6 Zusammenfassung

Die Sonogashira-Polykondensation kann, ausgehend von chiralen AB'-Monomeren zum Aufbau unterschiedlich substituierter, chiraler, defektfreier *Poly*(*meta*-phenylenethinylen)e verwendet werden. Die optischen Eigenschaften der Polymere wurden unter Verwendung der Absorptions-, Fluoreszenz-, sowie CD-Spektroskopie untersucht. Charakteristisch für die synthetisierten P*m*PE`s ist der Helix-Knäuel-Übergang, von einer helikalen geordneten, zu einer ausgedehnten, zufälligen Konformation, der sich auf solvophobe Wechselwirkungen mit dem Lösungsmittel gründet. Dabei zeigt sich ein unterschiedliches Verhalten zwischen Ester- und Amidpolymeren. Während Erstere in weniger polaren Lösungsmitteln, wie Chloroform, in einer nicht gefalteten Konformation vorliegen, bleibt die helikale Konformation der Amidpolymere stabil und kann auch durch erhöhte Temperaturen nicht denaturiert werden. Die hohe Stabilität resultiert aus der Ausbildung intramolekularer Wasserstoffbrückenbindungen zwischen einander überlagernden Amideinheiten. Die Amidpolymere liegen in den meisten Lösungsmitteln in einer helikalen Konformation vor, Trifluorethanol in Chloroform wirkt dagegen denaturierend, da sich intermolekulare Wasserstoffbrücken ausbilden können. Der Einfluss der Wasserstoffbrücken kann, durch Methylsubstitution am Stickstoffatom, irreversibel ausgeschaltet werden. Das entsprechende Methylamid-Polymer kann in keinem untersuchten polaren Lösungsmittel eine helikale Konformation einnehmen.

Der stabilisierende Einfluss intramolekularen Wasserstoffbrückenbindungen ist im Amidpolymer mit sterisch anspruchsvoller Seitenkette deutlich vermindert. Das Polymer liegt in Chloroform nicht in helikaler-, sondern in entfalteter Konformation vor, faltet sich jedoch in polaren Lösungsmitteln und ähnelt daher, seinen Eigenschaften nach, eher den Esterpolymeren. In statistischen Amid/Ester-Copolymeren wurde, statistisch gesehen, jede sechste Amid- durch Esterseitenketten ersetzt. Für dieses Polymer konnte eine erhebliche Destabilisierung der helikalen Konformation in Chloroform beobachtet werden.

Für das Amidpolymer mit unpolarer Seitenkette konnte eine sehr stabile helikale Konformation beobachtet werden, die durch Zugabe von Trifluorethanol denaturiert. Interessanterweise zeigt das analoge Esterpolymer, in Cyclohexan, einen inversen Signalverlauf im CD-Spektrum. Die Beobachtung konnte auch für die Esterpolymere mit variabler polarer Seitenkette gemacht werden. Die Umkehr des Helix-Drehsinns durch geringfügige Veränderungen der Seitenkettenarchitektur, ohne Verschiebung des chiralen Zentrums, stellt ein neues, bisher unbekanntes Phänomen dar.

6.1 Summary

The Sonogashira-Polycondensation, based on chiral AB'-monomers, can be used to construct different substituted and chiral, defect-free structures of P*m*PE`s. The optical properties of the polymers can be investigated by the methods of absorption-, fluorescence- or CD-spectroscopy. For synthesized P*m*PE`s the helix-coil-transition from a helical ordered state to an extended random conformation is characteristic, originating from solvophobic interactions with the solvent. Thereby, a different behavior of ester- and amid polymers can be observed. Since the ester substituted P*m*PE`s are in a unfolded conformation in poore solvents like chloroform, the helical conformation of amid polymers stays stable an can not be denatured by higher temperatures. The hight stability results from the formation of intramolecular hydrogen bonds between stacking amid units. The amid polymers are found in an helical conformation within most of the solvents, whereas trifluorethanol in chloroform acts denaturing, since intermolecular hydrogen bonds can be formed. The influence of hydrogen bonds can be turned off in an irreversible way by substitution of a methyl group at nitrogen atoms. The methyl amid polymer is not able to excist in a helical conformation in non of the polar solvents under investigation. The stabilizing influence of intramolecular hydrogen bonds is clearly reduced in amid polymers with steric demanding side chains. The polymer in chloroform appears not in an helical but in an unfolded conformation but is folding in polar solvents and shows therefore similar properties as ester polymers. In a statistic amid/ester-copolymer, every sixth unity of amid was replaced by an ester unity from a statistical point of view. For those polymers a clear destabilization of the helical conformation in chloroform could be observed. For the amid polymer with an unpolar side chain, a very stable helical conformation could be observed which denatured under addition of trifluorethanol in chloroform. It is remarkable, that the analog ester polymer shows an inverse shape of the signal within the CD-spectra. This observation could also be done for ester polymers with the different polar side chains. The reversal of the helical screw sense by a small change in the architecture of the side chains, maintaining des position of the chiral center, is a new, up to now unknown phenomena.

6.2 Ausblick

Kovalente Stabilisierung der helikalen Konformation

Zum Aufbau von „nanotubes“ konnte die tubulare sekundäre Struktur in einem gefalteten, helikalen P*m*PE-Derivat mit zimtsäureverknüpften Seitenketten durch eine topochemisch kontrollierte Photodimerisation intramolekular vernetzt werden.[1]

Die Bildung von Cyclobutanringen, als Folge der Vernetzung, führt jedoch zu einer leichten Verzerrung der helikalen Geometrie. Daher wurde nach alternativen Systemen gesucht, die sich ohne größeren Einfluss auf die Grundstruktur verlinken lassen. Die Verwendung von Acrylaten zum Aufbau radikalisch vernetzbarer P*m*PE`s, führte nicht zum Erfolg. Ausgehend von Acrylsäurechlorid konnte trotz instabiler Ausgangsverbindungen, in wenigen Syntheseschritten, zwar das A_2-Monomer **56** dargestellt werden (Abb.1), die Polykondensation von **56** mit TMS-Acetylen, unter Verwendung des A_2BB'-Protokolls, führte jedoch zu unlöslichem Produkt.

