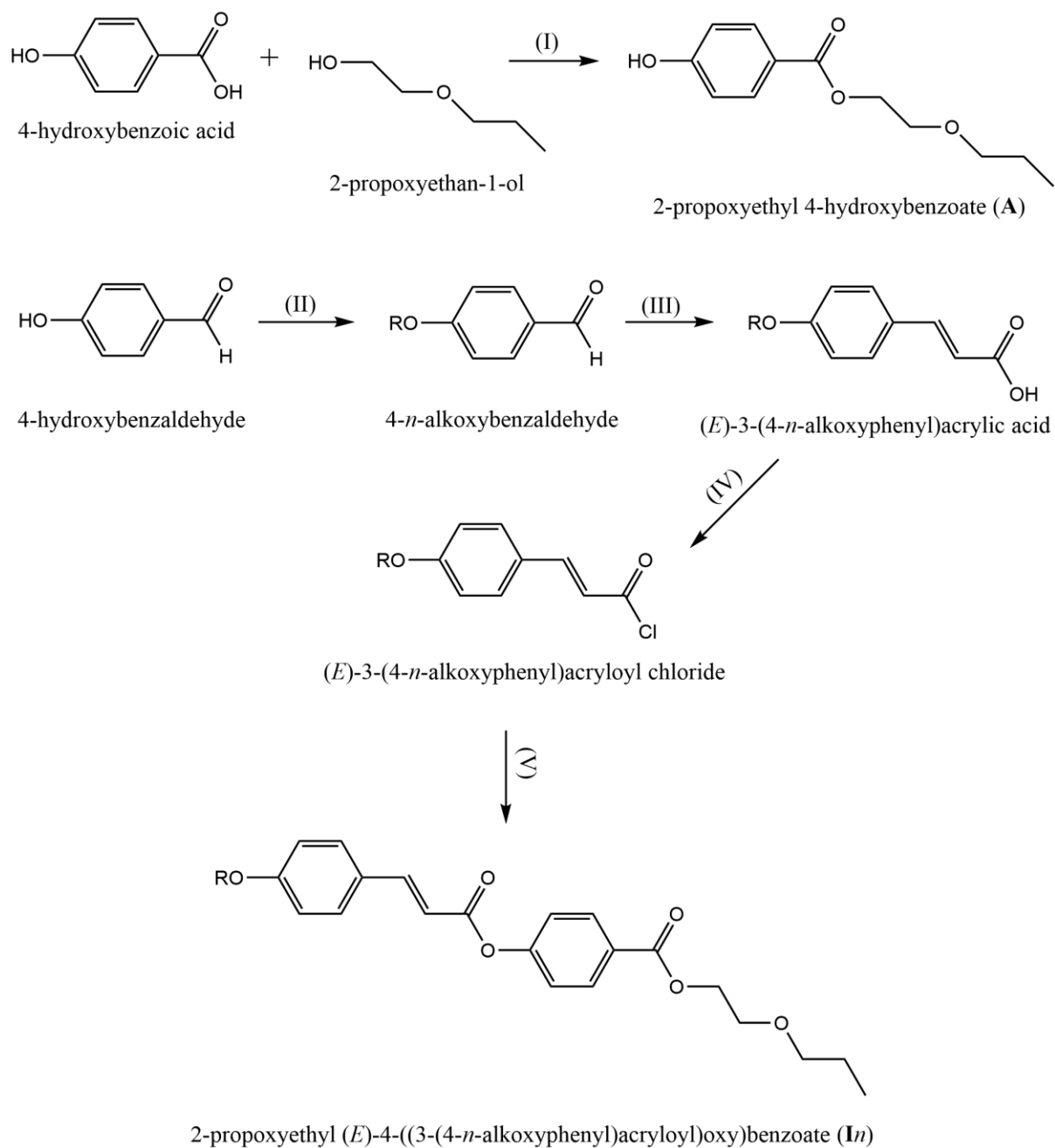
Scheme 1: Where, R= -C$_n$H$_{2n+1}$ (*n*=1 to 8,10,12,14,16 & 18)
Reagents & conditions: (i) Conc.H$_2$SO$_4$ (ii) R-Br, KOH, Methanol (iii) Malonic acid, Dry pyridine, Pipyridine (iv) Excess SOCl$_2$ (v) (**A**) in Dry pyridine, cold 1:1 HCl.

Table 1: Transition temperatures (ºC) of the series I compound

Compound No.	R= -C$_n$H$_{2n+1}$ *n* =	Cr		SmA		N		I
1	*1*	•	138			•	(111)	•

2	*2*	•	134			•	(108)	•
3	*3*	•	129			•	(104)	•
4	*4*	•	73	•	91	•	106	•
5	*5*	•	88	•	104	•	121	•
6	*6*	•	87	•	116			•
7	*7*	•	86	•	114			•
8	*8*	•	77	•	118			•
9	*10*	•	85	•	110			•
10	*12*	•	83	•	111			•
11	*14*	•	82	•	109			•
12	*16*	•	81	•	106			•

()= monotropic value; Cr=crystalline solid; SmA=smectic A phase; N=nematic phase; I=isotropic liquid phase; •=phase exists.

