

PART III

Experimental details

Pages 85-126

III.1 General methods of investigation

III.2 Physical methods

III.2.1 *Sample cell*

III.2.2 *Sample alignment*

III.2.3 *Experimental setup*

III.3 Synthetic procedures

III.3.1 *Monomers*

III.3.2 *Polymers*

References

III.1 General methods of investigation

Anhydrous solvents used were prepared from commercial solvents following the standard procedures. All solid starting materials were crystallised before use. Analytical tlc was carried out using ready made tlc-aluminium cards coated with silica gel with a fluorescent indicator (FLUKA AG, Switzerland). The spots on these plates were rendered visible by exposing them to UV-radiation at 254 and/or 366 nm (DESAGA HP-UVIS lamp). Silica gel 60-120 mesh, (ACME, India) was used for column chromatography.

Infrared absorption (IR) spectra of the compounds were recorded as nujol mull on a spectrophotometer (SHIMADZU IR-435), unless otherwise stated. The proton magnetic resonance spectra (^1H NMR) were recorded on a spectrometer (BRUKER WP80 SY FT NMR) using tetramethylsilane (TMS) as an internal reference standard. The chemical shifts are quoted as δ (parts per million) downfield from the reference. CDCl_3 was used as a solvent for all the compounds. Elemental analyses were carried out (CARLO-ERBA 1106 elemental analyser) and the values obtained are in close agreement with those calculated. Specific rotations $[\alpha]_D$ were measured (OPTICAL ACTIVITY digital polarimeter TYPE AA1000), at 589 nm sodium line. The transition temperatures were measured under a polarising microscope (LEITZ LABORLUX 12 POL) equipped with a heating stage (Mettler FP 82 HT) and a microprocessor controller (FP80 or FP90), by sandwiching the sample between a glass slide and a cover slip. Simultaneously, the mesophase textures were also observed. The enthalpies of transitions, reported as joules/g, were determined from thermograms obtained for the monomers, (PERKIN-ELMER, MODEL DSC-4 or DSC-7) and for the polymers, (RHEOMETRIC SCIENTIFIC differential scanning calorimeter). The heating and

cooling rates were 5.0°C/min and 3.0°C/min respectively for monomers and 10.0 °C/min or 20.0 °C/min for the polymers. The calorimeters were calibrated using pure indium as a standard.

Gel permeation chromatography (GPC) of the polymers was carried out in THF using μ -styragel columns with 10^4 , 10^3 and 10^2 Å particle size at room temperature. The concentration of the polymer solutions were 2mg/ml. The detection was made with a differential refractometer (WATERS 401). Elution (WATERS Pump, MODEL 510) volumes were converted to molecular weight based on calibration obtained with narrow molecular weight polystyrene standards.

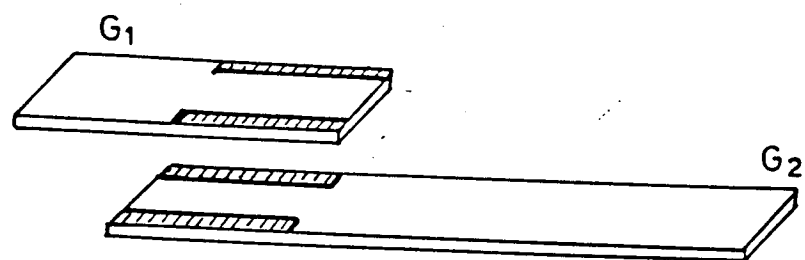
X-ray diffraction studies were carried out using a 18cm image plate (MARRESEARCH, Germany). A nickel filtered, graphite monochromated Cu-K α radiation was used.

III.2 Physical methods

III.2.1 The Sample Cell

The sample cell was made up of two thin (thickness 0.7 mm approx.), flat transparent glass plates, coated with indium-tin-oxide (ITO). The glass plates had a required electrode pattern of a predetermined active area (Fig. III.1) etched out of them using dilute hydrochloric acid and zinc dust. Electrically, the cell could be considered as a parallel plate capacitor.

Mylar spacer was used to control the thickness of the sample cell (3-5 μ m). The two glass plates were joined together by a non-reactive epoxy and cured at 150°C. While preparing the sample cell, care was taken to see that neither the mylar spacer nor the epoxy entered the active area of the cell. After preparing the cell, its thickness was



G_1, G_2 - ITO coated glass plates
Hatched portion - Etched part of the glass plates

Fig.III.1

measured to a high precision ($< 0.1 \mu\text{m}$) using an optical interference technique. Only those cells which had a uniform thickness throughout the active area were chosen for the experiments.

III.2.2 Sample alignment

A convenient way of measuring P_s is to have the sample aligned in the homogeneous (planar) bookshelf geometry.¹ Here the smectic layers are perpendicular to the glass plates (electrodes) and thus the field is applied parallel to the smectic layers and perpendicular to the director $\vec{n}$ (Fig. III.2). A proven method² for realising well oriented samples is by surface treatment of the substrate. For this purpose, the ITO coated plates were treated with polyimide solution, cured at 300°C for an hour and rubbed unidirectionally, after which the cell was assembled as described earlier. The sample was filled in the isotropic phase by capillary action. Care was taken to see that it was filled uniformly without any air bubbles. To obtain good alignment, the sample was heated to a temperature slightly above the isotropic point and cooled slowly, across the I-S_A transition, at a rate of $\sim 6^\circ\text{C}/\text{hour}$. This procedure generally resulted in a relatively well aligned sample.

III.2.3 Experimental setup

The triangular waves were generated by a waveform generator (HP 8116), amplified by an operational power supply (BOP 1000M, Kepco Inc.) (Fig.III.3). The maximum amplitude available is $\pm 1\text{kV}$, and waveforms upto 1kHz could be produced. The current was measured as a voltage drop across a $10\text{k}\Omega$ series resistor with a digital storage oscilloscope (Tektronix). The signal was amplified (ADA524 amplifier)

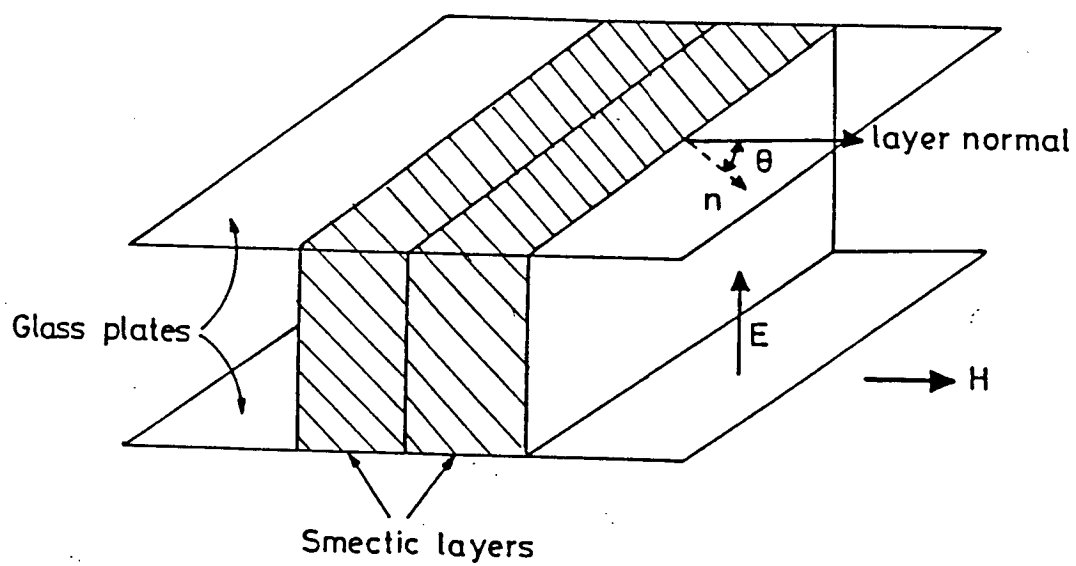


Fig.III.2

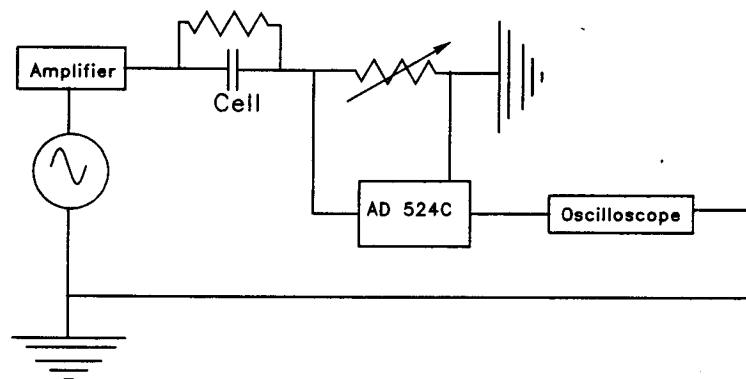
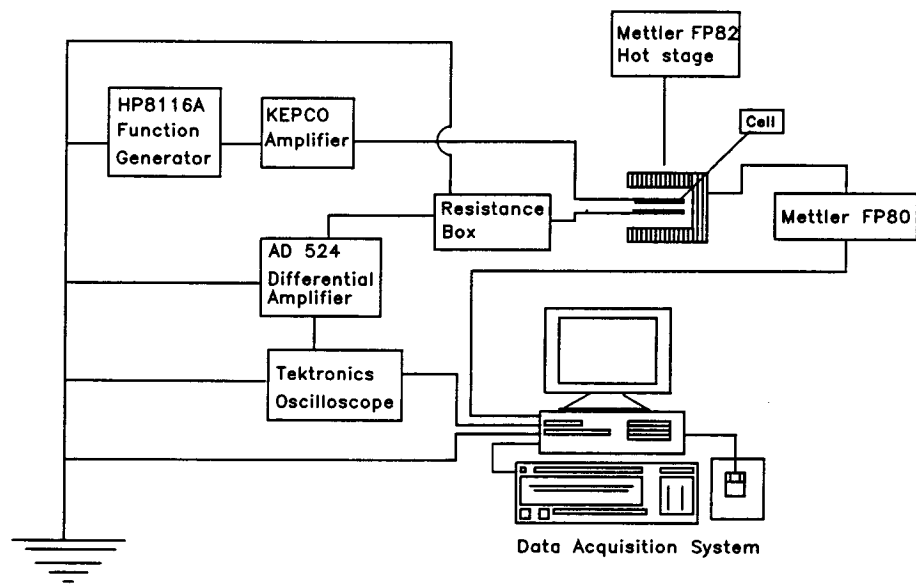


