SUPPORTING INFORMATION

Tuning Oxygen Permeability in Azobenzene-Containing Side-Chain Liquid Crystalline Polymers

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Experimental Section

Materials and Synthesis

Phenol, 4-aminobenzonitrile, dibromoalkanes, methacrylic acid, hydroquinone, 2,2'azoisobutyronitrile (AIBN), potassium carbonate, potassium bicarbonate sodium nitrite and all the solvents such as acetone, tetrahydrofuran (THF), hexanes, ethyl acetate, dimethylformamide (DMF) and benzene were purchased and used as received from Sigma Aldrich. ¹H-NMR was performed at 25 °C using a Bruker 500 MHz spectrometer using deuterated dimethyl sulfoxide (DMSO-*d*₆) and deuterated chloroform (CDCl₃) and teramethylsilane (TMS) (Cambridge Isotope Lab., Inc.) as the internal standard (δ H 0.00).

Synthesis of polymers

The polymers were synthesized using the scheme illustrated in **Fig. 2**, whereas "*n*" represents the number of methylene spacer groups in the side chain of the polymer. The general procedures used to prepare all the compounds were described in detail previously.^{1,2} Specific details unique to this work for synthesizing $poly(n-[4-(4'-cyanophenylazo)phenoxy]alkyl_n$ methacrylate) (azoLCP-C_n) where the spacer chain length, *n* was varied such that *n* = 5 or 8, 9, 10 and 12, is described in the following sections.

Synthesis of 4-(4'-hydroxy-phenylazo)benzonitrile (2)

Solution A was prepared by mixing 85 mmol of 4-aminobenzonitrile, 46 ml water and 46 ml of 37% Hydrochloric acid and heating the reaction mixture up to 40°C. The resulting amine-

chlorohydrate was then cooled in an ice bath to 0°C. 9.6g Sodium nitrite dissolved in 20 ml water was added dropwise in amine-chlorohydrate suspension to obtain corresponding diazonium salt. Solution B was prepared by dissolving 85 mmol of phenol in 15% (17.6g) aqueous solution of sodium hydroxide. Solution B was then added dropwise to suspension A at 0°C. Red precipitates were obtained that were filtered and recrystallized from 2-propanol. Resulting precipitates were kept under the vacuum overnight at 50°C. Yield was 12.5 g or 66%.

¹H NMR (500 MHz, DMSO-*d*₆) δ 10.55 (s, 1H), 8.05 (dd, *J* = 8.4, 2.0 Hz, 2H), 7.95 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.91 – 7.85 (m, 2H), 7.02 – 6.96 (m, 2H).

Synthesis of 1-Bromo-[4-(4'-cyanophenylazo)phenoxy]alkane (3)

13 mmol of 4-(4'-hydroxy-phenylazo)benzonitrile, 130 mmol of corresponding Dibromo Alkane, 97.5 mmol of Potassium-carbonate were stirred and heated to 68°C under reflux overnight. Reaction mixture was filtered hot and washed with acetone several times. Acetone was removed under reduced pressure at 55°C. Hexanes were added to the precipitates, and the resulting product was further purified using column chromatography. Starting mixture of 2% ethyl-acetate solution in hexanes was used to separate the desired product from the precipitates. The solution was removed under reduced pressure at 60°C and 45% product yield was obtained.

azoLCP₅:

¹H NMR (500 MHz, Chloroform-*d*, *δ* in ppm, *J* in Hz): 7.94 (m, 4H), 7.79 (d, 2H *J* = 9.0), 7.02 (d, 2H, *J* = 9.0 Hz), 4.08 (t, 2H *J* = 6.3), 3.46 (t, 2H *J* = 6.7), 2.00 – 1.93 (m, 2H), 1.91 – 1.84 (m, 3H), 1.68 (d, 2H), 1.52 (s, 2H).

azoLCP₈:

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, *J* in Hz): 7.9 (m, 4H), 7.5 (d, 2H, *J* = 9.0), 7.0 (d, 2H, *J* = 9.0), 4.0 (t, 2H, *J*= 6.5), 3.4 (t, 2H, *J*=6.5), 1.7-2.0 (m, 4H), 1.2-1.5 (m, 8H). ¹³C NMR (CDCl₃, δ in ppm): 162.7, 154.8, 146.7, 133.1, 125.4, 123.0, 118.6, 114.8, 113.1, 68.3, 33.9, 32.7, 29.1, 29.0, 28.6, 28.0, 25.8. FTIR (neat): 2923, 2859, 2218, 1599, 1581, 1499, 1467, 1337, 1246, 1222 cm⁻¹.