Table-2   Elemental analysis of butyloxy, octyloxy and dodecyloxy derivatives.

Sr.No.	Molecular Formula	Elements %Calculated (% found),		
		C	H	O
1	$C_{25}H_{30}O_6$	70.40(70.38)	7.09(6.99)	22.51(22.59)
2	$C_{29}H_{38}O_6$	72.17(72.11)	7.94(7.81)	19.89(19.81)
3	$C_{33}H_{46}O_6$	73.57(73.47)	8.61(8.70)	17.82(17.87)

Table 3: Enthalpy change, entropy change and normalized entropy of the series I*4* by DSC

Compound	Transition	Peak temp./℃	ΔH/kJmol^{-1}	ΔS/Jmol^{-1} K^{-1}
I4	Cr-SmA	72.88	61.1349	0.1767
	SmA-N	90.27	0.4279	0.0012
	N- I	105.44	0.9951	0.0026

Table1: 4 Comparison of the phase transition temperatures, smectic A \mesophase range and comparative molecular structures of compounds I*10*, A to F.

I10	83	111	28		C$_4$
A	94	133	39		C$_4$
B	78	125	47		C$_3$
C	62	70	08		C$_5$
D	86	117	31		C$_4$
E	60	87	27		C$_4$
F		49	67	18	C$_4$

2-propoxyethyl (*E*)-4-((3-(4-(dodecyloxy)phenyl)acryloyl)oxy)benzoate (I*12*)

