CHAPTER 3

SYNTHESIS AND CHARACTERISATION OF SIDE CHAIN POLYMERS WITH NLO GROUPS
3 Introduction

This chapter describes the synthesis of a new class of photocross-linkable NLO active side chain monomers and polymers based on unsymmetrically disubstituted donor-acceptor end functionalised charge transferable benzylidene cycloalkanone units. These function as NLO active mesogens and photoactive centres. These active molecules were linked to various polymerisable monomers like methacrylate, acrylate, maleimide and 4-chloromethyl styrene units through 2-6 methylene spacer units and subsequently polymerised in various organic solvents by free radical polymerisation. All monomers and polymers were characterised by spectroscopic techniques. Thermal transitions were studied by differential scanning calorimetry (DSC) and mesophases were observed by polarised light optical microscopy (POM). Some of the monomers and corresponding polymers, which are essentially based on push-pull bis(benzylidene) cycloalkanones, show mesophases. Transition temperatures were observed to decrease with increasing spacer length. Photolysis of the low molar mass liquid crystalline (LC) benzylidene cycloalkanones revealed that there are two kinds of photo reactions in these systems, the EZ isomerisation and $2 \pi + 2 \pi$ photocyclo-addition. The EZ photo-isomerisation in the LC phase disturbs the parallel stacking of the mesogens resulting in the transition from the LC phase to the isotropic phase. This also happens on heating the sample for several hours. The photo-reaction involving the $2\pi + 2\pi$ addition of the benzylidene alkanone units in the polymer results in the crosslinking of the chains, lowering of solubilities and loss of mesomorphic character.

Liquid Crystalline polymers have attracted considerable interest due to the unique combination of specific properties of polymer and anisotropic nature of liquid crystals. Among the polymers having side chains, mesogenic NLO active and photocrosslinkable liquid crystalline units in their structure are useful in fabricating anisotropic network and thin films.
information storage devices\textsuperscript{11,12} nonlinear optical devices\textsuperscript{13,14} aligned membranes for permeation of gases and drugs etc.\textsuperscript{15,16} During the last decade increasing attention has been paid to the design of new side chain liquid crystalline polymers (SCLCPs) with a high second order nonlinearity for applications in electro-optics. In this respect mesogenic groups having π-conjugated chains capped at both the ends with an electron donor and acceptor respectively as pendant groups in SCLCPs have been studied.\textsuperscript{17} For instance, incorporation of strong donor-acceptor functional groups to a bis(benzylidene) cycloalkanone greatly enhances its nonlinear optical properties\textsuperscript{18} mainly due to hyper-polarisability. However, production of useful NLO materials requires the supramolecular organisation of the molecules in SCLCP. For this we carried out an electric poling technique (corona poling) presented in Chapter 4. Providing NLO materials with liquid crystalline properties might also trigger the well defined supramolecular organisation.

A side chain liquid crystalline polymer comprises of three structural units: a polymer back-bone, a flexible spacer and a mesogenic core. The role of the flexible spacer is to decouple to some extent the relative tendencies of the mesogenic groups to self-assemble from those of the polymer and hence endowing upon the polymer a duality of properties.

Different design strategies have been worked out to synthesise polymers with desirable NLO properties. Typically the NLO phores attach themselves covalently into amorphous or liquid crystalline polymers. Crosslinkable polymers were used to enhance the orientational stability of the NLO phores.\textsuperscript{19,20} The photo-chemistry of these polymers is interesting from the topochemical aspects since the photo-reaction takes place in ordered LC media.\textsuperscript{21,22}

Among the two major classes of LCPs, namely, the main chain and the side chain LCPs, the latter exhibits lower transition temperature and tends to harden into glassy state with the retention of LC order when cooled from LC state. Besides, the side chain liquid crystalline
polymers (SCLCPs) have good solubility in common organic solvents displaying rich variety of LC phases and having quick response to an external field due to their low melt viscosity. Hence, side chain LCPs are widely studied for the applications in electro-optical devices.23

This chapter presents a new class of various mesogenic/non-mesogenic charge transferable NLO active unsymmetrically disubstituted push-pull end capped benzylidene cycloalkanone groups which are linked through a polymethylene spacer of repeat units n = 2, 3, 4 and 6 to various polymerisable monomeric units like methacrylate, acrylate, maleimide and 4-chloromethyl styrene. The monomers were isolated, purified, characterised and polymerised. Some of the new side chain Polymers so synthesised display mesophases and their thermal properties were found to be related to flexibility, nature of the backbone, spacer length, central cycloalkanone ring and end functional groups.

3.1 Experimentation

3.1.1 Materials

Maleimide, epichlorohydrin, methacryloylchloride, diethyl azodicarboxylate, triethyl amine, triphenyl phosphene, 4-chloromethyl styrene, acryloylchloride were used as received from Aldrich Chemical Co., USA. Tetrabutylammonium hydrogen sulphate (TBAH) was received from Fluka. Boron trifluoride etherate was distilled under nitrogen atmosphere. Azobisisobutyronitrile (AIBN) was recrystallised from methanol and dried under reduced pressure. The solvents used for the column chromatography was distilled before use.

3.1.2 Instrumentation

Proton and 13C NMR spectra were recorded on a Bruker ACF 200 MHz NMR spectrometer using CDCl3 and DMSO-d6 as solvents and tetramethylsilane (TMS) as internal standard. IR-spectra were recorded with Shimadzu IR-470 spectrometer. UV-Vis spectra were
recorded on a Shimadzu UV-Vis 160 spectrophotometer using chlorinated solvents. Mass spectra were recorded on Fermington mass spectrometer. Molecular weights were recorded in Knauer vapour pressure osmometer using recrystallised benzil as standard.

The transition temperatures were measured using a DuPont 1090 differential thermal analyser with a DSC 910 attachment and Mettler DSC-30 coupled to TA 4000 data station. Optical observations were made using a Olympus polarising microscope equipped with a Mettler FP-52 hot stage and FP-5 control unit.

3.2 2-[4-(ω-Methacryloyloxy alkyl-1-oxy) benzylidene]-6/5-(4-cyano/nitro benzylidene) cycloalkanones

All monomers were synthesised by a procedure involving the esterification of 2-[4-(ω-hydroxy alkyl-1-oxy) benzylidene]-6/5-(4-cyano/nitro benzylidene) cycloalkanones with methacryloyl chloride in the presence of an inhibitor to prevent polymerisation during the derivatisation reaction. The synthesis of 2-[4-(ω-hydroxy alkyl-1-oxy) benzylidene]-6/5-(4-cyano/nitro benzylidene) cycloalkanones are presented in Section 2.6. Scheme 3.1 outlines the synthesis of the described monomer and polymer.

3.2.1 2-[4-(6-Methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone (10a)

1.52 g (3.5 mmol) of 2-[4-(6-hydroxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone, prepared according to procedure in Section 2.6.12, was dissolved in 50 mL of dry dichloromethane (DCM) to which 3 mL of dry triethylamine (TEA) was added. The solution was then cooled to 0 °C and then 0.47 g (4.5 mmol) of methacryloyl chloride was added dropwise. The resulting mixture was stirred at room temperature for 30 hours and subsequently diluted with 60 mL of DCM. The organic phase was washed first with 30 mL of cold 5% hydrochloric acid, then twice with cold 5% sodium hydroxide solution and finally with cold
water. The organic phase was dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the resulting crude was column chromatographed on silica-gel column using 12%

**Scheme 3.1**

where \( Y = \text{CN, NO}_2 \); \( R = \text{Nil, CH}_2 \), \( \text{CH-CH}_3 \); and \( n = 2, 3, 4, 6 \).

acetone in petroleum ether as eluent to get pure product. This was further purified by recrystallisation from a mixture of benzene/hexane (50/50, V/V) to yield 1.412 g (80%) of 2-[4-(6-methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone. The IR, \(^1\text{H} \) NMR, \(^{13}\text{C} \) NMR and mass data are presented in support of the synthesised structures. A number of other methacrylates were synthesised, isolated and purified by the same procedure and analysed for purity. The analysis data on these methacrylates are presented in Sections 3.2.2 to 3.2.16. The yield, UV absorption maxima and cut-off, transition temperatures observed using
polarised optical microscopy and differential scanning calorimetry are compiled in Tables 3.1, 3.2 and 3.3 respectively.

IR (KBr) : 2930, 1719, 1662, 1597, 1554, 1506, 1467, 1338, 1240, 1159, 838 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)) : \(\delta\) 8.25 (d, 2H), 7.8 (ss, 2H), 7.55 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.2 (t, 2H), 4.0 (t, 2H), 2.95 (tt, 4H), 1.95 (s, 3H), 1.8 to 1.4 (m, 10H).

\(^13\)C NMR (CDCl\(_3\)) : \(\delta\) 18.28, 22.7, 25.7, 28.3, 28.4, 28.5, 29.06, 64.5, 67.9, 114.5, 123.5, 125.1, 128.1, 130.7, 130.8, 132.5, 133.2, 133.3, 136.4, 138.0, 139.5, 142.6, 147.0, 159.8, 167.3, 189.18.

Mass m/e : M\(^+(504)\), 504(18%), 486(40%), 474(5%), 334(21%), 318(15%), 288(10%), 278(9%), 260(4%), 215(6%), 185(4%), 128(12%), 107(13%), 83(22%), 69(100%), 55(96%).

Analysis calculated for C\(_{30}\)H\(_{33}\)O\(_6\)N

\[ C, 71.42\% \quad H, 6.54\% \quad N, 2.77\% \]

Found

\[ C, 71.68\% \quad H, 6.84\% \quad N, 2.80\% \]

Figure 3.1 DSC thermogram of 2-[4-(6-methacryloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone (Heating rate 10\(^{\circ}\)C/min)
3.2.2 2-[4-(4-Methacryloyloxy butyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone (10 b)

IR (KBr) : 2930, 1719, 1662, 1597, 1554, 1506, 1467, 1338, 1240, 1159, 838 cm⁻¹.

¹H NMR (CDCl₃) : δ 8.25 (d, 2H), 7.8 (ss, 2H), 7.55 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.25 (t, 2H), 4.05 (t, 2H), 2.95 (tt, 4H), 1.95 (s, 3H), 1.8 to 1.4 (m, 6H).

3.2.3 2-[4-(2-Methacryloyloxy ethyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone (10 c)

IR (KBr) : 2930, 1719, 1662, 1597, 1554, 1506, 1467, 1338, 1240, 1159, 838 cm⁻¹.