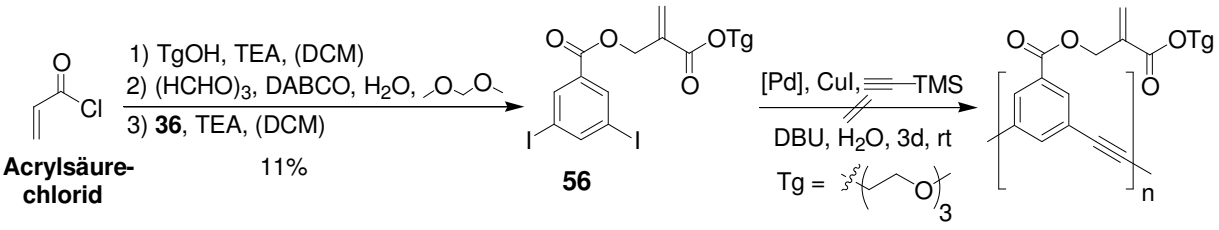


Abb. 1 Reaktionsschema zum Aufbau eines A_2-Monomers mit vernetzbarer Acrylat-Seitengruppe und versuchte Polykondensation.

Vermutlich vernetzen sich die sehr reaktiven Acrylate schon während der Reaktion. Eine alternative Strategie geht von der Vernetzung von Alkenen mittels RCM aus. Für die Synthese einer polaren Seitenkette mit Alkenylsubstituenten kann von D-Mannitol ausgegangen werden. In einer 7-stufigen Synthese erhält man den chiralen Alkohol **63** (Abb. 2).

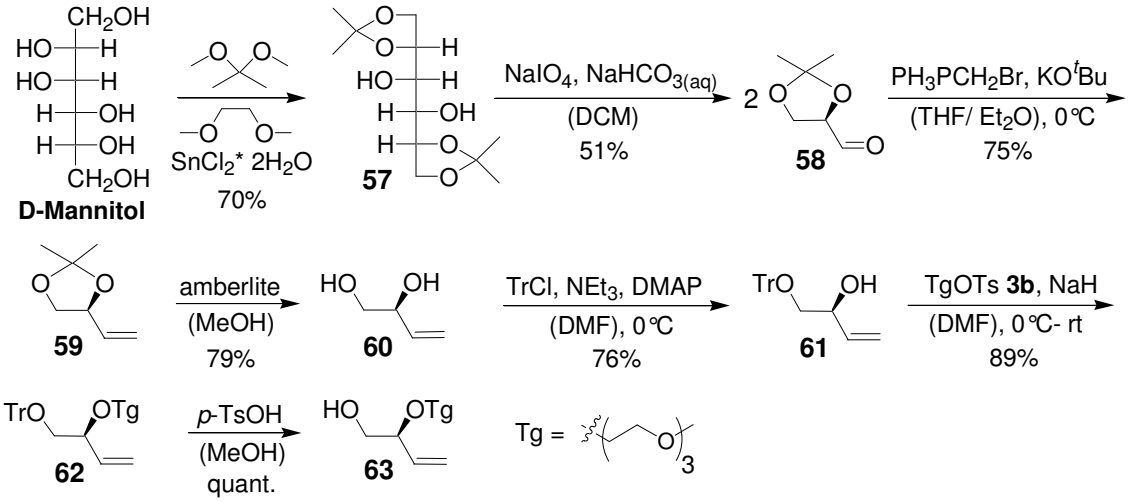


Abb. 2 Reaktionsschema zum Aufbau des chiralen Alkohols **63** mit Alkenylsubstituenten.

Die DCC-vermittelte Kupplung mit Benzoesäurederivat **16** führt zum AB'-Monomer **64** mit chiraler, polarer und vernetzbarer Seitenkette, das in einer Sonogashira-Polykondensation zu Polymer **P14** umgesetzt werden kann (Abb. 3).

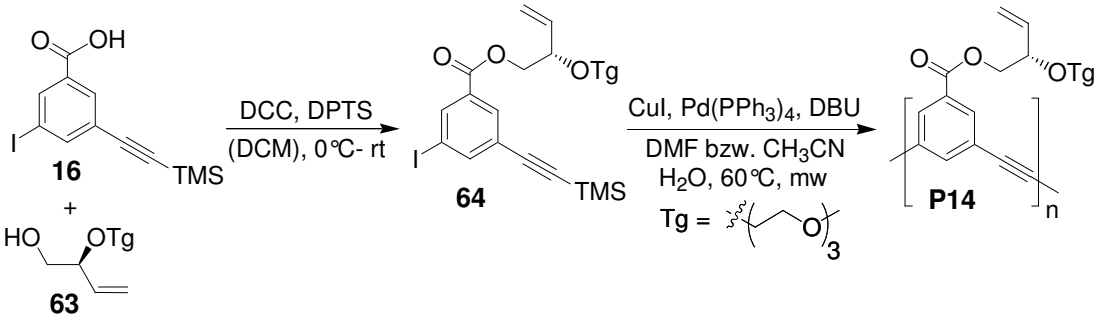


Abb. 3 Synthese des AB'-Monomers mit chiraler und vernetzbarer Seitengruppe und Sonogashira-Polykondensation.

Die Studien zur Seitengruppenvernetzung unter Verwendung von Grubbs-Katalysator sind noch nicht abgeschlossen und sollen fortgeführt werden (Abb. 4).

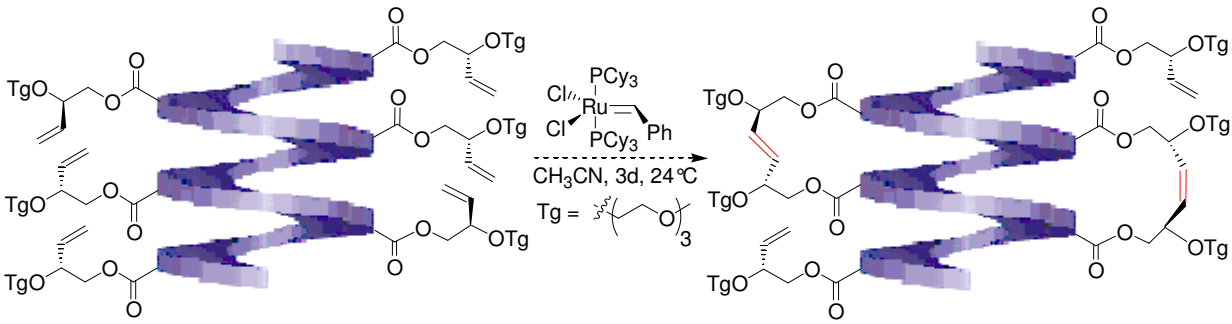


Abb. 4 Schematische Darstellung zur Seitenkettenvernetzung, unter Bildung von *cis*- bzw. *trans*-vernetzter Ringsystemen mit Grubbs[1st]-Katalysator.