2-methoxyethyl (*E*)-4-((3-(4-(dodecyloxy)phenyl)acryloyl)oxy)benzoate

2-chloroethyl (*E*)-4-((3-(4-(dodecyloxy)phenyl)acryloyl)oxy)benzoate

4-((2-methoxyethoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate

2-ethoxyethyl (*E*)-4-((3-(4-(dodecyloxy)phenyl)acryloyl)oxy)benzoate

2-butoxyethyl (*E*)-4-((3-(4-(dodecyloxy)phenyl)acryloyl)oxy)benzoate

4-((2-ethoxyethoxy)carbonyl)phenyl 4-(dodecyloxy)benzoate

FIgure 1:The phase behavior for Series I

Figure 2. Microphotograph of focal conic texture of SmA mesophase (Series I; *n*=14) at 80
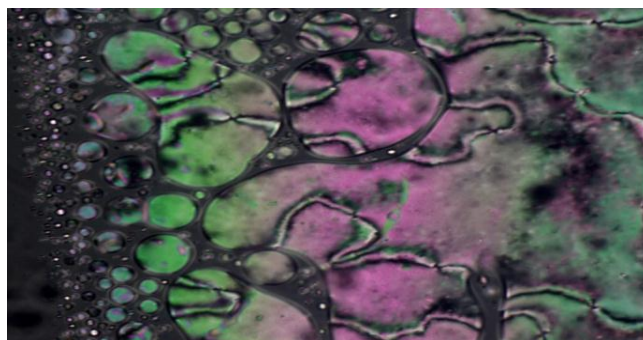
°C on cooling
Figure 3. Microphotograph of focal conic texture of Nematic mesophase (Series I; *n*=4) at 95 °C.
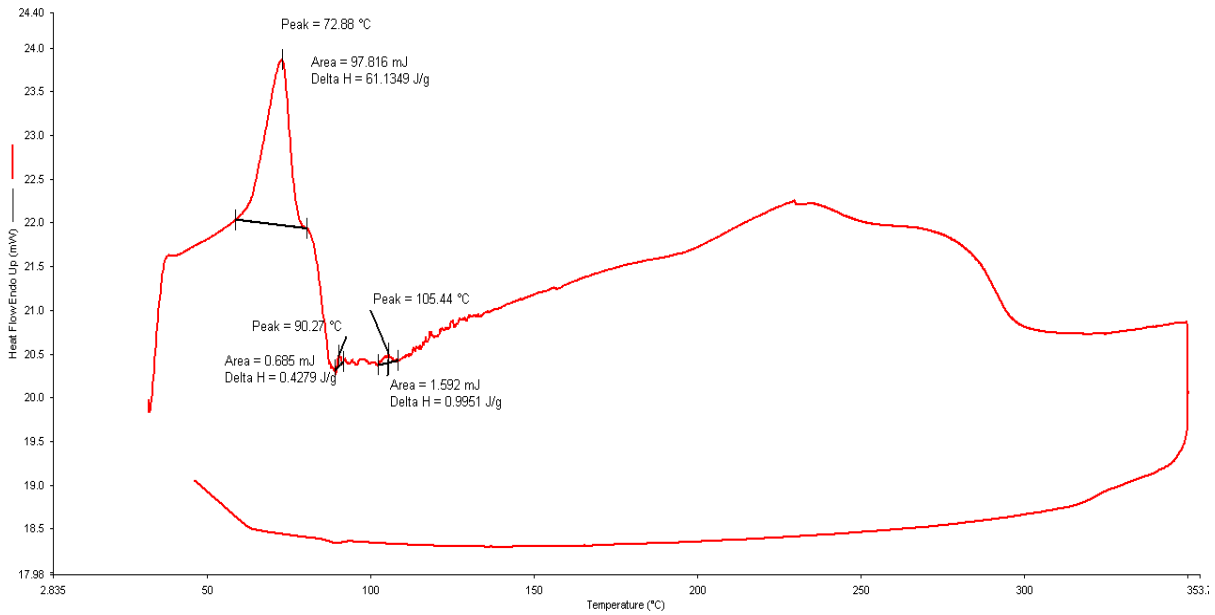
Figure 4: DSC Thermogram of series I (*n*=4)
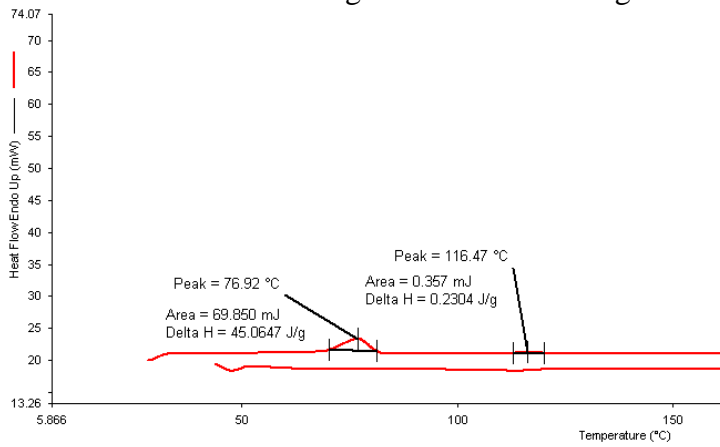
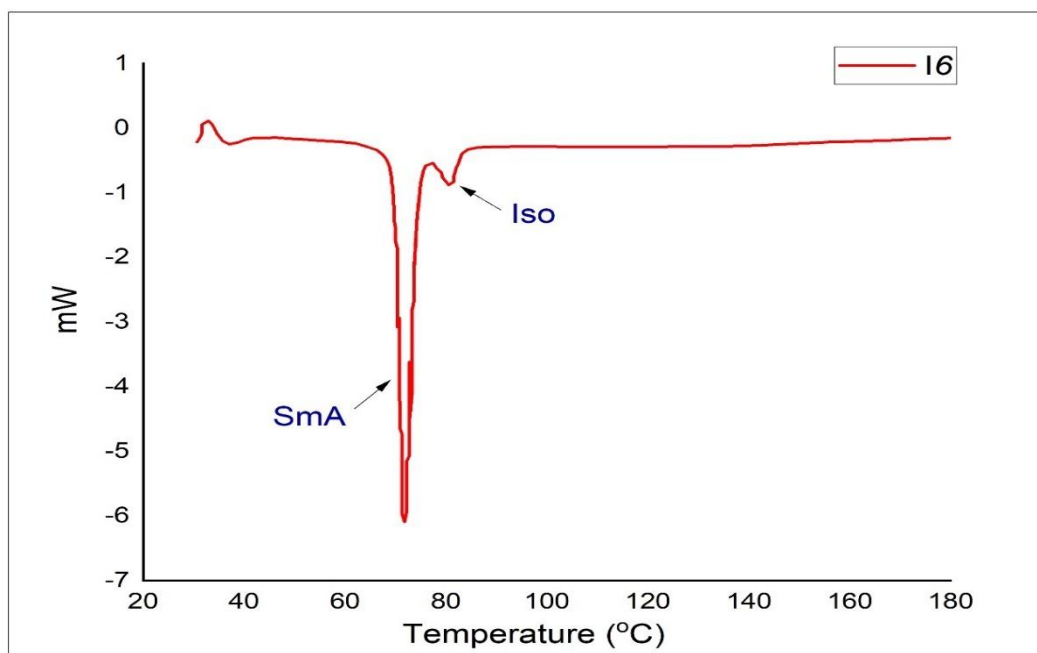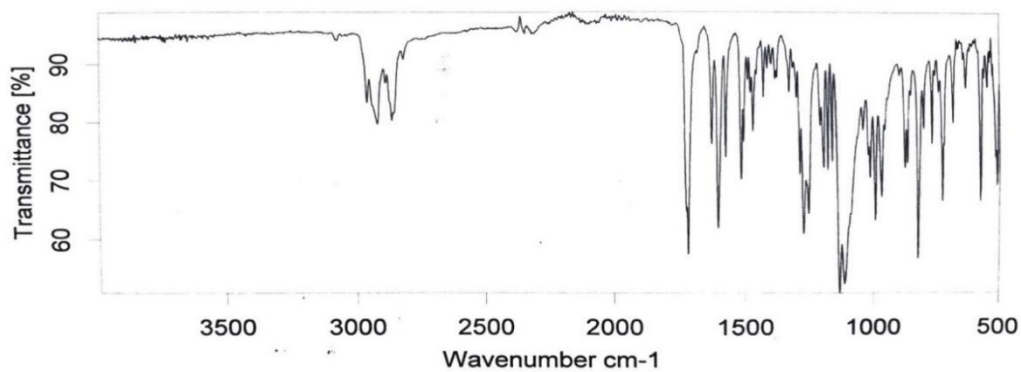Figure 5: DSC Thermogram of series I (*n*=8)
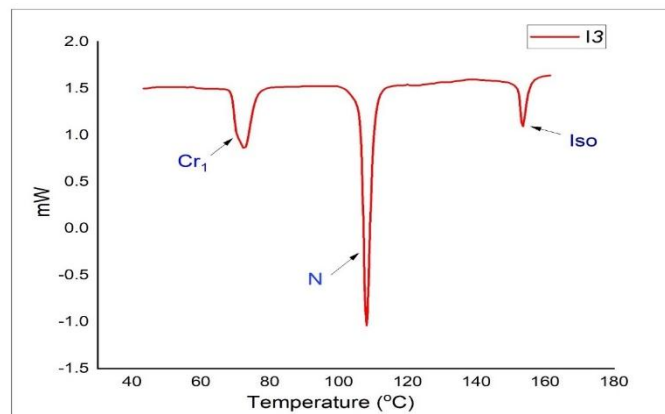
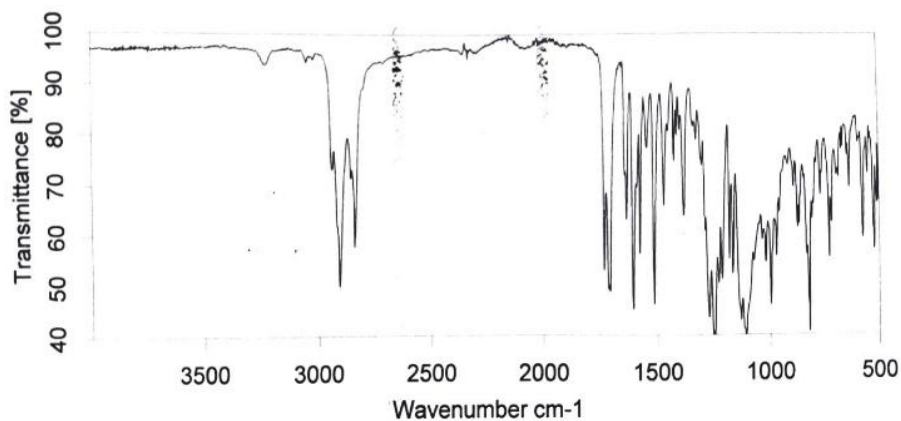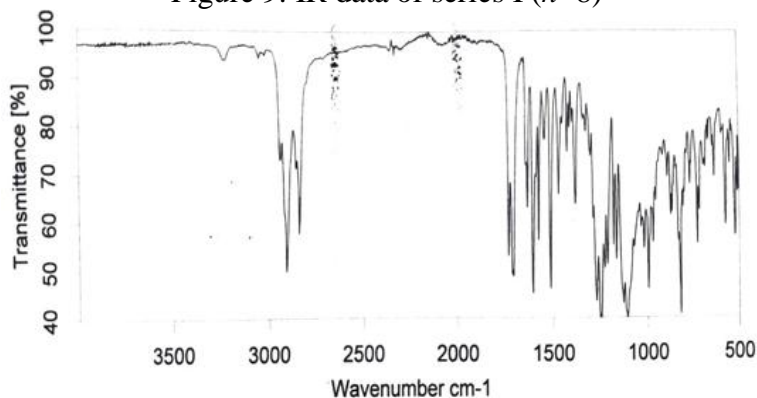Figure 6: DSC Thermogram of series I (*n*=3)