¹H NMR (CDCl₃) : δ 8.25 (d, 2H), 7.8 (ss, 2H), 7.55 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.55 (t, 2H), 4.3 (t, 2H), 2.95 (tt, 4H), 1.97 (s, 3H), 1.8 (m, 2H).

Analysis calculated for C₂₆H₂₅O₆N  C, 69.64 %  H, 5.58%  N, 3.12%
found  C, 69.62%  H, 5.64%  N, 3.15%

3.3.4 2-[4-(6-Methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone (10 d)

IR (KBr) : 2930, 2225, 1708, 1662, 1597, 1554, 1503, 1469, 1414, 1249, 838 cm⁻¹.

¹H NMR (CDCl₃) : δ 7.8 (s, 1H), 7.75 (s, 1H), 7.7 (d, 2H), 7.55 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.15 (t, 2H), 4.04 (t, 2H), 2.9 (t, 4H), 1.95 (s, 3H), 1.9 to 1.4 (m, 10H).

¹³C NMR (CDCl₃) : δ 18.17, 22.6, 25.6, 28.2, 28.4, 28.9, 64.4, 67.7, 111.3, 114.4, 125.0, 128.0, 130.0, 131.8, 132.3, 133.25, 133.5, 136.3, 137.7, 138.8, 140.4, 159.6, 167.1, 188.9.

Mass m/e : M⁺ (484), 484(28%), 414(16%), 323(100%), 314(37%), 296(20%), 281(6%), 267(40%), 253(14%), 240(12%), 228(11%), 208(20%), 194(21%), 180(20%), 166(31%), 154(36%), 140(80%), 127(65%), 116(44%), 101(20%), 89(21%), 77(29%), 73(21%), 69(42%), 55(46%).

3.2.5 2-[4-(4-Methacryloyloxy butyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone (10 e)

IR (KBr) : 2934, 2225, 1708, 1662, 1597, 1554, 1503, 1469, 1414, 1249, 838 cm⁻¹.

¹H NMR (CDCl₃) : δ 7.8 (s, 1H), 7.75 (s, 1H), 7.7 (d, 2H), 7.55 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.15 (t, 2H), 4.05 (t, 2H), 2.9 (t, 4H), 1.95 (s, 3H), 1.9 to 1.4 (m, 6H).
3.2.6 2-[4-(2-Methacryloyloxy ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone (10 f)

IR (KBr) : 2934, 2225, 1708, 1662, 1597, 1554, 1503, 1469, 1414, 1249, 838 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)) : \(\delta\) 7.84 (ss, 2H), 7.75 (d, 2H), 7.65 (d, 2H), 7.55 (d, 2H), 7.45 (d, 2H), 7.0 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.55 (t, 2H), 4.3 (t, 2H), 2.9 (t, 4H), 1.95 (s, 3H), 1.85 (m, 2H).

\(^13\)C NMR (CDCl\(_3\)) \(\delta\) : 18.4, 23.0, 28.6, 28.68, 63.1, 66.2, 11.8, 114.9, 118.8, 126.3, 129.1, 130.7, 132.3, 132.6, 134.1, 135.4, 136.2, 138.0, 139.0, 140.9, 159.4, 167.4, 184.8.

Mass: m/e: M\(^+\) (427), 427(16%), 358(12%), 323(76%), 298(19%), 281(8%), 267(21%), 256(15%), 240(14%), 228(13%), 215(10%), 208(11%), 190(14%), 185(12%), 180(19%), 171(11%), 166(22%), 154(31%), 140(92%), 127(74%), 113(100%), 69(82%), 55(34%).

3.2.7 2-[4-(6-Methacryloyloxy hexyl-1-oxy) benzylidene]-5-(4-nitro benzylidene) cyclopentanone (10 g)

IR (KBr) : 2945, 1699, 1642, 1592, 1569, 1509, 1478, 1173, 1002, 832 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)) : \(\delta\) 8.3 (d, 2H), 7.7 (d, 2H), 7.6 (s, 2H), 7.55 (s, 1H), 7.52 (d, 2H), 6.95 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.2 (t, 2H), 4.0 (t, 2H), 3.15 (s, 4H), 1.95 (s, 3H), 1.9 to 1.4 (m, 8H).

Mass m/e : M\(^+\) (489), 489(30%), 472(29%), 459(6%), 420(4%), 320(100%), 304(68%), 274(30%), 258(6%), 215(11%), 202(12%), 185(11%), 169(10%), 157(25%), 152(12%), 146(22%), 131(54%), 115(65%), 107(41%).

3.2.8 2-[4-(4-Methacryloyloxy butyl-1-oxy) benzylidene]-5-(4-nitro benzylidene) cyclopentanone (10 h)

IR (KBr) : 2945, 1699, 1642, 1592, 1569, 1509, 1478, 1173, 1002, 832 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)) : \(\delta\) 8.3 (d, 2H), 7.7 (d, 2H), 7.65 (s, 1H), 7.55 (s, 1H), 7.52 (d, 2H), 6.95 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.2 (t, 2H), 4.0 (t, 2H), 3.15 (s, 4H), 1.95 (s, 3H), 1.9 to 1.4 (m, 4H).

3.2.9 2-[4-(2-Methacryloyloxy ethyl-1-oxy) benzylidene]-5-(4-nitro benzylidene) cyclopentanone (10 i)

IR (KBr) : 2945, 1699, 1642, 1592, 1569, 1509, 1478, 1173, 1002, 832 cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\)) : \(\delta\) 8.3 (d, 2H), 7.75 (d, 2H), 7.62 (s, 2H), 7.6 (d, 2H), 6.95 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.15 (t, 2H), 4.0 (t, 2H), 3.15 (s, 4H), 1.95 (s, 3H).
3.2.10 2-[4-(3-Methacryloyloxy propyl-1-oxy) benzylidene]-5-(4-cyano benzylidene) cyclopentanone (10 j)

IR (KBr): 2945, 2225, 1704, 1642, 1592, 1509, 1478, 1173, 1002, 832 cm⁻¹.

¹H NMR (CDCl₃): δ 7.7 (d, 4H), 7.5 (ss, 2H), 7.45 (d, 2H), 6.95 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.35 (t, 2H), 4.1 (t, 2H), 3.1 (s, 4H), 2.15 (m, 2H), 1.95 (s, 3H).

3.2.11 2-[4-(2-Methacryloyloxy ethyl-1-oxy) benzylidene]-5-(4-cyano benzylidene) cyclopentanone (10 k)

IR (KBr): 2945, 2225, 1704, 1642, 1592, 1509, 1478, 1173, 1002, 832 cm⁻¹.

¹H NMR (CDCl₃): δ 7.7 (d, 4H), 7.5 (ss, 2H), 7.45 (d, 2H), 6.95 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.35 (t, 2H), 4.1 (t, 2H), 3.1 (s, 4H).

3.2.12 2-[4-(6-Methacryloyloxy hexyl-1-oxy) benzylidene]-5-(4-cyano benzylidene) cyclopentanone (10 l)

IR (KBr): 2945, 2225, 1704, 1642, 1592, 1509, 1478, 1173, 1002, 832 cm⁻¹.

¹H NMR (CDCl₃): δ 7.7 (d, 4H), 7.5 (ss, 2H), 7.45 (d, 2H), 6.95 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.35 (t, 2H), 4.1 (t, 2H), 3.1 (s, 4H), 1.95 to 1.54 (m, 8H).

3.2.13 4-Methyl-2-[4-(6-methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone (10 m)

IR (KBr): 2875, 1708, 1662, 1598, 1561, 1508, 1449, 1423, 1253, 861, 836 cm⁻¹.

¹H NMR (CDCl₃): δ 8.3 (d, 2H), 7.8 (s, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.0 (d, 2H), 6.15 (s, 1H), 5.6 (s, 1H), 4.55 (t, 2H), 4.3 (t, 2H), 3.0 (tt, 2H), 2.55 (tt, 2H), 1.95 (s, 3H), 1.8 to 1.4 (m, 9H), 1.1 (d, 3H).

3.2.14 4-Methyl-2-[4-(4-methacryloyloxy butyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone (10 n)

IR (KBr): 2875, 1708, 1662, 1598, 1561, 1508, 1449, 1423, 1253, 861, 836 cm⁻¹.

¹H NMR (CDCl₃): δ 8.3 (d, 2H), 7.8 (s, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.0 (d, 2H), 6.15 (s, 1H), 5.6 (s, 1H), 4.55 (t, 2H), 4.3 (t, 2H), 3.0 (tt, 2H), 2.55 (tt, 2H), 1.95 (s, 3H), 1.8 to 1.4 (m, 5H), 1.1 (d, 3H).

3.2.15 4-Methyl-2-[4-(2-methacryloyloxy ethyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone (10 o)

IR (KBr): 2875, 1708, 1662, 1598, 1561, 1508, 1449, 1423, 1253, 861, 836 cm⁻¹.
$^1$H NMR (CDCl$_3$) : $\delta$ 8.3 (d, 2H), 7.8 (s, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.1 (d, 2H), 6.15 (s, 1H), 5.6 (s, 1H), 4.55 (t, 2H), 4.3 (t, 2H), 3.0 (tt, 2H), 2.55 (tt, 2H), 1.95 (s, 3H), 1.8 (m, 1H), 1.1 (d, 3H).

$^{13}$C NMR (CDCl$_3$) : $\delta$ 21.6, 29.2, 36.4, 36.5, 62.9, 66.1, 114.7, 123.6, 126.1, 128.8, 130.8, 132.5, 133, 133.7, 136.0, 138.1, 142.7, 147.2, 159.3, 167.2, 189.2.

3.3.16 3-Methyl-2-[4-(3-methacryloyloxy propyl-l-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone (10 p)

IR (KBr) : 2938, 2225, 1714, 1689, 1597, 1571, 1504, 1419, 1309, 1249, 1160, 1103, 1040, 1001, 830 cm$^{-1}$.

$^1$H NMR (CDCl$_3$) : $\delta$ 7.7 (ss, 2H), 7.6 (d, 2H), 7.5 (d, 2H), 7.4 (d, 2H), 6.9 (d, 2H), 6.1 (s, 1H), 5.5 (s, 1H), 4.35 (t, 2H), 4.1 (t, 2H), 3.45 (t, 1H), 2.9 (m, 2H), 2.15 (m, 2H), 1.95 (s, 3H), 1.8 (m, 2H), 1.25 (d, 3H).

