New photoswitchable mesogenic polyurethanes with gelation ability

Neha Topnani, Miroslav Kašpar, Věra Hamplová, Ewa Gorecka and Damian Pociecha

1. Experimental

The ^{1}H and ^{13}C NMR spectra of all the compounds were recorded at a 300 MHz and 400 Hz Varian Unity Plus spectrometers, respectively. Proton chemical shifts (δ) are reported in ppm relative to the internal standard – tetramethylsilane (TMS, δ=0.00 ppm). Vario EL III (Heraeus) was used for determination of C, H and N contents by the catalytic combustion at 1150 ^{o}C in helium/oxygen atmosphere.

The phase transition and enthalpy changes were recorded by using the TA DSC Q200 machine, at a rate 5 deg/min for both heating and cooling cycles. Samples of mass 1-3 mg were sealed in standard aluminum pans (in case of gels hermetic aluminium pans) and kept in nitrogen atmosphere during the measurement.

X-ray diffractograms in broad angle range were obtained with Bruker D8 GADDS system equipped with Vantec 2000 area detector. A Parallel CuK_{α} line was formed with Goebel mirror and point collimator. The SAXS measurements were conducted with the Bruker Nanostar system. Samples were prepared either in thin-walled glass capillaries or as a droplet on a heated surface.

The optical studies were performed using Carl Zeiss Imager A2m polarizing microscope equipped with a Linkam TMS94 temperature controller and LTS350 hot stage. SEM images were recorded on Zeiss Merlin field emission microscope.

The samples were irradiated with the light source Hamamatsu LC8 equipped with interchangeable filters allowing for choosing UV or Vis illumination.

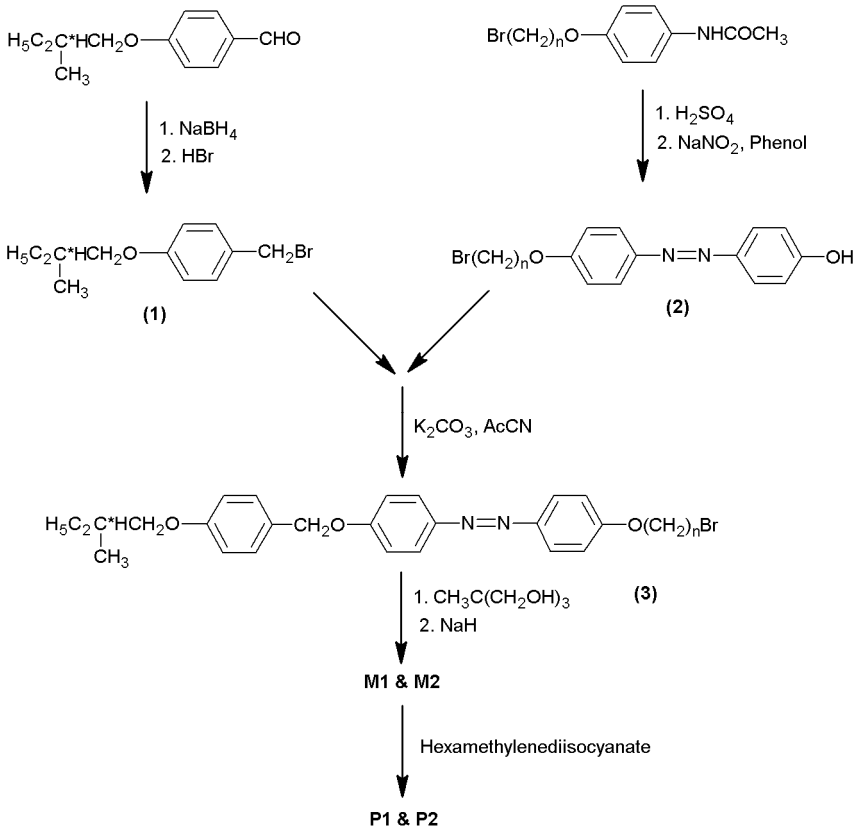
UV-Vis spectra were recorded with Shimadzu UV-3101PC spectrometer.