Figure 7: DSC Thermogram of series I (*n*=6)

IR Spectrum (KBr) $V_{max/Cm}^{-1}$: 2919, 2852, 1726 (-COO-), 1705, 1627 (-CH=CH-), 1600, 1509, 1467, 1248, 1104, 832.

Figure 8: IR data of series I (*n*=4)

. IR Spectrum (KBr) $V_{max/Cm}^{-1}$: 2919, 2852, 1726 (-COO-), 1705, 1627 (-CH=CH-), 1600, 1509, 1467, 1248, 1104, 832.

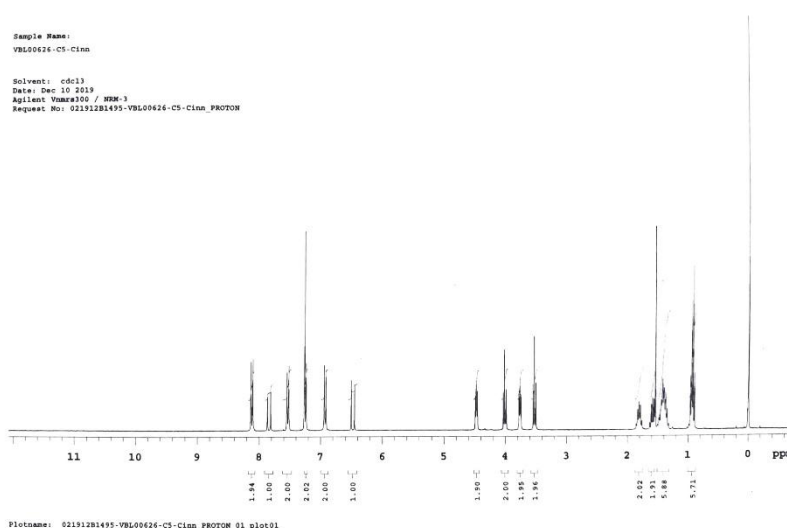Figure 9: IR data of series I (*n*=8)

