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EXPERIMENTAL SECTION

General Procedures: ^1H NMR (200 MHz) spectra were recorded on a Bruker ACF-200 instrument using the TMS/solvent signal as an internal reference. Differential scanning calorimetric studies were done on Rheometric Scientifics DSC Plus or Perkin Elmer DSC-7 instruments at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen. All the samples were heated to 250°C and then quenched to room temperature before recording the first scans. Subsequently, the second and third scans, recorded after the controlled cooling cycles, were found to be identical. Polarizing Light Microscopic studies were done on Leitz Ortho Lux 12POL-BK microscope attached with Mettler FP82 HT hot stage. Viscosity measurements were made using an Ubellhode viscometer in a constant temperature bath.

4-(4-Acetoxyphenyl) acetophenone (2): The synthesis was carried out starting from 4-phenyl phenol as described by Tanagaki et al.¹³

Yield = 97%, mp = $124.5\text{--}125.5^\circ\text{C}$.

4-(4-Methoxy phenyl) acetophenone (3): 2g (9.4 mmol.) of 4-(4-acetoxyphenyl) acetophenone (2) was refluxed in 50ml of water containing 3g (75.2 mmols) of sodium hydroxide till the initially insoluble starting material dissolved (ca. 6h). Dimethyl sulphate was then added to it dropwise with stirring till the solution becomes acidic to pH paper. The precipitate formed was filtered, washed with water and recrystallised from 2-propanol.

Yield = 90%, mp = $151\text{--}152^\circ\text{C}(\text{dec.})$

4-(4-Hydroxy phenyl) benzoic acid (5): 4-(4-Methoxy phenyl) acetophenone was oxidised to 4-(4-methoxy phenyl) benzoic acid and further demethylated under standard HBr/acetic acid conditions using a procedure similar to that described by Dauben et al,¹⁴

Overall yield = 89%, mp = $292\text{--}94^\circ\text{C}$.

Ethyl 4-(4-hydroxy phenyl) benzoate (6): 10g (47 mmols) of 4-(4-hydroxy phenyl) benzoic acid was refluxed in absolute ethanol for 15h in presence of ~4ml of concentrated sulfuric acid. The solution was poured into excess of water to get the crude product. The solid was filtered, washed with water and then recrystallised from aqueous ethanol to get light gray crystals.

Yield = 85% mp = 190-191°C. ¹H NMR(d₆DMSO, 200 MHz): 1.37(t, 3H, CH₃), 2.95(s, br., OH), 4.37(q, 2H, CH₂CH₃), 6.98(d, 2H, Ar.), 7.1(d, 2H, Ar.), 8.04(d, 2H, Ar.).

Ethyl 4-[4-(ω-hydroxy oligoethyleneoxy) phenyl] benzoates (BEO_n): 5g (20.7 mmols) of ethyl 4-[4-hydroxyphenyl] benzoate was stirred at 90°C in 50 ml DMF for 30h in the presence of 25g of potassium carbonate, 1.2 equivalent of the appropriate monochloro oligoethyleneoxy glycol and few crystals of potassium iodide. The reaction mixture was poured into water and extracted with chloroform. The chloroform layer was washed with 5% aqueous sodium hydroxide (2x100 ml) and then with water. It was dried over sodium sulfate and then chloroform was removed to get the product.

BEO1: Yield = 60%, mp = 155-156°C, ¹H NMR(CDCl₃): 1.33(t, 3H, CH₂CH₃), 3.94(t, 2H, CH₂CH₂OH), 4.04(t, 2H, PhOCH₂CH₂OH), 4.30(q, 2H, CH₂CH₃), 6.97(d, 2H, Ar.), 7.6-7.7(m, 4H, Ar.), 8.1(d, 2H, Ar.).

BEO2: Yield = 65%, mp = 116-117.5°C ¹H NMR(CDCl₃): 1.41(t, 3H, CH₂CH₃), 3.69(t, 2H, CH₂CH₂OH), 3.76(t, 2H, CH₂CH₂OH), 3.90(t, 2H, CH₂CH₂OPh), 4.19(t, 2H, CH₂OPh), 4.37(q, 2H, CH₂CH₃), 6.97(d, 2H, Ar), 7.6-7.7(m, 4H, Ar.), 8.10(d, 2H, Ar.).