SEM images were obtained from an FE-SEM Merlin (Zeiss, Germany) equipped with detectors: In-Lens, HE-SE, BSE and an EDS analyzer from Bruker. The samples for SEM imaging were deposited on glass with Au layer in gel state and left for 24 hours. After slow evaporation of solvent and formation of the xerogel the sample was covered with a thin layer of Pd/Au.

2. Organic synthesis

Synthesis of diols M1 and M2

The general synthetic procedure of diols M1(n=8) and M2 (n=10) is presented in the Scheme 1. Details of synthesis are given below for homologue n=10 (M2).



Scheme 1. The general route for the synthesis of compounds *M1 and M2,* and the respective polymers. It can be noted that n=8 for M1 and n=10 for M2.

Preparation of compound (1)

A solution of 4-hydroxybenzaldehyde, (S)-2-methylbutyl bromide and potassium hydroxide in ethanol/water was refluxed for several days. An excess of methylbutyl bromide was removed by extraction with n-hexane. The residual yellow liquid was reduced by natrium borohydride in dioxane at 40-50°C. Subsequently, the reaction mixture was poured into a very dilute HCl (1-2%) solution and extracted twice with dichloromethane. The organic extract was washed with water and evaporated. This compound was heated at 80°C in excess of concentrated hydrobromic acid for 2 hours without further purification. Then the reaction mixture was poured into a water/ice mixture, extracted with dichloromethane, dried over $CaCl_2$ and evaporated under vacuum.

*^{1}H NMR of **1***: 7.30 d (2H, *ortho* to CH_2Br); 6.87 d (2H, *ortho* to –OR); 4.51 s (2H, CH_2Br); 3.80 m (2H, CH_2O); 1.30 and 1.60 and 1.90 m (3H, C*H, CH_2); 1.02 d (3H, CH_3C*); 0.96 t (3H, CH_3).

*^{13}C NMR of **1***: 11.5, 16.44, 26.06, 34.06, 34.64, 73.87, 114.77, 129.41, 130.3, 159.36

Preparation of 4-ω-bromodecyloxy-4'-hydroxyazobenzene (2); n=10

4-ω-bromodecyloxy-4'-hydroxyazobenzene was obtained from 4-acetamidophenol using standard methods of alkylation, diazotization and coupling with phenol. The crude product was crystallized from ethanol.

*^{1}H NMR of **2*** : 7.82 dd (4H, *ortho* to –N); 6.99 d (2H, *ortho* to –OR); 6.90 d (2H, *ortho* to –OH); 4.02 t (2H, CH_2OAr); 3.40 t (2H, CH_2Br); 1.20-1.85 m (16H, CH_2).

Preparation of compound (3); n=10

Intermediates **1** and **2** were reacted in equal molar ratio in acetonitrile in the presence of an excess of dry potassium carbonate at room temperature for about 12 hours. The reacted mixture was poured into an excess of water and the precipitate was filtered off. The product was crystallized from 4:1 dioxane/ethanol mixture, separated and washed with ethanol (product is insoluble in ethanol). Finally, the product was dried at 90°C under vacuum. Yield: 55-60%.

*^{1}H NMR of **3*** : 7.85 d (4H, *ortho* to –N); 7.36 d (2H, *ortho* to $–CH_2O$); 7.06 d (2H, *ortho* to CH_2OAr); 6.98 d (2H, *ortho* to –OR); 6.90 d (2H, *ortho* to –OR); 5.07 s (2H, CH_2Ar); 4.02 t (2H, CH_2OAr); 3.80 m (2H, C^*CH_2OAr); 3.42 t (2H, CH_2Br); 1.20 -1.90 m (19H, CH_2, CH); 1.02 d (3H, CH_3C^*); 0.98 t (3H, CH_3).