azoLCP₉:

¹H NMR (500 MHz, Chloroform-*d*, *δ* in ppm, J in Hz): 7.9 (m, 4H), 7.7 (m, 2H), 7.0 (m, 2H), 4.6 (m, 4H), 1.7-2.2 (m, 6H), 1.2-1.6 (m, 11H).

azoLCP₁₀:

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, *J* in Hz): 1.21 – 1.39 (d, J = 9.4 Hz, 10H), 1.50 – 1.63 (m, 9H), 1.73 – 1.94 (m, 5H), 3.37 – 3.49 (m, 3H), 4.00 – 4.16 (m, 2H), 6.96 – 7.09 (td, J = 9.8, 8.8, 4.7 Hz, 2H), 7.75 – 7.85 (m, 2H), 7.87 – 8.04 (m, 4H).

azoLCP₁₂:

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, *J* in Hz) δ 8.04 (dd, *J* = 16.8, 8.2 Hz, 4H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 2H), 4.08 (t, *J* = 6.5 Hz, 1H), 3.41 (t, *J* = 6.8 Hz, 1H), 1.85 (qt, *J* = 8.8, 3.7 Hz, 4H), 1.53 – 1.27 (m, 24H).

Synthesis of n-[4-(4'-cyanophenylazo)phenoxy]alkyl methacrylate monomer (4)

The procedure used to synthesize the monomer was described in detail previously by Imrie *et al*³ and will be briefly described here. Methacrylic acid (7.7 mmol) was stirred with potassium hydrogen carbonate (7.4 mmol) for 5 min at room temperature to obtain the potassium methacrylate salt. This salt was added to 1-Bromo-[4-(4'-cyanophenylazo)phenoxy]alkane 5.2 mmol and 0.14mmol hydroquinone in N,N- dimethylformamide (DMF, 60 mL). This mixture was stirred at 100 °C under reflux overnight. After at least 12h the mixture was decanted into cold water (300 mL) and agitated to obtain the precipitates which were separated by filtration and dissolved in dichloromethane. The organic solution was washed with dilute (1:10) hydrochloric acid in a separating funnel. These steps were followed by subsequent washing with water and dilute brine solution. Dichloromethane was removed under pressure at 40°C to obtain precipitates of starting material for chromatography. Column chromatography was used further purify the monomer. 2% Ethyl acetate dissolved in hexane was used to separate the required monomer layer from starting material dispersed in silica gel. Yield of the monomer was 56% that was confirmed by NMR.

azoLCP₅:

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, *J* in Hz) δ 8.01 – 7.87 (m, 4H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 6.11 (s, 1H), 5.56 (s, 1H), 4.20 (t, *J* = 6.5 Hz, 2H), 4.08 (t, *J* = 6.3 Hz, 2H), 1.95 (s, 3H), 1.91 – 1.84 (m, 2H), 1.80 – 1.72 (m, 2H), 1.61 (p, *J* = 7.7, 7.3 Hz, 2H), 1.55 (s, 1H).

azoLCP₈:

¹H NMR (500 MHz, CDCl₃, δ in ppm, J in Hz): 7.9 (m, 4H), 7.7 (d, 2H, J = 9.0), 7.0 (d, 2H, J = 9.0), 5.6 (s), 6.1 (s), 4.1 (t, 2H, J= 6.5), 3.4 (t, 2H, J=6.5), 1.7-2.0 (m, 4H), 1.2-1.5 (m, 8H). ¹³C NMR (CDCl₃, δ in ppm): 167.5, 162.7, 154.8, 146.7, 133.1, 125.4, 123.0, 118.6, 114.8, 113.1,

68.3, 64.7, 33.9, 29.2, 29.1, 29.0, 28.6, 28.0, 25.8, 18.3. FTIR (neat): 2952, 2916, 2850, 2225, 1703, 1600, 1580, 1463, 1340, 1253 cm⁻¹.

azoLCP₉:

¹H NMR (500 MHz, CDCl₃, δ in ppm, J in Hz): 7.9 (m, 4H), 7.7 (d, 2H, J = 9.0), 7.0 (d, 2H, J = 9.0), 5.6 (s), 6.1 (s), 4.1 (t, 2H, J= 6.5), 3.4 (t, 2H, J=6.5), 1.7-2.0 (m, 4H), 1.2-1.5 (m, 8H).

azoLCP₁₀:

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, *J* in Hz) 1.22 – 1.44 (m, 15H), 1.52 – 1.61 (s, 3H), 1.60 – 1.73 (m, 3H), 1.77 – 1.87 (t, *J* = 7.4 Hz, 2H), 1.89 – 2.02 (s, 4H), 4.01 – 4.09 (s, 2H), 4.08 – 4.21 (t, *J* = 6.8 Hz, 3H), 5.47 – 5.64 (s, 1H), 6.04 – 6.15 (s, 1H), 6.94 – 7.11 (d, *J* = 8.5 Hz, 2H), 7.72 – 7.86 (d, *J* = 8.3 Hz, 2H), 7.86 – 8.03 (d, *J* = 8.2 Hz, 4H).

azoLCP₁₂:

¹H NMR (500 MHz, Chloroform-*d*, *δ* in ppm, *J* in Hz) *δ* 8.00 (s, 4H), 7.79 (d, *J* = 5.7 Hz, 2H), 7.26 (s, 2H), 7.06 – 7.01 (m, 2H), 6.09 (s, 1H), 5.54 (t, *J* = 2.0 Hz, 1H), 4.10 (dt, *J* = 32.0, 6.5 Hz, 4H), 1.94 (s, 3H), 1.83 (p, *J* = 6.6 Hz, 2H), 1.67 (p, *J* = 6.7 Hz, 2H), 1.48 (s, 6H), 1.41 – 1.28 (m, 18H).

Synthesis of Polymer (5)

Poly(n-[4-(4'-cyanophenylazo)phenoxy]alkyl methacrylate) (azoLCP-C₅) was synthesized according to previously reported procedures,^{1,2} and will be briefly described here. The reaction ampoule was charged with monomer (3.57 mmol), initiator 2,2'-azoisobutyronitrile (AIBN, 1/5th of the monomer), and 12mL of anhydrous benzene. After three freeze–pump–thaw cycles, the ampoule was sealed under argon gas, and the reaction mixture was heated at 68 °C for 48 h. Benzene from the resulting viscous solution was removed under reduced pressure at 70°C. Precipitates were dissolved in tetrahydrofuran (THF) and decanted into an excess of briskly agitated methanol. The precipitate formed was collected and redissolved in THF, and then reprecipitated several times from a THF/methanol system. Polymer was than dissolved in 2-3ml THF and added to hexane dropwise. The solution was centrifuged at 2000 rpm. Later the hexane was removed and polymer was dried overnight under vacuum at 50°C. NMR was used to confirm the product with the yield of 70%.

azoLCP₅:

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, J in Hz) δ 7.98 – 7.81 (m, 4H), 7.77 (s, 2H), 7.01 (d, J = 8.7 Hz, 2H), 4.03 (d, J = 35.8 Hz, 4H), 1.91 (d, J = 42.9 Hz, 2H), 1.79 (s, 3H), 1.60 – 1.43 (m, 3), 1.41 – 1.18 (m, 2H), 1.09 (s, 1H), 0.98 – 0.83 (m, 1H).

azoLCP₈:

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, *J* in Hz): 7.9 (m, 4H), 7.7 (m, 2H), 7.0 (m, 2H), 4.6 (m, 4H), 1.7-2.2 (m, 6H), 1.2-1.6 (m, 11H). FTIR (neat): 2927, 2854, 2226, 1722, 1597, 1499, 1472, 1282, 1214 cm⁻¹.

azoLCP₉:

¹H NMR (500 MHz, Chloroform-*d*, *δ* in ppm, *J* in Hz): 7.9 (m, 4H), 7.7 (m, 2H), 7.0 (m, 2H), 4.6 (m, 4H), 1.7-2.2 (m, 6H), 1.2-1.6 (m, 11H).

azoLCP₁₀:

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, *J* in Hz) 1.17 – 1.42 (s, 20H), 1.42 – 1.61 (s, 10H), 1.62 – 1.71 (t, *J* = 11.2 Hz, 3H), 1.74 – 1.91 (s, 3H), 3.93 – 4.23 (d, *J* = 7.1 Hz, 4H), 6.94 – 7.11 (s, 2H), 7.69 – 7.85 (s, 2H), 7.88 – 8.05 (s, 4H).

azoLCP₁₂

¹H NMR (500 MHz, Chloroform-*d*, δ in ppm, *J* in Hz) δ 7.96 (s, 4H), 7.78 (s, 2H), 7.26 (s, 4H), 7.01 (s, 2H), 4.06 (d, *J* = 7.0 Hz, 3H), 3.97 (s, 1H), 1.94 (s, 0H), 1.82 (s, 2H), 1.65 (t, *J* = 12.3 Hz, 3H), 1.55 (s, 0H), 1.47 (s, 10H), 1.33 (d, *J* = 37.2 Hz, 18H), 1.15 – 1.11 (m, 1H).