Mass m/e : M$^+$ (455), 455(16%), 386(32%), 328(34%), 312(18%), 213(18%), 185(9%), 165(14%), 141(22%), 127(82%), 115(30%), 105(52%), 99(48%), 85(26%), 77(18%), 69(82%), 57(100%).

Analysis calculated for C$_{29}$H$_{29}$O$_4$N

Found

Table 3.1 Yields, absorption, optical microscopy and DSC analysis of 2-[4-(o-methacryloyloxy alkyl-l-oxy) benzylidene]-6-(4-cyano/nitro benzylidene) cyclohexanones

<table>
<thead>
<tr>
<th>D</th>
<th>A</th>
<th>C. Code</th>
<th>Yield, %</th>
<th>$\lambda_{\text{max}}$</th>
<th>$\lambda_{\text{cut-off}}$</th>
<th>Heating $^\circ$C</th>
<th>Cooling $^\circ$C</th>
<th>$T_m$ $^\circ$C</th>
<th>$T_i$ $^\circ$C</th>
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<tr>
<td>mO-(CH$_2$)$_n$O-</td>
<td>-NO$_2$</td>
<td>10 a</td>
<td>84</td>
<td>354</td>
<td>426</td>
<td>N-I: 120-140</td>
<td>N-C: 90-80</td>
<td>125</td>
<td>130</td>
</tr>
<tr>
<td>mO-(CH$_2$)$_n$O-</td>
<td>-NO$_2$</td>
<td>10 b</td>
<td>82</td>
<td>358</td>
<td>430</td>
<td>N-I: 132-145</td>
<td>N-C: 100-95</td>
<td>140</td>
<td>145</td>
</tr>
<tr>
<td>mO-(CH$_2$)$_n$O-</td>
<td>-NO$_2$</td>
<td>10 c</td>
<td>80</td>
<td>352</td>
<td>428</td>
<td>N-I: 144-150</td>
<td>N-C: 112-108</td>
<td>149</td>
<td>153</td>
</tr>
<tr>
<td>mO-(CH$_2$)$_n$O-</td>
<td>-CN</td>
<td>10 d</td>
<td>85</td>
<td>356</td>
<td>440</td>
<td>N-I: 110-120</td>
<td>N-C: 85-94</td>
<td>110</td>
<td>115</td>
</tr>
<tr>
<td>mO-(CH$_2$)$_n$O-</td>
<td>-CN</td>
<td>10 e</td>
<td>81</td>
<td>348</td>
<td>436</td>
<td>N-I: 120-131</td>
<td>N-C: 92-98</td>
<td>123</td>
<td>128</td>
</tr>
<tr>
<td>mO-(CH$_2$)$_n$O-</td>
<td>-CN</td>
<td>10 f</td>
<td>83</td>
<td>345</td>
<td>435</td>
<td>N-I: 129-137</td>
<td>N-C: 101-108</td>
<td>131</td>
<td>138</td>
</tr>
</tbody>
</table>

where D is donor, A is acceptor, C is compound, POM is polarised optical microscopy, DSC is differential scanning calorimetry, m is methacrylate group, $T_m$ is melting temperature and $T_i$ is isotropic temperature.
Table 3.2 Yields, absorption, optical microscopy and DSC analysis of 2-[4-(ω-methacryloyloxy alkyl-1-oxy) benzylidene]-5-(4-cyano/nitro benzylidene) cyclopentanones

<table>
<thead>
<tr>
<th>D</th>
<th>A</th>
<th>C. Code</th>
<th>Yield %</th>
<th>( \lambda_{\text{max}} ) nm</th>
<th>Cutoff ( \lambda ) nm</th>
<th>Heating ( °C )</th>
<th>Cooling ( °C )</th>
<th>( T_m ) °C</th>
<th>( T_i ) °C</th>
</tr>
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<tbody>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>-NO₂</td>
<td>10 g</td>
<td>75</td>
<td>389</td>
<td>475</td>
<td>N-I: 160-176</td>
<td>N-C: 132-120</td>
<td>170</td>
<td>180</td>
</tr>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>-NO₂</td>
<td>10 h</td>
<td>72</td>
<td>382</td>
<td>470</td>
<td>N-I: 178-184</td>
<td>N-C: 146-135</td>
<td>179</td>
<td>187</td>
</tr>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>-NO₂</td>
<td>10 i</td>
<td>76</td>
<td>379</td>
<td>468</td>
<td>N-I: 189-196</td>
<td>N-C: 148-139</td>
<td>192</td>
<td>199</td>
</tr>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>-CN</td>
<td>10 i</td>
<td>70</td>
<td>380</td>
<td>482</td>
<td>N-I: 175-188</td>
<td>N-C: 130-118</td>
<td>174</td>
<td>184</td>
</tr>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>-CN</td>
<td>10 j</td>
<td>72</td>
<td>368</td>
<td>455</td>
<td>N-I: 186-200</td>
<td>N-C: 147-134</td>
<td>188</td>
<td>193</td>
</tr>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>-CN</td>
<td>10 k</td>
<td>67</td>
<td>375</td>
<td>470</td>
<td>N-I: 190-195</td>
<td>N-C: 150-141</td>
<td>192</td>
<td>199</td>
</tr>
</tbody>
</table>

where D is donor, A is acceptor, C is compound, POM is polarised optical microscopy, DSC is differential scanning calorimetry, m is methacrylate group, \( T_m \) is melting temperature and \( T_i \) is isotropic temperature.

Table 3.3 Yields, absorption, optical microscopy and DSC analysis of 4/3-methyl-2-[4- (ω-methacryloyloxy alkyl-1-oxy)benzyldiene]-6-(4-cyano/nitro benzylidene) cyclohexanones

<table>
<thead>
<tr>
<th>D</th>
<th>A</th>
<th>C. Code</th>
<th>yield, %</th>
<th>( \lambda_{\text{max}} ) nm</th>
<th>Cutoff ( \lambda ) nm</th>
<th>DSC ( T_m ) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>-NO₂</td>
<td>10 m</td>
<td>75</td>
<td>389</td>
<td>475</td>
<td>115</td>
</tr>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>-NO₂</td>
<td>10 n</td>
<td>69</td>
<td>382</td>
<td>470</td>
<td>130</td>
</tr>
<tr>
<td>mO-(CH₂)₆-O-</td>
<td>CN(C*)</td>
<td>10 o</td>
<td>74</td>
<td>368</td>
<td>455</td>
<td>123</td>
</tr>
</tbody>
</table>

where D is donor, A is acceptor, C is compound, DSC is differential scanning calorimetry, m is methacrylate group, \( T_m \) is melting temperature.
3.3 Poly\{2-[4-(6-(methacryloyloxy alkyl-1-oxy) benzylidene]-6-(4-nitro/cyano benzylidene) cyclalkanone

The homopolymerisation of these monomers were carried out using azobisisobutyronitrile (AIBN) as initiator.\(^{25}\) The general experimental procedure is given below.

3.3.1 Poly\{2-[4-(6-methacryloyloxy hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene)cyclo hexanone\} [SCLCPNO\(_2\)CH\(_6\)]

0.40 g of 2-[4-(6-methacryloyloxy hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene) cyclo-hexanone, prepared by procedure in Section 3.2.1, dissolved in 20 mL of dry tetrahydrofuran (THF) and 1 mol\% of AIBN were added in to a glass sample tube. The solution was degassed by several freeze-pump-thaw cycles under vacuum and sealed. The sample was then kept at 70 °C for 48 hours and subsequently opened and poured into 80 mL of methanol. The precipitated solid was separated by filtration and purified by repeated precipitation from chloroform into methanol.

\(\text{IR (KBr) : 2935, 1740, 1666, 1599, 1454, 1370, 1247, 1138, 1012, 828 cm}^{-1}\).

\(\text{\(^1H \text{NMR (CDCl}_3 \) : 8 8.25 (d, 2H), 7.8 (s, 2H), 7.6 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 4.0 (s, 4H), 2.9 (s, 4H), 2.0 to 1.5 (m, 12H), 1.05 (s, 3H).}\)

\(\text{Analysis calculated for C}_{30}\text{H}_{33}\text{O}_6\text{N} \quad \text{C, 71.42\%} \quad \text{H, 6.54\%} \quad \text{N, 2.77\%}\)

\(\text{Found} \quad \text{C, 71.68\%} \quad \text{H, 6.84\%} \quad \text{N, 2.87\%}\)
Figure 3.2 DSC thermogram of poly{2-[4-(6-methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene)cyclohexanone} [SCLCPNO_2CH_6] (Heating rate 10 °C/min)

3.3.2 Poly{2-[4-(4-methacryloyloxy butyl-1-oxy)benzylidene]-6-(4-nitro benzylidene) cyclohexanone} [SCLCPNO_2CH_4]

IR (KBr) : 2935, 1740, 1666, 1599, 1454, 1370, 1247, 1138, 1012, 828 cm⁻¹.

\( ^1H \) NMR (CDCl₃) : \( \delta 8.25 \) (d, 2H), 7.8 (s, 2H), 7.6 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 4.0 (s, 4H), 2.9 (s, 4H), 2.0 to 1.5 (m, 8H), 1.05 (s, 3H).

3.3.3 Poly{2-[4-(2-methacryloyloxy ethyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone} [SCLCPNO_2CH_2]

IR (KBr) : 2935, 1740, 1666, 1599, 1454, 1370, 1247, 1138, 1012, 828 cm⁻¹.

\( ^1H \) NMR (CDCl₃) : \( \delta 8.25 \) (d, 2H), 7.8 (s, 2H), 7.6 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 4.1 (s, 4H), 2.9 (s, 4H), 2.0 to 1.5 (m, 4H), 1.05 (s, 3H).

3.3.4 Poly{2-[4-(6-methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone} [SCLCPCNCH_6]

IR (KBr) : 2934, 2220, 1728, 1662, 1597, 1554, 1503, 1469, 1414, 1249, 838 cm⁻¹.

\( ^1H \) NMR (CDCl₃) : \( \delta 7.8 \) (s, 2H), 7.7 to 7.55 (d, 4H), 7.45 (d, 2H), 6.9 (d, 2H), 4.15 (s, 4H) 3.0 (s, 4H), 1.95 (s, 3H), 2.0 to 1.5 (m, 12H), 1.05 (s, 3H).
3.3.5 Poly{2-[4-(4-methacryloyloxy butyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone} [SCLPCNCNCH4]

IR (KBr): 2934, 2220, 1728, 1662, 1597, 1554, 1469, 1414, 1249, 838 cm⁻¹.