Durch Komplexierung getriebene Faltung

Der Helix-Knäuel-Übergang kann nicht nur durch ungerichtete solvophobe Wechselwirkungen in O*m*PE`s induziert werden,[2] sondern auch gezielt, durch Komplexbildung mit Silberionen, eines mit Nitrilgruppen funktionalisierten aromatischen Grundgerüstes.[3] Jede zweite aromatische Einheit trägt dabei eine Nitrilgruppe, die in gefalteter Konformation in den helikalen Käfig weisen, daraus resultiert eine trigonal planare Anordnung innerhalb jeder Windung die eine Komplexbildung mit Silberionen ermöglicht. Diese spezielle Architektur diente als Vorbild für die Herstellung nitrilfunktionalisierter P*m*PE`s. Um Untersuchungen zum Helix-Knäuel-Übergang auch im CD-Spektrum verfolgen zu können, sollte unter Einsatz der A_2B_2' Polykondensation eine chirale Polymerarchitektur aufgebaut werden.

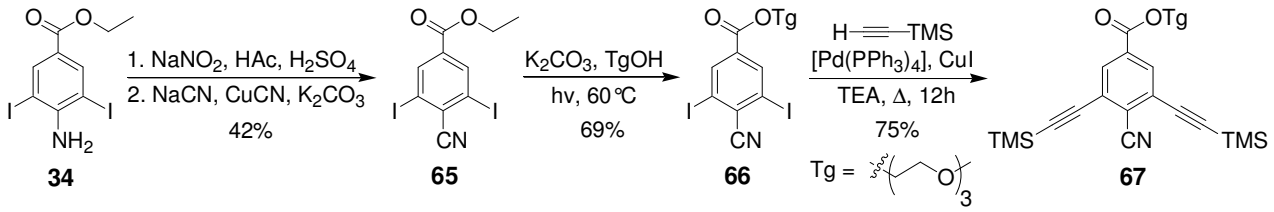


Abb. 5 Syntheseschema zum Aufbau des nitrilsubstituierten B_2'-Monomers **69**.

Als Ausgangsmaterial für die Synthese des B_2'-Monomers **67** konnte von Verbindung **34** ausgegangen werden (Abb.5). Durch eine Polykondensation von A_2-Monomer **39** mit **67** sollte ein chirales Polymer mit Nitrileinheiten zugänglich sein (Abb.6).

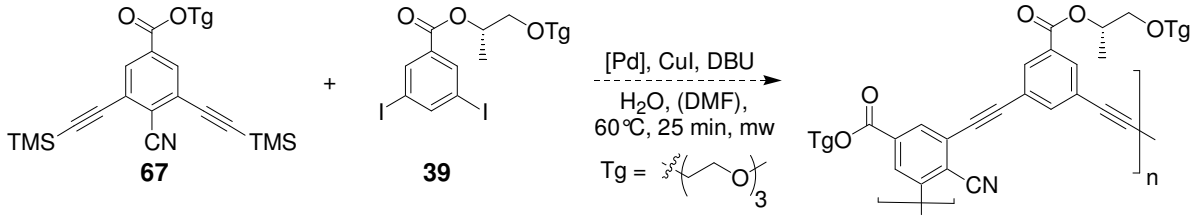


Abb. 6 A_2B_2'-Polykondensation zum Aufbau nitrilsubstituierter Polymere.

Erste Versuche zum Aufbau der gewünschten Polymerarchitektur verliefen nicht erfolgreich.

Untersuchungen zum Chiralitätstransfer

Chirale Seitenketten in O*m*PE`s können durch kooperative Wechselwirkungen Chiralität auf das achirale Polymerrückgrat übertragen. Es ist bekannt, dass bereits der Einbau einer kleinen Menge chiraler Seitenketten einen großen Einfluss auf das Gleichgewicht zwischen *M*- und *P*-helikaler Konformation hat, gemäß dem so genannten „Sergeant and Soldier"- Prinzip.[4]

Für Untersuchungen zum Chiralitätstransfer in P*m*PE`s wurden die chiralen und achiralen Amidmonomere **29** und **31** in unterschiedlichen Verhältnissen polykondensiert. Trotz zahlreicher Ansätze konnten nur zwei Polymere mit monomodaler, für spektroskopische Untersuchungen geeigneten, Molmassenverteilung erhalten werden, mit einen Chiralitätsanteil von ~17% in **P15** und ~ 8% im Fall von **P16** (Abb. 9).

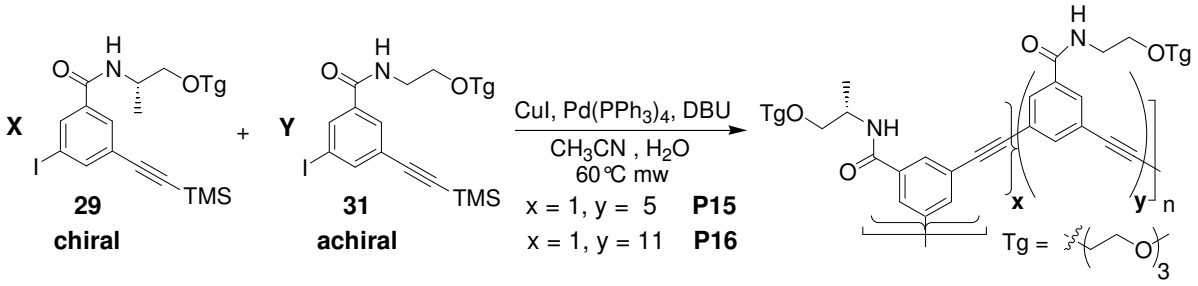


Abb. 9 Sonogashira-Polykondensation der polarer AB'-Monomere **29**, **31** unter Verwendung des „in situ" Aktivierungsprotokolls[5] und Mikrowelleneinstrahlung,[6] zum Aufbau statistischer Amidpolymere mit „verdünnter Chiralität".