^{1}HNMR Spectrum (400 MHz, CDCl$_3$): δ 0.88 (t, 3H, -CH$_3$), 1.26-1.37 (m, 10H, 5X-CH$_2$), 1.59-1.66(m, 5H,2H, of Ar-O-C-CH$_2$& 3H of (-O-C-C-CH$_3$), 3.47-3.78m (m, 4H of -CH$_2$-O-CH$_2$), 3.99.0 (t, 2H of Ar-O-CH$_2$), 4.47 (t, 2H, -COOCH$_2$), 6.47(d, 1H, -ArCH=), 6.92 (d, 2H, ArH), 7.24-7.33 (m, 2H or ArH), 7.53-7.55 (d, 2H, ArH),7.82-7.86 (d,1H, =CH-COO), 8.13 (d, 2H, ArH)

Figure 10: NMR data of series I (*n*=8)
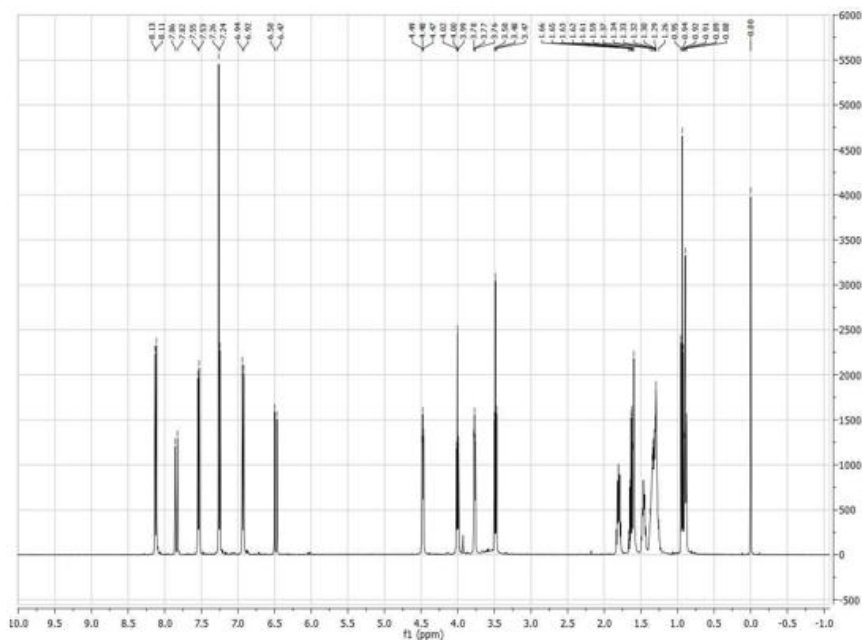
^{1}HNMR Spectrum (400 MHz, CDCl$_3$): δ 0.87 (t, 3H, -CH$_3$), 1.46-1.58 (m, 10H, 5X-CH$_2$), 1.61-1.82(m, 5H,2H, of Ar-O-C-CH$_2$& 3H of (-O-C-C-CH$_3$), 3.47-3.78m (m, 4H of -CH$_2$-O-CH$_2$), 3.99.0 (t, 2H of Ar-O-CH$_2$), 4.47 (t, 2H, -COOCH$_2$), 6.47(d, 1H, -ArCH=), 6.92 (d, 2H, ArH), 7.24-7.33 (m, 2H or ArH), 7.53-7.55 (d, 2H, ArH),7.82-7.86 (d,1H, =CH-COO), 8.13 (d, 2H, ArH)

Figure 11: NMR data of series I (*n*=12)

IR, ¹H-NMR & Elemental analysis data

2-Propyloxyethyl 4-((*E*)-3-(4-*n*-pentyloxyphenyl) acryloyloxy) benzoate (**I5**)
. IR Spectrum (KBr) $V_{max/Cm}^{-1}$: 2941, 2854, 1720 (-COO-), 1624 (-CH=CH-), 1601, 1511, 1463, 1271, 1124, 820.
¹H-NMR Spectrum (400 MHz,CDCl₃) δ in ppm: 0.92 (t, J=7.8 Hz, 6H, 2 X -CH₃), 1.34-1.47 (m, 6H, 3 X -CH₂-), 1.59-1.83 (m, 4H, 2 X -CH₂-), 3.52 (t, J=6.8 Hz, 2H, -O-CH₂-), 3.76 (t, J=6.4 Hz, 2H, -CH₂-O-), 4.00 (t, J=6.5 Hz, 2H, Ar-O-CH₂-), 4.47 (t, J=6.4 Hz, 2H, -COO-CH₂-), 6.50 (d, J=15.8 Hz, 1H, Olefinic H), 7.26 (d, J=8.8 Hz, 2H, ArH), 7.54 (d, J=8.7 Hz, 2H, ArH), 7.81 (d, J=15.7 Hz, 1H, Olefinic H), 8.10 (d, J=8.8 Hz, 2H, ArH). Yield: 69%