Fig.III.3

and accumulated to increase the S/N ratio and was processed to obtain P_s using a computer (Micronics 386). Usually a $7\text{--}10V_{pp}\mu\text{m}^{-1}$ amplitude triangular wave ($f = 4\text{--}10\text{ Hz}$) was sufficient to obtain saturation in measured value of polarisation. P_s values for the polymers were measured on cooling from the S_A phase, because a hysteresis effect was observed during the heating and cooling cycles. Such an effect has also been observed previously.³

III.3 Synthetic procedures

III.3.1 Synthetic procedures for monomers

2-Methoxynaphthalene (1)

2-Hydroxynaphthalene (51.0g, 350 mmol) was placed in a 500ml three-necked flask equipped with a pressure equalising funnel, a mechanical stirrer and a reflux condenser. A solution of sodium hydroxide (12.8g, 320mmol) in water (128ml) and ethyl alcohol (100ml) was added to it. This mixture was stirred and dimethylsulphate (37.8g, 300mmol) was added dropwise to it over a period of one hour. Then the reaction mixture was refluxed for one and half hours, when a clear solution was obtained. This was cooled, the solid product so obtained was filtered off, washed with water, dried and recrystallised from ethanol.

Yield 80%; m.p. 89.0°C (Reported¹⁰ m.p. 88.0°C).

2-Acetyl-6-methoxynaphthalene (2)

In a one litre three-necked flask fitted with a mechanical stirrer, a pressure equalising separatory funnel and a reflux condenser connected to a water trap through anhydrous calcium chloride guard tube, a mixture of 2-methoxynaphthalene (50g, 320mmol), anhydrous aluminium chloride (85g, 640mmol) and carbon disulphide (one liter) was placed. This was cooled in an ice-bath and while stirring freshly distilled acetyl chloride (24ml, 430mmol) was added dropwise to it over a period of one hour. After the addition was complete the reaction mixture was stirred at 35.0°C for five hours and then refluxed for one hour. After the removal of carbon disulphide, the residue was poured into a mixture of ice and concentrated hydrochloric acid. The solid

formed was filtered and boiled with ether (500ml) for thirty minutes and the ethereal solution was decanted off. The ether insoluble portion was crystallised from hexane.

Yield 49%; m.p. 103-104.5°C (Reported¹⁰ m.p. 104-105°C).

6-Methoxy-2-naphthoic acid (3)

A solution of sodium hypobromite was prepared by adding bromine (50ml, 40mmol) to a solution of sodium hydroxide (40g, 980 mmol) in water (600ml) at -5°C. This was added to a vigorously stirred solution of 2-acetyl-6-methoxynaphthalene (50g, 25mmol) in 1, 4-dioxane (500ml). The addition was carried out at 30-35°C during thirty minutes. Stirring was continued and the temperature raised to 60°C and held there for one hour to ensure completion of the reaction. Enough aqueous sodium metabisulphite was added to destroy the excess of hypobromite. Water (250ml) was added and about 220ml of the liquid was distilled. The residual portion was cooled and acidified with concentrated hydrochloric acid. The white precipitate obtained was filtered off, washed thoroughly with water and dried. This was crystallised from acetic acid.

Yield 76.6%; m.p. 207-208°C (Reported⁴ m.p. 205-206°C).

6-Hydroxy-2-naphthoic acid (4)

A mixture of 6-methoxy-2-naphthoic acid (20g, 88mmol), hydrobromic acid (48%, 150ml) and acetic acid (250ml) was refluxed for sixteen hours. It was then poured into ice-cold water and the precipitate formed was filtered, washed with water and dried. The crude product so obtained was crystallised from ethanol.

Yield 95%; m.p. 250°C (Reported⁴ m.p. 250°C).

Ethyl 6-hydroxy-2-naphthoate (5)

This was prepared following a classical esterification procedure.⁵ Thus, a mixture of 6-hydroxy-2-naphthoic acid (15.1g, 70 mmol), ethanol and a few drops of concentrated sulphuric acid was refluxed for eight hours. The excess alcohol was removed by distillation and the residue was poured into water. This was extracted with ether (3×60ml) and the combined ethereal solution was washed with 10% aqueous sodium bicarbonate (2×75ml), water (2×100ml) and dried (Na₂SO₄). The residue obtained on removing the solvent was chromatographed on silica gel and eluted with 30% chloroform-petroleum ether (b.p. 60-80°C) mixture. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol.

Yield 98%; m.p. 157°C (Reported¹⁰ m.p. 155°C).

Ethyl-6-(5-hexenyloxy)-2-naphthoate (6)

This was prepared following a procedure reported by Mitsunobu.⁶ Thus, diethylazodicarboxylate (4.76g, 27.3mmol) was added dropwise to a cold stirred solution of ethyl 2-hydroxynaphthalene-6-carboxylate (5.40g, 25mmol), 5-hexene-1-ol (2.25g, 24.9mmol), triphenyl phosphine (7.0g, 26.3mmol) and dichloromethane (56.0 ml) during one hour. The reaction mixture was stirred at room temperature for four hours and the solid formed during the reaction was filtered off. The residue obtained on removal of solvent from the filtrate was chromatographed on silica gel and eluted with 3:1 chloroform and petroleum ether (b.p. 60-80°C). On removal of solvent from the eluate, the required compound was obtained as a viscous liquid.

Yield 76%; $\nu_{\max}(\text{neat})$: 2980, 2850, 1725, 1640, 1480, 1240 and 1050 cm^{-1} ; δ :
0.7-2.0 (m, 11H, 1 $\times$ CH₃, 4 $\times$ CH₂), 4.2 (m, 2H, ArCOOCH₂), 4.5 (s, 2H, ArCH₂O),
5.10(m, 2H, CH₂=C), 5.75 (m, 1H, C=CH), 7.1-8.6 (m, 6H, ArH).

Elemental analysis: Found : C,76.58; H,7.50% C₂₀H₂₄O₃, requires
C,76.48; H,7.43%.

Cognate preparations were carried out for the following compounds.

Ethyl-6-(9-decenyloxy)-2-naphthoate (7)

Yield 72%; $\nu_{\max}(\text{neat})$: 2980, 2850, 1725, 1640, 1480, 1240 and 1050 cm^{-1} ; δ
: 0.7-2.1 (m, 17H, 1 $\times$ CH₃, 7 $\times$ CH₂), 4.2 (m, 2H, ArCOOCH₂), 4.5 (s, 2H, ArCH₂O),
5.10(m, 2H, CH₂=C), 5.75 (m, 1H, C=CH), 7.1-8.6 (m, 6H, ArH).

Elemental analysis: Found : C,78.06; H,8.49% C₂₃H₃₀O₃, requires
C,77.97; H,8.47%.

Ethyl-6-(10-undecenyloxy)-2-naphthoate (8)

Yield 77%; $\nu_{\max}(\text{neat})$: 2980, 2850, 1725, 1640, 1480, 1240 and 1050 cm^{-1} ; δ
: 0.7-2.0 (m, 19H, 1 $\times$ CH₃, 8 $\times$ CH₂), 4.2 (m, 2H, ArCOOCH₂), 4.5 (s, 2H, ArCH₂O),
5.10(m, 2H, CH₂=C), 5.75 (m, 1H, C=CH), 7.1-8.6 (m, 6H, ArH).

Elemental analysis: Found : C,78.33; H,8.74% C₂₄H₃₂O₃, requires
C,78.26; H,8.70%.

6-(5-Hexenyloxy)-2-naphthoic acid (9)

A mixture of ethyl 6-(5-hexenyloxy)-2-naphthoate (30.0g, 120mmol), potassium hydroxide (8.6g, 150mmol), water(20ml) and ethanol (50ml) was refluxed for six hours. Ethanol was removed by distillation and the residue poured into cold water. This was acidified by adding cold, concentrated hydrochloric acid. The white precipitate so obtained was filtered off, washed with water and dried. This was crystallised from ethanol.

Yield 90%; transition temperatures: K 135.8 S_C 137.3 N 186.7 I. $\nu_{\max}$: 3600, 3000, 1725, 1640, 1480, 1240 and 1050 cm⁻¹; δ : 0.7-2.0 (m, 8H, 4×CH₂), 4.2 (m, 2H, ArCOOCH₂), 4.5 (s, 2H, ArCH₂O), 5.10(m, 2H, CH₂=C), 5.75 (m, 1H, C=CH), 7.1-8.6 (m, 6H, ArH), 10.78 (s, 1H, COOH) .