Die Datenlage reicht daher nicht aus, um generelle Aussagen zum Chiralitätstransfer in den Amidpolymeren zu treffen. Für **P16** konnte jedoch, in Übereinstimmung mit dem „Sergeant and Soldier"- Prinzip[4] noch eine deutliche, temperaturstabile CD-Aktivität gemessen werden (Abb. 10). Die CD-Signale in Polymer **P15** zeigen darüber hinaus ein außergewöhnliches Temperaturverhalten. So kann in Chloroform/ Trifluorethanol, unter bestimmten Bedingungen, eine Helixinversion von *M*-helikal nach *P*-helikal, beobachtet werden (Abb. 10).

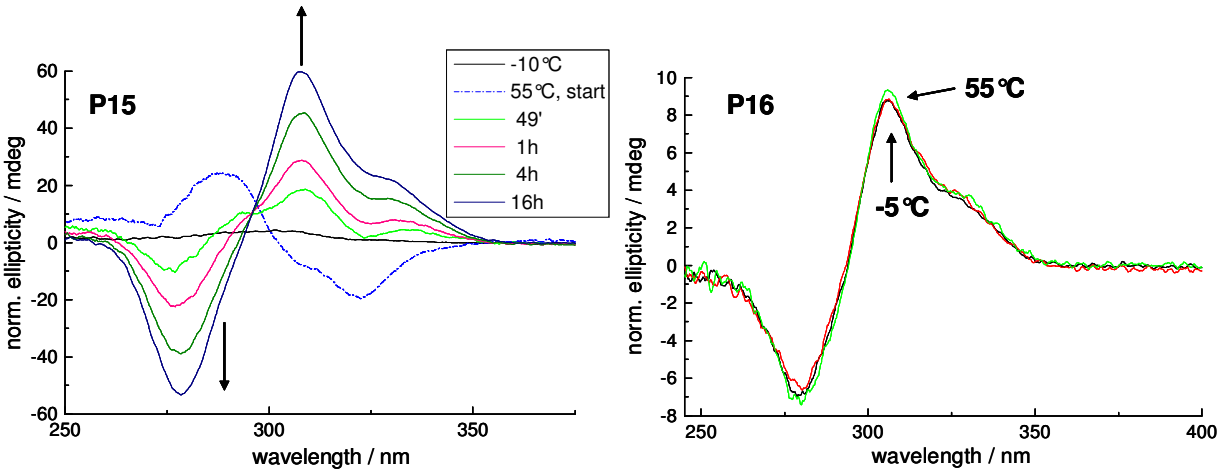


Abb. 10 links Temperaturexperiment mit Polymer **P15** in $CHCl_3$/1.5% TFE: zeitliche Entwicklung der CD-Intensität nach plötzlichem Erwärmen einer zuvor bei -10 °C gelagerten Probe auf 55 °C (Das Experiment wurde nur eine Stunde bei 55°C belassen, die weitere Signalintensivierung erfolgte bei Raumtemperatur); **rechts** temperaturstabile CD-Intensitäten von Polymer **P16** in Chloroform.

Die systematische Synthese weiterer chiralitätsverdünnter Amidpolymere und deren Charakterisierung könnte in Zukunft dazu beitragen, die kooperative Wechselwirkung der Amidseitenketten in P*m*PE`s besser verstehen zu lernen.

6.3 Experimentelle Daten

General methods

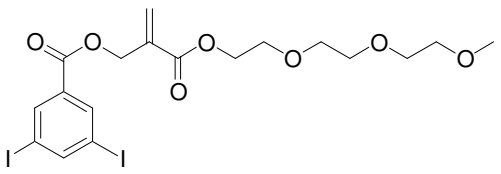
Diethylether and THF were refluxed with sodium and benzophenone under argon atmosphere. Toluene was refluxed with sodium and dichloromethan with calcium hydride under argon atmosphere and distilled. Triethlamin (TEA) was stored over NaOH pellets, acetonitrile over calcium hydride and both solvents were distilled prior to use under argon atmosphere. Column chromatography was carried out with silica gel 60 (0.04-0.063mm particle size), 230-400 mesh. ^{1}H NMR- and ^{13}C NMR-spectra were recorded on Bruker AC 250 (250.1 and 62.9 MHz for ^{1}H and ^{13}C, respectively) and AC 500 as well as Joel Eclipse 500 (500 and 126 MHz for ^{1}H and ^{13}C, respectively) spectrometers at 20 ± 5 ^{o}C using residual protonated solvent signal as internal standard (^{1}H: $\delta(CHCl_3)$ = 7.24 ppm, δ(DMSO) = 2.49, $\delta(CH_3CN)$ = 1.94 ppm and ^{13}C: $\delta(CHCl_3)$ = 77.0 ppm, δ(DMSO) = 39.7 ppm). ^{13}C NMR-spectra have been recorded with broadband ^{1}H-decoupling. Two dimensional correlation experiments that ^{1}H/^{1}H NMR-spectra (COSY) and ^{1}H/^{13}C NMR-spectra (HMBC, HMQC) have been made in order to determine exact structures. Mass-spectra (MS) were registered on *Perkin-Elmer Varian* Type: MAT 711 (EI, 80eV, 8kV) and CH5DF (FAB, 3kV). IR spectra were recorded as KBr pellets on Nicolet 5SXC FTIR-Interferometer equipped with DTGS-detector. Elemental analyses were performed on a C, H, N, S-Elementaranalysator Vario EL III. SEC measurements were performed on an Agilent 1100 series HPLC system equipped with three 300 x 8 mm SDV columns (1,000,000 Å, 100,000 Å, 1000 Å) and one 50 x 8 mm SDV column (100 Å) using both RI and UV (230 nm and 280 nm) detection. The measurements were performed in THF at 30 ^{o}C using a flow rate of 1 mL/min. The columns were calibrated with several narrow polydispersity polystyrene samples. Microwave-assisted polycondensations were performed in a multimode microwave reactor (typ: MTW-S) having a continuous microwave power delivery system from 0 to 800W. The reaction werde carried out in 10mL sealed glass vials, the temperature controlled by an extern IR sensor, that automatically adjust the microwave power to maintain the programmed temperature. All reaction were performed at 55°C-60°C (microwave power in a range of 0W - ~200W). UV/visible absorption spectra were recorded