2-Propoxyethyl 4-((*E*)-3-(4-*n*-pentyloxyphenyl) acryloyloxy) benzoate

Figure 12: IR spectrum of series I (n=5)
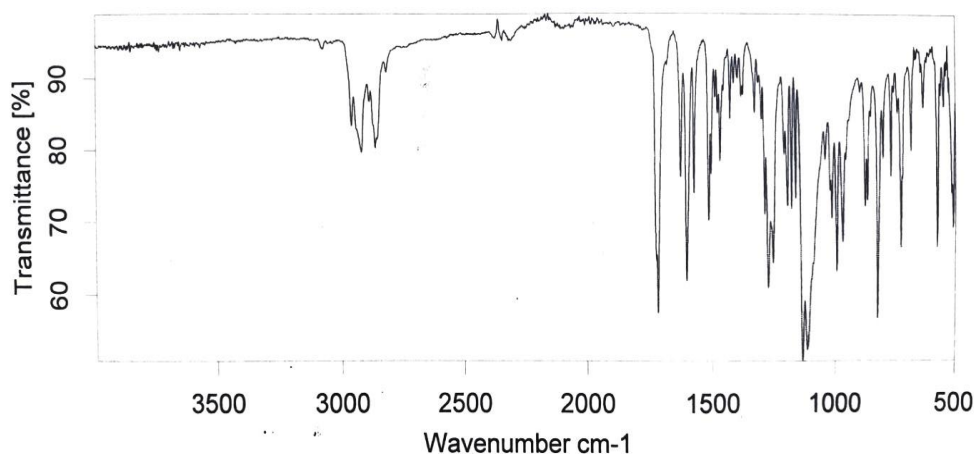
Figure 13: ^{1}H-NMR Spectrum of series I5.

2-Propyloxyethyl 4-((*E*)-3-(4-*n*-hexyloxyphenyl) acryloyloxy) benzoate (**I***6*)
UV-Vis. (THF) λ_{max}: 320 and 232 nm. IR Spectrum (KBr) $V_{max/Cm}^{-1}$: 2931, 2864, 1715 (-COO-), 1626 (-CH=CH-), 1601, 1513, 1469, 1275, 1114, 825. ^{1}H -NMR Spectrum (400 MHz,CDCl$_3$) δ in ppm: 0.93 (t, J=7.4 Hz, 6H, 2 X -CH$_3$), 1.37-1.46 (m, 8H, 4 X -CH$_2$-), 1.58-1.80 (m, 4H, 2 X -CH$_2$-), 3.53 (t, J=6.6 Hz, 2H, -O-CH$_2$-), 3.77 (t, J=6.2 Hz, 2H, -CH$_2$-O-), 4.02 (t, J=6.4 Hz, 2H, Ar-O-CH$_2$-), 4.45 (t, J=6.4 Hz, 2H, -COO-CH$_2$-), 6.49 (d, J=15.7 Hz, 1H, Olefinic H), 6.94 (d, J=8.8 Hz, 2H, ArH), 7.26 (d, J=8.8 Hz, 2H, ArH), 7.54 (d, J=8.8 Hz, 2H, ArH), 7.85 (d, J=15.6 Hz, 1H, Olefinic H), 8.12 (d, J=8.8 Hz, 2H, ArH). Yield: 67%
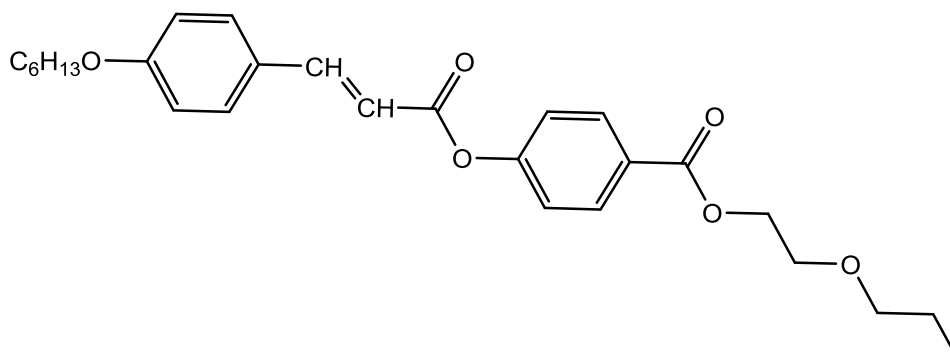
2-Propoxyethyl 4-((*E*)-3-(4-*n*-hexyloxyphenyl) acryloyloxy) benzoate .