Preparation of diol M2; n=10

0.5 M of pentaglycerine (1,1,1-trimethylol-ethane) was mixed with 4.0 g of sodium hydride in dry dimethylformamide (200 mL) at room temperature for 30 minutes. Then, dry mesogenic bromide (20 g) in DMF was added and the mixture was stirred for several hours at room temperature. The dry THF (200 mL) was added and the reaction mixture was refluxed for 48 hours, poured into water, cooled overnight in refrigerator and the solid was separated. The yellow product was crystallized twice from toluene and then dried under vacuum. Yield: 50%. Diol **M1 (n=8)** has been obtained in analogues way with yield 52%

*^{1}H NMR of **M2*** : 7.85 d (4H, *ortho* to –N); 7.36 d (2H, *ortho* to $–CH_2O$); 7.06 d (2H, *ortho* to CH_2OAr); 6.98 d (2H, *ortho* to –OR); 6.90 d (2H, *ortho* to –OR); 5.07 s (2H, CH_2Ar); 4.02 t (2H, CH_2OAr); 3.80 m (2H, C^*CH_2OAr); 3.70 dd (4H, CH_2OH); 3.42 m (4H, CH_2OCH_2); 1.20 -1.90 m (19H, CH_2, CH); 1.02 d (3H, CH_3C^*); 0.98 t (3H, CH_3); 0.83 s (3H, CH_3C).

*^{13}C NMR of **M2*** **:** 11.60, 16.83, 17.50, 25.19, 26.26, 26.3, 29.38, 29.44, 29.46, 29.52, 29.6, 29.72, 35.00, 40.51, 68.30, 68.61, 70.39, 72.26, 72.26, 73.20, 114.93, 114.93, 115.30, 124.58, 124.62, 128.52, 129.6, 147.16, 147.40, 159.63, 161.01, 161.40

Elemental analysis for $C_{39}H_{56}O_6N_2$ (M_{cz} = 648.9): calc. C 72.19, H 8.70, N 4.32; found C 72.26, H 8.80, N 4.34

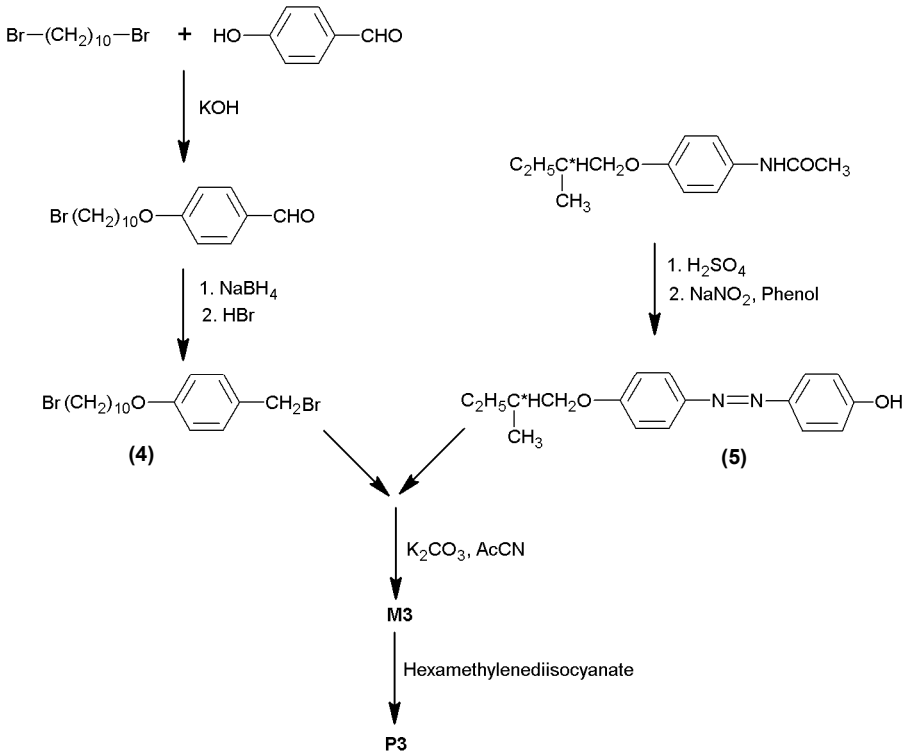
*^{1}H NMR of **M1*** **:** 7.83 d (4H, *ortho* to –N); 7.36 d (2H, *ortho* to $–CH_2O$); 7.05 d (2H, *ortho* to CH_2OAr); 6.99 d (2H, *ortho* to –OR); 6.92 d (2H, *ortho* to –OR); 5.06 s (2H, CH_2Ar); 4.04 t (2H, CH_2OAr); 3.81 m (2H, C^*CH_2OAr); 3.71 dd (4H, CH_2OH); 3.43 m (4H, CH_2OCH_2); 1.20 -1.90 m (15H, CH_2, CH); 1.01 d (3H, CH_3C^*); 0.98 t (3H, CH_3); 0.84 s (3H, CH_3C).