Elemental analysis: Found : C,75.46; H,6.78% C₁₈H₂₀O₃, requires
C,75.53; H,6.71%.

Cognate preparations were carried out for the following compounds.

6-(9-Decenyloxy)-2-naphthoic acid (10)

Yield 91%; transition temperatures: K 128.9 S_C 135.1 N174.1 I. $\nu_{\max}$: 3600, 3000, 1725, 1640, 1480, 1240 and 1050 cm⁻¹; δ : 0.7-2.2 (m, 16H, 8×CH₂), 4.2 (m, 2H, ArCOOCH₂), 4.5 (s, 2H, ArCH₂O), 5.10(m, 2H, CH₂=C-), 5.75 (m, 1H, C=CH), 7.1-8.6 (m, 6H, ArH), 10.78 (s, 1H, COOH) .

Elemental analysis: Found : C,77.36; H,7.94% C₁₈H₂₀O₃, requires
C,77.30; H,7.98%.

6-(10-Undecenyl-oxy)-2-naphthoic acid (11)

Yield 88%; transition temperatures: K 125.8 S_C 135.6 N 170.2 I. $\nu_{\max}$: 3600, 3000, 1725, 1640, 1480, 1240 and 1050 cm⁻¹; δ : 0.7-2.0 (m, 8H, 4×CH₂), 4.2 (m, 2H, ArCOOCH₂), 4.5 (s, 2H, ArCH₂O), 5.10 (m, 2H, CH₂=C), 5.75 (m, 1H, C=CH), 7.1-8.6 (m, 6H, ArH), 10.78 (s, 1H, COOH) .

Elemental analysis: Found : C,77.61; H,8.22% C₁₈H₂₀O₃, requires C,77.65; H,8.24%.

3-Chloro-4-hydroxyacetophenone (12)

This compound was prepared using a Fries rearrangement.⁷ Thus, a mixture of 2-chlorophenylacetate (37.6g, 200mmol) and anhydrous aluminium chloride (58.8g, 400mmol) was heated for two hours at 120°C in an oil bath. It was then poured into a mixture of ice and concentrated hydrochloric acid. The precipitate formed was filtered, washed with water until the washings were neutral and dried. The crude product so obtained was crystallised from toluene.

Yield 64%; m.p. 100.0°C (Reported¹⁰ m.p. 100.0-100.5°C).

3-Chloro-4-benzoyloxyacetophenone (13)

A mixture of 3-chloro-4-hydroxyacetophenone (2g, 11.7mmol), benzylchloride (2.85g, 12.9mmol), anhydrous potassium carbonate (4.85g, 35.1mmol) and anhydrous butan-2-one (35ml) was refluxed for twenty-four hours. Then the butan-2-one was distilled off from the reaction mixture and the residue poured into a mixture of ice and concentrated hydrochloric acid and extracted with chloroform (3×50 ml). The combined chloroform solution was washed with water (3×30 ml) and dried (CaCl₂).

The solvent was removed and the residue was chromatographed on silica gel and eluted with 30% chloroform-petroleum ether (b.p. 60-80°C) mixture. The required material obtained on removal of solvent was crystallised from ethanol.

Yield 71%; m.p. 111.5°C (Reported⁸ 111.5°C).

***3-Chloro-4-benzyloxybenzoic acid* (14)**

A solution of sodium hypobromite was prepared by adding bromine (4.36g, 27.2mmol) to a solution of sodium hydroxide (3.81g, 95.5mmol) in water (25ml) at -5°C. This was added to a vigorously stirred solution of 3-chloro-4-benzyloxyacetophenone (2.0g, 5.4mmol) in 1, 4-dioxane (20ml). The addition was carried out at 30-35°C during thirty minutes, then the temperature was raised to 60°C and held there for one hour. Enough aqueous sodium metabisulphite was added to destroy the excess of hypobromite. Water (30ml) was added and about 30ml of the liquid was distilled. The residual portion was cooled and acidified with concentrated hydrochloric acid. The white precipitate obtained was filtered off, washed thoroughly with water and dried. This was crystallised from isopropanol.

Yield 70.2%; m.p. 209.0°C (Reported¹⁰ m.p. 209.0°C).

***[S]-2-Chloro-4-methylpentanoic acid* (15)**

This was prepared following the procedure of Fu *et al.*⁹ Thus, a mixture of l-leucine (52.4 g, 0.4mol) and 6N hydrochloric acid (500ml) contained in a one litre three-necked flask fitted with a mechanical stirrer and cooled in an ice-salt bath was stirred vigorously. Sodium nitrite (44.0g, 0.64mol) was added to this mixture in small portions over a period of one hour. The temperature of the reaction mixture was not

allowed to exceed 0°C during the addition. The stirring was continued for a further period of five hours at 0°C after the completion of the addition. The reaction mixture was then extracted with ether (3×150 ml) and the combined ether solution was dried (Na₂SO₄). The residual liquid obtained on removal of the solvent was distilled under reduced pressure to yield the pure product.

Yield 50%; b.p. 90.0 °C/2.5mm; [α] = -25.0 (c = 5 in C₂H₅OH); (Reported⁶ b.p. 112.4 °C/20 mm; [α] = -24.6 (c = 5 in C₂H₅OH).

[S]-Methyl 2-chloro-4-methylpentanoate (16)

A mixture of [S]-2-chloro-4-methylpentanoic acid (15.1g, 0.1mol), methanol and a few drops of concentrated sulphuric acid was refluxed for eight hours. The excess alcohol was removed by distillation and the residue was poured into water. This was extracted with ether (3×60ml) and the combined ethereal solution was washed with 10% aqueous sodium bicarbonate (2×75ml), water (2×100ml) and dried (Na₂SO₄). Removal of the solvent afforded the required ester which was purified by distillation under reduced pressure.

Yield 98%; b.p. 105°C/20mm. (Reported¹⁰ b.p. 72°C/11 mm.).

[S]-2-Chloro-4-methylpentanol (17)

Lithium aluminium hydride (2.28g, 0.06mol) was added to sodium dried ether (200ml) contained in a three-necked flask fitted with a condenser and a dropping funnel. This was cooled in an ice-bath and magnetically stirred. To this cold mixture was added dropwise a solution of [S]-methyl-2-chloro-4-methylpentanoate (16.45g, 0.1mol) in anhydrous ether. After completion of addition, the mixture was stirred at

room temperature for a period of two hours. The reaction mixture was again cooled thoroughly in an ice-bath and the excess lithium aluminium hydride was decomposed by a careful addition of damp ether (100ml) followed by ice-cold water (4ml). The stirring was continued till the decomposition was complete. The gelatinous white precipitate was filtered and washed thoroughly with warm ethyl acetate. The filtrate was dried (Na_2SO_4) and the solvent removed. The crude product so obtained was purified by distillation under reduced pressure.

Yield 90%; b.p. $80^\circ\text{C}/3\text{mm}$; $[\alpha] = -30.0$ ($c = 2$ in CHCl_3); $\nu_{\text{max}}(\text{neat})$: 3370, 2950, 2850, 1480, 1360 and 1070 cm^{-1} ; δ : 0.9 (dd, 6H, $(\text{CH}_3)_2\text{-C-}$), 1.2-1.9 (m, 3H, $-\text{CH-CH}_2$), 2.7 (s, 1H, $-\text{OH}$), 3.5-4.2 (m, 3H, $-\text{CH-CH}_2\text{O-}$).

[S]-2-Chloro-4-methylpentyl-4'-benzyloxybenzoate (18)

This was prepared following the esterification procedure of Hassner and Alexanian.⁵ Thus, a mixture of 4-benzyloxybenzoic acid (11.4g, 0.05mol), N,N' -dicyclohexylcarbodiimide (11.3g, 0.055 mol), [S]-2-chloro-4-methylpentanol (7.5g, 0.055mol), 4- N,N' -dimethylaminopyridine (0.74g, 0.005mol) and anhydrous dichloromethane (25ml), protected from moisture through anhydrous calcium chloride guard tube was stirred for six hours at room temperature. N,N' -Dicyclohexyl urea formed was filtered and the filtrate was washed successively with water ($2 \times 50\text{ml}$), 5% aqueous acetic acid ($2 \times 70\text{ml}$), water ($2 \times 50\text{ml}$), and dried (Na_2SO_4). The residue obtained on removal of the solvent was chromatographed on silica gel and eluted with 30% chloroform-petroleum ether (b.p. $60-80^\circ\text{C}$) mixture. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol.

Yield 64 %; m.p. 51-52°C; $[\alpha] = +3.92$ ($c = 2$ in CHCl_3); ν_{max} : 2950, 1700, 1605, 1585, 1510, 1280, 1240, 1175 and 1010 cm^{-1} ; δ : 0.75 (dd, 6H, $-(\text{CH}_3)_2-\text{C}-$), 1.23-1.7 (m, 3H, $-\text{CH}_2-\text{CH}-\text{C}-$), 3.3-3.7 (m, 3H, $-\text{COOCH}_2\text{CHCl}$), 4.1(s, 2H, $-\text{OCH}_2$), 5.6 (d, 2H, ArH), 5.9 (s, 5H, ArH), 6.4 (d, 2H, ArH).