in various solvents of spectroscopic grade using silylated[1] quartz cuvettes of 1 cm path length on a Cary 50 Spectrophotometer and a Cary Eclipse Fluorescence Spectrophotometer. Unless stated otherwise, all experiments were carried out at 25 ± 0.5 °C. For titration experiments, stock solutions in $CHCl_3$ and CH_3CN with optical densities OD(λ_{max}) ~ 0.8 - 1.0 were used to prepare samples with varying solvent composition. Circular dichroism spectra were recorded on a JASCO 700, equipped with Peltier thermostated cell holders (ΔT = ± 0.05 °C), using silylated[1] quartz cuvetts of 1 cm path length. Unless stated otherwise, all experiments were carried out at 25 ± 0.05 °C.The corrected CD spectra were normalized by the exact OD_{max} (range from ~275nm-292nm). Optical rotation were registered on a *Perkin-Elmer* 241-Polarimeter at room temperatur. Specific optical rotation wer calculated from $[\alpha]_D^{23} = \alpha \cdot 100 / c \cdot d$; D = Na-D-line (λ = 589.3 nm), d = layer thickness (1dm), c = concentration in g/100 mL.

Building blocks for covalente connection

Acrylate system

3,5-Diiodo 2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxycarbonyl}-allyl benzoate 56



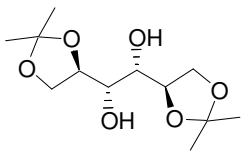
3g (8mmol) 3,5- Diiodobenzoic acid were suspended in 20mL $SOCl_2$ and refluxed for a hour. The excess of thionylchloride was evaporated under reduced pressure and the pale yellow acid chlorid dried at the oil pump. A solution of 3,5- diiodobenzoic acid chlorid **36** in 20mL dry dichloromethane was dropped to a mixture of 1.80g (0.91eq, 7.3mmol, 92.6%) 2-hydroxymethyl- 2-[2-(2-methoxy-ethoxy)-ethoxy] acrylate and 4.8ml NEt_3 (4.7eq, 34.3mmol) in 10mL dichloromethane, white precipitate. After stirring at room temperature over night 25mL satt. NH_4Cl were added, the aqueous phase 3 times extracted with 20mL dichloromethane, the combined organic layers twice washed with satt. NH_4Cl, satt. $NaHCO_3$ and brine, dried over $MgSO_4$ and the solvent evaporated under reduced pressure. The yellow crude product was purified by column chromatography (dichloromethane/ 3% MeOH R_f: 0.5) to yield 1.86g (42%) of a white solid, m.p. 37.5- 38.5°C. ^{1}H NMR (500 MHz, $CDCl_3$, 296±2K): δ 8.29 (d, $^4J_{(H,H)}$ = 1.6 Hz, 2H, Ar-

[1] Cuvetts were cleaned with a 1:1 mixture of conc. H_2SO_4 / 30% H_2O_2, washed with water and acetonitrile, and a 10vol% solution of *silyl-501* (BSTFA: N, O-Bis(trimethylsilyl)acetamide, 1%TMS-Cl) in acetonitrile added, stirred for 10 min at rt and 20min at 50°C, washed twice with acetonitrile and chloroform.

H), 8.22 (t, $^{4}J_{(H,H)}$ = 1.6 Hz ,1H, Ar-H), 6.45 (s, 1H, =C-H), 5.91 (bs, 1H, =C-H), 5.04 (s, 2H, OCH_2), 4.35-4.33 (m, 2H, OCH_2), 3.74-3.72 (m, 2H, OCH_2), 3.65-3.61 (m, 6H, OCH_2), 3.53-3.51 (m, 2H, OCH_2), 3.35 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.93, 163.09, 149.45, 137.75, 134.79, 133.04, 128.61, 94.41, 71.92, 70.63, 70.62, 70.58, 68.96, 64.25, 63.54, 59.02; MS (EI, 80eV, 200°C): *m/z* (%) = 559 (0.1) $[C_{16}H_{17}O_6I_2]^+$, 485 (100) $[C_{13}H_{11}O_4I_2]^+$, 441 (10) $[C_{11}H_7O_3I_2]^+$, 357 (84) $[C_7H_3OI_2]^+$, 329 (13) $[C_6H_3I_2]^+$, 59 (20) $[C_3H_7O]^+$; *pos*FAB-MS (matrix: MNBA/ CH_2Cl_2) *m/z* (%) = 605 (2) $[M+H]^+$, 485 (2) $[C_{13}H_{11}O_4I_2]^+$, 441 (3) $[C_{11}H_7O_3I_2]^+$, 357 (2) $[C_7H_3OI_2]^+$; HRMS (EI, 80eV, 200°C): *m/z* = 558.91355 (calcd. 558.91144 for $[C_{16}H_{17}O_6I_2]^+$), 484.87622 (calcd. 484.87469 for $[C_{13}H_{11}O_4I_2]^+$), 440.84466 (calcd. 440.84848 for $[C_{11}H_7O_3I_2]^+$), 356.82588 (calcd. 356.82733 for $[C_7H_3OI_2]^+$), 328.83444 (calcd. 328.83243 for $[C_6H_3I_2]^+$); HPLC (90% MeOH/ 10% H_2O, 1ml/ min): 99.3% in the peak area; IR (KBr) 3421, 3067, 3048, 2961, 2903, 2875, 2821, 1740, 1712, 1639, 1573, 1546, 1513, 1494, 1459, 1444, 1414, 1398, 1374, 1364, 1352, 1326, 1305, 1257, 1247, 1195, 1157, 1142, 1118, 1104, 1042, 1029, 1007, 1000, 958, 912, 892, 873, 845, 818, 756, 720, 710, 671, 660, 650, 576, 550, 513, 470cm^{-1}.

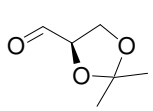
RCM-building blocks

1,2:5,6-Diisopropyliden-D-mannitol 57



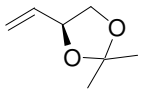
75g D-mannitol were suspended in 180mL freshly distilled glyme, 120mL 2,2-dimethoxypropane and 84mg $SnCl_2*2H_2O$ were added. Mixture was stirred and heated to reflux until a clear solution could be obtained, then stirred 30min at this temperature, cooled to ambient temperature and 0.9mL pyridine was added. The solvents were removed, the white solid was slurried in 540mL dichloromethane for 1h, filtrated and the solvent evaporated at low pressure. The crude product contains the 1,2;3,4;5,6-protected mannitol-compound. The yield was calculated by NMR: ~79g (73%). For NMR characterization a small portion of the crude product was recrystallized from *n*-butyl-ether, to obtain the pure product as a white solid. ^{1}H NMR (250.13 MHz, $CDCl_3$, 296±2K): δ 4.18-4.05 (m, 4H), 3.94 (dd, $^{3}J_{(H,H)}$ = 5.2 Hz, 8.1 Hz, 2H), 3.71 (d, $^{3}J_{(H,H)}$ = 6.6 Hz, 2H), 2.64 (bs, 1H, OH), 1.38 (s, 6H, CH_3), 1.32 (s, 6H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 109.33, 76.28, 71.26, 66.73, 26.67, 25.18.

