

SUPPORTING INFORMATION

High Refractive Index Polymers by Design

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1. Monomer and polymer syntheses

1.1 Reagents

Chemicals purchased were at least of analytical quality and used as received.

1.2 Instrumentation

Calculations were performed using the software ACD/Physchem Profiler, ACD/Labs percepta, version 2016.2, by ADVANCED CHEMISTRY DEVELOPMENT, Inc., Toronto, 2016, further referred to as ACD/Labs.

All NMR measurements were recorded in 0.6 mL dimethyl sulfoxide d_6 (DMSO- d_6) (SIGMA ALDRICH) solution. The spectra were measured on an AV-300 (BRUKER) at 300 MHz (^1H -NMR) and 75 MHz (^{13}C -NMR), respectively. The solvent signal of DMSO- d_6 was used for calibrating the spectra (^1H : δ = 2.50 ppm, ^{13}C : δ = 39.52 ppm).

UV/Vis spectra were measured on a Lambda 1050 (PERKIN ELMER), in the range from 200 to 800 nm at a scan rate of 100 nm/min. For liquid samples quartz glass cuvettes (HELLMA, 1.0 cm thickness) were used. Polymer samples were mounted on object holder for positioning.

IR measurements were carried out with a FT-IR spectrometer Spectrum Two (PERKIN ELMER) in the wave number range from 4000 to 600 cm^{-1} .

For high pressure liquid chromatography (HPLC) an UltiMate 3000 (DIONEX) equipped with a Nucleosil C18 reversed phase column (5 μm , 250 mm x 4 mm, MACHEREY-NAGEL) was employed. The isocratic eluent was a mixture of acetonitrile:water (75:25) with 300 $\mu\text{L/L}_{\text{water}}$ H_3PO_4 .

Mass spectra were measured on a LTQ-FT Ultra (THERMO FISCHER SCIENTIFIC) with electron spray ionization (ESI).

Glass transition temperatures T_g of the samples were measured via differential scanning calorimetry (DSC) using a DSC 1 STAR[®] (METTLER TOLEDO). Approximately 20 mg sample in a closed aluminum crucible was used for each analysis. Two cycles in the range between min. -100 $^{\circ}\text{C}$ and max. +150 $^{\circ}\text{C}$ at a heating rate and cooling rate of (-)10 $^{\circ}\text{C}/\text{min}$ were recorded. The T_g value of the sample was determined from the minimum of the first derivative of the second cooling cycle.

Refraction index and ABBE number were measured each in the range between 20 $^{\circ}\text{C}$ and 80 $^{\circ}\text{C}$ on a DSR- λ multi-wavelength refractometer (SCHMIDT+HAENSCH). The used wavelengths were 399.0, 435.8, 486.1, 541.5, 589.3, 656.3 and 702.5 nm.

Column chromatography was carried out using silica gel 60 (MACHEREY-NAGEL) as static phase. For thin layer chromatography (TLC) precoated silica gel 60 aluminum cards with fluorescence indicator F254 (MERCK) were used. For detection either a UV lamp at 254 nm or staining with a KMnO_4 solution was used.

Lightfastness test were run in a Suntest XLS+ (ATLAS) with filter F installed. Energy sensor and in addition blue wool strips (DEK – DEUTSCHE ECHTHEITSKOMMISSION, NMP 511) according to DIN EN ISO 105 B01 – B06, category 1 – 8, were used for reference.

An air circulated furnace (TK LE 117, EHRET) was used for drying of the polymer samples.

1.3 Allyl precursor syntheses

The syntheses of all allyl precursors were identical except for minor variations due to the different acidities of the protons involved in the substitution reactions.

a) Heteroatom containing precursors: The precursor syntheses were done using modified procedures taken from literature for diphenylamine¹, carbazole² and phenylphenol³. After mixing the corresponding starting material, potassium carbonate, allyl bromide, and tetrabutylammonium chloride in a flask with acetonitrile / acetone, the solution was refluxed at 90 °C (respectively 60 °C) for 120 h (DPA), 72 h (Cz) and 20 h (oPP).

b) Heteroatom free precursors: Diphenylmethane⁴ and fluorene⁵ were processed to their allyl precursors using modified reactions from literature. The starting materials were dissolved in dry tetrahydrofuran under inert gas conditions and *n*-butyl lithium was added as base.

1.3.1 Synthesis of *N*-allyldiphenylamine

Diphenylamine (10.03 g, 59.3 mmol), dry potassium carbonate (20.46 g, 148.0 mmol), tetrabutylammonium chloride (1.11 g, 4.0 mmol), and allyl bromide (13.2 mL, 152.0 mmol) were dissolved in acetonitrile (120 mL) under argon atmosphere. The solution was refluxed under stirring for 120 h at 90 °C. The crude product was purified via column chromatography with a mixture of pentane and triethylamine (98:2). Destillation was used to remove the last remaining impurities (0.06 mbar, 86 – 100 °C). Thus 10.40 g *N*-allyldiphenylamine (49.69 mmol, 84.0% yield, 99.3% purity) was obtained as a pale yellow oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.28-7.21 (*m*, 4H, 4x CH_{arom.}), 7.01-6.98 (*m*, 4H, 4x CH_{arom.}), 6.94-6.88 (*m*, 2H, 2x CH_{arom.}), 5.97-5.85 (*m*, 1H, -CH=CH₂), 5.25-5.18 (*m*, 1H, -CH=CHH_a), 5.15-5.10 (*m*, 1H, -CH=CHH_b), 4.37-4.34 (*m*, 2H, -N-CH₂-)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 147.4 (C_{arom.}), 134.5 (CH₂=CH-), 129.2 (C_{arom.}), 121.0 (C_{arom.}), 120.3 (C_{arom.}), 116.2 (CH₂=CH-), 54.0 (-CH₂-N-)

R_f (Pentane:Et₃N 98:2): 0.60

1.3.2 Synthesis of 9-allyl-9*H*-carbazole

Carbazole (10.06 g, 60.2 mmol), tetrabutylammonium chloride (1.05 g, 3.8 mmol), allyl bromide (10.2 mL, 118.1 mmol), and dried potassium carbonate (19.95 g, 138.2 mmol) were dissolved in 90 mL dry

acetonitrile under argon atmosphere. The solution was refluxed for 72 h at 90 °C. The crude brown product was collected, washed with ice cold methanol, recrystallized from diethyl ether and dried *in vacuo*. 9.60 g 9-Allyl-9*H*-carbazole (46.31 mmol, 77.0% yield, 99.9% purity) was obtained as a white solid.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 8.17-8.15 (*m*, 2H, 2x CH_{arom.}), 7.57-7.55 (*m*, 2H, 2x CH_{arom.}), 7.47-7.41 (*m*, 2H, 2x CH_{arom.}), 7.23-7.18 (*m*, 2H, 2x CH_{arom.}), 6.05-5.93 (*m*, 1H, CH₂=CH-), 5.13-4.93 (*m*, 4H, CH₂=CH-CH₂-)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 139.9 (C_{arom.}), 133.1 (CH₂=CH-), 125.6 (C_{arom.}), 122.1 (C_{arom.}), 120.2 (C_{arom.}), 118.8 (C_{arom.}), 116.3 (CH₂=CH-), 109.3 (C_{arom.}), 44.5 (-CH₂-N-)

R_f (Pentane:Et₃N 99:1): 0.47

1.3.3 Synthesis of 4,4-diphenyl-1-butene

Diphenyl methane (9.9 mL, 59.4 mmol) was mixed with 150 mL dry tetrahydrofuran in a flask under argon atmosphere. The mixture was cooled down to – 78 °C and *n*-butyl lithium (28.0 mL, 2.5 M in hexane, 70.0 mmol) was added dropwise over a period of 20 minutes. The solution was stirred for another 16 h whilst slowly raising to room temperature. After cooling to 0 °C allyl bromide (6.2 mL, 71.7 mmol) was added dropwise and stirred for further 4 hours. The mixture was quenched with 10 mL H₂O, extracted twice with diethyl ether and the combined organic phases were concentrated using a rotary evaporator. The remaining oil was dissolved in diethyl ether, washed twice with brine, dried over magnesium sulfate, filtered, and then the solvent was removed *in vacuo*. The crude product was purified by column chromatography. 11.78 g 4,4-Diphenyl-1-butene (56.55 mmol, 95.1% yield, 98.0% purity) was obtained as a colorless oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.33-7.24 (*m*, 8H, 8x CH_{arom.}), 7.18-7.12 (*m*, 2H, 2x CH_{arom.}), 5.74-5.60 (*m*, 1H, CH₂=CH-), 5.07-5.00 (*m*, 1H, CH_aH=CH-), 4.93-4.89 (*m*, 1H, CH_bH=CH-), 4.05 (*t*, 1H, -CH₂-CH-), 2.81 (*m*, 2H, -CH₂-CH-)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 144.6 (C_{arom.}), 136.8 (CH₂=CH-), 128.2 (C_{arom.}), 127.6 (C_{arom.}), 125.9 (C_{arom.}), 116.3 (CH₂=CH-), 50.3 (-CH₂-CH-), 38.9 (-CH₂-CH-)