*^{13}C NMR of **M1*** **:** 11.6, 16.85, 17.5, 25.19, 26.27, 26.3, 29.38, 29.52, 29.6, 29.72, 35.02, 40.5, 68.3, 68.6, 70.39, 72.24, 73.2, 114.9, 114.9, 115.32, 124.58, 124.63, 128.5, 129.6, 147.14, 147.4, 159.65, 161.0, 161.4

Elemental analysis for $C_{37}H_{52}O_6N_2$ (M_{cz} = 620.8): calc. C 71.58, H 8.44, N 4.51; found C 71.69, H 8.50, N 4.49

Synthesis of diol M3

The procedure for the synthesis of diol M3 is presented in Scheme 2.



Scheme 2. The schematic synthetic route for the synthesis of compound *M3* and polymer *P3*.

Preparation of compound (4)

4-ω-bromodecyloxy benzaldehyde was obtained from 4-hydroxy-benzaldehyde and 1,10-dibromodecane in water/dioxane solution in the presence of potassium hydroxide. The reaction mixture was stirred and refluxed for 24hrs, poured into water and extracted twice with dichloromethane. The organic layer was evaporated and shook threefold in cool n-hexane (for the removal of excess of dibromodecane) until the product was solid (in refrigerator). The product was reduced with $NaBH_4$ and brominated similarly as 4-(2-methylbutyl)benzaldehyde.

*^{1}H NMR of **1*** : 7.31 d (2H, *ortho* to CH_2Br); 6.85 d (2H, *ortho* to –OR); 4.51 s (2H, CH_2Br); 3.93 t (2H, CH_2OAr); 3.41 t (2H, CH_2Br) 1.7- 2.0 m (4H, CH_2CH_2O and CH_2CH_2Br); 1.2-1.5m (12H, CH_2).

Preparation of 4-((S)-2-methylbutyloxy)-4'-hydroxyazobenzene (5)

4-((S)-2-methylbutyloxy)-4'-hydroxyazobenzene was synthesized by the similar method, as previously azo-dye (compound **2** in Scheme 1) was obtained.

*^{1}H NMR of **5*** : 7.82 dd (4H, *ortho* to –N); 7.00 d (2H, *ortho* to –OR); 6.91 d (2H, *ortho* to –OH); 3.8 and 3.9 m+m (2H, CH_2O); 1.3 and 1.6 and 1.9, m+m+m (3H, CH_2CH); 1.02 d (3H, CH_3C*); 0.95 t (3H, CH_3).

Preparation of M3 diol

The diol **M3** was obtained by the same synthetic method as **M2** and **M1**.

*^{1}H NMR of **M3*** : 7.86 d (4H, *ortho* to –N); 7.39 d (2H, *ortho* to –CH_2OAr); 7.08 d (2H, *ortho* to OCH_2Ar); 7.00 d (2H, *ortho* to –OR*); 6.92 d (2H, *ortho* to –OR); 5.06 s (2H, $ArCH_2$); 3.98 t