Figure 14: IR spectrum of series I *(n=6)*.
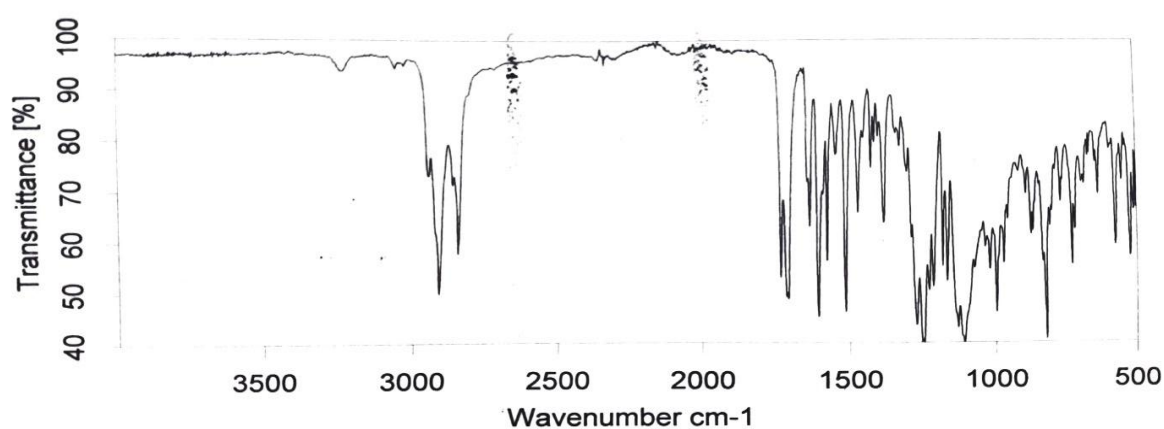
Figure 15: ^{1}H-NMR Spectrum of series I *(n=6)*.
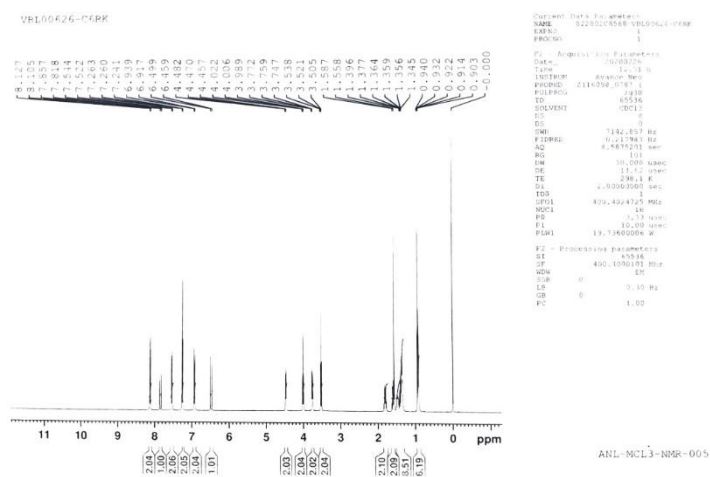
2Propyloxyethyl 4-((*E*)-3-(4-*n*-decyloxyphenyl) acryloyloxy) benzoate **I** (n=10)
UV-Vis. (THF) λ_{max}: 320 and 232 nm. IR Spectrum (KBr) $V_{max/Cm}^{-1}$: 2919, 2852, 1726 (-COO-), 1705, 1627 (-CH=CH-), 1600, 1509, 1467, 1248, 1104, 832. ^{1}H -NMR Spectrum (400 MHz, CDCl$_3$) δ in ppm: 0.94 (t, J=7.6 Hz, 6H, 2 X -CH$_3$), 1.25-1.45 (m, 16H, 8 X -CH$_2$-), 1.58-1.80 (m, 4H, 2 X -CH$_2$-), 3.50 (t, J=6.8 Hz, 2H, -O-CH$_2$-), 3.76 (t, J=6.4 Hz, 2H, -CH$_2$-O-), 4.01 (t,