¹H NMR (CDCl₃): δ 7.8 (s, 2H), 7.7 to 7.55 (d, 4H), 7.45 (d, 2H), 6.9 (d, 2H), 4.15 (s, 4H), 3.0 (s, 4H), 1.95 (s, 3H), 2.0 to 1.5 (m, 8H), 1.05 (s, 3H).

3.3.6 Poly{2-[4-(2-methacryloyloxy ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone} [SCLPCCNCH2]

IR (KBr): 2934, 2223, 1728, 1662, 1597, 1554, 1503, 1469, 1414, 1249, 838 cm⁻¹.

¹H NMR (CDCl₃): δ 7.8 (s, 2H), 7.7 to 7.55 (d, 4H), 7.45 (d, 2H), 6.9 (d, 2H), 4.15 (s, 4H), 3.0 (s, 4H), 1.95 (s, 3H), 2.0 to 1.5 (m, 4H), 1.05 (s, 3H).

3.3.7 Poly{2-[4-(6-methacryloyloxy hexyl-1-oxy) benzylidene]-5-(4-cyano benzylidene) cyclopentanone} [SCLPCNCNCP6]

IR (KBr): 2934, 2223, 1730, 1658, 1597, 1554, 1503, 1469, 1414, 1249, 838 cm⁻¹.

¹H NMR (CDCl₃): δ 7.8 (s, 2H), 7.7 to 7.55 (d, 4H), 7.45 (d, 2H), 6.9 (d, 2H), 4.15 (s, 4H), 3.0 (s, 4H), 1.95 (s, 3H), 2.0 to 1.5 (m, 12H), 1.05 (s, 3H).

3.3.8 Poly{4-methyl-2-[4-(6-methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone} [SCP4HNO₂CH6]

IR (KBr): 2935, 1740, 1668, 1599, 1454, 1370, 1247, 1138, 1012, 828 cm⁻¹.

¹H NMR (CDCl₃): δ 8.25 (d, 2H), 7.8 (s, 2H), 7.6 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 4.2 (s, 4H), 2.9 (s, 4H), 2.0 to 1.5 (m, 12H), 1.05 (s, 6H).

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Yield</th>
<th>UV-vis nm</th>
<th>Mol. weight Mₙ</th>
<th>Transition temperatures °C</th>
<th>POM</th>
<th>DSC</th>
<th>T₄</th>
<th>T₅</th>
</tr>
</thead>
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<tr>
<td>SCLCPNO₂CH₂</td>
<td>24%</td>
<td>385</td>
<td>5800</td>
<td>N-1.112-136</td>
<td>54</td>
<td>162</td>
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<td></td>
</tr>
<tr>
<td>SCLCPNO₂CH₄</td>
<td>18%</td>
<td>380</td>
<td>4300</td>
<td>N-1.120-132</td>
<td>50</td>
<td>151</td>
<td></td>
<td></td>
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<tr>
<td>SCLCPNO₂CH₆</td>
<td>26%</td>
<td>390</td>
<td>5600</td>
<td>N-1.110-145</td>
<td>47</td>
<td>144</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4 Yields, molecular weight, UV-vis and thermal transition temperatures of poly{2-[4-(ω-methacryloyloxy alkyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanones}

where POM is polarised optical microscopy, DSC is differential scanning calorimetry, T₄ is glass transition temperature and T₅ is isotropic temperature.
Table 3.5  Yields, UV-Vis absorption, molecular weight and thermal transition temperatures of poly{2-[4-(co-methacryloyloxy alkyl-l-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanones}

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Yield</th>
<th>UV-vis nm</th>
<th>Mol. weight $M_n$</th>
<th>Transition temperatures $^0$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCLCPCNCH2</td>
<td>32%</td>
<td>389</td>
<td>5700</td>
<td>N-I: 98-114 38 118</td>
</tr>
<tr>
<td>SCLCPCNCH4</td>
<td>30%</td>
<td>386</td>
<td>3000</td>
<td>N-I: 89-105 42 112</td>
</tr>
<tr>
<td>SCLCPCNCH6</td>
<td>28%</td>
<td>374</td>
<td>4300</td>
<td>N-I: 88-96 34 96</td>
</tr>
</tbody>
</table>

where POM is polarised optical microscopy, DSC is differential scanning calorimetry, $T_g$ is glass transition temperature and $T_i$ is isotropic temperature.

Table 3.6  Yields, UV-Vis, molecular weight and thermal transition temperatures of poly{2-[4-(co-methacryloyloxy alkyl-l-oxy benzylidene]-5-(4-nitro benzylidene) cyclopentanones}

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Yield</th>
<th>UV-vis nm</th>
<th>Mol. weight $M_n$</th>
<th>Transition temperatures $^0$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCLCPNO2CP4</td>
<td>18%</td>
<td>395</td>
<td>6600</td>
<td>N-I: 134-145 48 158</td>
</tr>
<tr>
<td>SCLCPNO2CP6</td>
<td>26%</td>
<td>390</td>
<td>7500</td>
<td>N-I: 125-142 40 164</td>
</tr>
</tbody>
</table>

where POM is polarised optical microscopy, DSC is differential scanning calorimetry, $T_g$ is glass transition temperature and $T_i$ is isotropic temperature.

Table 3.7  Yields, molecular weight and thermal transition temperatures of poly{4-methyl-2-[4-(co-methacryloyloxy alkyl-l-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone}

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Yield</th>
<th>UV-vis nm $\lambda_{max}$</th>
<th>Mol. weight $M_n$</th>
<th>Transition temperatures $^0$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCLCPCN4MCH6</td>
<td>36%</td>
<td>385</td>
<td>7400</td>
<td>DSC Heating $T_g$ 35 $T_i$ 134</td>
</tr>
</tbody>
</table>

where $T_g$ is glass transition temperature and $T_i$ is isotropic temperature.
3.4 Thermal Properties

3.4.1 Monomers

Among the monomers, those with 4-methyl cyclohexanone in the central cycloalkanone ring (10 m-p) did not exhibit mesomorphic behaviour. Tables 3.1, 3.2 and 3.3 show the transition temperatures of 2-[4-(ω-methacryloyloxy alkyl-1-oxy) benzylidene]-6-(4-cyano/nitro benzylidene) cyclohexanones, 2-[4-(ω-methacryloyloxy alkyl-1-oxy) benzylidene]-5-(4-cyano/nitro benzylidene) cyclopentanones and 4/3-methyl-2-[4-(ω-methacryloyloxy alkyl-1-oxy)benzylidene]-6-(4-cyano/nitro benzylidene) cyclohexanones. Fig. 3.1 shows the DSC heating and cooling traces for the monomer 2-[4-(6-methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone. The first heating scan curve(a) showed an endotherm at 125 °C for the transition to nematic phase. Clear transition peaks were seen on cooling from the isotropic state. However, in polarising optical microscope (POM) studies, the isotropic to nematic transition was observed at 78 °C. The crystallisation endotherm during the second heating scan appeared at 120 °C. The newly formed crystallites then melt into nematic fluid at 124 °C and on further heating change over to an isotropic liquid at 140 °C. All monomers exhibit nematic mesophases are shown in annexure 1.

Clear trends were noticeable within the structurally similar systems. These were dictated by the flexible spacer length, the type of the central cycloaliphatic ring system and the substitution on it as well as the type of acceptor end groups. From the thermal data presented in Tables 3.1, 3.2 and 3.3 it can be inferred that 2-[4-(ω-methacryloyloxy alkyl-1-oxy) benzylidene]-6-(4-cyano/nitro benzylidene) cyclohexanones, 2-[4-(ω-methacryloyloxy alkyl-1-oxy) benzylidene]-5-(4-cyano/nitro benzylidene) cyclopentanones were liquid crystalline while 3-/4-methyl-2-[4-(ω-methacryloyloxy alkyl-1-oxy) benzylidene]-5-(4-cyano/nitro benzylidene)
cyclohexanones were normal crystals. With in each homologous series, the mesomorphic transition temperatures were seen to decrease with increasing spacer length. The nitro analogues displayed a higher transition temperature relative to the cyano. On shifting from a cyclohexanone central ring to cyclopentanone, the transition temperatures were seen to increase due to the planarity of the cyclopentanone ring. The presence of an additional methyl group in the cyclohexanone group provides just enough of additional disturbance to the already non-planar cyclohexanone that liquid crystallinity disappears, as seen for the monomers presented in Table 3.3.

The absorption of the NLO chromophore in Tables 3.1 to 3.3 are indicative of an electronic delocalisation between the donor and acceptor groups. The size and nature of the central cycloalkanone ring strongly affects the relative charge transfer absorption of the conjugated chain for the same spacer length and donor-acceptor groups. The absorption maxima for monomers with planar cyclopentanone central ring are red shifted, indicating that planarity of the structural moiety responsible for the conjugation between the donor and acceptor is of importance for polarisability as well.

3.4.2 Polymers

The yield, Uv absorbance, molecular weight and transition temperatures of the polymers are presented in Tables 3.4 to 3.7. All polymers except 4-methyl cyclohexanone analogues exhibit liquid crystallinity. These polymers did not show any tendency to crystallise. In comparison to the monomers, the LC Phase was stabilised in the polymers. Both the temperatures and the widths of the transitions were higher in the polymers. The DSC heating thermograms for these polymers were characterised by Tg above which the polymer changes over to the anisotropic fluid and the following endotherm was assigned for the anisotropic to isotropic
transition. Similarly, in the cooling scan, an exo-therm is seen for the isotropic to anisotropic phase change followed by a T_g, below which polymer chains lose their mobility and solidify retaining the anisotropic order. Fig. 3.2 shows the DSC heating and cooling traces for poly{2-[4-(6-methacryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone} [SCLCPNO_2CH6]. The first heating scan showed a T_g at 47 °C and small endotherm at 110 °C for the crystal to nematic phase. This is followed by endotherm at 142 °C for nematic to isotropic transition. Clear transition peaks were not seen on cooling from the isotropic state probably because of thermal curing reaction between exocyclic double bonds present in benzylidene cyclohexanones hooked to two adjacent chains. Additionally, isomerisms (eg. EZ and ZZ) are also known to occur at these temperatures. These isomerisms would disturb the planarity of the structure. However, in POM studies, the isotropic to nematic transition was observed at 115 °C. The sample on reheating shows transition to an isotropic liquid at 165 °C. The DSC of this reheated sample does not show any T_g. This confirms the thermal crosslinking of the polymer during the first heating. All polymers exhibit nematic mesophases in the first heating. The T_g of the polymers showed a decrease with increasing spacer length. However, no clear dependence of T_i on structure was noted.