R_f (pentane:Et₃N 99:1): 0.50

1.3.4 Synthesis of 9-allyl-9*H*-fluorene

Fluorene (10.06 g, 60.3 mmol) was dissolved in 150 mL dry tetrahydrofuran under argon atmosphere. After cooling to -78 °C, *n*-butyl lithium (28.0 mL, 2.5 M in hexane, 70.0 mmol) was added dropwise over 20 minutes. Whilst stirring for 16 h the solution was slowly warming up to room temperature. After cooling to 0 °C allyl bromide (6.2 mL, 71.7 mmol) was added dropwise to the solution and stirred for further 4 hours. Then the reaction was quenched with 10 mL H₂O. After two-fold extraction with diethyl ether twice the organic phases were combined, the solvent removed, and the remaining oil dissolved in diethyl

ether. After washing with brine, drying with magnesium sulfate and filtration the product was concentrated in a rotary evaporator. The crude product was purified by column chromatography. 11.70 g 9-Allyl-9H-fluorene (56.72 mmol, 94.1% yield, 96.7% purity) was obtained as a yellow oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.86-7.84 (*m*, 2H, 2x CH_{arom.}), 7.61-7.58 (*m*, 2H, 2x CH_{arom.}), 7.39-7.28 (*m*, 4H, 4x CH_{arom.}), 5.66-5.52 (*m*, 1H, CH₂=CH-), 5.00-4.87 (*m*, 2H, CH₂=CH-), 4.04 (*t*, 1H, -CH₂-CH-), 2.72 (*m*, 2H, -CH₂-CH-)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 146.4 (C_{arom.}), 140.4 (C_{arom.}), 135.3 (CH₂=CH-), 126.9 (C_{arom.}), 126.8 (C_{arom.}), 124.5 (C_{arom.}), 119.8 (C_{arom.}), 117.0 (CH₂=CH-), 46.1 (-CH₂-CH-), 36.6 (-CH₂-CH-)

R_f (pentane:Et₃N 99:1): 0.50

1.3.5 Synthesis of 2-(allyloxy)-biphenyl

2-Phenylphenol (10.00 g, 58.8 mmol) and dry potassium carbonate (20.30 g, 146.9 mmol) were dissolved in 100 mL acetone and then allyl bromide (12.7 mL, 146.9 mmol) was added. The reaction mixture was heated to 60 °C and refluxed for 20 h. The reaction process was monitored via HPLC and TLC. The suspension was filtered through a BÜCHNER funnel and concentrated using a rotary evaporator. The remaining oil was purified via column chromatography and the combined organic phases were dried and the solvent was removed *in vacuo*. 12.24 g 2-(Allyloxy)-biphenyl (58.2 mmol, 99.0% yield, 99.1% purity) was obtained as a colorless oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.52-7.48 (*m*, 2H, 2x CH_{arom.}), 7.43-7.38 (*m*, 2H, 2x CH_{arom.}), 7.35-7.29 (*m*, 3H, 3x CH_{arom.}), 7.11-7.09 (*m*, 1H, CH_{arom.}), 7.06-7.01 (*m*, 1H, CH_{arom.}), 6.05-5.93 (*m*, 1H, CH₂=CH-), 5.34-5.26 (*m*, 1H, CH_aH=), 5.21-5.16 (*m*, 1H, CH_bH=), 4.59-4.56 (*m*, 2H, -CH₂-)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 154.9 (C_{arom.}), 138.1 (C_{arom.}), 133.6 (CH₂=CH-), 130.4 (C_{arom.}), 130.0 (C_{arom.}), 129.2 (C_{arom.}), 128.7 (C_{arom.}), 127.8 (C_{arom.}), 126.7 (C_{arom.}), 120.9 (C_{arom.}), 116.6 (CH₂=CH-), 113.0 (C_{arom.}), 68.4 (-CH₂-O-)

R_f (pentane:Et₃N 99:1): 0.40

1.4 Siloxane monomer syntheses

1.4.1 Synthesis of *N*-(diphenyl)-3-aminopropyl-dimethoxy(methyl)silane (SX-DPA)

N-Allyldiphenylamine (11.10 g, 53.04 mmol) was transferred to a flask and dried *in vacuo* at elevated temperature. Then it was dissolved in dry toluene (100 mL) before adding KARSTEDT's catalyst solution (1.0 mL, in Xylene, Pt ~2%) and dimethoxy(methyl)silane (15.0 mL, 121.66 mmol). The reaction mixture was stirred refluxing at 120 °C until the reaction was completed under HPLC and TLC control. The remaining silane starting material and the solvent were removed at low pressure. The crude product was distilled and fractionated at 0.001 mbar. 5.81 g *N*-(Diphenyl)-3-aminopropyl-dimethoxy-(methyl)silane (18.43 mmol, 35.1% yield, 98.0% purity) was obtained as a yellow oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.28-7.23 (*m*, 4H, 4x *CH*_{arom.}), 6.96-6.88 (*m*, 6H, 6x *CH*_{arom.}), 3.65 (*t*, 2H, -N-*CH*₂-), 3.38 (*s*, 6H, -O-*CH*₃), 1.59 (*m*, 2H, -Si-*CH*₂-*CH*₂-), 0.59 (*m*, 2H, -Si-*CH*₂-), 0.01 (*s*, 3H, -Si-*CH*₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 147.5 (*C*_{arom.}), 129.2 (*C*_{arom.}), 120.9 (*C*_{arom.}), 120.4 (*C*_{arom.}), 54.0 (-*CH*₂-N-), 49.5 (-Si-(O-*CH*₃)₂), 20.1 (-Si-*CH*₂-*CH*₂-), 9.6 (-Si-*CH*₂-), -5.8 (-Si-*CH*₃)

²⁹Si-NMR (100 MHz, DMSO-*d*₆): δ(ppm) = -1.51

MS (ESI+): 316.1728, calculated: 316.1727 (C₁₈H₂₅NO₂Si + H⁺)

Mp.: -65 °C

1.4.2 Synthesis of 3-(9*H*-carbazol)-1-dimethoxy(methyl)silyl-propane (SX-Cz)

9-Allyl-9*H*-carbazole (11.00 g, 53.07 mmol) was transferred to a flask and heated under reduced pressure to remove potential water in the sample. After dissolving in 70 mL dry toluene KARSTEDT's catalyst (1.0 mL, in Xylene, Pt ~2%) and dimethoxy(methyl)silane (15.8 mL, 128.06 mmol) were added. The reaction mixture was stirred and refluxed at 120 °C until completion. The reaction progress was checked via HPLC and TLC. After removing the remaining silane educt and the solvent at reduced pressure (low vacuum) the crude product was purified in high vacuum by distillation at 0.001 mbar. 8.57 g 3-(9*H*-Carbazol)-1-dimethoxy(methyl)silyl-propane (27.35 mmol, 51.5% yield, 99.5% purity) was obtained as a pale yellow oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 8.14 (*d*, 2H, 2x *CH*_{arom.}), 7.60 (*d*, 2H, 2x *CH*_{arom.}), 7.47-7.42 (*m*, 2H, 2x *CH*_{arom.}), 7.21-7.16 (*m*, 2H, 2x *CH*_{arom.}), 4.36 (*t*, 2H, -N-*CH*₂-), 3.35 (*s*, 6H, 2x -O-*CH*₃), 1.80 (*m*, 2H, -Si-*CH*₂-*CH*₂-), 0.60 (*m*, 2H, -Si-*CH*₂-), 0.01 (*s*, 3H, -Si-*CH*₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 140.0 (*C*_{arom.}), 125.7 (*C*_{arom.}), 122.0 (*C*_{arom.}), 120.3 (*C*_{arom.}), 118.6 (*C*_{arom.}), 109.2 (*C*_{arom.}), 49.6 (-Si-(O-*CH*₃)₂), 44.7 (-*CH*₂-N-), 22.0 (-*CH*₂-*CH*₂-), 10.1 (-Si-*CH*₂-), -5.9 (-Si-*CH*₃)

²⁹Si-NMR (100 MHz, DMSO-*d*₆): δ(ppm) = -1.76

MS (ESI+): 336.1392, calculated: 336.1390 (C₁₈H₂₃NO₂Si + Na⁺)

Mp.: -53 °C

1.4.3 Synthesis of 4,4-diphenyl-1-dimethoxy(methyl)silyl-butane (SX-DPM)

4,4-Diphenyl-1-butene (11.04 g, 53.00 mmol) was dried in a flask *in vacuo* under heating. Dry toluene (100 mL) was added to the starting material and stirred until it was fully dissolved. The KARSTEDT's catalyst solution (1.0 mL, in Xylene, Pt ~2%) and dimethoxy(methyl)silane (15.0 mL, 121.66 mmol) were added to the flask. The mixture was refluxed at 120 °C until completion of the reaction which was monitored by HPLC and TLC. Remaining low boiling educts were removed *in vacuo*. The obtained crude

product was purified by fractionated distillation at 0.001 mbar. 7.13 g 4,4-Diphenyl-1-dimethoxy(methyl)silyl-butane (22.67 mmol, 43.0% yield, 98.5% purity) was obtained as a colorless oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.31-7.23 (*m*, 8H, 8x CH_{arom.}), 7.17-7.11 (*m*, 2H, 2x CH_{arom.}), 3.94 (*t*, 1H, -CH-CH₂-), 3.34 (*s*, 6H, 2x -O-CH₃), 2.03 (*m*, 2H, -CH-CH₂-), 1.23 (*m*, 2H, -Si-CH₂-CH₂-), 0.60 (*t*, 2H, -Si-CH₂-), 0.04 (*s*, 3H, -Si-CH₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 145.2 (C_{arom.}), 128.4 (C_{arom.}), 127.6 (C_{arom.}), 125.9 (C_{arom.}), 50.2 (-CH-CH₂-), 49.5 (-Si-(O-CH₃)₂), 38.2 (-CH-CH₂-), 20.7 (-CH₂-CH₂-), 12.4 (-Si-CH₂-), -5.7 (-Si-CH₃)

²⁹Si-NMR (100 MHz, DMSO-*d*₆): δ(ppm) = -1.45

MS (ESI+): 337.1593, calculated: 337.1593 (C₁₉H₂₆O₂Si + Na⁺)