Elemental analysis: Found : C,69.15; H,6.54% $\text{C}_{20}\text{H}_{23}\text{ClO}_3$, requires C,69.26; H,6.64%.

[S]-2-Chloro-4-methylpentyl-4'-hydroxybenzoate (19)

A mixture of [S]-2-chloro-4-methylpentyl 4'-benzyloxybenzoate (10.4g, 0.03mol) dissolved in ethylacetate (100ml) and 5% Pd-C catalyst (5.2g) was stirred in an atmosphere of hydrogen till the calculated amount of hydrogen was absorbed. The reaction mixture was filtered and ethylacetate removed by distillation under reduced pressure. The residual product so obtained was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol.

Yield 91%; m.p. 60°C; $[\alpha] = -6.2$ ($c = 2$ in $\text{C}_2\text{H}_5\text{OH}$); ν_{max} : 3420, 2950, 1690, 1590, 1460, 1285, 1165 cm^{-1} ; δ : 0.65-2.22 (m, 9H, $2\times\text{CH}_3$, CH_2 and $-\text{CH}-$), 3.57-4.6 (m, 3H, $-\text{COOCH}_2\text{CHCl}$), 6.57 (s, 1H, $-\text{OH}$), 6.92 (d, 2H, ArH), 8.0 (d, 2H, ArH).

Elemental analysis: Found : C,60.94; H,6.73% $\text{C}_{13}\text{H}_{17}\text{ClO}_3$, requires C,60.82; H,6.63%.

[S]-2-Chloro-4-methylpentyl-(4'-(4-benzyloxybenzoyloxy))benzoate (20)

A mixture of 4-benzyloxybenzoic acid (2.64g, 11.6mmol), [S]-2-chloro-4-methylpentyl-(4'-hydroxybenzoyloxy)benzoate (2.96g 11.6mmol), N,N'-dicyclohexylcarbodiimide (2.36g, 11.6mmol), 4 - N,N'-dimethylaminopyridine (0.14g, 1.16mmol) and anhydrous dichloromethane was stirred for two hours at room temperature. N,N'-Dicyclohexylurea formed was filtered off and the filtrate diluted with dichloromethane (50ml). The combined organic solution was washed successively with water (2×30ml), 5% aqueous acetic acid (3×50ml), water (3×50ml) and dried (Na₂SO₄). The residue obtained on removal of solvent was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol.

Yield 83%; m.p. 61.2°C; $[\alpha] = -5.7$ ($c = 2$ in CH₂Cl₂); $\nu_{\max}$: 2950, 1690, 1590, 1460, 1285, 1165 cm⁻¹; δ : 0.65-2.22 (m, 9H, 2×CH₃, CH₂ and -CH-), 3.57-4.6 (m, 3H, -COOCH₂CHCl), 5.09 (s, 2H, ArOCH₂Ph), 6.92-8.0 (m, 13H, ArH).

Elemental analysis: Found : C,69.86; H,5.90% C₂₇H₂₇O₅ Cl, requires C,69.45; H,5.79%.

[S]-2-Chloro-4-methylpentyl (4-(3'-chloro-4'-benzyloxybenzoyloxy))benzoate (21)

Following a procedure similar to the one described above for the compound [S]-2-chloro-4-methylpentyl-4-benzyloxybenzoate, 3-chloro 4-benzyloxybenzoic acid was esterified with [S]-2-chloro-4-methylpentyl-(4'-hydroxybenzoyloxy)benzoate in presence of N, N'-dicyclohexylcarbodiimide and 4-N,N'-dimethylaminopyridine using anhydrous dichloromethane as solvent.

Yield 77%; m.p. 58.3°C; $[\alpha] = -12.7$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1690, 1590, 1460, 1285, 1165 cm^{-1} ; δ : 0.65-2.22 (m, 9H, $2\times\text{CH}_3$, CH_2 and $-\text{CH}-$), 3.57-4.6 (m, 3H, $-\text{COOCH}_2\text{CHCl}$), 5.09 (s, 2H, ArOCH_2Ph), 6.92-8.0 (m, 12H, ArH).

Elemental analysis: Found : C,64.76; H,5.29% $\text{C}_{27}\text{H}_{26}\text{O}_5\text{Cl}_2$, requires C,64.67; H,5.19%.

[S]-2-Chloro-4-methylpentyl-(4'-(4-hydroxybenzoyloxy))benzoate (22)

Hydrogenolysis was carried out for [S]-2-chloro-4-methylpentyl(4-(4'-benzyloxybenzoyloxy))benzoate in ethylacetate solution as described previously for compound (20).

Yield 84%; m.p. 67.5°C; $[\alpha] = -5.3$ ($c = 2$ in CH_2Cl_2); ν_{max} : 3420, 2950, 1690, 1590, 1460, 1285, 1165 cm^{-1} ; δ : 0.70-2.12 (m, 9H, $2\times\text{CH}_3$, CH_2 and $-\text{CH}-$), 3.45-4.7 (m, 3H, $-\text{COOCH}_2\text{CHCl}$), 6.45 (s, 1H, $-\text{OH}$), 6.85-8.3 (m, 8H, ArH).

Elemental analysis: Found : C,63.75; H,5.12% $\text{C}_{20}\text{H}_{21}\text{O}_5\text{Cl}$, requires C,63.39; H,5.58%.

[S]-2-Chloro-4-methylpentyl-(4'-(3'-chloro-4-hydroxybenzoyloxy))benzoate (23)

Hydrogenolysis was carried out for [S]-2-chloro-4-methylpentyl(4-(3'-chloro-4'-benzyloxybenzoyloxy))benzoate in ethylacetate solution as described previously for compound (20).

Yield 84%; m.p. 64.5°C; $[\alpha] = -5.3$ ($c = 2$ in CH_2Cl_2); ν_{max} : 3420, 2950, 1690, 1590, 1460, 1285, 1165 cm^{-1} ; δ : 0.70-2.12 (m, 9H, $2\times\text{CH}_3$, CH_2 and $-\text{CH}-$), 3.45-4.7 (m, 3H, $-\text{COOCH}_2\text{CHCl}$), 6.45 (s, 1H, $-\text{OH}$), 6.85-8.3 (m, 7H, ArH).

Elemental analysis: Found : C,58.58; H,5.12% $\text{C}_{20}\text{H}_{20}\text{O}_5\text{Cl}_2$, requires C,58.39; H,4.87%.

[2S, 3S]-2-Chloro-3-methylpentanoic acid (24)

This was prepared from l-isoleucine following a procedure similar to the one described above for the compound [S]-2-chloro-4-methylpentanoic acid.

Yield, 49%; b.p. 84.0 °C/3 mm; $[\alpha] = -2.62$ ($c = 5$ in $\text{C}_2\text{H}_5\text{OH}$); (Reported¹⁰, b.p. 88-90°C/1-2 mm; $[\alpha] = -2.92$ ($c = 5$ in $\text{C}_2\text{H}_5\text{OH}$).

[2S, 3S]-Methyl 2-chloro-3-methylpentanoate (25)

Following a procedure similar to the one described above, [2S, 3S]-methyl 2-chloro-3-methylpentanoic acid was esterified with methanol in the presence of catalytic amount of concentrated sulphuric acid.

Yield, 98%; b.p. 94-98°C/ 20-25 mm. (Reported¹⁰ b.p. 71-72°C/10 mm.).

[2S, 3S]-2-Chloro-3-methylpentanol (26)

Following a procedure similar to the one described above for compound [S]-2-chloro-4-methylpentanol, [2S, 3S]-methyl-2-chloro-3-methylpentanoate was reduced to the corresponding alcohol by lithium aluminium hydride.

Yield 90%; b.p. 60°C/7mm; $[\alpha] = -5.0$ ($c = 2$ in CHCl_3); $\nu_{\text{max}}(\text{neat})$: 3370, 2960, 2880, 1480, 1465, 1380 and 1075 cm^{-1} ; δ : 0.7-1.1 (m, 6H, $-(\text{CH}_3)\text{C}-\text{C}(\text{CH}_3)-$), 1.1-2.0 (m, 3H, $-\text{CH}_2-\text{CH}$), 2.6 (s, 1H, $-\text{OH}$), 3.55-4.1 (m, 3H, $-\text{CH}(\text{Cl})-\text{CH}_2\text{O}$).

[2S, 3S]-2-Chloro-3-methylpentyl-4'-benzyloxybenzoate (27)

Following a procedure similar to the one described above for the compound [S]-2-chloro-4-methylpentyl-4-benzyloxybenzoate, 4-benzyloxybenzoic acid was esterified with [2S, 3S]-2-chloro-3-methylpentanol in presence of N, N'-dicyclohexylcarbodiimide and 4-N,N'-dimethylaminopyridine using anhydrous dichloromethane as solvent.

Yield 64 %; m.p. 48-50°C; $[\alpha] = +3.13$ ($c = 2$ in CHCl_3); ν_{max} : 2950, 1715, 1605, 1510, 1460, 1260, 1170 and 1100 cm^{-1} ; δ : 0.8-2.0 (m, 9H, $2\times(\text{CH}_3)$, CH_2 and CH), 4.06-4.68 (m, 3H, $-\text{COOCH}_2\text{CHCl}$), 5.09 (s, 2H, ArOCH_2Ph), 6.82-8.18 (m, 9H, ArH).