All polymers crosslink at and above isotropic transition temperatures during the first DSC heating scan. The polymers in the as synthesised form were found to be crosslinked when DMSO was used as the polymerisation solvent and hence were not soluble. This may be due to the attack of highly reactive methacrylate radicals on the benzylidene exocyclic double bonds. Medium polarity enhances the unwanted side reactions and this may also lead to the crosslinking between chains resulting in the formation of a polymeric gel.

3.5 Photo-crosslinking study
The photolysis of the polymers was conducted in film form and analysed by UV-visible spectral studies. These films were cast from chloroform solution on to the outer surface of a 1 cm quartz plate. For the FT-IR measurements, a thin film of the polymer was formed on one side of a KBr pellet of 10 mm diameter and 0.5 mm thickness and was adjusted to get the absorbance between 0.05 and 0.10. The photochemical studies were carried out in a discontinuous mode. The samples were exposed to UV-irradiation from a 125 W medium pressure mercury lamp, kept at a distance of 15 cm from the sample for varying time intervals. The irradiated films were subsequently subjected to UV-vis and FT-IR spectral analysis.

Figure 3.3 shows the UV-visible spectral changes during the photo-irradiation of poly{2-[4-(6-methacryloyloxy hexyl-l-oxy)benzylidene]-6-(4-nitro benzylidene)cyclohexane} at 35 °C. Before irradiation, the UV-visible spectrum shows an absorption maxima at 365 nm corresponding to the \( \pi - \pi^* \) transition of donor-acceptor end functionalised bis(benzylidene) cyclohexanone entity. There is a gradual decrease in the intensity of the absorption band at 365 nm with increasing exposure time. After 25 minutes of irradiation, the film completely insoluble indicating that crosslinking has taken place. The extent of crosslinking was obtained by weighing the dried insoluble polymer after washing the irradiated film to remove uncrosslinked polymer. The extent of cross-linking after irradiating for 12 minutes was 70%. The DSC thermogram of the crosslinked polymer did not show any peaks or baseline shifts for the glass transition, indicating that the photo-crosslinking suppresses the thermal transitions in these polymers.

The absorbence at 365 nm (\( \lambda_{\text{max}} \)) slowly decreases while an absorbence peak starts to appear at 246 nm and its intensity keeps on increasing indicating a gradual loss in extended \( \Pi \)
conjugation in the system. The $2\Pi + 2\Pi$ cycloaddition reaction consumes the C=C bonds and this decreases the intensity of the $\Pi-\Pi'$ transition at the later stages of the photolysis.

![Graph showing changes in UV-spectral characteristics during photolysis](image)

**Figure 3.3** Changes in the UV-spectral characteristics during the photolysis of films of poly{2-[4-(6-methacyroyloxy hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene) cyclohexanone} at $35^\circ C$

### 3.6 2-[4-N-(\(\omega\)-Methacyroyloxy alkyl)-N-methyl amino benzylidene]-5/6-(4-nitro/ cyano benzylidene) cycloalkanone

The two monomers were synthesised by a procedure involving the esterification of the corresponding 2-[4-N-(\(\omega\)-hydroxy alkyl)-N-methyl amino] benzylidene]-5/6-(4-nitro/cyano benzylidene) cycloalkanones, synthesised according to procedure in Section 2.12, with methacryloyl chloride. Scheme 3.2 outlines the synthesis of the described monomers. The details of the synthesis is presented in Section 3.6.1. The characterisations are presented in Sections 3.6.1 and 3.6.2.
where, $Y = \text{CN, NO}_2$; $R = \text{CH}_2$; Conditions Used : (i) TEA, DCM, 34 h, RT.

### 3.6.1 2-[4-N-(2-Methacryloyloxy ethyl)-N-methyl amino benzylidene]-6-(4-nitro benzylidene) cyclohexanone (11 a)

1.568 g (3.5 mmol) of 2-[4-N-(2-hydroxy ethyl)-N-methyl amino benzylidene]-6-(4-nitro benzylidene) cyclohexanone was dissolved in 50 mL of dry DCM and 3 mL of dry TEA was added. The solution was then cooled to 0°C and 0.63 g (6 mmol) of methacryloylchloride was added drop-wise. The resulting mixture was stirred at room temperature for 30 hours and subsequently diluted with 60 mL of DCM. The reaction mixture was filtered and washed first with 30 mL of cold aqueous 5% hydrochloric acid, twice with cold aqueous 5% sodium hydroxide solution, finally with cold water and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. The crude product was purified by and subsequent column chromatography on silica-gel column using 12% acetone in petroleum ether as eluent to get pure 65% of 2-[4-N-(2-methacryloyloxy ethyl-1-oxy)-N-methyl benzylidene]-6-(4-nitro benzylidene)cyclohexanone. The purity was checked by thin layer chromatography. The purified
sample was characterised by elemental analysis, IR, $^1$H NMR and mass. The data is presented below.

**IR (KBr)**: 2915, 1713, 1653, 1598, 1554, 1513, 1452, 1375, 1159, 850, 811 cm$^{-1}$.

**$^1$H NMR (CDCl$_3$)**: $\delta$ 8.25 (d, 2H), 7.72 (ss, 2H), 7.55 (d, 2H), 7.45 (d, 2H), 6.75 (d, 2H), 6.1 (s, 1H), 5.5 (s, 1H), 4.6 (t, 2H), 3.7 (t, 2H), 3.1 (s, 3H), 2.9 (t, 4H), 1.95 (s, 3H), 1.85 (m, 2H).

**Mass** m/e: M$^+$ 460(14%), 410(19%), 361(100%), 331(8%), 272(4%), 228(5%), 198(8%), 165(10%), 157(14%), 128(14%), 115(20%), 91(9%), 77(10%), 69(31%), 55(11%).

**Analysis calculated for C$_{27}$H$_{28}$O$_5$N$_2$**

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<td>N</td>
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**Found**

<table>
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<td>N</td>
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</table>

### 3.6.2 2-[4-N-(3-Methacryloyloxy propyl)-N-methyl amino benzylidene]-5-(4-cyano benzylidene) cyclopentanone (11 b)

**IR (KBr)**: 2915, 1743, 1671, 1598, 1554, 1513, 1452, 1375, 1159, 850, 811 cm$^{-1}$.

**$^1$H NMR (CDCl$_3$)**: $\delta$ 7.7 (d, 4H), 7.6 (s, 2H), 7.52 (d, 2H), 6.95 (d, 2H), 6.1 (s, 1H), 5.55 (s, 1H), 4.4 (t, 2H), 4.1 (t, 2H), 3.1 (s, 4H), 2.2 (m, 2H), 1.95 (s, 3H).

#### Table 3.8 Yields, absorption, optical microscopy and DSC analysis of 2-[4-N-(3-Methacryloyloxy propyl)-N-methyl amino benzylidene]-5-(4-cyano benzylidene) cycloalkanone

<table>
<thead>
<tr>
<th>Donor Acceptor</th>
<th>C.Code</th>
<th>Yield %</th>
<th>$\lambda_{max}$ nm</th>
<th>Cut-off $\lambda$ nm</th>
<th>$T_m$, °C</th>
<th>$T_i$, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-O-(CH$_2$)$_2$-N-CH$_3$ -NO$_2$</td>
<td>11 a</td>
<td>44</td>
<td>468</td>
<td>534</td>
<td>131</td>
<td>138</td>
</tr>
<tr>
<td>m-O-(CH$_2$)$_2$-N-CH$_3$ -CN</td>
<td>11 b</td>
<td>32</td>
<td>475</td>
<td>528</td>
<td>123</td>
<td>128</td>
</tr>
</tbody>
</table>

where c is compound, m is methacrylate group, $T_m$ is start of melting temperature and $T_i$ is complete isotropisation temperature.

### 3.6.3 Thermal Properties 2-[4-N-(3-Methacryloyloxy propyl)-N-methyl amino benzylidene]-5/6-(4-nitro/ cyano benzylidene) cycloalkanone

The monomers were normal crystals and did not exhibit liquid crystallinity. The transitions were studied by DSC and POM. In the DSC thermogram, at the highest transition temperature a single endotherm was noted which corresponded to the transition from crystal to isotropic
phase as observed by the POM studies. The temperature range over which the polymers melted ($T_m$) and isotropised ($T_i$) were quite narrow.

3.7 Poly{2-[4-(ω-acryloyloxy alkyl-1-oxy) benzylidene]-6-(4-nitro benzylidene)cyclohexanone}

3.7.1 2-[4-(ω-Acryloyloxy alkyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cycloalkanones

All monomers were synthesised by a procedure involving the esterification of 2-[4-(ω-hydroxy alkyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cycloalkanones with acryloyl chloride. Scheme 3.3 outlines the synthesis of the described monomer and polymer:

Scheme 3.3

Reagents: (I) TEA, DCM, 30 h, (ii) AIBN, THF, 70 °C.
3.7.2 2-[4-(6-Acryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone (12 a)

1.52 g (3.5 mmol) of 2-[4-(6-hydroxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone [Section 2.6.12] was dissolved in 50 mL of dry DCM to which 3 mL of dry TEA was added. The solution was then cooled to 0 °C and then 0.40 g (4.5 mmol) of acryloylchloride was added drop-wise. The resulting mixture was stirred at room temperature for 30 hours and subsequently diluted with 60 mL of DCM. The organic phase was washed first with 30 mL of cold 5% hydrochloric acid, twice with cold 5% sodium hydroxide solution and finally with cold water. This was dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure and the resulting crude was column chromatographed on silica gel column using 12% acetone in petroleum ether as eluent to get pure 1.51 g (89%) of the product. This was further purified by recrystallisation from a mixture of benzene/hexane (50/50, V/V) to yield 80% of 2-[4-(6-acryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone.

IR (KBr) : 2945, 1703, 1642, 1592, 1509, 1478, 1173, 1002, 832 cm⁻¹.

'H NMR (CDCl₃) : δ 8.3 (d, 2H), 7.7 (d, 2H), 7.65 (s, 1H), 7.55 (s, 1H), 7.52 (d, 2H), 6.95 (d, 2H), 6.56 (d, 1H), 6.34 (d, d 1H), 6.2 (s, 1H), 4.2 (t, 2H), 4.0 (t, 2H), 3.15 (s, 4H), 1.9 to 1.4 (m, 8H).