Mp.: -72 °C

1.4.4 Synthesis of 9-(3-(dimethoxymethylsilyl)propyl)-9H-fluorene (SX-FI)

9-Allyl-9H-fluorene (11.00 g, 53.33 mmol) was degassed under heating *in vacuo* and dissolved in 100 mL dry toluene. KARSTEDT's catalyst solution (1.0 mL, in Xylene, Pt ~2%) and dimethoxy(methyl)silane (14.9 mL, 120.85 mmol) were added during stirring. The mixture was refluxed at 120 °C. The reaction progress was monitored HPLC and TLC. After completion of the reaction the remaining low boiling components were removed under reduced pressure before fractionated distillation at 0.001 mbar. 9.49 g 9-(3-(Dimethoxymethylsilyl)propyl)-9H-fluorene (30.38 mmol, 57.0% yield, 97.5% purity) was obtained as a colorless oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.86-7.84 (*m*, 2H, 2x CH_{arom.}), 7.56-7.54 (*m*, 2H, 2x CH_{arom.}), 7.39-7.29 (*m*, 4H, 4x CH_{arom.}), 3.99 (*t*, 1H, -CH-CH₂-), 3.33 (*s*, 6H, 2x -O-CH₃), 2.00 (*m*, 2H, -CH-CH₂-), 1.15 (*t*, 2H, -CH₂-CH₂-CH₂-), 0.52 (*t*, 2H, -Si-CH₂-), 0.05 (*s*, 3H, -Si-CH₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 147.0 (C_{arom.}), 140.5 (C_{arom.}), 126.9 (C_{arom.}), 126.9 (C_{arom.}), 124.3 (C_{arom.}), 120.0 (C_{arom.}), 49.5 (-Si-(O-CH₃)₂), 46.7 (-CH-CH₂-), 35.7 (-CH-CH₂-), 18.4 (-CH₂-CH₂-), 12.9 (-Si-CH₂-), -5.7 (-Si-CH₃)

²⁹Si-NMR (100 MHz, DMSO-*d*₆): δ(ppm) = -1.57

MS (ESI+): 335.1437, calculated: 335.1438 (C₁₉H₂₄O₂Si + Na⁺)

Mp.: -63 °C

1.4.5 Synthesis of 3-(*o*-biphenoxy)-1-dimethoxy(methyl)silyl-propane (SX-oPP)

2-(Allyloxy)-biphenyl (10.98 g, 52.22 mmol) was dried in a flask under heating before adding 100 mL dry toluene and KARSTEDT's catalyst (1.0 mL, in Xylene, Pt ~2%) and dimethoxy(methyl)silane (15.0 mL, 121.66 mmol) were added slowly to the solution. The reaction was heated to 120 °C and refluxed until HPLC- and TLC-control showed no further progress of the reaction. The remaining low boiling

components were removed *in vacuo* before final purification was done by fractionated distillation under decreased pressure (0.001 mbar). 4.77 g 3-(*o*-Biphenoxy)-1-dimethoxy(methyl)silyl-propane (15.07 mmol, 28.9% yield, 99.5% purity) was obtained as a colorless oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.52-7.49 (*m*, 2H, 2x CH_{arom.}), 7.41-7.36 (*m*, 2H, 2x CH_{arom.}), 7.34-7.28 (*m*, 3H, 3x CH_{arom.}), 7.08-6.98 (*m*, 2H, 2x CH_{arom.}), 3.93 (*t*, 2H, -O-CH₂-), 3.38 (*s*, 6H, 2x -O-CH₃), 1.66 (*m*, 2H, -Si-CH₂-CH₂-), 0.62 (*m*, 2H, -Si-CH₂-), 0.02 (*s*, 3H, -Si-CH₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 155.4 (C_{arom.}), 138.2 (C_{arom.}), 130.4 (C_{arom.}), 129.9 (C_{arom.}), 129.3 (C_{arom.}), 128.8 (C_{arom.}), 127.8 (C_{arom.}), 126.7 (C_{arom.}), 120.7 (C_{arom.}), 112.7 (C_{arom.}), 69.8 (-CH₂-O-), 49.6 (-Si-(O-CH₃)₂), 22.2 (-CH₂-CH₂-), 8.7 (-Si-CH₂-), -5.8 (-Si-CH₃)

²⁹Si-NMR (100 MHz, DMSO-*d*₆): δ(ppm) = -1.39

MS (ESI+): 339.1387, calculated: 339.1387 (C₁₈H₂₄O₃Si + Na⁺)

Mp.: -64 °C

1.5 Polymerization of siloxanes

Polymerization initiation by sulfuric acid has proven to be our favored method in preliminary tests. An alternative route was also carried out, which proceeds from the synthesized allyl species of the HRI structures and pre-polymerized polymethylhydrosiloxane (pMHS).

1.5.1 Sulfuric acid promoted polycondensation

The polycondensation was performed using sulfuric acid to promote the co-hydrolysis/condensation via an identical procedure for each monomer.⁶ The respective dimethoxy silane precursor (3.18 mmol each) was transferred into a flask which was purged with argon and the sulfuric acid (1.09 mmol, 0.5 mol/L) was added dropwise. After stirring for 2 h at 60 °C 5 mL toluene were added and the reaction stirred for another 48 h at 60 °C. After cooling down to room temperature and filtration through a 0.5 μm PTFE syringe filter, the solvent was removed *in vacuo*. The polymers were cured at 150 °C for 12 h.

1.5.2 Hydrosilylation with pMHS

The second route to synthesize the allyl structures a platonic-catalyst was employed to pre-polymerize the polymethylhydrosiloxane (pMHS). This hydrosilylation reaction was performed using a dichlorodicyclopentadienyl platinum catalyst according to a reaction adapted from literature.⁷ This route was described for the carbazole-propyl-substituted polysiloxane derivative (pSX-Cz) by Strohriegl et al.⁸ The allyl species (5.00 mmol each) and pMHS (1900 g/mol, 0.17 mmol, in average 31.6 Si-H/chain) were thoroughly dried and degassed. After solving in 5 mL dry toluene a solution of dichlorodicyclopentadienyl platinum in toluene was added (0.0005 mmol Pt). The reaction was heated to 60 °C and stirred for 23 h under argon atmosphere. Finally toluene and residues of the HRI allyl derivatives were removed *in vacuo* at 150 °C. After 48 h the polymers were completely purified and analyzed.

1.6 Methacrylate precursor syntheses

1.6.1 Synthesis of *N*-(2-hydroxyethyl)-diphenylamine

Dry diphenylamine (10.00 g, 59.1 mmol, 0.5 eq base) was melted under argon atmosphere in a flask at 100 °C. 2-Bromoethanol (2.1 mL, 29.6 mmol) was added to the hot melt and stirred for 12 h at 100 °C. After cooling to room temperature 20 mL of distilled water were added to the reaction. The aqueous solution was extracted with 100 mL ethyl acetate three times before drying the combined organic phases over sodium sulfate and removing the solvent *in vacuo*. The crude product was purified via column chromatography with a mixture of *n*-pentane and ethyl acetate (8:1) as eluent. After removing the solvent under reduced pressure, 2.70 g *N*-(2-Hydroxyethyl)-diphenylamine (12.6 mmol, 42.6% yield, 97.1% purity) was obtained as a slightly brown oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.28-7.22 (*m*, 4H, 4x CH_{arom.}), 7.01-6.99 (*m*, 4H, 4x CH_{arom.}), 6.93-6.89 (*m*, 2H, 2x CH_{arom.}), 4.76 (*t*, 1H, -OH), 3.76 (*t*, 2H, -CH₂-N-), 3.57 (*q*, 2H, -CH₂-OH)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 147.6 (C_{arom.}), 129.2 (C_{arom.}), 120.9 (C_{arom.}), 120.5 (C_{arom.}), 57.7 (-CH₂-OH), 53.2 (-CH₂-N-)

R_f (pentane:EtOAc 8:1): 0.21, (DCM): 0.30

1.6.2 Synthesis of 9-(2-hydroxyethyl)-9*H*-carbazole

Carbazole (10.08 g, 60.3 mmol) was dried at reduced pressure and added to a flask of dry sodium hydride (1.45 g, 60.3 mmol) under argon atmosphere. Then 100 mL dimethylformamide were added to the mixture and stirred for 16 h at 20 °C. Then 2-bromoethanol (4.7 mL, 66.3 mmol) was added dropwise to the solution which was stirred for another 24 h at 20 °C. The reaction solution was slowly poured into 1 L of cold deionized water. The obtained white solid was separated from the solution by filtration. The crude product was dried under reduced pressure and then purified by column chromatography in dichloromethane. 1.38 g 9-(2-Hydroxyethyl)-9*H*-carbazole (6.5 mmol, 10.8% yield, 97.5% purity) was obtained as a colorless solid.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 8.15-8.12 (*m*, 2H, 2x CH_{arom.}), 7.62-7.59 (*m*, 2H, 2x CH_{arom.}), 7.46-7.40 (*m*, 2H, 2x CH_{arom.}), 7.21-7.16 (*m*, 2H, 2x CH_{arom.}), 4.86 (*t*, 1H, -OH), 4.43 (*t*, 2H, -CH₂-N-), 3.79 (*q*, 2H, -CH₂-OH)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 140.4 (C_{arom.}), 125.5 (C_{arom.}), 122.0 (C_{arom.}), 120.0 (C_{arom.}), 118.5 (C_{arom.}), 109.5 (C_{arom.}), 59.4 (-CH₂-OH), 45.2 (-CH₂-N-)

R_f (Pentane:EtOAc 8:1): 0.14, (DCM): 0.27

1.6.3 Synthesis of 3,3-diphenylpropan-1-ol

Diphenyl methane (10.1 mL, 59.4 mmol) was dried in a flask *in vacuo* before adding 50 mL dry tetrahydrofuran under argon atmosphere. The solution was cooled down to -78 °C before adding

n-butyllithium (28.5 mL, 2.5 M in hexane, 71.3 mmol) slowly over 15 min. The reaction was stirred for 14 h under inert gas whilst slowly warming up to room temperature. After cooling to 0 °C, 2-chloroethanol (4.7 mL, 71.3 mmol) was added dropwise and stirred for 8 h. The reaction was quenched by adding 50 mL H₂O. After removing the solvent *in vacuo*, the remaining product was extracted with 100 mL dichloromethane, washed twice with brine and dried over magnesium sulfate. After extracting the solvent, the crude product was purified via column chromatography in dichloromethane. 5.30 g 3,3-Diphenylpropan-1-ol (25.0 mmol, 42.0% yield, 99.0% purity) was obtained as a yellow oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.32-7.24 (*m*, 8H, 8x CH_{arom.}), 7.18-7.12 (*m*, 2H, 2x CH_{arom.}), 4.49 (*t*, 1H, -OH), 4.11 (*t*, 1H, -CH-), 3.33 (*q*, 2H, -CH₂-OH), 2.20 (*q*, 2H, -CH₂-CH-)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 145.1 (C_{arom.}), 128.3 (C_{arom.}), 127.6 (C_{arom.}), 125.9 (C_{arom.}), 58.8 (-CH₂-OH), 46.6 (-CH-), 38.0 (-CH₂-CH-)