2,3-*O*-(Isopropyliden)-D-glyceraldehyd 58



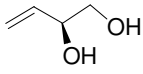
Approximately 39.4g (150mmol) of 1,2;5,6-diisopropylidene-D-mannitol **57**, were suspended in 450mL dichloromethane, 15mL satturated aqueous $NaHCO_3$ were added and 45g (1.4eq, 210mmol) powdered $NaIO_4$ added, in 10 portions within two hours, with vigorous stirring, maintaining the temperature below 25°C. The mixture was stirred for additional two hours, the solution was decanted and the remaining solids twice extracted with 120mL dichloromethane. The solvent was removed at low pressure and the crude product fractionally distilled, using a vigreux column, to yield 20g (51%, b.p. 45-50°C, ~2mbar) of a colourless oily liquid. ^{1}H NMR (250.13 MHz, $CDCl_3$, 296±2K): δ 9.68 (d, $^3J_{(H,H)}$ = 1.5 Hz, 1H, CHO), 4.38-4.32 (m, 1H, CH), 4.17-4.03 (m, 2H, CH_2), 1.45 (s, 3H, CH_3), 1.38 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.47, 111.02, 79.68, 65.34, 26.03, 24.93.

(*S*)-1,2-*O*-Isopropyliden-but-3-en-1,2-diol 59



To a solution of 60g Ph_3PH_2Br in 210mL dry tetrahydrofurane were added 18.4g ^{tert}BuOK at 0°C under a N_2-atmosphere. The yellow suspension was stirred for 90 minutes at 0°C, a solution of 20g 2,3-O-isopropylidene-D-glyceraldehyde **58** in 81mL dry diethylether added and stirring over night at room temperature, colourless mixture. The reaction was quenched with ether satturated with water and water, the organic layer separated, washed with brine and concentrated at the rotvap (~450mbar). Fractionated destillation at ~80mbar gave 3 fractions with different solvent/ product ratios, to yield 14.8g (75% estimated by NMR) colourless liquid. $[\alpha]_D^{23}$ = +24.6° (c = 8, $CHCl_3$); ^{1}H NMR (250.13 MHz, $CDCl_3$, 296±2K): δ 5.80 (ddd, $J_{(H,H)}$ = 6.9 Hz, 10.3 Hz, 17.3 Hz, 1H), 5.31 (bd, $J_{(H,H)}$ = 16.9 Hz, 1H), 5.18 (bd, $^3J_{(H,H)}$ = 10.3 Hz, 1H), 4.47 (q, $^3J_{(H,H)}$ = 6.6 Hz, 1H), 4.1-4.04 (m, 1H), 3.57 (t, $^3J_{(H,H)}$ = 8.1 Hz, 1H), 1.40 (s, 3H, CH_3), 1.36 (s, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 135.96, 117.82, 109.35, 77.35, 69.29, 26.62, 25.82.

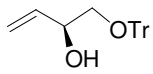
(*S*)-But-3-en-1,2-diol 60



(*S*)-1,2-O-Isopropylidenbut-3-en-1,2-diol **59** was solved in 100mL MeOH, 1g amberlite was added and stirred at room temperature for 6h. The ion changer was removed by filtration, the solvent evaporated and the crude product destilled (b.p. 40-45°C, 2mbar) to yield 5.9g (79%) of a colourless liquid. $[\alpha]_D^{23}$ = -7.6° (c = 0.97, $CHCl_3$); ^{1}H NMR (250.13 MHz, $CDCl_3$, 296±2K): δ 5.81 (ddd, $J_{(H,H)}$ = 6.9 Hz, 10.3 Hz, 17.3 Hz, 1H),

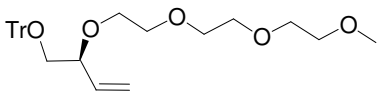
5.32 (dt, $J_{(H,H)}$ = 17.7 Hz, 1.5 Hz, 1H), 5.21-5.16 (m, 1H), 4.25-4.17 (m, 1H), 3.63 (dd, $J_{(H,H)}$ = 11.4 Hz, 3.3 Hz, 1H), 3.45 (dd, $J_{(H,H)}$ = 11.4 Hz, 7.7 Hz, 1H), 3.31 (bs, 2H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 136.74, 116.65, 73.29, 66.23.

(*S*)-1-*O*-Trityl-but-3-en-1,2-diol 61



A mixture of 2.64g (30mmol) but-3-ene-1,2-diol **60**, 9.20g (1.1eq, 33mmol) tritylchloride and 0.15g (0.04eq, 1.2mmol) DMAP were solved in 25mL dry dimethyl formamide and 6.5mL NEt_3 added. The mixture was stirred at room temperature over night under nitrogen, poured into icecold water and extracted three times with 25mL dichloromethane. The organic layers were washed with satt. NH_4Cl and brine, dried with $MgSO_4$, the solvent evaporated and the yellow crude product purified by column chromatography (dichloromethane, R_f: 0.26) to yield 7.5g (75.7%) of a colourless liquid with high viscosity. $[\alpha]_D^{23}$ = +0.55° (c = 1.12, $CHCl_3$); ^{1}H NMR (250.13 MHz, $CDCl_3$, 296±2K): δ 7.46-7.21 (m, 15H, Ar-H), 5.80 (ddd, $J_{(HH)}$ = 5.9 Hz, 10.3 Hz, 16.9 Hz, 1H), 5.34-5.26 (m, 1H), 5.18-5.13 (m, 1H), 4.32-4.24 (m, 1H), 3.22 (dd, $J_{(H,H)}$ = 9.6 Hz, 3.7 Hz, 1H), 3.11 (dd, $J_{(H,H)}$ = 9.6 Hz, 7.4 Hz, 1H), 2.41 (d, $^3J_{(H,H)}$ = 3.7 Hz, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.84, 137.15, 128.68, 127.87, 127.13, 116.20, 86.84, 72.03, 67.53.