Elemental analysis: Found : C, 69.38; H, 6.70% $\text{C}_{20}\text{H}_{23}\text{ClO}_3$, requires C, 69.26; H, 6.64%.

[2S, 3S]-2-Chloro-3-methylpentyl-4'-hydroxybenzoate (28)

Following a procedure described above for compound [S]-2-chloro-4-methylpentyl-4-hydroxybenzoate, [2S, 3S]-2-chloro-3-methylpentyl 4-benzyloxybenzoate was subjected to hydrogenolysis in ethylacetate using 5% Pd-C as a catalyst.

Yield 90%; m.p. 59.0°C; $[\alpha] = -6.5$ ($c = 2$ in C_2H_5OH); ν_{max} : 3360, 2980, 1690, 1590, 1515, 1450, 1270, 1165 cm^{-1} ; δ : 0.72-2.12 (m, 9H, 2 $\times$ CH₃, CH₂ and -CH-), 4.04-4.76 (m, 3H, -COOCH₂CHCl), 6.80 (s, 1H, -OH), 6.88-8.48 (d, 4H, ArH).

Elemental analysis: Found : C,61.03; H,6.80% $C_{13}H_{17}ClO_3$, requires C,60.82; H,6.63%.

[2S, 3S]-2-Chloro-3-methylpentyl-(4'-(4-hydroxybenzoyloxy))benzoate (29)

Hydrogenolysis was carried out for [2S, 3S]-2-chloro-3-methylpentyl-(4'-(4-benzyloxybenzoyloxy))benzoate in ethylacetate solution as described above for compound (20).

Yield 81%; m.p. 67.4°C; $[\alpha] = -3.2$ ($c = 2$ in CH_2Cl_2); ν_{max} : 3420, 2950, 1690, 1590, 1460, 1285, 1165 cm^{-1} ; δ : 0.70-2.12 (m, 9H, 2 $\times$ CH₃, CH₂ and -CH-), 3.45-4.7 (m, 3H, -COOCH₂CHCl), 6.45 (s, 1H, -OH), 6.85-8.3 (m, 8H, ArH).

Elemental analysis: Found : C,63.48; H,5.32% $C_{20}H_{21}O_5Cl$, requires C,63.75; H,5.58%

[2S, 3S]-2-Chloro-3-methylpentyl-(4'-(4-hydroxybenzoyloxy))benzoate (30)

Hydrogenolysis was carried out for [2S, 3S]-2-chloro-3-methylpentyl(4-(4'-benzyloxybenzoyloxy))benzoate in ethylacetate solution as described previously for compound (20).

Yield 88%; m.p. 64.5°C; $[\alpha] = -3.3$ ($c = 2$ in CH_2Cl_2); ν_{max} : 3420, 2950, 1690, 1590, 1460, 1285, 1165 cm^{-1} ; δ : 0.70-2.12 (m, 9H, $2\times\text{CH}_3$, CH_2 and $-\text{CH}-$), 3.45-4.7 (m, 3H, $-\text{COOCH}_2\text{CHCl}$), 6.45 (s, 1H, $-\text{OH}$), 6.85-8.3 (m, 8H, ArH).

Elemental analysis: Found : C,58.58; H,5.12% $\text{C}_{20}\text{H}_{20}\text{O}_5\text{Cl}$, requires
C,58.39; H,4.87%

4-Methoxybiphenyl (31)

4-Hydroxybiphenyl (51.0g, 300mmol) was placed in a 500ml three-necked flask equipped with a pressure equalising funnel, a mechanical stirrer and a reflux condenser. A solution of sodium hydroxide (12.8g, 320mmol) in water (128ml) and ethyl alcohol (100ml) was added to it. This mixture was stirred and dimethylsulphate (37.8g, 300mmol) was added dropwise to it over a period of one hour. Then the reaction mixture was refluxed for two hours. A clear solution was obtained. This was cooled and the solid product so obtained was filtered off, washed with water, dried and recrystallised from ethanol.

Yield 80%; m.p. 89.0°C (Reported¹⁰ m.p. 91.0°C).

4-Methoxy-4'-acetylbiphenyl (32)

In a 500ml three-necked flask fitted with a mechanical stirrer, a pressure equalising separatory funnel and a reflux condenser connected to a water trap through anhydrous calcium chloride guard tube, a mixture of 4-methoxybiphenyl (18.4g, 100mmol), anhydrous aluminium chloride (18.7g, 140mmol) and carbon disulphide (175ml) was placed. This was cooled in an ice-bath and while stirring freshly distilled acetyl chloride (7.8g, 100mmol) was added dropwise to it. After the addition was

complete the reaction mixture was stirred at 35.0°C for five hours and then refluxed for one hour. After the removal of carbon disulphide, the residue was poured into a mixture of ice and concentrated hydrochloric acid. The solid formed was filtered and boiled with ether (50ml) for fifteen minutes and the ethereal solution was decanted off. The ether insoluble portion was crystallised from isopropanol.

Yield 65%; m.p. 157.0°C (Reported¹¹ m.p. 156.5°C).

4-Hydroxy-4'-acetylbiphenyl (33)

A mixture of 4-methoxy-4'-acetylbiphenyl (10.0g, 44.0mmol), hydrobromic acid (48%, 75ml) and acetic acid (125ml) was refluxed for sixteen hours. It was then poured into ice-cold water and the precipitate formed was filtered, washed with water and dried. The crude product so obtained was crystallised from ethanol.

Yield 95%; m.p. 146-147°C (Reported¹² m.p. 146-147°C).

4-Benzoyloxy-4'-acetylbiphenyl (34)

A mixture of 4-hydroxy-4'-acetylbiphenyl (4.24g, 20mmol), benzylchloride (3.03g, 24 mmol), potassium carbonate (8.28g, 60mmol) and anhydrous acetone (100ml) was refluxed for forty-eight hours. Then the acetone was distilled off from the reaction mixture and the residue poured into a mixture of ice and concentrated hydrochloric acid and extracted with chloroform (3×100ml). The combined chloroform solution was washed with water (3×100ml) and dried (Na₂SO₄). The solvent was removed and the residue was purified by column chromatography on silica gel using chloroform as eluent. The required material so obtained after removal of solvent was crystallised from t-butanol.

Yield 70%; m.p. 162-165.0°C (Reported¹⁰ m.p. 162-164°C).

***4'-Benzyloxybiphenyl-4-carboxylic acid* (35)**

A solution of sodium hypobromite was prepared by adding bromine (6.4g, 40mmol) to a solution of sodium hydroxide (3.2g, 80 mmol) in water (40ml) at -5°C. This was added to a vigorously stirred solution of 4'-benzyloxy-4-acetylbiphenyl (3.0g, 10mmol) in 1,4-dioxane (20ml). The addition was carried out at 30-35°C during 30 minutes. Stirring was continued and the temperature was raised to 60°C and held there for one hour to ensure the completion of the reaction. Enough aqueous sodium metabisulphite solution was added to destroy the excess of hypobromite. Water (50ml) was added and about 40ml of the liquid was distilled. The residual portion was cooled and acidified with concentrated hydrochloric acid. The white precipitate obtained was filtered off, washed thoroughly with water and dried. This was crystallised from acetic acid.

Yield 76.6%; transition temperatures K 267 N 286 (decomposes).

***[R]-[-]-1-Methylheptyl-4'-benzyloxybiphenyl-4-carboxylate* (36)**

This was prepared following a esterification procedure of Hassner and Alexanian.⁵ Thus, a mixture of 4-benzyloxybiphenyl-4'-carboxylic acid (1g, 3.28mmol), R-[-]-2-octanol (0.42g, 3.28 mmol), 4-N,N'-dimethylaminopyridine (0.25g, 1.96mmol) and anhydrous dichloromethane (16.0ml) was stirred for five minutes. To the mixture, was added N,N'-dicyclohexylcarbodiimide (1.3g, 6.3mmol) and stirring was continued for six hours at room temperature. The solid N,N'-dicyclohexylurea formed was filtered off and the filtrate was diluted with dichloromethane (50ml). The solution was

washed with 5% aqueous acetic acid (2×30ml), water (3×30ml) and dried over anhydrous Na₂SO₄. After the solvent was removed, the residue was purified by column chromatography on silica gel using chloroform as eluent.

Yield 87%; m.p. 104.6-105.7°C; [α] = -36.9 (c = 2 in CH₂Cl₂); $\nu_{\max}$: 3000, 1710, 1610, 1580, 1280, 1050 cm⁻¹; δ : 0.63-2.39 (m, 16H, 2× -CH₃, 5×CH₂), 4.15 (m, 1H, COOCH), 5.12 (s, 2H, ArCH₂OAr), 6.91-8.15 (m, 13H, ArH)

Elemental analysis: Found : C,80.68; H,7.64% C₂₈H₃₂O₃, requires
C,80.78; H, 7.69%.

[R]-[-]-1-Methylheptyl-4'-hydroxybiphenyl-4-carboxylate (37)

A mixture of [R]-[-]-1-methylheptyl-4'-benzyloxybiphenyl-4-carboxylate (3.0g, 7.21mmol) in ethylacetate (20ml) and 5% Pd-C catalyst (1.2g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was then filtered off and ethylacetate removed by distillation under reduced pressure. The residual solid was chromatographed on silica gel and eluted with chloroform : ethylacetate (9:1) mixture. Removal of solvent from the eluate afforded a white crystalline solid. This was crystallised from ethanol.