R_f (Pentane:EtOAc 8:1): 0.20, (DCM): 0.33

1.6.4 Synthesis of 9-(2-hydroxyethyl)-9H-fluorene

Dry fluorene (10.05 g, 60.2 mmol) was solved in 50 mL dry tetrahydrofuran in a flask under argon atmosphere. After cooling down the solution to -78 °C, *n*-butyllithium (28.7 mL, 2.5 M in hexane, 71.9 mmol) was slowly added over 15 min. The mixture was stirred for 14 h under inert gas and warmed up to room temperature. 2-Chloroethanol (4.8 mL, 71.9 mmol) was added dropwise after cooling down to 0 °C. The solution was stirred for another 8 h. The reaction was quenched by adding 50 mL H₂O. The solvent was removed *in vacuo* and the product extracted with 100 mL dichloromethane. The organic phase was washed with brine twice and dried over magnesium sulfate followed by column chromatography in dichloromethane for further purification. After solvent removal, 2.75 g 9-(2-hydroxyethyl)-9H-fluorene (13.1 mmol, 21.7% yield, 98.1% purity) was obtained as a colorless solid.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.87-7.84 (*m*, 2H, 2x CH_{arom.}), 7.60-7.58 (*m*, 2H, 2x CH_{arom.}), 7.39-7.29 (*m*, 4H, 4x CH_{arom.}), 4.62 (*t*, 1H, -OH), 4.07 (*t*, 1H, -CH-), 3.49 (*q*, 2H, -CH₂-OH), 2.03 (*q*, 2H, -CH₂-CH-)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 147.2 (C_{arom.}), 140.2 (C_{arom.}), 126.9 (C_{arom.}), 126.9 (C_{arom.}), 124.6 (C_{arom.}), 119.9 (C_{arom.}), 58.3 (-CH₂-OH), 43.9 (-CH-), 36.2 (-CH₂-CH-)

R_f (Pentane:EtOAc 8:1): 0.14, (DCM): 0.25

1.6.5 Synthesis of 2-(*o*-biphenyl)oxyethanol

Ground *ortho*-phenylphenol (10.00 g, 58.8 mmol) was dissolved in 10% aqueous sodium hydroxide solution (42.4 mL, 117.5 mmol) in a flask equipped with a reflux condenser. The mixture was heated to 60 °C and maintained at this temperature for 30 minutes. 2-Chloroethanol (7.8 mL, 117.5 mmol) was slowly added to the reaction solution before stirring at 60 °C for 72 h. After solvent extraction twice with 100 mL dichloromethane each the solution was cooled down to 20 °C. The organic phases were washed

twice with brine, dried over magnesium sulfate and solvent was removed *in vacuo*. The crude product was purified via column chromatography using dichloromethane as mobile phase. Finally 9.80 g 2-(2-biphenyl)oxyethanol (45.8 mmol, 78.0% yield, 99.0% purity) was obtained as a colorless solid.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.58-7.55 (*m*, 2H, 2x CH_{arom.}), 7.42-7.37 (*m*, 2H, 2x CH_{arom.}), 7.34-7.29 (*m*, 3H, 3x CH_{arom.}), 7.13-7.10 (*m*, 1H, 1x CH_{arom.}), 7.05-7.00 (*m*, 1H, 1x CH_{arom.}), 4.76 (*t*, 1H, -OH), 4.03 (*t*, 2H, -CH₂-O-), 3.67 (*dt*, 2H, -CH₂-OH)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 155.5 (C_{arom.}), 138.1 (C_{arom.}), 130.4 (C_{arom.}), 129.9 (C_{arom.}), 129.2 (C_{arom.}), 128.7 (C_{arom.}), 127.9 (C_{arom.}), 126.7 (C_{arom.}), 120.8 (C_{arom.}), 113.1 (C_{arom.}), 69.9 (-CH₂-O-), 59.5 (-CH₂-OH)

R_f (Pentane:EtOAc 8:1): 0.14, (DCM): 0.25

1.7 Methacrylate monomer syntheses

1.7.1 Synthesis of diphenylaminoethyl-methacrylate (MA-DPA)

Dry N-(2-hydroxyethyl)-diphenylamine (9.98 g, 46.8 mmol) was dissolved in 80 mL dry dichloromethane. After cooling down to 0 °C triethylamine (6.8 mL, 49.1 mmol) was slowly added to the solution. Methacryloyl chloride (4.7 mL, 49.1 mmol) was added dropwise before stirring the reaction for 16 h and slowly warming up to 20 °C. 100 mL dichloromethane were added to the reaction solution. The organic phase was washed twice with brine and dried over magnesium sulfate. After concentrating the solvent *in vacuo*, the crude product was purified using column chromatography in dichloromethane. After drying, 8.20 g diphenylaminoethyl-methacrylate (29.1 mmol, 62.3% yield, 95.0% purity) was obtained as a light brown oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.29-7.23 (*m*, 4H, 4x CH_{arom.}), 7.01-6.99 (*m*, 4H, 4x CH_{arom.}), 6.95-6.91 (*m*, 2H, 2x CH_{arom.}), 5.87 (*m*, 1H, =CHH_{trans}), 5.60 (*m*, 1H, =CHH_{cis}), 4.29 (*t*, 2H, -CH₂-N-), 4.04 (*t*, 2H, -CH₂-O-), 1.78 (*s*, 3H, -CH₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 166.5 (-COO-), 147.3 (C_{arom.}), 135.6 (-C=CH₂), 129.3 (C_{arom.}), 125.9 (-C=CH₂), 121.3 (C_{arom.}), 120.5 (C_{arom.}), 62.0 (-CH₂-O-), 49.8 (-CH₂-N-), 17.8 (-CH₃)

R_f (DCM): 0.88, (Pentane:EtOAc 8:1): 0.78

MS (ESI⁺): 282.1490, calculated: 282.1489 (C₁₈H₁₉NO₂ + H⁺)

Mp.: -60 °C

1.7.2 Synthesis of 2-carbazolyethyl-methacrylate (MA-Cz)

9-(2-Hydroxyethyl)-9*H*-carbazole (9.97 g, 47.2 mmol) was dried in a flask and dissolved in 160 mL dry dichloromethane. Triethylamine (6.9 mL, 49.6 mmol) was slowly added to the solution at 0 °C. After stirring for 15 min. methacryloyl chloride (4.8 mL, 49.6 mmol) was added dropwise before stirring for 16 h and slowly warming up to 20 °C. The crude product was extracted with 200 mL dichloromethane

before washing the organic phases twice with brine and drying over magnesium sulfate. The solvent was removed *in vacuo* and purified via column chromatography in dichloromethane. 6.62 g 2-Carbazolyethyl-methacrylate (23.7 mmol, 50.2% yield, 99.9% purity) was obtained as a crystalline white solid.

¹H-NMR (300 MHz, DMSO-*d*₆): δ (ppm) = 8.15-8.13 (*d*, 2H, 2x *CH*_{arom.}), 7.67-7.64 (*d*, 2H, 2x *CH*_{arom.}), 7.47-7.42 (*m*, 2H, 2x *CH*_{arom.}), 7.23-7.18 (*m*, 2H, 2x *CH*_{arom.}), 5.74 (*s*, 1H, =*CHH*_{trans}), 5.51 (*m*, 1H, =*CHH*_{cis}), 4.74 (*t*, 2H, -CH₂-N-), 4.47 (*t*, 2H, -CH₂-O-), 1.64 (*s*, 3H, -CH₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ (ppm) = 166.3 (-COO-), 140.1 (*C*_{arom.}), 135.4 (-C=CH₂), 126.0 (-C=CH₂), 125.6 (*C*_{arom.}), 122.1 (*C*_{arom.}), 120.2 (*C*_{arom.}), 118.9 (*C*_{arom.}), 109.4 (*C*_{arom.}), 62.8 (-CH₂-O-), 41.2 (-CH₂-N-), 17.7 (-CH₃)

R_f (DCM): 0.85, (Pentane:EtOAc 8:1): 0.57

MS (ESI⁺): 280.1333, calculated: 280.1343 (C₁₈H₁₇NO₂ + H⁺)

Mp: 86 °C

1.7.3 Synthesis of 3,3-diphenylpropyl-methacrylate (MA-DPM)

Dry 3,3-Diphenylpropan-1-ol (10.10 g, 47.6 mmol) was transferred to an flask filled with and dissolved in 80 mL dichloromethane. The solution was cooled down to 0 °C before adding triethylamine (6.9 mL, 50.0 mmol) and stirring for 15 minutes. Methacryloyl chloride (4.9 mL, 50.0 mmol) was added dropwise. After stirring for 16 h and warming up to room temperature, the crude product was dissolved in 100 mL dichloromethane. The organic phases were washed twice with brine and dried over magnesium sulfate. After removal of the solvent, side products were separated using column chromatography with a mixture of pentane:ethyl acetate (8:1) as eluent. 9.70 g 3,3-Diphenylpropyl-methacrylate (34.6 mmol, 72.7% yield, 94.6% purity) was obtained as a colorless oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ (ppm) = 7.35-7.25 (*m*, 8H, 8x *CH*_{arom.}), 7.19-7.14 (*m*, 2H, 2x *CH*_{arom.}), 5.99 (*m*, 1H, =*CHH*_{trans}), 5.63 (*m*, 1H, =*CHH*_{cis}), 4.10 (*t*, 1H, -CH-CH₂-), 4.01 (*t*, 2H, -CH₂-O-), 2.41 (*q*, 2H, -CH₂-CH-), 1.85 (*s*, 3H, -CH₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ (ppm) = 166.4 (-COO-), 144.2 (*C*_{arom.}), 135.8 (-C=CH₂), 128.4 (*C*_{arom.}), 127.5 (*C*_{arom.}), 126.1 (-C=CH₂), 125.5 (*C*_{arom.}), 62.8 (-CH₂-O-), 47.2 (-CH-CH₂-), 33.4 (-CH-CH₂-), 17.9 (-CH₃)