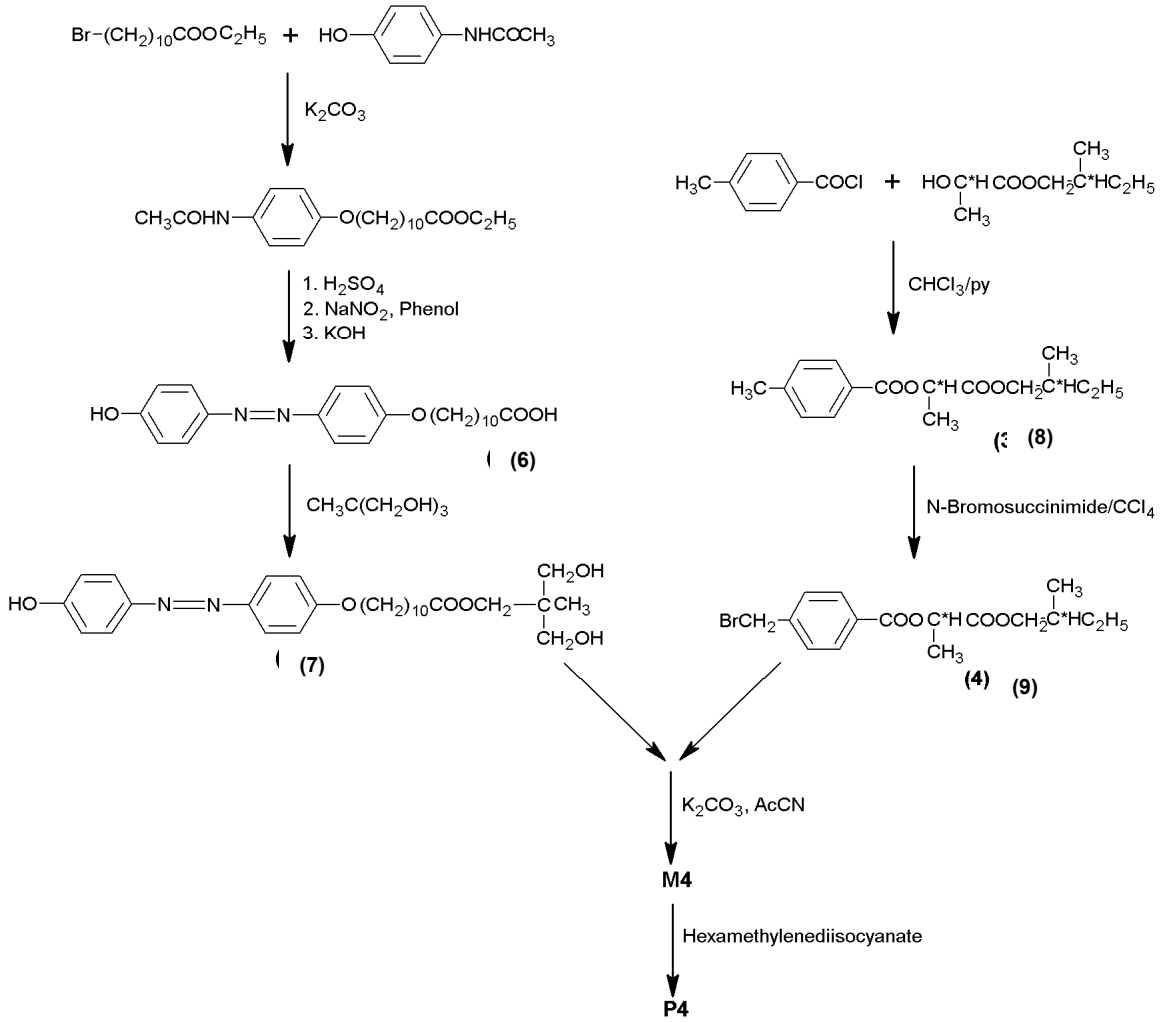
(2H, CH_2OAr); 3.85 m (2H, C^*CH_2O); 3.60 and 3.70 dd (4H, CH_2OH); 3.40 m (4H, CH_2OCH_2); 1.20 -1.90 m (19H, CH_2, CH); 1.02 d (3H, CH_3C^*); 0.98 t (3H, CH_3); 0.82 s (3H, CH_3C).

*^{13}C NMR of **M3*** **:** 11.30, 16.44, 17.50, 25.20, 26.06, 26.26, 29.39, 29.44, 29.46, 29.54, 29.60, 29.70, 34.64, 40.50, 67.79, 68.30, 72.28, 72.28, 73.09, 78.03, 114.57, 114.63, 115.00, 124.22, 124.26, 128.33, 129.21, 146.80, 147.10, 159.02, 160.71, 161.36

Elemental analysis for $C_{39}H_{56}O_6N_2$ (M_{cz} = 648.9): calc. C 72.19, H 8.70, N 4.32; found C 72.31, H 8.75, N 4.39

Synthesis of diol M4

The diol **M4** has been synthesized according to the procedure presented in the Scheme 3.



Scheme 3. The general schematic procedure for the synthesis of compound *M4* and its polymer *P4*.