Yield 81.5%; m.p. 84-86°C (Reported¹³ m.p. 84-86°C); [α] = - 43.5 (c = 2 in CH₂Cl₂); $\nu_{\max}$: 3350, 2960, 1740, 1690, 1600, 1510, 1450, 1275 and 1050 cm⁻¹; δ : 0.75-2.0 (m, 16H, 2×CH₃, 5×CH₂), 4.2 (m, 1H, COOCH), 6.9 (d, 2H, ArH), 7.2 (s, 1H), 7.5 (d, 2H, ArH), 7.6 (d, 2H, ArH), 8.1 (d, 2H, ArH).

Elemental analysis: Found : C,77.41; H,7.96% C₂₁H₂₆O₃, requires
C,77.30; H,7.98%

Ethyl 4-benzyloxybenzoate (38)

A solution of sodium ethoxide was prepared by dissolving sodium (4.6g, 200mmol) in absolute ethanol (150ml). Ethyl 4-hydroxybenzoate (33.2g, 200mmol) was added to it. The resulting reaction mixture was stirred and refluxed for thirty minutes. Benzylchloride (27.8g, 220mmol) was then added to it. The stirring and refluxing was continued for a further period of twelve hours. Excess ethanol was distilled off, the residue poured into cold water and extracted with ether (3×100ml). The combined ethereal solution was washed with 10% aqueous sodium hydroxide (2×75ml) and water (2×60ml). The ethereal solution was dried (Na₂SO₄) and the solvent removed. The solid residue was crystallised from ethanol.

Yield 78%; m.p. 46.0°C (Reported¹⁴ m.p. 46.0°C).

4-Benzyloxybenzoic acid (39)

A mixture of ethyl 4-benzyloxybenzoate (30.0g, 120mmol), potassium hydroxide (8.6g, 150mmol), water (20ml) and ethanol (50ml) was refluxed for six hours. Ethanol was removed by distillation and the residue poured into cold water. This was acidified by adding cold, concentrated hydrochloric acid. The white precipitate so obtained was filtered off, washed with water and dried. This was crystallised from ethanol.

Yield 90%; m.p. 191-192°C (Reported¹⁵ m.p. 188.0°C).

[R]-[-]-1-Methylheptyl-4-benzyloxybenzoate (40)

This was prepared following a esterification procedure of Hassner and Alexanian⁵. Thus, a mixture of 4-benzyloxybenzoic acid (4.0g, 17.54mmol), [R]-[-]-2-

octanol (2.3g, 17.54mmol), 4-N,N'-dimethylaminopyridine (1.3g, 10.5mmol) and anhydrous dichloromethane (80ml) was stirred for five minutes. To the mixture, was added N,N'-dicyclohexylcarbodiimide (5.4g, 26.7mmol) and stirring was continued for six hours at room temperature. The solid N,N'-dicyclohexylurea formed was filtered off and the filtrate diluted with dichloromethane (100ml). The solution was washed with 5% aqueous acetic acid (2×30ml), water (3×30ml) and dried (Na₂SO₄). After the solvent was removed, the residue was purified by column chromatography on silica gel using chloroform as eluent. [R]-[-]-1-Methylheptyl-4-benzyloxybenzoate was obtained as a viscous liquid.

Yield 87%; $[\alpha] = -21.8$ ($c = 2$ in CH₂Cl₂); $\nu_{\max}$: 3000, 1710, 1610, 1580, 1280, 1050 cm⁻¹; δ : 0.63-2.39 (m, 14H, 2×-CH₃, 4×CH₂), 4.15 (m, 1H, COOCH), 5.12 (s, 2H, ArCH₂OAr), 6.91-8.15 (m, 9H, ArH).

Elemental analysis: Found : C,77.81; H,8.31% C₂₂H₂₈O₃, requires C,77.64; H,8.23%.

[R]-[-]-1-Methylheptyl-4-hydroxybenzoate (41)

A mixture of [R]-[-]-1-methylheptyl-4-benzyloxybenzoate (5.0g, 14.7mmol) dissolved in ethanol (40ml) and 5% Pd-C catalyst (2.0g) was stirred in an atmosphere of hydrogen till the calculated quantity of hydrogen was absorbed. The reaction mixture was then filtered and ethanol removed by distillation under reduced pressure. The residual liquid was chromatographed on silica gel and eluted with chloroform : ethylacetate (9:1) mixture. Removal of the solvent from the eluate afforded a viscous liquid.

Yield 82.0%; $[\alpha] = -39.7$ ($c = 2$ in CH_2Cl_2); ν_{max} : 3310, 2950, 1740, 1690, 1600, 1510, 1450, 1275 and 1050 cm^{-1} ; δ : 0.75-2.0 (m, 16H, $2\times\text{CH}_3$, $5\times\text{CH}_2$), 4.2 (m, 1H, COOCH), 6.9 (d, 2H, ArH), 7.2 (s, 1H), 7.9 (d, 2H, ArH).

Elemental analysis: Found : C,71.86; H,8.78% $\text{C}_{15}\text{H}_{22}\text{O}_3$, requires
C,72.00; H,8.80%.

[R]-[-]-1-Methylheptyl 4-(4'-benzyloxybenzoyloxy)benzoate (42)

A mixture of 4-benzyloxybenzoic acid (2.64g, 11.6mmol), [R]-[-]-1-methylheptyl-4-hydroxybenzoate (2.9g, 11.6mmol), N,N'-dicyclohexylcarbodiimide (2.36g, 11.6mmol), 4 - N,N'-dimethylaminopyridine (0.14g, 1.16mmol) and anhydrous dichloromethane was stirred for two hours at room temperature. N,N'-Dicyclohexylurea formed was filtered off and the filtrate was diluted with dichloromethane (50ml). The combined organic solution was washed successively with water ($2\times 30\text{ml}$), 5% aqueous acetic acid ($3\times 50\text{ml}$), water ($3\times 50\text{ml}$) and dried (Na_2SO_4). The residue obtained on removal of solvent was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white solid which was crystallised from ethanol.

Yield 87%; m.p. 111.1°C ; $[\alpha] = -25.7$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 2850, 1720, 1620, 1600, 1480, 1280 and 1050 cm^{-1} ; δ : 0.94-2.28 (m, 16H, $2\times\text{CH}_3$, $5\times\text{CH}_2$), 4.35 (m, 1H, COOCH), 5.18 (s, 2H, ArCH_2OAr), 7.02-8.6 (m, 13H, ArH).

Elemental analysis: Found : C,76.26; H,7.12% $\text{C}_{29}\text{H}_{32}\text{O}_5$, requires
C,76.48; H,7.03%.

[R]-[-]-1-Methylheptyl 4-(4'-hydroxybenzoyloxy)benzoate (43)

Hydrogenolysis was carried out for [R]-[-]-1-methylheptyl-4'-(4-benzyloxybenzoyloxy)benzoate in ethylacetate solution as described for the previous compound (20).

Yield 81.0%; m.p. 82.6°C; $[\alpha] = -33.2$ ($c = 2$ in CH_2Cl_2); ν_{max} : 3310, 2950, 1740, 1690, 1600, 1510, 1450, 1275 and 1050 cm^{-1} ; δ : 0.75-2.0 (m, 16H, $2\times\text{CH}_3$, $5\times\text{CH}_2$) 4.1 (m, 1H, COOCH), 6.2(s, 1H, OH), 6.5-8.1 (m, 8H, ArH).

Elemental analysis: Found : C,72.28; H,7.18% $\text{C}_{22}\text{H}_{26}\text{O}_5$, requires C,72.31; H,7.12%.

Cognate preparations were carried out for all the final compounds. A typical procedure for one of the compounds, [R]-[-]-1-methylheptyl 4(6-(10-undecenylloxynaphthalene-2-carbonyloxy) 4'-benzoyloxy)benzoate, is given below followed by physical data for all others.

[R]-[-]-1-Methylheptyl 4-[4'-(6-(10-undecenylloxynaphthalene-2-carbonyloxy)-benzoyloxy]benzoate (44)

A mixture of 6-(10-undecenylloxy)-2-naphthoic acid (142mg, 0.46mmol) and [R]-[-]-1-methylheptyl-4-(4'-hydroxybenzoyloxy)benzoate (180mg, 0.46mmol), N,N'-dicyclohexylcarbodiimide (94mg, 0.46mmol), 4 - N,N'-dimethylaminopyridine (5mg, 0.046mmol) and anhydrous dichloromethane (10ml) was stirred for two hours at room temperature. N,N'-Dicyclohexylurea formed was filtered off and the filtrate was diluted with dichloromethane (25ml) and this solution was washed successively with water ($2\times 30\text{ml}$), 5% aqueous acetic acid ($3\times 50\text{ml}$), water ($3\times 50\text{ml}$) and dried (Na_2SO_4). The

residue obtained on removal of solvent was chromatographed on silica gel and eluted with chloroform. Removal of solvent from the eluate afforded a white solid which was crystallised repeatedly from ethanol.

Yield 82%; $[\alpha] = -14.67$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 35H, $3\times\text{CH}_3$, $13\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 14H, ArH and vinyl-H).

Elemental analysis: Found : C,76.17; H,7.77% $\text{C}_{44}\text{H}_{52}\text{O}_7$, requires
C,76.30; H,7.51%.