R_f (DCM): 0.85, (Pentane:EtOAc 8:1): 0.81

MS (ESI⁺): 303.1357, calculated: 303.1356 (C₁₉H₂₀O₂ + Na⁺)

Mp.: -56 °C

1.7.4 Synthesis of 9*H*-fluorene-9-ethyl-methacrylate (MA-FI)

Dry 9-(2-Hydroxyethyl)-9*H*-fluorene (10.01 g, 47.6 mmol) was dissolved in 160 mL dry dichloromethane under argon atmosphere. Triethylamine (6.9 mL, 50.0 mmol) was added to the solution at 0 °C and stirred for 15 min. After dropwise addition of methacryloyl chloride (4.9 mL, 50.0 mmol), the reaction solution was stirred for 16 h. 200 mL Dichloromethane was added to the solution at room temperature and the organic phase was washed twice with brine. After drying over magnesium sulfate and solvent removal, the crude product was purified by column chromatography in pentane:ethyl acetate (9:1). 9.88 g 9*H*-fluorene-9-ethyl-methacrylate (35.5 mmol, 74.6% yield, 94.9% purity) were obtained as a light yellow oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.88-7.86 (*m*, 2H, 2x *CH*_{arom.}), 7.61-7.59 (*m*, 2H, 2x *CH*_{arom.}), 7.40-7.30 (*m*, 4H, 4x *CH*_{arom.}), 5.74 (*m*, 1H, =*CHH*_{trans}), 5.52 (*m*, 1H, =*CHH*_{cis}), 4.13 (*t*, 1H, -*CH*-CH₂-), 3.93 (*t*, 2H, -CH₂-O-), 2.42 (*q*, 2H, -CH₂-CH-), 1.71 (*s*, 3H, -CH₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 166.3 (-COO-), 146.1 (*C*_{arom.}), 140.4 (*C*_{arom.}), 135.5 (-C=CH₂), 127.1 (*C*_{arom.}), 127.0 (*C*_{arom.}), 125.5 (-C=CH₂), 124.4 (*C*_{arom.}), 120.0 (*C*_{arom.}), 61.5 (-CH₂-O-), 44.1 (-CH-CH₂-), 30.5 (-CH-CH₂-), 17.7 (-CH₃)

R_f (DCM): 0.88, (Pentane:EtOAc 8:1): 0.78

MS (ESI⁺): 279.1381, calculated: 279.1380 (C₁₉H₁₈O₂ + H⁺)

Mp.: -48 °C

1.7.5 Synthesis of *o*-biphenyloxyethyl methacrylate (MA-oPP)

2-(*o*-Biphenyl)oxyethanol (10.04 g, 46.9 mmol) was dried in a flask before dissolving it in 80 mL dry dichloromethane. Triethylamine (6.8 mL, 49.6 mmol) was slowly added to the solution at 0 °C. After dropwise addition of methacryloyl chloride (4.7 mL, 49.6 mmol), the reaction was stirred under argon atmosphere for 16 h. After warming up to room temperature, the crude product was extracted with 100 mL dichloromethane. The organic phases were washed twice with brine before drying over magnesium sulfate and purification via column chromatography with pentane:EtOAc (8:1). After solvent removal, 7.77 g *o*-Biphenyloxyethyl methacrylate (31.4 mmol, 67.0% yield, 98.2% purity) was obtained as a colorless oil.

¹H-NMR (300 MHz, DMSO-*d*₆): δ(ppm) = 7.52-7.49 (*m*, 2H, 2x *CH*_{arom.}), 7.39-7.29 (*m*, 5H, 5x *CH*_{arom.}), 7.16-7.13 (*m*, 1H, 1x *CH*_{arom.}), 7.08-7.02 (*m*, 1H, 1x *CH*_{arom.}), 6.01 (*m*, 1H, =*CHH*_{trans}), 5.69 (*m*, 1H, =*CHH*_{cis}), 4.37 (*t*, 2H, -CH₂-O-*C*_{arom.}), 4.26 (*t*, 2H, -CH₂-O-CO), 1.87 (*s*, 3H, -CH₃)

¹³C-NMR (75 MHz, DMSO-*d*₆): δ(ppm) = 166.3 (-COO-), 154.9 (*C*_{arom.}), 137.9 (*C*_{arom.}), 135.7 (-C=CH₂), 130.5 (*C*_{arom.}), 129.9 (*C*_{arom.}), 129.1 (*C*_{arom.}), 128.8 (*C*_{arom.}), 127.8 (*C*_{arom.}), 126.7 (*C*_{arom.}), 125.9 (-C=CH₂), 121.3 (*C*_{arom.}), 113.0 (*C*_{arom.}), 66.0 (-CH₂-O-*C*_{arom.}), 62.8 (-CH₂-O-CO), 17.8 (-CH₃)

R_f (DCM): 0.83, (Pentane:EtOAc 8:1): 0.68

MS (ESI⁺): 283.1330, calculated: 283.1329 (C₁₈H₁₈O₃ + H⁺)

Mp.: -47 °C

1.8 Syntheses of polymethacrylates

1.8.1 Photochemical radical polymerization

The monomers were fully dried and degassed prior to the polymerization. The samples were mixed with 0.5 wt.% of an initiator system containing 50 wt.% camphor quinone and 50 wt.% ethyl-4-dimethyl-aminobenzoate. As crosslinking agent 1.0 wt.% ethylene glycol dimethacrylate were added. The solution was mixed and filtered using a 0.5 μm PTFE syringe filter before transferring it to a polymerization mold made of two PET films (DUPONT TEIJIN FILMS) and medical grade silicone spacers (REIFF). The mold was degassed and heated to 50 °C (respective 100 °C for the MA-Cz monomer) before starting the 16 h lasting photochemical polymerization using an LED array ($\lambda_{\text{max}} = 465 \text{ nm}$, 100 W).

1.8.2 Post-treatment of the samples

Following the polymerization, the polymethacrylate samples were soaked in isopropanol/acetonitrile at 35 °C for 3 days whilst changing the solvent daily and analyzing it via HPLC chromatography. The drying of the polymer samples was performed at 85 °C in an air circulated furnace for 6 days. The polymers were analyzed by IR spectroscopy to ensure complete removal of low molecular weight side products.

1.9. Analytics over all syntheses stages

Starting with the five HRI groups all components included in the syntheses routes were fully characterized with respect to their optical and physicothermal properties. The chemical syntheses first converts the HRI units to their respective methacrylate and siloxane precursors. Using 2-bromoethanol respectively 2-chloroethanol and an appropriate base, five methacrylate precursors with ethanol spacers were prepared. The synthesis procedure is shown in Chapter 1.6, Supporting Information, in detail for every aromatic unit. The siloxane precursors were also prepared using suitable bases and allyl bromide to form five HRI-allyl derivatives (Supporting Information, Chapter 1.3). Following this preparation, the monomers of the siloxane and methacrylate type were synthesized. In case of the methacrylates, a reaction with methacryloyl chloride in presence of triethylamine as auxiliary base lead to the desired monomers in good yields (Supporting Information, Chapter 1.7). Using the KARSTEDT'S catalyst, we were able to convert the allyl precursors to the respective siloxane monomers by reaction with dimethoxy(methyl)silane (Supporting Information, Chapter 1.4). The catalyst tends to induce the terminal hydrosilylation selectively⁹, leading to high amounts of the desired *anti*-MARKOWNIKOW product in our case. An overview of the obtained purities and yields for the different precursors and monomers based on methacrylate and siloxane is given in Table 1.

Table 1. Overview of the obtained yields **Y** and purities **P** in each reaction step to the monomers.

	Siloxane synthesis (SX)				Methacrylate synthesis (MA)			
	Precursor		Monomer		Precursor		Monomer	
HRI unit	Y / %	P / %	Y / %	P / %	Y / %	P / %	Y / %	P / %
DPA	84.0	99.3	35.1	98.0	42.6	97.1	62.3	95.0
Cz	77.0	99.9	51.5	99.5	10.8	97.5	50.2	99.9
DPM	95.1	98.0	43.0	98.5	42.0	99.0	72.7	94.6
FI	94.1	96.7	57.0	97.5	21.7	98.1	74.6	94.9
oPP	99.0	99.1	28.9	99.5	78.0	99.0	67.0	98.2

After preparation of the monomers, the corresponding polymers were synthesized via two individual routes. The siloxanes were polymerized via polycondensation (for detail see Supporting Information, Chapter 1.5.1) and the methacrylate derivatives via free radical polymerization. This reaction was initiated using a two-component photo starter system (see Supporting Information, Chapter 1.8.1). After polymerization, the obtained polymers were characterized extensively.

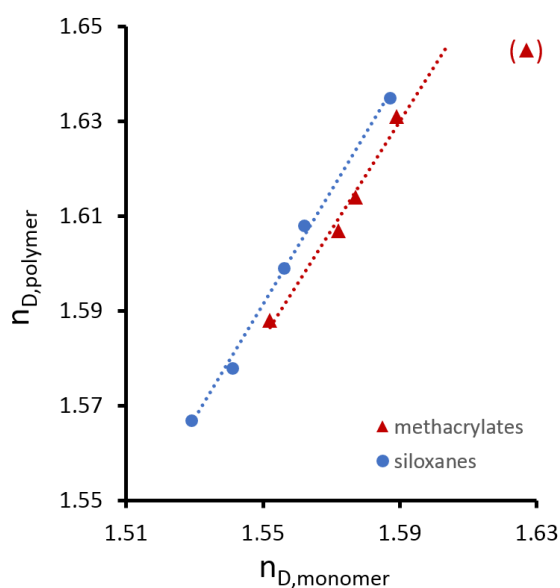


Figure 1. Comparison between measured refractive indices of all polymers and monomers synthesized.