Preparation of compound (6)

4-hydroxy-4´-(11-oxyundecanoic acid)-azobenzene (**6)** was obtained from 4-acetamidophenol and ethyl-11-bromoundecanoate using standard methods of alkylation in ethylmethylketone and potassium carbonate and subsequent hydrolysis of the amide with a 20% solution of sulfuric acid. The intermediate free amine was diazotized and coupled with phenol to give ethylester of acid **6**. Acid **6** was obtained after hydrolysis with potassium hydroxide in hot ethanol/water mixture and subsequent acidification by hydrochloric acid. The product was

crystallized from methanol, washed with chloroform (the acid being insoluble) and then dried at 100 °C under vacuum.

*^{1}H NMR of **6*** : 7.75 dd (4H, *ortho* to -N); 7.08 d (2H, *ortho* to –OR); 6.90 d (2H, *ortho* to -OH); 4.01 t (2H, CH_2OAr); 2.18 t (2H, CH_2COOH); 1.20-1.80 m (16H, CH_2).

Preparation of compound (7)

39.8 g (0.1 M) of acid **6** was boiled in dioxane solution with 60 g (0.5 M) of pentaglycerine and 2 mL of concentrated sulphuric acid for 3 hours. The reaction mixture was neutralized by $CaCO_3$, dioxane was removed by evaporation in vacuum and the residue was extracted four times with chloroform at 40°C. The warm extract was filtered, evaporated on rotavapor and crystallized from dry acetonitrile and dry toluene. The final product was dried under vacuum. Yield: 22 g (45 %) of yellow solid.

*^{1}H NMR of **7*** : 7.82 dd (4H, *ortho* to –N); 7.00 d (2H, *ortho* to –OR); 6.90 d (2H, *ortho* to –OH); 4.20 s (2H, $COOCH_2$); 4.02 t (2H, CH_2OAr); 3.60 dd (4H, CH_2OH); 2.37 t (2H, CH_2COO); 1.20-1.80 m (16H; CH_2); 0.82 s (3H, CH_3).

*^{13}C NMR of **7*** : 16.86, 25.19, 26.26, 26.46, 29.38, 29.44, 29.52, 29.6, 29.72, 33.76, 40.75, 66.01, 67.75, 68.31, 114.97, 115.94, 127.81, 128.05, 133.34, 133.6, 155.58, 158.39, 175.16

Preparation of compound (9)

32 g (0.2 M) of (S,S)-2- methylbutyl-2-hydroxypropionate was dissolved in 100 mL of dry dichloromethane with 20 mL of pyridine followed by the addition of 30.8 g (0.2 M) of toluoylchloride in 50 mL of dichloromethane. The reaction mixture was stirred at room temperature for two days, refluxed for four hours, poured into dilute hydrochloric acid (5%). After the extraction with chloroform it was dried with calcium chloride and evaporated to dryness. The dry toluic ester (**8**) was dissolved in 300 mL of dry tetrachloromethane along with the addition of the mixture of 38 g of N-bromsuccinimide and 5 g of benzoylperoxide in small portions under reflux. The mixture was then refluxed for subsequent 1 hour. To remove the succinimide, the cold reaction mixture was filtered and washed twice with cold water. The solution was dried by calcium chloride and evaporated under vacuum. Yield: 38 g (52 %) of yellow liquid.

*^{1}H NMR of **9*** : 8.08 d (2H, *ortho* to –COO); 7.48 d (2H, *ortho* to $–CH_2Br$); 5.35 q (1H, C*HCOO); 4.50 s (2H, CH_2Br); 4.00 m (2H, C*CH_2) ; 1.64 d (3H, CH_3C*); 1.20+1.40+1.70 m+m+m (3H; $CHCH_2O$); 0,90m (6H, CH_3).

*^{13}C NMR of **9*** : 11.2, 16.31, 17.16, 26.02, 32.42, 34.15, 69.13, 69.84, 126.91, 129.3, 130.61, 143.25, 165.62, 170.9

Preparation of diol M4

15 g (0.03 M) of diol **7** was dissolved in 200 mL of dry acetonitrile with 20 g of dry K_2CO_3. Bromide **9** (15 g, 0,042 M) was added under reflux and the mixture was heated under intensive stirring for 8 hrs. The mixture was poured into 1 L of water, cooled in refrigerator and filtered under vacuum. The diol was crystallized from toluene and dry ethanol, dried at 60°C under vacuum for 24 hours. Yield: 6 g (27 %) of dry product.