[S] 2-Chloro-4-methylpentyl 4-[4'-(6-(5-hexenyloxy)naphthalene-2-carbonyloxy) 3'-chlorobenzoyloxy]benzoate (45)

Yield 88%; $[\alpha] = 9.12$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2960, 1745, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 15H, $2\times\text{CH}_3$, $4\times\text{CH}_2$, CH), 4.0 (t, 2H, ArOCH_2), 4.1-4.64 (m, 3H, $\text{COOCH}_2\text{CHCl}$), 6.34-8.46 (m, 16H, ArH and vinyl-H).

Elemental analysis: Found : C,67.14; H,5.18% $\text{C}_{37}\text{H}_{36}\text{O}_7\text{Cl}_2$, requires
C,66.97; H,5.43%.

[S] 2-Chloro-4-methylpentyl 4-[4'-(6-(9-decenyloxy)naphthalene-2-carbonyloxy) 3'-chlorobenzoyloxy]benzoate (46)

Yield 80%; $[\alpha] = 10.27$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 23H, $2\times\text{CH}_3$, $8\times\text{CH}_2$, CH), 4.0 (t, 2H, ArOCH_2), 4.1-4.64 (m, 3H, $\text{COOCH}_2\text{CHCl}$), 6.34-8.46 (m, 16H, ArH and vinyl-H).

Elemental analysis: Found: C,68.56; H,6.08% C₄₁ H₄₄ O₇ Cl₂, requires
C,68.43; H,6.12%

[S] 2-Chloro-4-methylpentyl 4-[4'-(6-(10-undecenyloxy)naphthalene-2-carbonyloxy) 3'-chlorobenzoyloxy]benzoate (47)

Yield 78%; $[\alpha] = 10.36$ ($c = 2$ in CH₂Cl₂); $\nu_{\max}$: 2950, 1745, 1730, 1720, 1600, 1490, 1270 and 1050 cm⁻¹; δ : 0.7-2.0 (m, 25H, 2×CH₃,9×CH₂,CH), 4.0 (t, 2H, ArOCH₂), 4.1-4.64 (m, 3H, COOCH₂CHCl), 6.34-8.46 (m, 16H, ArH and vinyl-H).

Elemental analysis: Found : C,68.47; H,6.08% C₄₂ H₄₆ O₇ Cl₂, requires
C,68.76; H,6.28%

[S] 2-Chloro-4-methylpentyl 4-[4'-(6-(5-hexenyloxy)naphthalene-2-carbonyloxy) benzoyloxy]benzoate (48)

Yield 81%; $[\alpha] = 2.21$ ($c = 2$ in CH₂Cl₂); $\nu_{\max}$: 3000, 1740, 1730, 1720, 1590, 1490, 1270 and 1050 cm⁻¹; δ : 0.7-2.0 (m, 15H, 2×CH₃,4×CH₂,CH), 4.0 (t, 2H, ArOCH₂), 4.1-4.64 (m, 3H, COOCH₂CHCl), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,70.57; H,5.80% C₃₇ H₃₇ O₇ Cl, requires
C,70.64; H,5.89%.

[S] 2-Chloro-4-methylpentyl 4-[4'-(6-(9-decenyloxy)naphthalene-2-carbonyloxy)benzoyloxy]benzoate (49)

Yield 88%; $[\alpha] = 3.27$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 23H, $2\times\text{CH}_3, 8\times\text{CH}_2, \text{CH}$), 4.0 (t, 2H, ArOCH_2), 4.1-4.64 (m, 3H, $\text{COOCH}_2\text{CHCl}$), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C, 71.71; H, 6.18% $\text{C}_{41}\text{H}_{45}\text{O}_7\text{Cl}$, requires C, 71.88; H, 6.57%.

[S] 2-Chloro-4-methylpentyl 4-[4'-(6-(10-undecenyloxy)naphthalene-2-carbonyloxy)benzoyloxy]benzoate (50)

Yield 88%; $[\alpha] = 3.97$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1745, 1730, 1720, 1605, 1500, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 25H, $2\times\text{CH}_3, 9\times\text{CH}_2, \text{CH}$), 4.0 (t, 2H, ArOCH_2), 4.1-4.64 (m, 3H, $\text{COOCH}_2\text{CHCl}$), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C, 72.57; H, 6.38% $\text{C}_{42}\text{H}_{47}\text{O}_7\text{Cl}$, requires C, 72.15; H, 6.73%.

[2S, 3S] 2-Chloro-3-methylpentyl 4-[4'-(6-(5-hexenyloxy)naphthalene-2-carbonyloxy)benzoyloxy]benzoate (51)

Yield 80%; $[\alpha] = 3.21$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 15H, $2\times\text{CH}_3, 4\times\text{CH}_2, \text{CH}$), 4.0 (t, 2H, ArOCH_2), 4.1-4.64 (m, 3H, $\text{COOCH}_2\text{CHCl}$), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,70.51; H,5.50% $C_{37}H_{37}O_7Cl$, requires
C,70.64; H,5.89%.

[2S, 3S] 2-Chloro-3-methylpentyl 4-[4'-(6-(9-decenyloxy)naphthalene-2-carbonyloxy) benzoyloxy]benzoate (52)

Yield 87%; $[\alpha] = 4.25$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1745, 1730, 1725, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 23H, $2\times CH_3, 8\times CH_2, CH$), 4.0 (t, 2H, $ArOCH_2$), 4.1-4.64 (m, 3H, $COOCH_2CHCl$), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,71.67; H,6.34% $C_{41}H_{45}O_7Cl$, requires
C,71.88; H,6.57%.

[2S, 3S] 2-Chloro-3-methylpentyl 4-[4'-(6-(10-undecenyloxy)naphthalene-2-carbonyloxy) benzoyloxy]benzoate (53)

Yield 85%; $[\alpha] = 4.79$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 25H, $2\times CH_3, 9\times CH_2, CH$), 4.0 (t, 2H, $ArOCH_2$), 4.1-4.64 (m, 3H, $COOCH_2CHCl$), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,72.57; H,6.38% $C_{42}H_{47}O_7Cl$, requires
C,72.15; H,6.73%.

[2S, 3S] 2-Chloro-3-methylpentyl 4-[4'-(6-(5-hexenyloxy)naphthalene-2-carbonyloxy]benzoate (54)

Yield 86%; $[\alpha] = 3.12$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 15H, $2\times\text{CH}_3, 4\times\text{CH}_2\text{CH}$), 4.0 (t, 2H, ArOCH_2), 4.1-4.64 (m, 3H, $\text{COOCH}_2\text{CHCl}$), 6.34-8.46 (m, 13H, ArH and vinyl-H).

Elemental analysis: Found : C, 70.48; H, 6.88% $\text{C}_{30}\text{H}_{33}\text{O}_5\text{Cl}$, requires C, 70.80; H, 6.49%.

[2S, 3S] 2-Chloro-3-methylpentyl 4-[4'-(6-(9-decenyloxy)naphthalene-2-carbonyloxy]benzoate (55)

Yield 85%; $[\alpha] = 3.92$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 23H, $2\times\text{CH}_3, 8\times\text{CH}_2\text{CH}$), 4.0 (t, 2H, ArOCH_2), 4.1-4.64 (m, 3H, $\text{COOCH}_2\text{CHCl}$), 6.34-8.46 (m, 13H, ArH and vinyl-H).

Elemental analysis: Found : C, 72.47; H, 7.08% $\text{C}_{34}\text{H}_{41}\text{O}_5\text{Cl}$, requires C, 72.28; H, 7.26%.

[2S, 3S] 2-Chloro-3-methylpentyl 4-[4'-(6-(10-undecenyloxy)naphthalene-2-carbonyloxy]benzoate (56)

Yield 81%; $[\alpha] = 4.12$ ($c = 2$ in CH_2Cl_2); ν_{max} : 3000, 1745, 1735, 1720, 1590, 1500, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 25H, $2\times\text{CH}_3, 9\times\text{CH}_2\text{CH}$), 4.0 (t, 2H, ArOCH_2), 4.1-4.64 (m, 3H, $\text{COOCH}_2\text{CHCl}$), 6.34-8.46 (m, 13H, ArH and vinyl-H).

Elemental analysis: Found : C, 72.57; H, 7.68% $\text{C}_{35}\text{H}_{43}\text{O}_5\text{Cl}$, requires C, 72.73; H, 7.27%.

[R]-[-]-1-Methylheptyl 4-[6-(5-hexenyloxy)naphthalene-2-carbonyloxy]

benzoate (57)

Yield 81%; $[\alpha] = -10.23$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 22H, $2\times\text{CH}_3$, $8\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 13H, ArH and vinyl-H).

Elemental analysis: Found : C,76.47; H,7.48% $\text{C}_{32}\text{H}_{38}\text{O}_5$, requires
C,76.49; H,7.57%.

[R]-[-]-1-Methylheptyl 4-[6-(9-decenyloxy)naphthalene-2-carbonyloxy]

benzoate (58)

Yield 90%; $[\alpha] = -12.12$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 30H, $2\times\text{CH}_3$, $12\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 13H, ArH and vinyl-H).

Elemental analysis: Found : C,77.17; H,8.58% $\text{C}_{36}\text{H}_{46}\text{O}_5$, requires
C,77.42; H,8.24%.

[R]-[-]-1-Methylheptyl 4-[6-(10-undecenyloxy)naphthalene-2-carbonyloxy]

benzoate (59)

Yield 88%; $[\alpha] = -13.24$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1745, 1730, 1720, 1600, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 24H, $2\times\text{CH}_3$, $9\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 13H, ArH and vinyl-H).