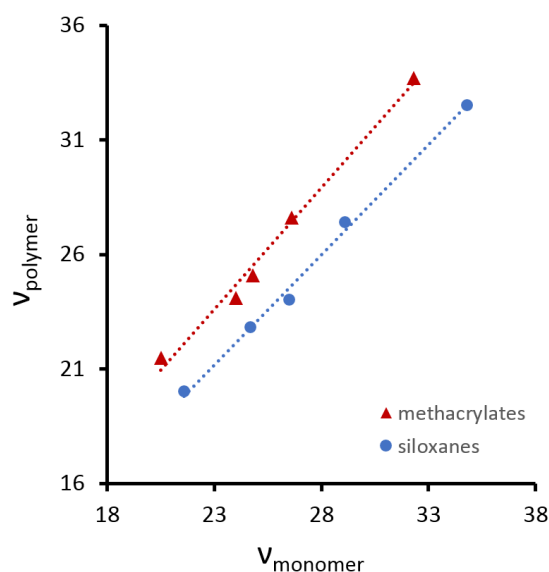


Figure 2. Comparison between measured Abbe numbers of all polymers and monomers prepared.

The polysiloxanes show a higher rise of the refractive index n_D than the methacrylates compared to their monomeric forms (Figure 1). The loss of the low refractive methoxy groups during polymerization results in an increasing HRI group mol.wt.% during polycondensation and higher refractive index changes than expected from sole chain packing. Inspite the HRI structures used in both polymer systems are identical,

the dependencies between both polymer types significantly differ. MA-Cz was excluded from fitting in the Figure 1, symbolized by brackets, because it is not in the glassy state at room temperature.

The ABBE number depends primarily on the structural elements and for this reason the dependencies are parallel over all samples studied (Figure 2). The siloxane monomers show better ABBE numbers than their corresponding methacrylate derivatives.

The thermal properties of the monomers and polymers of both species reveal clear dependencies. Whilst the siloxanes show the lowest melting temperatures, only slightly increasing over the whole index range, the acrylate monomers show a significantly stronger dependence on the characteristics of the HRI group. We measured the highest melting point of $T_m = 80\text{ }^{\circ}\text{C}$ for MA-Cz, compared to a literature value of $T_{m,\text{lit}} = 76 - 83\text{ }^{\circ}\text{C}$.^{10,11} A distinct difference between the melting temperature of MA-FI and MA-Cz is observed ($\Delta T_m = 113\text{ }^{\circ}\text{C}$). The temperature gap is noticeably less distinct in case of MA-DPA ($T_m = -60\text{ }^{\circ}\text{C}$) and MA-DPM ($T_m = -56\text{ }^{\circ}\text{C}$). The effect is dominated by the aromatic stacking of the stiff HRI group in combination with a higher polarity.

After polymerization, the free volume in the materials is minimized and the energetic interactions are mainly dominated by the applied HRI groups. The difference between the glass transition temperatures of pSX and pMA containing the same HRI-unit is about $\Delta T_g = 72\text{ }^{\circ}\text{C}$ in average in the final polymers.

A good accordance of our measurements for pSX-Cz to those available in literature is observed. The glass transition temperature was determined to be $T_{g,\text{exp.}} = 49\text{ }^{\circ}\text{C}$, whilst a value of $T_{g,\text{lit.}} = 51\text{ }^{\circ}\text{C}$ was presented by other groups.^{12,13} The measured refractive index of pSX-Cz, $n_{D,\text{exp.}} = 1.630$ is equal to data taken from literature ($n_{D,\text{lit.}} = 1.63$).¹⁴ The condensation rate of all polymers was very promising, showing a value of $c > 99\%$, except pSX-Cz ($c = 98\%$), determined via IR measurements of the $-\text{O}-\text{CH}_3$ -stretching vibration band at 2820 cm^{-1} . The surprisingly good result of the lightfastness test for pSX-Cz can be ascribed to its already present staining prior to the test which did not change much in the process. We also did lightfastness tests starting with a colorless polymer. A lightfastness of blue wool scale 2 was found. Further we observed that the amine species pSX-DPA was colorless in monomeric form, but turned blue shortly after the polymerization was accomplished. This leads to the conclusion that side products with extended aromatic system were formed, causing a bathochromic shift in the visible wavelength range.

The methacrylates were also determined to be highly polymerized. Nevertheless, the glass transition temperature of pMA-Cz ($T_g = 110\text{ }^{\circ}\text{C}$) is a bit lower than expected from literature ($T_{g,\text{lit.1}} = 131\text{ }^{\circ}\text{C}$ ¹⁵, $T_{g,\text{lit.2}} = 118\text{ }^{\circ}\text{C}$ ¹⁶). This is very likely referred to the usage of cross linker, preventing the large aromatic units to align freely and form dense π -stacking areas. A refractive index at $20\text{ }^{\circ}\text{C}$ is hardly described in literature due to the brittleness of the material, but experiments with thin films exceeded $n_D = 1.625$ ¹⁷, which we can fully support ($n_D = 1.645$). The measured glass transition temperature of the polymer pMA-DPA ($T_g = 69\text{ }^{\circ}\text{C}$), showing a higher structural flexibility, corresponds with the temperature available in literature very well ($T_{g,\text{lit.}} = 65\text{ }^{\circ}\text{C}$ ¹⁸).

2. Calculation of monomer refractive indices

The refractive indices of all siloxane and methacrylate monomers were calculated theoretically using *ACD/Labs*.¹⁹ Starting from tabulated additive atomic increments for the molar volume V_m and molar refraction R the refractive indices were obtained using the LORENTZ-LORENZ equation.^{20,21} The calculated values predicted by our WT%-model and the experimental data are compared in Table 2 and 3.

Table 2. Physical properties of the siloxane monomers synthesized.

Monomer		SX-DPA	SX-Cz	SX-DPM	SX-FI	SX-oPP
calc. refr. index ($n_{D,calc}$)	-	1.540	1.539	1.514	1.537	1.511
calc. refr. index ($n_{D,WT\%}$)	-	1.562	1.599	1.531	1.563	1.548
refract. index ($n_{D,exp.}$)	-	1.556	1.587	1.529	1.562	1.541
ABBE number (v)	-	24.7	21.6	34.8	26.5	29.1
melting point (T_m)	°C	-65	-53	-72	-63	-64
color	-	clear	clear	clear	clear	clear

Values given in grey shaded rows were calculated using *ACD/Labs*.

Table 3. Physical properties of the methacrylate monomers synthesized.

Monomer		MA-DPA	MA-Cz	MA-DPM	MA-FI	MA-oPP
calc. refr. index ($n_{D,calc}$)	-	1.580	1.585	1.547	1.577	1.545
calc. refr. index ($n_{D,WT\%}$)	-	1.586	1.629	1.551	1.588	1.570
refractive index ($n_{D,exp.}$)	-	1.577	1.627 ^a	1.552	1.589	1.572
ABBE number (v)	-	24.0	20.5 ^a	32.3	25.0	26.6
melting point (T_m)	°C	-60	80	-56	-33	-47
color	-	light brown	clear	clear	light yellow	clear

^a Determined via extrapolation of measured values taken around melting temperature.

Values given in grey shaded rows were calculated using *ACD/Labs*.

It could be determined that the refractive indices of both models show similar deviations in case of the methacrylate monomers. Since MA-Cz is the only monomer which appears in a different transition state by having a very high melting temperature of $T_m = 80$ °C, it shows the largest discrepancy to the theoretical values. In case of the siloxane monomers, our first calculation provides overall low values, whilst a very good accordance can be determined for the values based on the WT%-model.

3. Deduction of the correction term $n_{R'-C}$

All monomers were calculated starting with their respective HRI-unit and SPG via WT%-method with an n_{R-C} correction term for the formation of an $R'-C$ bond. Independently from the HRI-group, a formal unit H_2 is released every time during the molecule coupling. The term was determined by observing the behavior of the refractive index of pure alkanes C_nH_{2n+2} ($n > 5$) at 20 °C starting from literature data (Table 4).^{22,23}

Table 4. Refractive indices of several alkanes and cycloalkanes, values obtained from literature.^{22,23}

Chain length n		5	6	7	8	9
refractive index ($n_{D,20}$)	linear	1.3575	1.3727	1.3878	1.3980	1.4050
refractive index ($n_{D,20}$)	cyclic	1.4064	1.4262	1.4436	1.4586	---

These values were compared with the respective values for cyclic alkanes of the same chain length n . Both tangential functions were derived and the difference at a chain length of $n = 0$ was determined (Fig. 3). This should correspond to the formation of an $R'-C$ -bond, respective the refractive index increase during the mentioned formal loss of one unit H_2 . The value for this term is $n_{R'-C} = f(n=0) - g(n=0) = 0.039$.

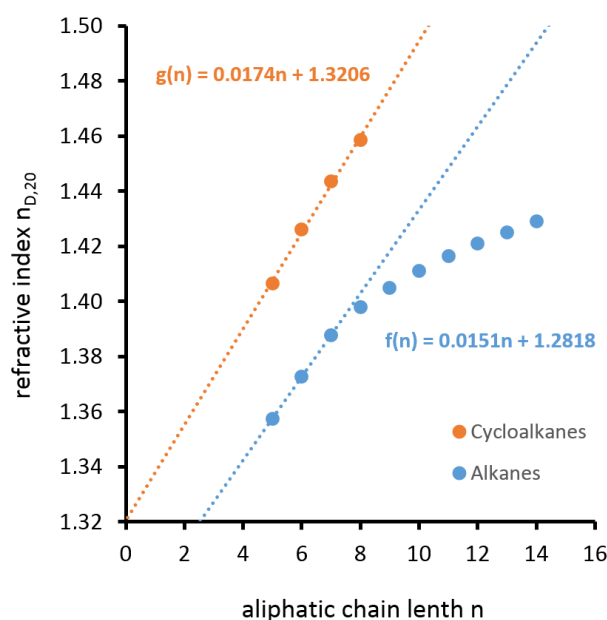


Figure 3. Comparison of the refractive indices of linear (f) and cyclic (g) alkanes.