2-[4-(6-Acryloyloxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone is nematic. The DSC heating and cooling traces are shown in Fig. 3.4. The first heating scan curve(a) showed an endotherm at 118 °C for the melting to nematic phase. This is followed by a small endotherm at 124 °C for nematic to isotropic transition. Clear transition peaks were not seen on cooling from the isotropic state. However, in POM studies, the isotropic to nematic transition was observed at 74 °C. On second heating the newly formed crystallites turn nematic at 112 °C and on further heating change over to isotropic liquid at 126 °C.
3.7.3 Poly{2-[4-(6-acryloyloxy hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene) cyclohexanone} (12 p)

0.40 g of 2-[4-(6-acryloyloxy hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene)cyclohexanone was dissolved in 20 mL dry THF and 1 mol% AIBN was added. The solution was degassed by freeze-pump-thaw cycles under vacuum and sealed. The sample was then kept at 70 °C for 48 hours. Subsequently it was opened and poured into the 80 mL of methanol. The precipitated solid was separated by filtration and purified by repeated precipitation from chloroform into methanol.

IR (KBr) : 2930, 1730, 1662, 1597, 1554, 1506, 1467, 1338, 1240, 1159, 838 cm⁻¹.

$^1$H NMR (CDCl₃) : δ 8.25 (d, 2H), 7.8 (s, 2H), 7.6 (d, 2H), 7.45 (d, 2H), 6.9 (d, 2H), 4.0 (s, 2H), 2.95 (s, 4H), 2.1 to 1.6 (m, 12H).

Analysis calculated for C$_{29}$H$_{31}$O$_6$N

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated</td>
<td>71.60%</td>
<td>6.33%</td>
<td>2.86%</td>
</tr>
<tr>
<td>Found</td>
<td>72.58%</td>
<td>6.64%</td>
<td>2.98%</td>
</tr>
</tbody>
</table>
This polymer did not show any tendency to crystallise. The DSC thermogram for the poly{2-[4-(6-acryloyloxy hexyl-1-oxy)benzyldiene]-6-(4-nitro benzyldiene) cyclohexanone} in the heating cycle was characterised by $T_g$. Anisotropic flow behaviour was observed above this temperature. The endotherm at $68^\circ C$ was assigned for the anisotropic to isotropic transition. DSC thermogram is shown in Fig. 3.5.

This polymer degrades at and above isotropic transition temperature during the first DSC heating scan. The polymer synthesised with DMSO as the solvent was cross-linked and hence were not soluble in solvents. This may be due to the attack of highly reactive acrylate radicals on the benzyldene exocyclic double bonds.

Figure 3.5  DSC thermogram of poly{2-[4-(6-acryloyloxy hexyl-1-oxy)benzyldiene]-6-(4-nitro benzyldiene)cyclohexanone
Scheme 3.4 outlines the synthesis of the described monomers and polymers. All these p-Vinylbenzylethers were prepared by the phase transfer catalysed Williamson etherification of the corresponding phenols with p-chloromethylstyrene in THF at room temperature.\textsuperscript{26-28} An experimental procedure is as follows:

\textbf{Scheme 3.4}

\begin{align*}
\text{CH}_2\text{Cl}^+ \quad \text{HO-} & \quad \text{O} \quad \text{(i)} \quad \text{CH}_2\text{O} \\
\text{CH}_2\text{O} & \quad \text{Y} \quad \text{(ii)} \quad \text{CH}_2\text{O}
\end{align*}

where, $Y = \text{CN, NO}_2$; $R = \text{Nil, CH}_3$, Chiral CH-CH$_3$; Reagents : (i) TBAH, NaOH (50%), 45 h; (ii) AIBN, Dioxane, 70 °C.

3.8.1 2-[(4-Vinylbenzyl oxy)benzylidene]-6-(4-cyano benzylidene) cyclohexanone (13 a)

1.26 g (4 mmol) of 2-(4-hydroxy benzylidene)-6-(4-cyano benzylidene) cyclohexanone, 0.765 g (5 mmol) p-chloromethylstyrene and 0.28 g (0.82 mmol) tetrabutylammonium hydrogen sulphate were dissolved in 70 mL of THF and 20 mL of 50 Wt.% aqueous sodium hydroxide solution was added. The reaction mixture was stirred at room temperature for 45 hours and then the organic phase was washed with water. Organic solvent was removed under reduced pressure
at room temperature. The resulting crude product was column chromatographed on silica-gel using 13% ethyl acetate in petroleum ether as eluent to give 2-[(4-vinylbenzyl oxy)benzylidene]-6-(4-cyano benzylidene)cyclohexanone. It was further purified by recrystallisation from a mixture of benzene/cyclohexane (50/50, V/V) to yield 60% of pure product as yellow crystals. Similarly, 2-[(4-vinylbenzyl oxy)benzylidene]-6-(4-nitro benzylidene)cyclohexanone, 2-[(4-vinylbenzyl oxy) benzylidene]-5-(4-cyano benzylidene) cyclopentanone, 3-methyl-(2-[(4-vinylbenzyl oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone were synthesised. The IR and $^1$H NMR data of these purified monomers are presented in Sections 3.8.2 to 3.8.4.

**IR** (KBr) : 2855, 2225, 1655, 1597, 1557, 1506, 1408, 1341, 1270, 1166, 1065, 882, 828 cm$^{-1}$.

$^1$H NMR (CDCl$_3$) : $\delta$ 7.8 (s, 1H), 7.73 (s, 1H), 7.6 (d, 2H), 7.55 to 7.3 (m, 8H), 7.0 (d,d 2H), 6.8 to 6.62 (dddd, 1H), 5.8 (dd, 1H), 5.72 (d,d, 1H), 5.25 (dd, 1H), 5.1 (s, 2H), 2.9 (m, 2H), 1.85 (m, 2H).

$^{13}$C NMR (CDCl$_3$) : $\delta$ 19.6, 22.9, 28.4, 28.5, 69.9, 111.7, 114.5, 114.9, 115, 118.7, 125.4, 126.0, 126.5, 126.9, 127.7, 128.7, 128.9, 129.1, 130.6, 131.5, 132.1, 132.3, 132.6, 133.8, 133.9, 134.5, 136.5, 136.6, 136.9, 137.0, 137.9, 138.1, 139.1, 140.7, 159.5, 189.5.

**Mass** m/e : $M^+$ 431(8%), 314(9%), 117(100%), 141(8%), 128(6%), 105(12%), 97(10%), 85(15%), 77(11%), 71(32%), 57(83%).

Figure 3.6 DSC thermogram of 2-[(4-vinylbenzyl oxy)benzylidene]-6-(4-cyano benzylidene) cyclohexanone (13 a)

3.8.2 2-[(4-Vinylbenzyl oxy)benzylidene]-6-(4-nitro benzylidene)cyclohexanone (13 b)
IR (KBr): 2855, 1655, 1557, 1506, 1408, 1341, 1270, 1166, 1065, 882, 828 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta$ 8.25 (d, 2H), 7.8 (s, 2H), 7.6 (d, 4H), 7.4 (d, 2H), 7.0 (d, 2H), 6.75 (dddd, 1H), 5.8 (dd, 1H), 5.72 (dd, 1H), 5.25 (dd, 1H), 5.1 (s, 2H), 3.0 (t, 4H), 1.8 (m, 2H).

3.8.3 2-[(4-Vinylbenzyl oxy) benzylidene]-5-(4-cyano benzylidene)cyclopentanone (13 c)

IR (KBr): 2855, 2225, 1662, 1597, 1557, 1506, 1408, 1341, 1270, 1166, 882, 828 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta$ 7.75 to 7.25 (m, 10H), 7.0 (d, 2H), 6.7 (dddd, 1H), 5.8 (dd, 1H), 5.6 (dd, 1H), 5.1 (s, 2H), 3.1 (s, 4H).

3.8.4 3-Methyl-2-[(4-vinylbenzyl oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone (13 d)

Optical rotation: -38.2 in DCM

IR (KBr): 2855, 2225, 1658, 1597, 1557, 1506, 1408, 1341, 1270, 1065, 882, 828 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta$ 7.7 to 7.3 (m, 12H), 7.0 (d, 2H), 6.85 to 6.6 (dddd, 1H), 5.8 (d, 1H) and 5.72 (d, 1H), 5.35 to 5.25 (dd, 1H), 5.1 (s, 2H), 3.5 (m, 1H), 3.0 (m, 2H), 1.85 (m, 2H), 1.32 (d, 3H).

Table 3.9  Absorption, optical microscopy and DSC analysis of 2-[(4-vinylbenzyl oxy) benzylidene]-6/5-(4-cyano/nitro benzylidene) cycloalkanones

<table>
<thead>
<tr>
<th>C.Code</th>
<th>Yield</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>Cutoff $\lambda$ (nm)</th>
<th>Heating, $^\circ$C</th>
<th>Cooling, $^\circ$C</th>
<th>$T_m$, $^\circ$C</th>
<th>$T_i$, $^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>13 a</td>
<td>60</td>
<td>386</td>
<td>473</td>
<td>N-I: 115-128</td>
<td>I-N : 111-97</td>
<td>120</td>
<td>136</td>
</tr>
<tr>
<td>13 b</td>
<td>54</td>
<td>389</td>
<td>485</td>
<td>N-I: 121-135</td>
<td>I-N : 108-95</td>
<td>126</td>
<td>142</td>
</tr>
<tr>
<td>13 c</td>
<td>51</td>
<td>394</td>
<td>496</td>
<td>N-I: 146-151</td>
<td>I-N : 134-122</td>
<td>148</td>
<td>153</td>
</tr>
<tr>
<td>13 d</td>
<td>48</td>
<td>378</td>
<td>470</td>
<td>C-I : 118-136</td>
<td>I-C : 84.7</td>
<td>115</td>
<td>120</td>
</tr>
</tbody>
</table>

where c is compound, $T_m$ is melting temperature and $T_i$ is isotropic temperature.
3.8.5 Poly{2-[(4-vinylbenzyl oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone} [SCLCPVCN]

0.50 g (1.5 mmol) of 2-[(4-vinylbenzyl oxy)benzylidene]-6-(4-cyano benzylidene) cyclohexanone and 3.85 mg of AIBN were dissolved in 5 mL of dry THF. The solution was thoroughly degassed several times by the freeze-thaw technique and then heated up to 70 °C in an oil bath. Polymerisation was allowed to proceed for 35 hours. The solution was cooled to room temperature and poured in to 100 mL of methanol. The precipitated polymer was then separated by filtration as yellow solid and purified by two further reprecipitation from THF solution in to methanol. It was then dried under reduced pressure for about 24 h to give 0.125 g of poly{2-[(4-vinylbenzyl oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone}.