Elemental analysis: Found : C,77.55; H,8.28% $\text{C}_{37}\text{H}_{48}\text{O}_5$, requires
C,77.62; H,8.39%.

[R]-[-]-1-Methylheptyl 4-[4'-(6-(5-hexenyloxy)naphthalene-2-carbonyloxy)benzoyloxy]benzoate (60)

Yield 81%; $[\alpha] = -12.42$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 22H, $2\times\text{CH}_3$, $8\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,75.17; H,6.58% $\text{C}_{39}\text{H}_{42}\text{O}_7$, requires C,75.24; H,6.75%.

[R]-[-]-1-Methylheptyl 4-[4'-(6-(9-decenyloxy)naphthalene-2-carbonyloxy)benzoyloxy]benzoate (61)

Yield 88%; $[\alpha] = -14.25$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1725, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 30H, $2\times\text{CH}_3$, $12\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,76.45; H,7.52% $\text{C}_{43}\text{H}_{50}\text{O}_7$, requires C,76.11; H,7.37%.

[R]-[-]-1-Methylheptyl 4'-[6-(5-hexenyloxy)naphthalene-2-carbonyloxy]biphenylcarboxylate (62)

Yield 88%; $[\alpha] = -13.47$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1745, 1735, 1720, 1605, 1485, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 22H, $2\times\text{CH}_3$, $8\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,78.67; H,7.38% $\text{C}_{38}\text{H}_{42}\text{O}_5$, requires C,78.89; H,7.27%.

[R]-[-]-1-Methylheptyl 4'-[6-(9-decenyloxy)naphthalene-2-carbonyloxy]

biphenylcarboxylate (63)

Yield 86%; $[\alpha] = -15.12$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 30H, $2\times\text{CH}_3$, $12\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,79.71; H,8.08% $\text{C}_{42}\text{H}_{50}\text{O}_5$, requires
C,79.50; H,7.89%

[R]-[-]-1-Methylheptyl 4'-[6-(10-undecenyloxy)naphthalene-2-carbonyloxy]

biphenylcarboxylate (64)

Yield 87%; $[\alpha] = -19.27$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1725, 1600, 1500, 1270 and 1050 cm^{-1} ; δ : 0.7-2.0 (m, 32H, $2\times\text{CH}_3$, $13\times\text{CH}_2$), 4.0 (t, 2H, ArOCH_2), 5.0-5.34 (m, 1H, COOCH), 6.34-8.46 (m, 17H, ArH and vinyl-H).

Elemental analysis: Found : C,74.7; H,8.08% $\text{C}_{43}\text{H}_{52}\text{O}_5$, requires
C,75.0; H,7.92%

III.3.1 Synthetic procedures for polymers

All the polymers examined were prepared by the same procedure. A typical procedure for one of the polymers RP-4, is given below followed by physical constants for all other polymers.

Polymer RP-4

To a dry round bottomed flask flushed with dry nitrogen, was introduced poly(hydrogenmethylsiloxane) 0.17g (0.65 mmol counted on SiH) and monomer, [S]-2-Chloro-4-methylpentyl 4-[4'-(6-(5-hexenyloxy)naphthalene-2-carbonyloxy)3'-chlorobenzoyloxy]benzoate, 0.46g (0.7 mmol). Anhydrous toluene (4ml) was added, the mixture was heated to 80°C. A solution of the catalyst was prepared by dissolving chloroplatinic acid, $\text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$ (0.12mg), in isopropanol (10ml), so that the ratio of catalyst to monomer is $1:1 \times 10^{-5}$ to 1×10^{-6} . A solution of this catalyst (10 μ l) was added to the reactants through a hypodermic syringe and the mixture stirred for two days. If the reaction was not complete, as indicated by IR spectrum, an additional 10 μ l of the catalyst was added and stirred further. After the completion of the reaction, as indicated by the absence of Si-H band at 2100cm^{-1} , the reaction mixture was added to methanol (250ml), and the polymer so obtained was collected by centrifugation. This was dissolved in dichloromethane (75ml) and washed well with water ($3 \times 50\text{ml}$). The organic solution was filtered through a microfilter (0.2 μm) prior to repeated reprecipitation with methanol to obtain the pure polymer.

Yield 20%, $[\alpha] = 3.9$ ($c = 2$ in CHCl_3), ν_{max} : 2960, 1745, 1730, 1724, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl}-$), 6.8-8.2 (m, ArH).

Polymer RP-8

Yield 80%; $[\alpha] = 4.12$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1600, 1495, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer RP-9

Yield 17%; $[\alpha] = 5.6$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2925, 1735, 1725, 1715, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer KP-4

Yield 18%; $[\alpha] = 2.7$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer KP-8

Yield 21%; $[\alpha] = 3.5$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2945, 1745, 1730, 1720, 1600, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer KP-9

Yield 23%; $[\alpha] = 2.7$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1735, 1730, 1720, 1590, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer IP-4

Yield 12%; $[\alpha] = 3.1$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2940, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer IP-8

Yield 17%; $[\alpha] = 5.5$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer IP-9

Yield 22%; $[\alpha] = 4.0$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer SP-4

Yield 16%; $[\alpha] = 2.2$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1735, 1725, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer SP-8

Yield 15%; $[\alpha] = 3.1$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2945, 1735, 1725, 1715, 1585, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer SP-9

Yield 18%; $[\alpha] = 4.1$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 4.04-4.76 (m, $\text{COOCH}_2\text{CHCl-}$), 6.8-8.2 (m, ArH).

Polymer HP-4

Yield 18%; $[\alpha] = -6.3$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1745, 1735, 1725, 1615, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer HP-8

Yield 19%; $[\alpha] = -7.2$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2955, 1740, 1735, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer HP-9

Yield 19%; $[\alpha] = -8.1$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2945, 1740, 1730, 1715, 1605, 1490, 1260 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer NP-4

Yield 20%; $[\alpha] = -7.2$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1745, 1735, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer NP-8

Yield 18%; $[\alpha] = -8.4$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1250 and 1100 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer NP-9

Yield 22%; $[\alpha] = -12.5$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2945, 1740, 1730, 1715, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer AP-4

Yield 23%; $[\alpha] = -7.7$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1735, 1730, 1715, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer AP-8

Yield 20%; $[\alpha] = -9.1$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2945, 1740, 1730, 1720, 1600, 1500, 1250 and 1100 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer AP-9

Yield 17%; $[\alpha] = -11.2$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1730, 1720, 1605, 1490, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si-CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C-}$), 5.2 (s, COOCHC-) 6.8-8.5 (m, ArH).

Polymer MP-25

Yield 22%; $[\alpha] = -8.2$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1740, 1725, 1715, 1605, 1490, 1265 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C}-$), 5.2 (s, $\text{COOCHC}-$) 6.8-8.5 (m, ArH).

Polymer MP-50

Yield 23%; $[\alpha] = -8.6$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2950, 1745, 1735, 1720, 1605, 1500, 1270 and 1050 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C}-$), 5.2 (s, $\text{COOCHC}-$) 6.8-8.5 (m, ArH).

Polymer MP-75

Yield 20%; $[\alpha] = -8.1$ ($c = 2$ in CH_2Cl_2); ν_{max} : 2945, 1735, 1730, 1720, 1600, 1490, 1260 and 1060 cm^{-1} ; δ : 0.00-2.12 [m, methylenes and $(\text{Si}-\text{CH}_3)_n$], 3.9-4.1 (d, $\text{COOCH}_2\text{C}-$), 5.2 (s, $\text{COOCHC}-$) 6.8-8.5 (m, ArH).

References

- 1 N. A. Clark and S. T. Lagerwall, *Appl. Phys. Lett.*, **36**, 899 (1980).
- 2 J. S. Patel, T. M. Leslie and J. W. Goodby, *Ferroelectrics*, **59**, 137 (1984).
- 3 H. Poths and R. Zentel, *Liq. Cryst.*, **16**, (5), 749 (1994).
- 4 G. W. Gray and J. Jones, *J. Chem. Soc.*, 678 (1954).
- 5 A. Hassner and V. Alexanian, *Tetrahedron Lett.*, 4475 (1978).
- 6 O. Mitsunobu, *Synthesis*, 1, (1981).
- 7 K. Fries and G. Finck, *Ber.*, **41**, 4271 (1908).
- 8 B. Shivkumar, *Ph. D. thesis*, Bangalore University, Bangalore, 1991.
- 9 S. J. Fu, S. N. Birnbaum and J. P. Greenstein, *J. Am. Chem. Soc.*, **76**, 6054 (1954).
- 10 *Dictionary of Organic Chemistry*, Fifth Edition, (Chapmann and Hall, 1982).
- 11 G. W. Gray, J. B. Hartley and B. Jones, *J. Chem. Soc.*, 1412 (1955).
- 12 R. Otter and R. L. Shriver, *J. Am. Chem. Soc.*, **73**, 887 (1951).
- 13 C. J. Booth, D. A. Dunmur, J. W. Goodby, J. S. Kang and K. J. Toyne, *J. Mater. Chem.*, **4**, 747 (1993).
- 14 B. Jones and J. Robinson, *J. Chem. Soc.*, 3845 (1955).
- 15 Chemical Abstracts, **38**, 81 (1944).