4. Refraction change during polymerization

The prepared siloxane and methacrylate monomers were polymerized via a sulfuric acid promoted polycondensation (Supporting Information, Chapter 1.5.1) or photochemical radicalic polymerization (Supporting Information, Chapter 1.8.1), respectively. In order to calculate the optical properties prior to the synthesis, the changes in refractivity during the polymerization process have to be considered. The alterations in molar refraction per repetitive unit R/n can be derived theoretically from the tabulated values for each functional group (Table 5).

Table 5. Atomic mol. refraction R_D of selected functional organic groups.^{24–26}

Substituent	$R_D / (\text{cm}^3/\text{mol}^{-1})$	Substituent	$R_D / (\text{cm}^3/\text{mol}^{-1})$
–H	1.100	N (sec-aliph.)	2.499
O (–O–H)	1.525	N (tert-aliph.)	2.840
O (–C–O–)	1.643	N (sec-arom.)	3.590
C=C	1.733	N (tert-arom.)	4.360
C=O	2.211	–Si–	9.000
C≡C	2.336	phenyl	25.46
>C<	2.418	naphthyl	43.00

For the acrylate polymerization the structural loss of a double bond during sp^2 to sp^3 conversion at the terminal C-atoms has to be considered (eq. 1).

$$R_{pMA} = -1.733 \quad (1)$$

The polymerization of the siloxanes proceeds in presence of H_2O and H^+ . This polycondensation generates one unit of Me-O-Me per repetitive unit, which needs to be subtracted from the molar refraction, leading to the following correction term (eq. 2).

$$R_{pSX} = -(2 \cdot (3 \cdot 1.100 + 2.418) + 1.643) = -13.079 \quad (2)$$

5. Correction terms for HRI group attachment

For the theoretical treatment of the HRI group attachment to the pSPG unit, different correction terms were derived for the molar refraction and molar dispersion for the different units. This model can be applied to the pSX as well as the pMA groups, since these molecules all have a loss of one C-H bond during coupling. For the HRI units different groups at the coupling site need to be considered, i.e. different R'-H bonds (R' = N, C, O) lead to different correction terms for the molar refraction ($R_{R'-C}$) and the molar dispersion ($\Delta R_{R'-C}$).

Table 6. Correction terms for molar refraction $R_{R'-C}$ and molar dispersion $\Delta R_{R'-C}$ of five HRI units.

HRI unit	R'	pSPG	$R_{R'-C}$	$\Delta R_{R'-C}$
DPA	N	pSX / pMA	-1.430	+0.052
Cz	N	pSX / pMA	-1.430	+0.052
DPM	C	pSX / pMA	-2.200	-0.046
FI	C	pSX / pMA	-2.200	-0.046
oPP	O	pSX / pMA	-2.082	-0.040

For example, the substitution of oPP leads to the formal loss of two hydrogens and the conversion of a phenolic oxygen to an ether group (eq. 3). The respective tabulated values are shown in Table 5.

$$R_{O-C} = -(2 \cdot 1.100) + (1.643 - 1.525) = -2.082 \quad (3)$$

Not only is the refraction changed during this substitution, but also the dispersion. Therefore the same calculation was performed again, using ΔR values instead of R for each group (eq. 4).

$$\Delta R_{O-C} = -(2 \cdot 0.023) + (0.012 - 0.006) = -0.040 \quad (4)$$

The values of molar dispersion ΔR are tabulated for many functional groups.^{26,27} The calculated correction terms shown in Table 6 were applied individually in the prediction of the ABE numbers using eq. 5.

$$v_{polymer} = \frac{6 \cdot n_{D,calc} \cdot (R_{HRI} + R_{pSPG} + R_{R'-C})}{(n_{D,calc}^2 + 2) \cdot (n_{D,calc} + 1) \cdot (\Delta R_{HRI} + \Delta R_{pSPG} + \Delta R_{R'-C})} \quad (5)$$

6. Thermal properties of the HRI polymers

The glass transition temperatures of all polymer samples were measured via differential scanning calorimetry (DSC). The samples went through two heating and cooling cycles with a heating and cooling rate of ± 10 °C/min. The measured thermograms for the prepared polysiloxane and polymethacrylate samples are displayed in Figure 4 and 5.

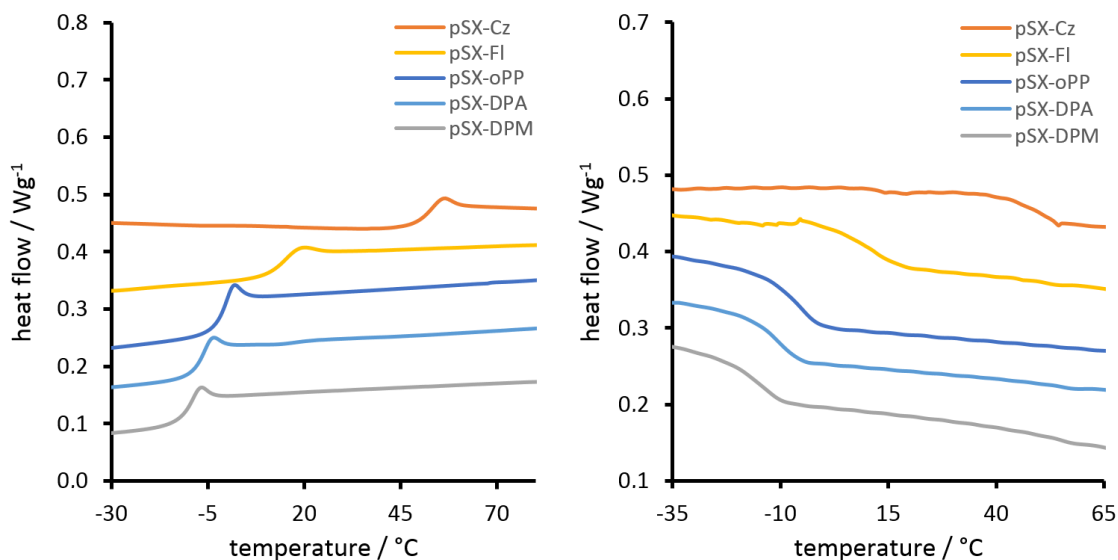


Figure 4. DSC curves of the HRI polysiloxanes, second heating run (left) and second cooling run (right).

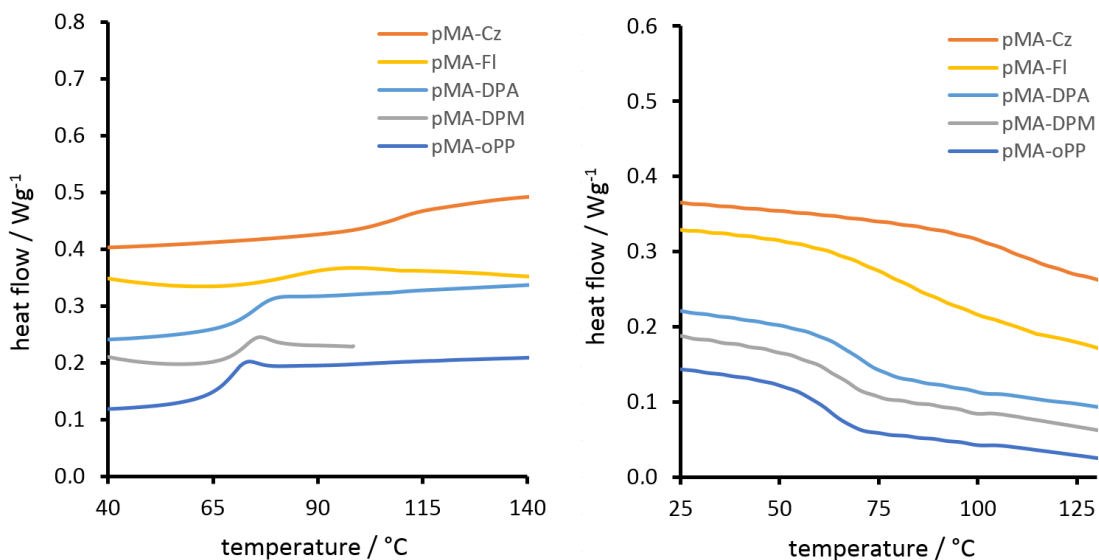


Figure 5. DSC curves of the HRI polymethacrylates, second heating run (left) and second cooling run (right).

7. Optical properties and SELLMIEER function

Because of all IOLs containing a UV absorber, the effective absorption spectrum of the polymers ready for application is dominated by this absorber in the end. We prepared our homopolymers without an absorber to determine the pure influence of the HRI group on the optical properties. The UV-vis spectra of the sole HRI groups were measured in acetonitrile to determine the starting conditions in respect to the material absorption (Figure 6).

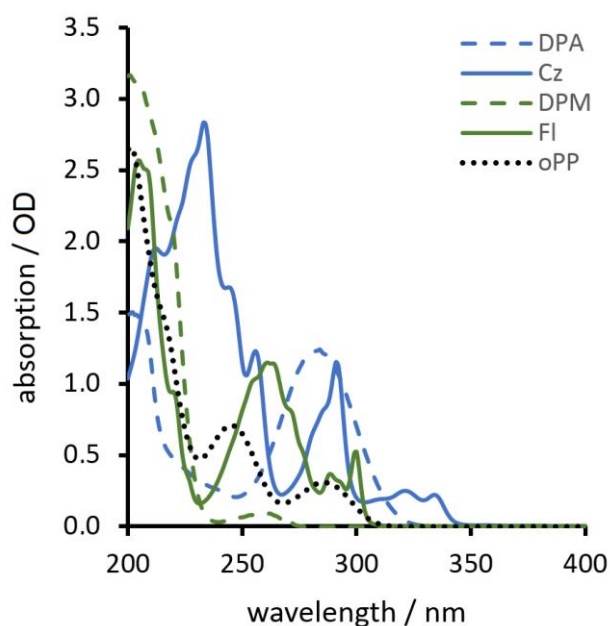


Figure 6. UV/VIS absorption curves of the HRI-educts, measured in acetonitrile at a concentration of 0.055 mmol/L each at 20 °C.