IR (KBr) : 2855, 2225, 1655, 1597, 1557, 1506, 1408, 1341, 1270, 1065, 882, 828 cm⁻¹.

¹H NMR (CDCl₃) : δ 7.8 to 7.6 (m, 4H), 7.55 to 7.3 (m, 8H), 7.0(d, 2H), 5.0 (s, 2 H), 2.9 (s ,4H), 1.85 (b, 3H), 1.45(b, 2H).

![Figure 3.7 DSC thermogram of poly{2-[(4-vinylbenzyl oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone}](image)
The DSC trace is characterised by a marked glass transition at 89 °C. The first endotherm at 136 °C corresponds to a mesophase to isotropic liquid transition. POM observations show that the polymer is still nematic at 138 °C.

3.9 Polyepichlorohydrin with pendent 2-[4-(2-ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone

The synthetic pathway used for the preparation involved the phase transfer catalysed etherification of chloromethyl group of epichlorohydrin with 2-[4-(2-hydroxy ethyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone.\textsuperscript{26,27} The subsequent ring opening polymerisation of the same with BF\textsubscript{3}.(Et\textsubscript{2}O)\textsubscript{2} would result in poly{2-[(4-ethylene oxy methyl-2-ethyl-1-oxy ether) benzylidene]-6-(4-cyano benzylidene)cyclohexanone. Scheme 3.5 outlines the synthetic methodology followed for the described monomer and the attempted polymerisation.

**Scheme 3.5**

![Scheme 3.5](image)

Reagents: (i) TBAH, 50% NaOH, 45 h; (ii) BF\textsubscript{3}.(Et\textsubscript{2}O)\textsubscript{2}, benzene
3.9.1 2-[4-(Epoxy propoxy-2-ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone (14a)

1.256 g (3.5 mmol) of 2-[4-(2-hydroxy ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone, 1.0 g (10 mmol) of epichlorohydrin and 0.28 g (0.82 mmol) of TBAH were dissolved in 70 mL of THF and 20 mL of 50 wt.% aqueous sodium hydroxide solution was added. The reaction mixture was stirred at room temperature for 45 hours and then the organic phase was separated and poured into water. The precipitated product was filtered and dried under reduced pressure at room temperature. The resulting crude product was column chromatographed on silica-gel using 13% ethyl acetate in petroleum ether as eluent to get 2-[4-(epoxy propoxy-2-ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone. It was further purified by recrystallisation from a mixture of benzene/cyclohexane (50/50, V/V) to yield 0.90 g (60%) of yellow crystals. The characterisation by IR, $^1$H NMR are presented below. The DSC is presented in Figure 3.8.

IR (KBr) : 2930, 2230, 1665, 1600, 1505, 1451, 1298, 1254, 1159, 1047, 835 cm$^{-1}$.

$^1$H NMR (CDCl$_3$) : $\delta$ 7.75 to 7.35 (m, 8H) 6.9 (d, 2H), 4.2 (t, 2H), 3.85 (m, 4H), 3.4 (m, 1H), 3.2 (m, 1H), 3.0 to 2.7 (m, 4H), 2.6 (m, 1H), 1.85 (m, 2H).

![Figure 3.8 DSC thermogram of 2-[4-(epoxy propoxy-2-ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone](image-url)
3.9.2 Poly{2-[4-(epoxy propyloxy-2-ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone} [SCLCPECN]

0.40 g of 2-[4-(epoxy propyloxy-2-ethyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone was dissolved in 10 mL of benzene and 0.015 mmol of ethereal solution of boron trifluoride etherate was added. The mixture was kept at 20°C for 24 hours. The system became viscous and so it was diluted with benzene and precipitated in methanol. NMR data was not clear. Molecular weight was not found to increase perhaps due to BF$_3$(Et$_2$O)$_2$ activating the α,β-unsaturated carbonyl carbon of reactive bisbenzylidene cycloalkanone instead of the epoxy to start the ring opening polymerisation. Thus, the ring opening polymerisation is inhibited, due to the formation of stable boron chelate with the α,β-unsaturated carbonyl oxygen. The polymerisation was not successful and hence synthesis was discontinued.

3.10 Poly{2-[4-(ω-maleimido) alkyl-1-oxy) benzylidene]-6/5-(4-nitro/cyano benzylidene) cycloalkanones}

These monomers were synthesised by a procedure involving the Mitsunobu reaction between 2-[4-(ω-hydroxy alkyl-1-oxy) benzylidene]-6/5-(4-nitro/cyano benzylidene) cycloalkanones and maleimide. Polymerisation was carried out by free radical initiation. Scheme 3.6 outlines the synthesis of the described monomer and polymer.
Scheme 3.6

Reagents: (i) DEAD, THF, Ph₃P, 38 h; (ii) AIBN, THF, 70 °C, 74 h.

The Mitsunobu reaction between the maleimide and the 2-[4-(ω-hydroxy alkyl-1-oxy) benzylidene]-6/5-(4-cyano/nitro benzylidene) cycloalkanones results in intermolecular dehydration on treatment with triphenyl phosphate (Ph₃P) and diethylazodicarboxylate (DEAD). In order to minimise the formation of ylide adduct between Ph₃P and maleimide (Michael addition on maleimide double bond) the following experimental procedure given below in Section 3.10.1 was adopted.

3.10.1 2-[4-(6-Maleimido hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene) cyclohexanone (15a)

1.063 g (6.1 mmol) DEAD was added to a solution of 2.26 g (5.2 mmol) of the 2-[4-(6-hydroxy hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene)cyclohexanone and 0.60 g (6.1 mmol) of maleimide in 200 mL of dry THF. The solution was cooled to 0 °C and kept under nitrogen
overflow. 1.66 g (6.1 mmol) of triphenyl phosphine (Ph₃P) in 10 mL dry THF was added dropwise over a period of 45 minutes with stirring. After addition was completed, the solution was allowed to come to room temperature and stirred for 38 hours. THF was removed under reduced pressure, residue was dissolved in DCM, washed with water and dried over anhydrous sodium sulphate. DCM was evaporated under reduced pressure and column chromatographed in silica-gel column with 19% acetone in petroleum ether as eluent to get pure 1.91 g (61%) of 2-[4-(6-maleimido hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene)cyclohexanone. This was purified by recrystallisation from a mixture of benzene/hexane (80/20, V/V) to get yellow needles. The characterisation by IR, 1H NMR and mass are presented below. The DSC thermogram is presented in Figure 3.9. Thermal data is presented in Table 3.10. The procedure was adopted to synthesise 2-[4-(6-maleimido hexyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexanone and 2-[4-(6-maleimido hexyl-1-oxy) benzylidene]-5-(4-nitro benzylidene) cyclopentanone. The characterisation data are presented in 3.10.2 and 3.10.3.

**IR (KBr)**: 2935, 1715, 1660, 1590, 1339, 1159, 825 cm⁻¹.

**¹H NMR (CDCl₃)**: δ 8.25 (d, 2H), 7.8 (ss, 2H), 7.6 (d, 2H), 7.45 (d, 2H), 6.95 (d, 2H), 6.7 (s, 2H), 4.0 (t, 2H), 3.55 (t, 2H), 2.9 (tt, 4H), 1.9 to 1.4 (m, 10H).

**Mass m/e**: M⁺ 514(12%), 497(30%), 347(6%), 334(34%), 31(28%), 288(20%), 278(15%), 260(6%), 232(16%), 215(18%), 202(11%), 180(11%), 165(12%), 150(31%), 128(18%), 115(25%), 110(100%), 98(21%), 82(26%), 77(22%), 55(60%).

**Figure 3.9** DSC thermogram of 2-[4-(6-maleimido hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene) cyclohexanone (15 a)
3.10.2 2-[4-(6-Maleimido hexyl-1-oxy) benzylidene]-6-(4-cyano benzylidene) cyclohexa-
none (15 b)

IR (KBr) : 2984, 2225, 1747, 1696, 1616, 1586, 1529, 1442, 1407, 1251, 1066, 825 cm⁻¹.

¹H NMR (CDCl₃) : δ 7.73 (d, 2H), 7.5 (ss, 2H), 7.45 (d, 2H), 7.35 (d, 2H), 6.90 (d, 2H), 6.7 (s, 2H), 4.0 (t, 2H), 3.55 (t, 2H), 2.9 (tt, 4H), 1.9 to 1.4 (m, 10H).

3.10.3 2-[4-(6-Maleimido hexyl-1-oxy) benzylidene]-5-(4-nitro benzylidene) cyclopenta-
none (15 c)

IR (KBr) : 2985, 1747, 1654, 1696, 1616, 1586, 1529, 1442, 1407, 1337, 1175, 1066, 825 cm⁻¹.

¹H NMR (CDCl₃) : δ 8.3 (d, 2H), 7.8 (s, 1H), 7.76 (s, 1H), 7.65 to 7.5 (d,d, 4H), 6.9 (d, 2H), 6.65 (s, 2H), 4.0 (t, 2H), 3.55 (t, 2H), 3.15 (s, 4H), 1.85 to 1.4 (m, 8H).

Mass m/e : M⁺ 500(28%), 483(10%), 470(4%), 453(6%), 320(64%), 304(45%), 274(20%), 215(6%), 185(10%), 180(125), 157(14%), 131(20%), 115(22%), 110(100%), 97(23%), 83(39%), 69(30%), 55(75%).

Table 3.10 Yields, absorption, optical microscopy and DSC analysis of 2-[4-(ω-
(maleimido benzylidene)cycloalkanones)

<table>
<thead>
<tr>
<th>D</th>
<th>A</th>
<th>C.Code</th>
<th>Yield %</th>
<th>λmax nm</th>
<th>Cutoff λ nm</th>
<th>Heating</th>
<th>Tm °C</th>
<th>Ti °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ma-O-(CH₂)₆-O-</td>
<td>-NO₂</td>
<td>15 a</td>
<td>61</td>
<td>384</td>
<td>486</td>
<td>S-I: 102.3</td>
<td>108</td>
<td>124</td>
</tr>
<tr>
<td>Ma-O-(CH₂)₆-O-</td>
<td>-CN</td>
<td>15 b</td>
<td>54</td>
<td>367</td>
<td>457</td>
<td>S-I: 122.6</td>
<td>136</td>
<td>154</td>
</tr>
<tr>
<td>Ma-O-(CH₂)₆-O-</td>
<td>-NO₂</td>
<td>15 c</td>
<td>46</td>
<td>395</td>
<td>508</td>
<td>S-I: 145.4</td>
<td>153</td>
<td>168</td>
</tr>
</tbody>
</table>

where D is donor, A is acceptor, C is compound, DSC is differential scanning calorimetry, m is methacrylate group, Ma is Maleimide, Tm is melting temperature and Ti is isotropic temperature.