*^{1}H NMR of **M4*** : 8.10 d (2H, *ortho* to –COO), 7.82 m (4H, *ortho* to –N; 7.55 d (2H, *ortho* to –CH_2); 7.02d (2H, *ortho* to $ArCH_2O$); 7.00 d (2H, *ortho* to –OR); 5.34 q (1H, C*HCOO) ; 5.20 s

(2H, $ArCH_2O$); 4.18 s (2H, $COOCH_2$); 4.00 m (4H, C^*CH_2 and CH_2OAr); 3.55 dd (4H, CH_2OH); 2.38 t (2H, CH_2COO); 1.64 d (3H, CH_3C^*); 1.20-1.80 m (19H; CH_2CH); 0.90 m (6H, CH_3) ; 0.82 s (3H, c-CH_3).

*^{13}C NMR of **M4*** **:** 11.21, 16.75, 16.86, 17.31, 26.30, 26.20-29.80, 34.35, 34.47, 40.74, 65.54, 67.82, 68.53, 69.25, 69.47, 69.92, 114.63, 115.02, 124.48, 124.52, 126.96, 129.13, 130.18, 142.12, 146.80, 147.35, 160.22, 161.25, 165.20, 170.84, 175.20

Elemental analysis for $C_{44}H_{60}O_{10}N_2$ (M_{cz} = 777.0): calc. C 68.02, H 7.78, N 3.61; found C 68.14, H 7.71, N 3.60

Synthesis of Polymers

Polymerization was done by the reaction of as-obtained monomeric diols with hexamethylenediisocyanate under argon atmosphere to achieve respective polymers. As an example, preparation of P4 polymer is described in details.

Preparation of polyurethane P4

6.00 g (8.02 mM) of the diol M4 and 1.30 g (7.74 mM) of hexamethylenediisocyanate was dissolved in 50 mL of toluene (dried with CaH_2) and the mixture was heated under dry argon to the boiling point. One additional drop of hexamethylenediisocyanate was added every hour (overall three times) and the reaction mixture was refluxed for another 6 hours. The reaction mixture was evaporated, the solid was dissolved in tetrahydrofurane and precipitated in cold methanol. The procedure was repeated twice, then the polymer was separated and dried under vacuum.

*^{1}H NMR of **P1*** : 7.86 d (4H, *ortho* to –N); 7.35 d (2H, *ortho* to $–CH_2O$); 7.07 d (2H, *ortho* to OCH_2Ar); 6.99 d (2H, *ortho* to –OR); 6.91 d (2H, *ortho* to –OR*); 5.06 s (2H, CH_2Ar); 4.02 m (6H, CH_2OAr and CH_2OCONH); 3.80 m (2H, C^*CH_2OAr); 3.44 m (4H, CH_2OCH_2); 3.22 m (4H, CH_2NHCO); 1.20 -1.90 m (23H, CH_2, CH); 1.02 d (3H, CH_3C^*); 0.98 t (3H, CH_3); 0.83 s (3H, CH_3C).

*^{13}C NMR of **P1*** : 1.66, 3.44, 11.32, 16.52, 17.08, 26.04, 26.12, 29.53, 29.85, 34.69, 39.58, 41.74, 60.75, 66.67, 68.06, 70.10, 73.14, 101.05, 109.99, 114.16, 114.62, 114.67, 115.03, 124.26, 124.31, 129.28, 141.26, 141.61, 146.85, 147.13, 149.52, 155.25, 156.61, 159.14,160.76, 161.38, 165.08, 169.04, 173.69, 232.47

*^{1}H NMR of **P2*** : 7.85 d (4H, *ortho* to –N); 7.36 d (2H, *ortho* to $–CH_2O$); 7.06 d (2H, *ortho* to OCH_2Ar); 6.98 d (2H, *ortho* to –OR); 6.90 d (2H, *ortho* to –OR*); 5.07 s (2H, CH_2Ar); 4.02 m (6H, CH_2OAr and CH_2OCONH); 3.80 m (2H, C^*CH_2OAr); 3.42 m (4H, CH_2OCH_2); 3.20 m (4H, CH_2NHCO); 1.20 -1.90 m (27H, CH_2, CH); 1.02 d (3H, CH_3C^*); 0.98 t (3H, CH_3); 0.83 s (3H, CH_3C).