Whilst the spacer and the polymerizable group do not show any absorption in the visible range, the absorption spectrum remains nearly unchanged for aliphatic spacers. Only both amine structures pSX-DPA and pSX-Cz show a slight bathochromic shift during process. This in turn has an impact on the refractive index of the final polymer and its dispersion, defined by the ABBE number. All corresponding UV/vis spectra of the prepared polysiloxanes and polymethacrylates are displayed in Figure 7a and 7b.

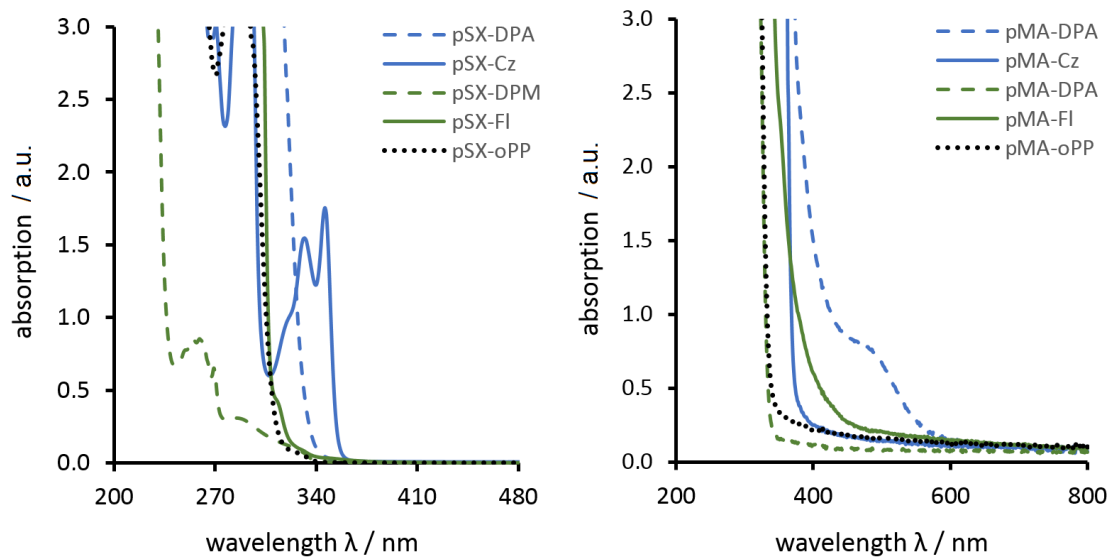


Figure 7. UV/vis spectra of (a, left) polysiloxane thin films (about 100 μm) and (b, right) polymethacrylates (1 mm slabs), each with no UV absorber added.

The measured refractive indices of all polymers in dependence on the wavelength were measured using a digital refractometer. The received indices were fitted with the respective SELLMEIER plot and represented in Figure 8a for the polysiloxanes and in Figure 8b for the polymethacrylates.

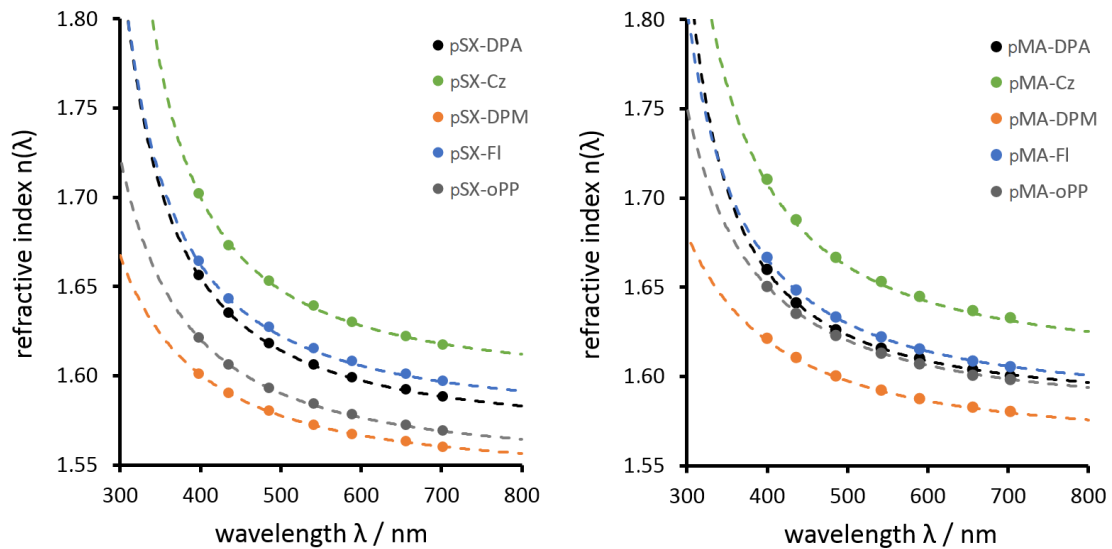


Figure 8. Wavelength-dependent refractive indices of the synthesized (a, left) polysiloxanes and (b, right) polymethacrylates.

It was observed that all refractive indices proceed most widely parallel, except for pMA-DPA in the range of $\lambda < 500$ nm. Since this polymer shows the largest absorption in the visible area by far (Figure 7b), at this point also the biggest deviation can be measured, reaching known limitations for the SELLMEIER transparent function.

8. Alternative pathway for pSX derivatives

The preparation of the polysiloxanes was performed over two parallel routes to determine the influence of the synthesis on the material properties. The first route was completed with a polycondensation of the prepared siloxane precursor, whilst the alternative pathway proceeded with a hydrosilylation or grafting process of a polysiloxane pre-polymer (Figure 9). This method was also performed starting from diphenylamine (R_1), carbazole (R_2), diphenylmethane (R_3), fluorene (R_4) and o-phenylphenol (R_5).

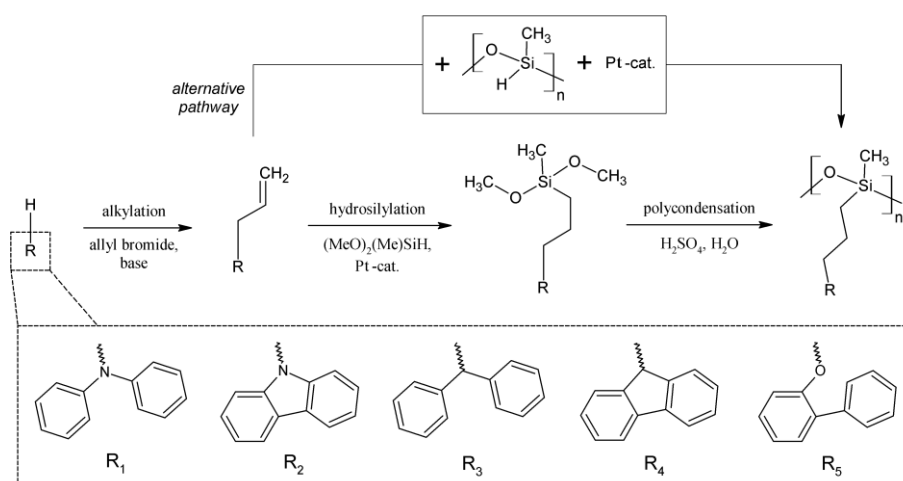


Figure 9. Reaction overview for the alternative synthesis route of the five HRI polysiloxane derivatives.

The second route started from the synthesized allyl derivatives of the five HRI units. Using a platinum-catalyst, the hydrosilylation with polymethylhydrosiloxane (pMHS, average $M_w = 1900$ g/mol) was performed in solution at 60 °C. The conversion rate of each reaction was monitored via IR spectroscopy of the characteristic vibration band for Si-H (2158 cm^{-1}) in relation to the Si-O-Si band (1082 cm^{-1}). The reaction was performed until maximal conversion and described in detail in Chapter 1.5.2.

Table 7. Physical properties of the hydrosilylated polysiloxanes synthesized.

Polymer		pSX-DPA	pSX-Cz	pSX-DPM	pSX-FI	pSX-oPP
degr. of conversion (IR)	%	91	86	95	>99	>99
degr. of conversion (NMR)	%	85	83	85	92	95
glass trans. (T_g) / °C	°C	-7	53	-13	24	-6
refract. index ($n_{D,20}$)		1.598	1.635	1.562	1.608	1.578
ABBE number (v)		23.2	20.4	32.8	23.8	27.5
UV vis spectra (color)		clear	light brown	clear	clear	clear
wt.% HRI group (p)	%	62	62	62	62	63
lightfastness (blue wool scale, 353 h)		2	2	5	5	5

Every conversion degree was also determined via ^1H -NMR spectroscopy. We monitored the signal of Si-*H* at $\delta = 4.72$ ppm and calculated the ratio between the unsubstituted $\text{CH}_3\text{-Si-H}$ signal ($\delta = 0.21$ ppm) and the converted $\text{CH}_3\text{-Si-R}$ signal. All physical parameters of the polymers obtained via the second route are summarized in Table 7.

A good accordance is found to the properties for pSX-Cz available in literature ($T_g = 51$ °C¹², $n_D = 1.63$ ¹⁴). Furthermore, the properties of the polysiloxanes prepared via hydrosilylation show very small deviations only from those obtained via polycondensation. The determined refractive indices and ABBE numbers are almost identical, despite having slightly less absorption in the visible range. The differences of the glass transition temperatures are also only marginal and within the uncertainties of the measurements, showing a minor difference in case of pSX-Fl.

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