The data presented in Table 3.10 indicates that all three monomers showed smectic mesophases. In DSC thermogram, at the highest transition temperature there was only single endotherm corresponding to the transition from the smectic phase to the isotropic phase. The transition in some cases from crystal to LC was marked by more than one endotherm. When such multiple peaks were observed, the one at the highest temperature was attributed to the crystal to
Poly{2-[4-(6-maleimido hexyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone} exhibits smectic phase like the corresponding monomer but did not show any tendency to crystallise. The DSC thermogram of the polymer is characterised by a $T_g$ at 72 °C. The endotherm at 97 °C corresponds to a smectic to isotropic transition. POM observations indicated that this polymer was smectic at 92 °C.

### 3.11 General Discussions

The synthetic routes for the donor-acceptor end functionalised bis(benzylidene)cycloalkanone based monomers and polymers are shown in Schemes 3.1 to 3.6. The polymerisable methacrylate, acrylate, 4-methyl styrene, epichlorohydrin, maleimide moieties were linked to the various donor-acceptor end functionalised bis(benzylidenes)cycloalkanones through polymethylene units of varying lengths. The resulting monomers excepting the epichlorohydrin could be polymerised in various polar organic solvents to obtain the respective polymers. The yields and molecular weights are presented in Tables 3.4 to 3.8. The $^1$H NMR, $^{13}$C NMR and optical micrographs are presented in annexure 1. In most cases conversions were poor and this is in agreement with the reported literature data. Attempt to synthesise polymers with an acrylate, instead of methacrylate backbone resulted in very poor yields and the polymers formed were cross-linked, probably due to the attack of highly reactive (meth)acrylate radicals on the benzylidene exocyclic double bonds.

The polymers were soluble in common organic solvents like 1,1,2,2-tetrachloroethane, N,N-dimethyl formamide and tetrahydrofuran. The molecular weights of all the polymers were low. This is because of the extensive chain transfer reactions attributable to the benzylidene units and the inhibitive effects of the nitro and cyano groups (used as the acceptor) on the free radical
polymerisation. So in all cases the yields were rather poor even after sufficiently long polymerisation times with extensive precautions and the molecular weights were also quite low.

3.11.1 Thermal Studies

The thermal transitions were investigated using DSC and POM. The monomers and polymers with pendent 2-[4-(ω-alkyl-1-oxy)benzyldiene]-6/5-(4-cyano/nitro benzylidene) cycloalkanones were found to be liquid crystalline but the monomers and polymers with pendent 2-[4-(N-ω-alkyl-1-oxy)-N-methyl amino benzyldiene]-6/5-(4-cyano/ nitro benzylidene) cycloalkanones were not liquid crystalline. Generally, in the DSC thermogram, a single endotherm corresponding to the transition from the liquid crystalline phase to the isotropic state was noticed. In a few cases the transition from crystal to liquid crystal state was marked by more than one endotherm. In case of such multiple peaks in DSC, POM observations were used to identify the temperature corresponding to the crystal to mesophase transition. Peaks at lower temperature were assigned to unidentified crystal-crystal transformations since no flow was observable in POM within the time scale of the experimentation. Transitions in a few of the monomers and polymers showed large dependence on the thermal history of the sample due to the simultaneous unavoidable thermal curing. Annealing at a temperature between T_g and T_m seems to be essential for observing the transitions clearly in such cases.

One important observation was that all polymers lost the liquid crystallinity on storage for a long period at the ambient temperature, perhaps due to addition reaction between adjacent chromophores pointed in the same direction. The polar end groups probably enhance the reactivity of the benzyldienic double bond. Additional complications arise from EZ, ZZ isomerisation which induces a non-mesogenic character to the polymer.
The glass transition temperature of all these polymers with different spacer lengths were close to each other unlike that reported in literature. On replacing the polymethacrylate backbone with polystyrene back-bone while keeping the spacer length constant, the glass transition temperature increased while the isotropisation temperature was found to decrease, since the main chain interferes with organisation of a lateral side groups and hence the Tg increases. The Tg of the polymers depended on the nature of the back-bone attached to the NLO units with styrene and polymaleimide displaying higher Tg than the methacrylate. The mesophase type formed was also influenced by the polymer back-bone. Thus, polymers with 2-[4-(ω-alkyl-1-oxy)benzylidene]-6/5-(4-cyano/nitro benzylidene) cycloalkanone units exhibit nematic/smectic mesophases depending on the polymer back-bone, akin to the corresponding monomers. The Tg also depends on the spacer length and central cycloalkanone ring. However, no clear dependence of T1 on structure was observed.

The emergence of smectic phase was observed when the same mesogen (10 a) was hooked through the same number of polymethylene spacer to polymaleimide back-bone instead of methacrylate back-bone. The decoupling of the side chain was perhaps the least with maleimide back-bone. It is not possible at the moment to establish an exact correlation between the molecular structure and mesomorphism.

3.12 Conclusion

A new class of side chain liquid crystalline monomers and polymers containing 2-[4-(ω-alkyl-1-oxy)benzylidene]-6/5-[4-cyano/nitro benzylidene)cycloalkanone and 2-[4-N-(ω-alkyl-1-oxy) N-methyl amino benzylidene]-6/5-(4-cyano/nitro benzylidene) cycloalkanone groups were synthesised. The structure was varied by altering the spacer length, polymerisable backbones and end functional groups. These variations influence the thermal characteristics and the phase types.
References:


Annexure 1
FIGURE 3.11: $^1$H NMR Spectrum of 2-[4-(6-Methacryloyloxy hexyl-1-oxy benzylidene)-6-(4-nitro benzylidene) cyclohexanone
FIGURE 3.12: $^{13}$C NMR Spectrum of 2-[4-(6-Methacryloyloxy hexyl)-1-oxy benzylidene]-6-(4-nitro benzylidene) cyclohexanone

FIGURE 3.13: $^1$H NMR Spectrum of 2-[4-(6-Methacryloyloxy hexyl)-1-oxy benzylidene]-5-(4-nitro benzylidene) cyclopentanone
FIGURE 3.14: $^1$H NMR Spectrum of 2-[4-(3-Methacryloyloxy propyl-1-oxy benzylidene]-5-(4-cyano benzylidene) cyclopentanone

FIGURE 3.15: $^1$H NMR Spectrum of 4-Methyl-2-[4-(2-methacryloyloxy ethyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone
FIGURE 3.16: $^{13}$C NMR Spectrum of 4-Methyl-2-[4-(2-methacryloyloxy ethyl-1-oxy) benzylidene]-6-(4-nitro benzylidene) cyclohexanone

FIGURE 3.17: $^1$H NMR Spectrum of 2-[4-(6-Methacryloyloxy hexyl-1-oxy benzylidene]-6-(4-cyano benzylidene) cyclohexanone
FIGURE 3.18: $^{13}$C NMR Spectrum of 2-[4-(6-Methacryloxy hexyl-1-oxy benzylidene)-6-(4-cyano benzylidene) cyclohexanone
FIGURE 3.19: $^1$H NMR Spectrum of 2-[4-(3-Methacryloyloxy propy-1-oxo benzylidene]-6-(4-cyano benzylidene) cyclohexanone

FIGURE 3.20: $^1$H NMR Spectrum of 2-[4-(2-Methacryloyloxy ethyl-1-oxo benzylidene]-6-(4-cyano benzylidene) cyclohexanone
FIGURE 3.21: $^{13}$C NMR Spectrum of 2-[4-(2-Methacryloyloxy ethyl-1-oxy benzylidene)-6-(4-cyano benzylidene) cyclohexanone
**FIGURE 3.22** : $^1$H NMR Spectrum of 3 methyl 2-[4-(3-Methacryloyloxy propy-1-oxy benzylidene)-6-(4-cyano benzylidene) cyclohexanone

**FIGURE 3.23** : $^1$H NMR Spectrum of Poly 2-[4-(6-Methacryloyloxy hexyl-1-oxy benzylidene)-6-(4-nitro benzylidene) cyclohexanone
FIGURE 3.24: $^1$H NMR Spectrum of 2-\{4-(2-N-Methacryloyloxy-N-methyl ethyl-1-oxy) benzylidene\}-6-(4-nitro benzylidene) cyclohexanone

FIGURE 3.25: $^1$H NMR Spectrum of 2-\{(4-vinylbenzyl oxy)benzylidene\}-6-(4-cyano benzylidene)cyclohexanone
FIGURE 3.26: $^{13}$C NMR Spectrum of 2-[(4-vinylbenzyl oxy)benzylidene]-6-(4-cyano benzylidene)cyclohexanone

FIGURE 3.27: $^1$H NMR Spectrum of 4 methyl 2-[(4-vinylbenzyl oxy)benzylidene]-6-(4-cyano benzylidene)cyclohexanone
FIGURE 3.28: $^1$H NMR Spectrum of 2-[(4-epoxy propyl)-2-ethyl-1-oxy ether) benzylidene]-6-(4-cyano benzylidene)cyclohexanone

FIGURE 3.29: $^1$H NMR Spectrum of 2-[4-(6-Maleimido hexyl-1-oxy)benzylidene]-6-(4-nitro benzylidene) cyclohexanone
FIGURE 3.47: Optical Micrograph of SCLCPCNCH2 at 108°C

FIGURE 3.48: Optical Micrograph of SCLCPCNCH4 at 98°C

FIGURE 3.49: Optical Micrograph of SCLCPCNCH6 at 91°C

FIGURE 3.50: Optical Micrograph of 12a at 128°C

FIGURE 3.51: Optical Micrograph of 12p at 65°C

FIGURE 3.52: Optical Micrograph of 13a at 121°C
FIGURE 3.53: Optical Micrograph of 13b at 1320°C

FIGURE 3.54: Optical Micrograph of 13c at 1490°C

FIGURE 3.55: Optical Micrograph of SCLCPVCN at 1230°C

FIGURE 3.56: Optical Micrograph of SCLCPVNC at

FIGURE 3.57: Optical Micrograph of 15a at 1180°C

FIGURE 3.58: Optical Micrograph of 15b at 980°C
FIGURE 3.59: Optical Micrograph of 15c at 1400°C
FIGURE 3.60: Optical Micrograph of SCLCPMNO_{2}CH_{6} at 1280°C