*^{13}C NMR of **P2*** : 1.66, 3.44, 11.32, 16.52, 17.08, 23.07, 26.04, 26.12, 29.53, 29.85, 34.69, 39.58, 41.74, 53.64, 60.75, 66.67, 68.06, 70.10, 73.14, 101.05, 109.99, 114.16, 114.62, 114.67, 115.03, 124.26, 124.31, 129.28, 141.26, 141.61, 146.85, 147.13, 149.52, 155.25, 156.61, 159.14,160.76, 161.38, 165.08, 169.04, 173.69, 232.47

*^{1}H NMR of **P3*** : 7.86 d (4H, *ortho* to –N); 7.39 d (2H, *ortho* to –CH_2OAr); 7.08 d (2H, *ortho* to OCH_2Ar); 7.00 d (2H, *ortho* to –OR*); 6.92 d (2H, *ortho* to –OR); 5.06 s (2H, $ArCH_2$); 4.00 m (6H, CH_2OAr and CH_2OCONH); 3.85 m (2H, C*CH_2O); 3.40 m (4H, CH_2OCH_2); 3.20 m (4H, CH_2NHCO); 1.20 -1.90 m (27H, CH_2, CH); 1.02 d (3H, CH_3C*); 0.98 t (3H, CH_3); 0.82 s (3H, CH_3C).

*^{13}C NMR of **P3*** **:** 1.66, 3.44, 11.32, 16.52, 17.08, 23.07, 26.04, 26.12, 29.53, 29.85, 34.69, 39.58, 41.74, 53.64, 60.75, 66.67, 68.06, 70.10, 73.14, 101.05, 109.99, 114.16, 114.62, 114.67, 115.03, 124.26, 124.31, 129.28, 141.26, 141.61, 146.85, 147.13, 149.52, 155.25, 156.61, 159.14,160.76, 161.38, 165.08, 169.04, 173.69, 232.47

*^{1}H NMR of **P4*** : 8.10 d (2H, *ortho* to -COO); 7.82 m (4H, *ortho* to –N); 7.55 d (2H, *ortho* to –CH_2); 7.02 d (2H, *ortho* to $ArCH_2O$); 7.00 d (2H, *ortho* to –OR); 5.34 q (1H, C*HCOO); 5.20 s (2H, $ArCH_2O$); 4.18 s (2H, $COOCH_2$); 4.00 m (8H, C*CH_2 and CH_2Oar and $NHCOOCH_2$); 3.10 m (4H, CH_2NHCO; 2.38 t (2H, CH_2COO); 1.64 d (3H, CH_3C*); 1.20-1.80 m (27H; CH_2, CH); 0.90m (6H, CH_3); 0.82 s (3H, C-CH_3).

*^{13}C NMR of **P4*** **:** 1.66, 3.44, 11.32, 16.52, 17.08, 23.07, 24.50, 26.04, 26.12, 28.20, 29.53, 29.85, 34.69, 39.58, 41.74, 53.64, 60.75, 66.67, 68.06, 70.10, 73.14, 101.05, 109.99, 114.16, 114.62, 114.67, 115.03, 124.26, 124.31, 129.28, 135.20, 137.80, 141.26, 141.61, 146.85, 147.13, 149.52, 155.25, 156.61, 159.14,160.76, 161.38, 165.08, 169.04, 173.69, 232.47

Table S1. Sol-gel phase transition temperatures for polymers in menthone. In the table only phase transition temperatures are presented (taken as peak position in heating runs), as the enthalpies are measured with large error due to some evaporation of the solvent at elevated temperatures, despite the sealing of the sample.

Polymer	Sol-gel phase transition temperature (in menthone)
P1	38.6 °C
P2	44.4 °C
P3	40.9 °C
P4	39.9 °C

Figure S1. Planar texture of M4 in the SmC phase observed under a polarizing microscope at T=75ºC. (a) without applied electric field and (b) under applied electric field of 10 V/micron.