BEO3: Yield = 79%, mp = 83-84°C, ¹H NMR(CDCl₃): 1.4(t, 3H, CH₂CH₃), 3.6(t, 2H, CH₂OH), 3.73(t, 2H, CH₂CH₂OH), 3.90(t, 2H, PhOCH₂CH₂O), 4.19(t, 2H, PhOCH₂CH₂), 4.37(q, 2H, CH₂CH₃), 6.95(d, 2H, Ar.), 7.6-7.7(m, 4H, Ar.), 8.10(d, 2H, Ar.).

Ethyl 3,5-dihydroxy benzoate (8): 15g (97.4 mmol) of 3,5-dihydroxy benzoic acid was refluxed in 200ml of absolute ethanol, in the presence of 5ml of conc. sulphuric acid, for 20h. Ethanol was removed after neutralising the sulphuric acid and the residue was poured into excess of water. The product was extracted into ether, and the ether layer was washed with water, dried over anhydrous sodium sulphate and then concentrated to get a viscous liquid which crystallised out on keeping in the freezer for 3h

Yield = 15.1g(85%), mp = 128°C, ¹H NMR (d6-Acetone): 1.33(t,3H,CH₂CH₃), 4.27(q,2H,CH₂CH₃), 6.58(t,1H,Ar), 7.0(d,2H,Ar).

Ethyl 3,5-bis-(ω-hydroxy diethyleneoxy) benzoates (EBHDB) 9: 5g (27.5 mmol) of ethyl 3,5-dihydroxy benzoate was stirred at 90°C for 24h in the presence of 56 mmol. of the 2-(2-chloro ethoxy) ethanol, 25g of anhydrous potassium carbonate, and few crystals of potassium iodide in 100 ml of DMF. The reaction mixture was poured into excess of water and extracted with chloroform. The organic layer was washed with 5% aqueous sodium hydroxide (2x100ml) and then with water, dried over sodium sulphate and concentrated to get the product. The product was dried in a vacuum oven at 100°C for 1 day.

Yield = 52%, ¹H NMR (CDCl₃): 1.38(t,3H,CH₂CH₃), 2.5(s,broad,OH), 3.66(t,4H,HO-CH₂), 3.77(t,4H,HO-CH₂CH₂O-), 3.85(t,4H,PhOCH₂CH₂O-), 4.16(t,4H,PhOCH₂CH₂O-), 4.35(q,2H,CH₂CH₃), 6.72(t,1H,Ar), 7.22(d,2H,Ar).

Ethyl 3-hydroxy benzoate (11): Same procedure as for 8 was used.

Yield- 90%, mp = 70-72°C.

¹H NMR(CDCl₃): 1.37(t,3H,-COOCH₂CH₃), 4.35(q,2H,-COOCH₂CH₃), 7.05-7.1(m,1H,Ar), 7.26-7.32(m,1H,Ar), 7.56-7.63(m,2H,Ar).

Ethyl 3-(ω-hydroxy diethyleneoxy) benzoate (EHDB) : Same procedure as for 9 was used.

Yield = 69% $^1\text{H NMR}(\text{CDCl}_3)$: 1.36(t, 3H, CH_2CH_3),
3.65(t, 2H, $\text{CH}_2\text{CH}_2\text{OH}$), 3.76(t, 2H, $\text{CH}_2\text{CH}_2\text{OH}$), 3.91(t, 2H, $\text{PhOCH}_2\text{CH}_2$),
4.17(t, 2H, $\text{PhOCH}_2\text{CH}_2$), 4.41(q, 2H, CH_2CH_3), 4.49(t, 1H, OH),
7.06-7.85(m, 4H, Ar).

Preparation of PBEO_n : 500 mg of the monomer BEOn was heated to 200°C, under dry nitrogen, in the presence of ca. 1 mole% of the tetra isopropyl ortho titanate for 2h. The melt became quite viscous by this time. It was cooled to room temperature and then a vacuum (.05 mbar) was applied. It was then heated gradually to 200°C under dynamic vacuum and the heating was continued for additional 15h to get the solid polymers, PBEO_n, after cooling. PBEO2 and PBEO3 were purified by reprecipitating a p-chlorophenol solution in methanol and PBEO1 was purified by extracting with p-chlorophenol at 90°C for 2 days, and further washed with acetone and dried. All the polymers were dried in a vacuum oven at 100°C for 1 day.

Preparation of PBEO2-M-X and PBEO2-B-X: Appropriate amounts of the two monomers, BEO2 and EIBHDB or EIHDB were taken and polymerized in a similar fashion as described for PBEO_n. All the polymers were extracted with p-chlorophenol at 90°C for 2 days and then were washed with acetone before drying in the vacuum oven at 100°C for 1 day.