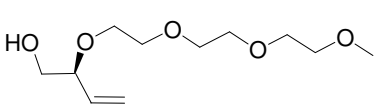
(*S*)-1-*O*-Trityl-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-but-3-en 62



To a solution of 4.58g (13.9mmol) (*S*)-1-*O*-trityl-but-3-en-1,2-diol **61** in 10mL dry dimethylformamide were added 0.37g (1.1eq, 15.2mmol, 95%) NaH under nitrogen at 0°C. The white suspension was stirred at room temperature for 30min and a solution of 4.63g (1.05eq, 14.5mmol) 2-(2-(2-methoxyethoxy)ethoxy)ethyl tosylate in 15mL dry dimethylformamide was added slowly at 0°C. The mixture was stirred over night at room temperature and the reaction was treated with 10mL satt. aqueous NH_4Cl. The solvent was removed at low pressure and the residue several times extracted with 25mL dichloromethane, the combined organic layers dried over $MgSO_4$, filtrated and the solvent evaporated. The orange crude product was purified by column chromatography (dichloromethane/ 4% MeOH, R_f: 0.71) to yield 1.1g (16.7%) of a highly viscos, colourless liquid. Around 20% of the product was detritylated by $NH_4Cl_{(aq)}$ and/ or silica gel. Isolated fractions containing deprotected product and byproducts: 4.7g. $[\alpha]_D^{23}$ = -9.0° (c = 1.2, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 296±2K): δ 7.49-7.42 (m, 6H, Ar-H), 7.31-7.20 (m, 9H, Ar-H), 5.73 (ddd, $^3J_{(H,H)}$ = 6.9 Hz, 10.4 Hz, 17.3 Hz, 1H, H_{vinyl}), 5.28 (dt,

$J_{(H,H)}$ = 17.3 Hz, 1.4 Hz, 1H, H_{vinyl}), 5.20 (ddd, J = 6.9 Hz, 10.4 Hz, 17.3 Hz, 1H, H_{vinyl}), 3.91 (dd, $J_{(H,H)}$ = 10.4 Hz, 1.5 Hz, 1H), 3.73-3.57 (m, 12H, OCH_2), 3.52-3.49 (m, 2H, OCH_2), 3.35 (s, 3H, OCH_3), 3.26 (dd, $J_{(H,H)}$ = 6.6 Hz, 9.5 Hz, 1H, CH_2), 3.05 (dd, $^3J_{(H,H)}$ = 5.1 Hz, 9.5 Hz, 1H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$, 296±2K): δ 144.06, 136.34, 128.72, 127.66, 126.84, 117.52, 86.46, 80.80, 71.87, 70.67, 70.61, 70.46, 68.59, 66.51, 58.94; MS (EI, 80eV, 150°C): *m/z* (%) = 243 (100) $[C_{19}H_{15}]^+$), 59 (25) $[C_3H_7O]^+$, 103 (6) $[C_5H_{11}O_2]^+$, 147 (11) $[C_7H_{15}O_3]^+$, 165 (22) $[C_{13}H_9]^+$, 203 (29) $[C_{10}H_{19}O_4]^+$; HRMS (EI, 80eV, 150°C): *m/z* = 243.11733 (calcd. 243.11737 for $[C_{19}H_{15}]^+$), 203.12769 (calcd. 203.12834 for $[C_{10}H_{19}O_4]^+$), 147.10177 (calcd. 147.10213 for $[C_7H_{15}O_3]^+$), 103.07633 (calcd. 103.07590 for $[C_5H_{11}O_2]^+$), 59.04933 (calcd. 59.04969 for $[C_3H_7O]^+$); *pos*FAB-MS (matrix: MNBA / CH_2Cl_2): *m/z* (%) = 515 (1) $[M+K]^+$, 499 (9) $[M+Na]^+$, 243 (100) $[Ph_3C]^+$; Anal. C: 75.49 H: 7.57 (calcd. C: 75.60 H: 7.61); HPLC (80% MeOH/ 20% H_2O, 1ml/ min): 98.0% in the peak area.

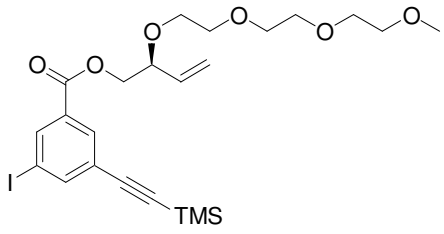
2-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy}-but-3-en-1-ol 63



App. 4.70g (~10mmol) (*S*)-1-*O*-trityl-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-but-3-en **62** were solved in 150mL methanol and 1.90g TsOH- hydrate were added. The mixture was stirred at room temperature for 6h, neutralized with satt. aqueous $NaHCO_3$ and the solvent evaporated at low pressure. Thr residue was solved in 30mL water and extracted three times with 50mL ethyl acetate. The combined organic phases were washed twice with satt. $NaHCO_3$, satt. NH_4Cl and brine, dried over $MgSO_4$ and the solvent evaporated at low pressure. The yellow crude product was purified by column chromatography (dichloromethane/ 4% MeOH, R_f: 0.35) to yield: 2.11g (quantitativ conversion) of a colorless liquid. (mosher Ester: ≥ 98.4% ee, ^{19}F NMR, 298K); ^{1}H NMR (500 MHz, $CDCl_3$, 291K): δ 5.65 (ddd, $^3J_{(H,H)}$ = 6.9 Hz, 10.4 Hz, 17.3 Hz, 1H, H_{vinyl}), 5.28 (dt, $J_{(H,H)}$ = 17.4 Hz, 1.3 Hz, 1H, H_{vinyl}), 5.21 (ddd, J = 10.4 Hz, 1.3 Hz, 1H, H_{vinyl}), 3.87-3.83 (m, 1H, CH), 3.75-3.71 (m, 1H, *CH*), 3.69-3.59 (m, 8H, OCH_2), 3.52-3.47 (m, 5H, *OCH_2, CH*), 3.33 (s, 3H, OCH_3), 2.76 (bs, 1H, OH); ^{13}C NMR (125 MHz, $CDCl_3$, 296±2K): δ 135.12, 118.22, 82.31, 71.87, 70.53, 70.50, 70.46, 70.464, 70.457, 68.17, 65.25, 58.93; MS (EI, 80eV, 70°C): *m/z* (%) = 203 (7) [M- OCH_3 = $C_{10}H_{19}O_4]^+$,147 (15) $[C_7H_{15}O_3]^+$, 103 (20) $[C_5H_{11}O_2]^+$, 59 (100) $[C_3H_7O]^+$, 45 (48) $[C_2H_5O]^+$, 71 (9) $[C_4H_7O]^+$; HRMS (EI, 80eV, 70°C): *m/z* = 203.12755 (calcd. 203.12834 for [M- OCH_3 = $C_{10}H_{19}O_4]^+$); *pos*FAB-MS (matrix: MNBA / CH_2Cl_2): *m/z* (%) = 235 (36) $[M+H]^+$, 257 (51) $[M+Na]^+$, 59 (100) $[C_3H_7O]^+$, 45 (45) $[C_2H_5O]^+$, 103 (31) $[C_5H_{11}O_2]^+$; Anal. C: 54.17 H: 9.41 (calcd. C: 56.39 H: 9.46); GC