J=6.4 Hz, 2H, Ar-O-CH$_2$-), 4.43 (t, J=6.8 Hz, 2H, -COO-CH$_2$-), 6.93 (d, J=8.8 Hz, 2H, ArH), 7.25 (d, J=8.8 Hz, 2H, ArH), 7.54 (d, J=8.8 Hz, 2H, ArH), 7.85 (d, J=15.7 Hz, 1H, Olefinic H), 8.10 (d, J=8.6 Hz, 2H, ArH). Yield: 66%
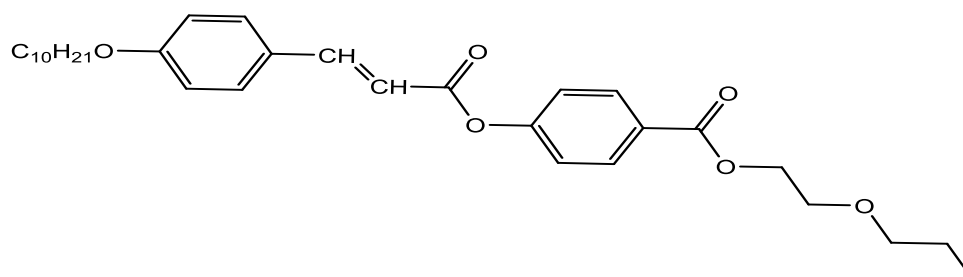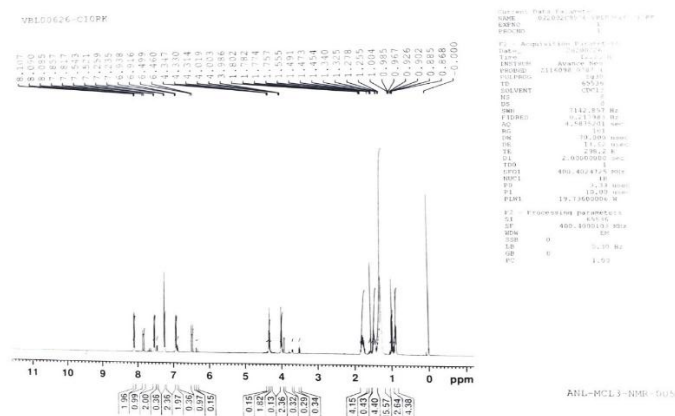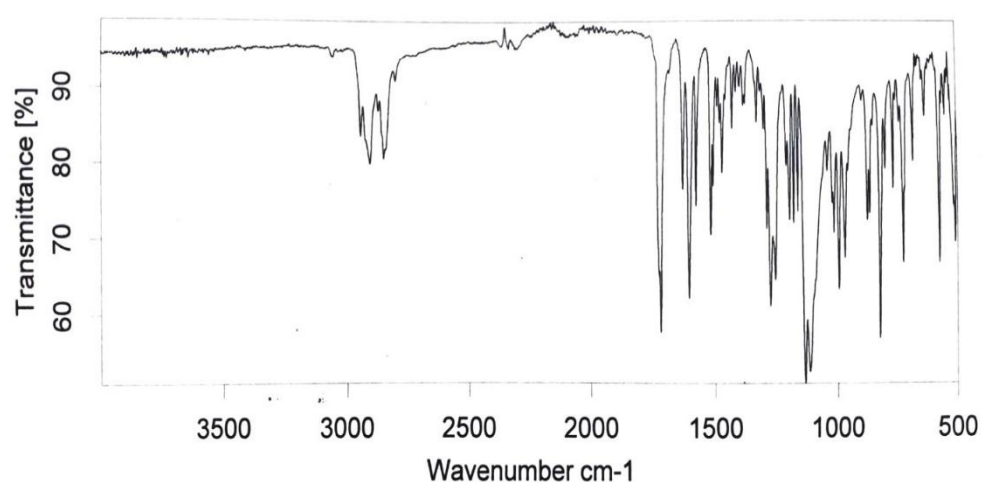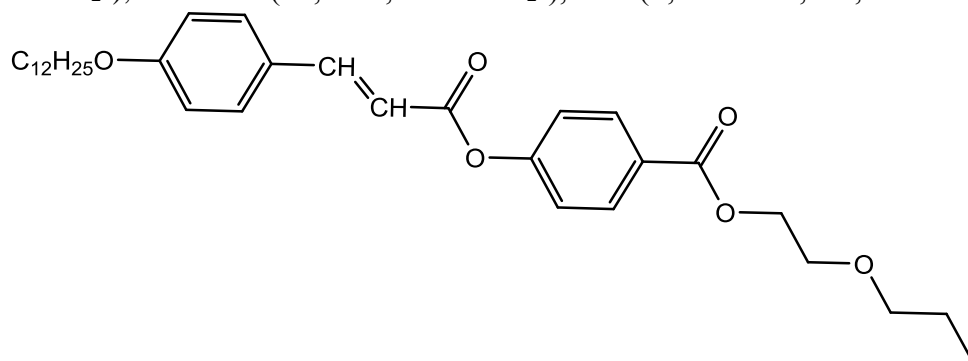

Figure 16: IR spectrum of series I(n=10).

Figure 17: ^{1}H-NMR Spectrum of series I (*n*=10).

2-Butoxyethyl 4-((*E*)-3-(4-*n*-dodecyloxyphenyl) acryloyloxy) benzoate (**I***12*)
UV-Vis. (THF) λ$_{max}$: 320 and 232 nm. IR Spectrum (KBr) V$_{max/Cm}$$^{-1}$: 2914, 2850, 1730 (-COO-), 1711, 1632 (-CH=CH-), 1604, 1512, 1470, 1246, 1108, 821.^{1}H -NMR Spectrum (400 MHz,CDCl$_3$) δ in ppm: 8.10 (d, J=8.6 Hz, 2H, ArH), 7.84 (d, J=15.8 Hz, 1H, Olefinic H), 7.55 (d, J=8.8 Hz, 2H, ArH), 7.24 (d, J=8.6 Hz, 2H, ArH), 6.93 (d, J=8.8 Hz, 2H, ArH), 6.49 (d, J=15.6 Hz, 1H, Olefinic H), 4.45 (t, J=6.8 Hz, 2H, -COO-CH$_2$-),4.02 (t, J=6.4 Hz, 2H, Ar-O-

CH$_2$-), 3.76 (t, J=6.4 Hz, 2H, -CH$_2$-O-), 3.50 (t, J=6.8 Hz, 2H, -O-CH$_2$-), 1.55-1.80 (m, 4H, 2 X -CH$_2$-), 1.26-1.47 (m, 20H, 10 X -CH$_2$-), 0.94 (t, J=7.2 Hz, 6H, 2 X -CH$_3$). Yield: 65%

2-Propoxyethyl 4-((*E*)-3-(4-*n*-dodecyloxyphenyl) acryloyloxy) benzoate.

Figure 18: IR spectrum of series I (*n*=12*)*.