Chemical Composition by Fourier Transform Infrared Spectroscopy

Infrared spectra were obtained using a Nicolet 4700 Fourier transform infrared (FTIR) spectrometer. In the FTIR spectrum of azoLCP-C₈ (**Fig. S7**†), where the olefinic C-H stretching is observed at 2960 cm⁻¹, the azo (-N=N-) stretching at 2200 cm⁻¹, the ester carbonyl absorption (-(C=O)-) at 1730 cm⁻¹, and multiple bands at 1130-1220 cm⁻¹ is due to C-O stretching of the unsaturated ester.

Molecular Weight Determination by Gel Permeation Chromatography

AzoLCP samples were prepared for number-average molecular weight (M_n) , weightaverage molecular weight (M_w) , and polydispersity indices $((M_w/M_n)$ or PDIs) analysis by first vortexing them such that the samples were suspended in solution, then centrifuged at 13.4 kRPM for 15 min. The supernatant (0.5-1 mL) was filtered through a PTFE syringe filter (0.45 um pore size) into a vial containing ~20-30 uL methanol to ensure complete dissolution. The molecular weights and dispersity relative to polymethyl methacrylate standards were then determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) (1.0 mL min⁻¹) using a PL GPC 50 system equipped with two PL Resipore columns (3μ m, 300 mm × 7.5 mm) and an online viscometer detector, along with a differential refractive index (*d*RI) detector to directly obtain molecular weights from a universal calibration curve.

Thermal Stability Characterization by Thermogravimetric Analysis

The polymer degradation temperatures were recorded using thermal gravimetric analysis (TGA). Samples of 10-12mg were loaded into the platinum sample pan of a TA Instruments Q50 thermal gravimetric analyzer at room temperature. The oven was purged with air and the mass was recorded while heating the sample at the rate of 15°C/min to 1000°C.

Thermal Phase Behavior Characterization by Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to determine the liquid crystalline and isotropic transition in the azoLCPs. The TA Instruments Q200 DSC was calibrated against an indium standard at 10 °C/min heating rate and cooled using liquid nitrogen. Polymer samples of 5 mg to 12 mg were sealed in aluminum pans. The heat flow required to raise the temperature of the sample was recorded after a full heating and cooling run to remove sample thermal history. Typical procedures were: (1) heat -60 °C to 200 °C at 10 °C/min (2) Cool to -60 °C at a cooling rate 10 °C/min (3) Heat from -60 °C to 200 °C at 10 °C/min.

Polarizing Optical Microscopy

POM was used to identify and study the mesophase behavior of the azoLCPs. The azoLCP films were ~10µm thick. The films were dried in the oven to remove the solvent. An Olympus BX61 optical microscope equipped with a Linkam warm stage. Phase assignments were made by cooling at a rate of 0.1 °C/min from 10 °C above the isotropic temperature; to below the glass transition temperature identified using the DSC.

Wide Angle X-ray Diffraction Analysis

A Scintag PAD X diffractometer with a Peltier detector was used to collect X-ray diffraction (WAXD) data on the polymers. Typical samples were thin films spin cast onto 9 cm² silicon wafers from 8-10 wt% solution of polymer in chloroform. The polymer films were coated on a zero-diffraction substrate and subject to analysis at room temperature or as cast, above their respective glass transition temperature. Diffraction scans were taken from scattering angle 20 of 1° to 40° at a resolution of 0.1° and a scanning rate of 3 seconds per point. Thin film samples were measured after drying at 50 °C for 30 minutes, after annealing for 25 minutes and three hours at 70 °C, and after melting at 120 °C and quenching in liquid nitrogen.

Film Preparation and Casting

For the WAXD, thin films were coated by spin-casting the azoLCPs on silicon wafers. Polymer coated discs and silicon wafers were allowed to dry in vacuum at 45 °C for 30 min before preparation of the films to exhibit liquid-crystalline or isotropic mesophase.

Since both the WAXD and the oxygen permeation analyzer (OPA) instruments do not have heating capability, in order to make permeation measurements on films above their clearing temperature T_c or T_{NI} , where the azoLCP will be in an isotropic phase, the films were first heated above T_c , held for 30 min for thermal equilibrium to be reached, followed by rapid quenching in liquid N₂ (*melt-liquid* N₂ quenched) in order to "freeze-in" the isotropic phase. The assumption is made that the measurement time is less than the time taken for the film to return to temperatures above its T_c and thus its liquid-crystalline mesomorphic phase (nematic). Measurements where the films are in a liquid-crystalline phase were made by annealing the films for 30 min just below their T_c and above their glass transition temperature, T_g to induce high liquid crystallinity.

For O₂ permeation analysis, solution casting was done on unsupported AnoporeTM discs (25 mm diameter) from a polymer concentration of 8-10 wt% in tetrahydrofuran. The azoLCPs were spin-coated on AnoporeTM discs to form uniform films that were used as testing samples. Based on thin-film thicknesses measured by Contact stylus (surface) profilometry using a Veeco Dektek 150 Instrument, average film thickness of the polymer over the AnoporeTM discs was found to be between 0.56 and 1.10 µm.

Oxygen Permeation Analysis

The O_2 permeability experiments were conducted according to the method described previously⁴ and will be briefly described here. O_2 gas permeability properties were measured using an Illinois instruments Model 8001 oxygen permeation analyzer (OPA). Ultra-high purity nitrogen and oxygen were used for the analyses. Each testing sample was placed to cover 11 mm diameter hole in a solid brass masking plate. Two analyses were performed simultaneously at 23 °C and 0% RH. Initially, nitrogen was purged to the instrument with an initial oxygen concentration of ~0.14 ppm which is equivalent to an oxygen transmission rate (OTR) of 4 cm³/m².day.atm is preset in the instrument software. Later O_2 gas was introduced on the opposite side of the sample. The sampling interval used was 30 min and each test was set to terminate after three consistent reading (i.e., within ±1% of one another). Testing times are varied from 2 to 3h. Each sample was measured at five different points and the results were averaged.

The OTR of the polymer films only was determined by taking into consideration the average pore size of the AnodiscTM, which is 212 Å and which corresponds to ~37.5 % porosity. That is, to determine the OTR of the polymer only, the values measured by the OPA are divided by 0.375. The O₂ permeability coefficient (Po_2) was then calculated by multiplying the average thickness of the film by the OTR of the polymer film only.



Figure S1. ¹HNMR spectra of the synthesized monomer and polymer at each step for poly[4-(4'cyanophenylazo)phenoxy]pentyl methacrylate polymer (azoLCP-C₅).



Figure S2. ¹HNMR spectra of the synthesized monomer and polymer at each step for poly[4-(4'cyanophenylazo)phenoxy]Octyl methacrylate polymer (azoLCP-C₈).



Figure S3. ¹HNMR spectra of the synthesized monomer and polymer at each step for poly[4-(4'- cyanophenylazo)phenoxy]dodacyl methacrylate polymer (azoLCP-C₉).



Figure S4. ¹HNMR spectra of the synthesized monomer and polymer at each step for poly[4-(4'- cyanophenylazo)phenoxy]dodacyl methacrylate polymer (azoLCP-C₁₀).



Figure S5. ¹HNMR spectra of the synthesized monomer and polymer at each step for poly[4-(4'cyanophenylazo)phenoxy]dodacyl methacrylate polymer (azoLCP-C₁₂).



Fig. S6. ¹³C NMR of 4-(4'-Hydroxyphenylazo)benzonitrile, 4-[4'-(n-bromooctyloxy)phenylazo] benzonitrile , monomer used to synthesize azoLCP-C₈.



Figure S7. FTIR spectra of 4-(4'-Hydroxyphenylazo)benzonitrile starting compound,

intermediates, and the corresponding final polymer, azoLCP-C8.



Figure S8. DSC thermographs of poly[4-(4'-cyanophenylazo)phenoxy]alkyl methacrylate polymers (azoLCP-C₅,) indicating T_{SN} during the first heating cycle. The exotherm is up in the heat flow axis.



Figure S9. DSC thermographs of poly[4-(4'-cyanophenylazo)phenoxy]alkyl methacrylate polymers (azoLCP-C₈,) indicating T_{SN} during the first heating cycle. The exotherm is up in the heat flow axis.



Figure S10. DSC thermographs of poly[4-(4'-cyanophenylazo)phenoxy]alkyl methacrylate polymers (azoLCP-C₉,) indicating T_{SN} during the first heating cycle. The exotherm is up in the heat flow axis.



Figure S11. DSC thermographs of poly[4-(4'-cyanophenylazo)phenoxy]alkyl methacrylate polymers (azoLCP-C₁₀,) indicating T_{SN} during the first heating cycle. The exotherm is up in the heat flow axis.



Figure S12. DSC thermographs of poly[4-(4'-cyanophenylazo)phenoxy]alkyl methacrylate polymers (azoLCP-C₁₂,) indicating T_{SN} during the first heating cycle. The exotherm is up in the heat flow axis.

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