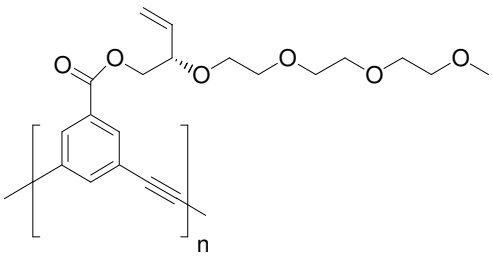
(13m DB-Wax, 0.25 / 0.15df, G/249, 220/60 6°C/min 250°C/ 350°C, t_R 19.5min): 93.6% in the peak region. Chiral GC (30m BGB-176/ BGB-15 0.25/0.1 G/ 494, t_R ~67min): ≥98% ee.

(2*S*)-2-Vinyl-3,6,9,12-tetraoxatridec-1-yl-3-iodo-5-[(trimethylsilyl)ethynyl]benzoate 64



0.37g (1.07mmol) 3-Iodo-5-(2-(trimethylsilyl)ethynyl-benzoic acid **16**, 0.27g (1.05eq, 1.12mmol) (*S*)-2-{2-[2-(2-methoxy-ethoxy)-ethoxy]-ethoxy}-but-3-en-1-ol **63**, 0.09g (0.3eq, 0.32mmol) DPTS were mixed and a solution of 0.28g (1.25eq, 1.34mmol) DCC in 1mL dry dichloromethane added at 0°C, white precipitate. The mixture was stirred over night at room temperature, filtrated, the solvent evaporated, 10mL toluene were added and the suspension stored over night at 8°C. The white residue was removed by filtration, the solvent evaporated and the yellow crude product purified by column chromatography (ethyl acetate, R_f: 0.56) to yield 0.5g (88%) of a slightly yellow liquid. $[\alpha]_D^{23}$ = +5.6° (c = 1.58, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 8.25 (t, $^4J_{(H,H)}$ = 1.6 Hz, 1H, Ar-H), 8.03 (t, $^4J_{(H,H)}$ = 1.6 Hz, 1H, Ar-H), 7.94 (t, $^4J_{(H,H)}$ = 1.6 Hz, 1H, Ar-H), 5.74 (ddd, $^3J_{(H,H)}$ = 7 Hz, 10.4 Hz, 17.4 Hz, 1H, H_{vinyl}), 5.37 (dt, $^3J_{(H,H)}$ = 17.4 Hz, $^2J_{(H,H)}$ = 1.3 Hz, 1H, H_{vinyl}), 5.30 (ddd, $^2J_{(HH)}$ = 1.3 Hz, $^3J_{(HH)}$ = 10.4 Hz, 1H, H_{vinyl}), 4.34-4.28 (m, 2H, CH_2), 4.15-4.11 (m, 1H, CH), 3.72-3.68 (m, 1H, CH), 3.64-3.57 (m, 8H, OCH_2), 3.53-3.56 (m, 1H, CH), 3.50-3.49 (m, 2H, OCH_2), 3.33 (s, 3H, OCH_3), 0.22 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (125 MHz, $CDCl_3$, 296±2K): δ 164.17, 144.39, 138.22, 134.61, 132.19, 131.78, 125.39, 119.23, 102.02, 97.18, 93.07, 79.03, 71.89, 70.63, 70.60, 70.49, 68.41, 66.96, 58.97, -0.27; MS (EI, 80eV, 90°C): *m/z* (%) = 45 (12) $[C_2H_5O]^+$, 59 (100) $[C_3H_7O]^+$, 73 (15) $[C_3H_9Si]^+$, 103 (37) $[C_5H_{11}O_2]^+$, 147 (57) $[C_7H_{15}O_3]^+$, 203 (44) $[C_{10}H_{19}O_4]^+$, 397 (10) $[C_{16}H_{18}O_2SiI]^+$, 327 (51) $[C_{12}H_{12}OSiI]^+$, 515 (6) $[C_{21}H_{28}O_5SiI]^+$, 560 (3) $[M]^+$; HRMS (EI, 80eV, 90°C): *m/z* = 560.10868 (calcd. 560.10913 for $[C_{23}H_{33}O_6SiI]^+$); HPLC (CH_2Cl_2, 3% MeOH, 1ml/ min): 99.4% in the peak area; Anal. C: 49.27 H: 5.93 (calcd. C: 49.29 H: 5.93); IR (KBr) 3439, 3072, 2955, 2920, 2898, 2874, 2817, 2720, 2160, 1950, 1818, 1728, 1644, 1587, 1556, 1451, 1427, 1376, 1351, 1326, 1280, 1250, 1204, 1141, 1114, 1041, 1030, 995, 933, 908, 882, 846, 764, 725, 700, 674, 656, 472cm^{-1}.

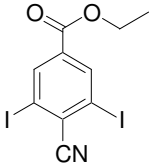
Poly(*m*-aryleneethynylene) P14



102mg (0.182mmol) (2*S*)-2-Vinyl-3,6,9,12-tetra-oxatridec-1-yl 3-iodo-5-[(trimethylsilyl)ethynyl]-benzoate **16** and 4mg CuI (0.12eq, 0.022mmol) were loaded under argon in a 25mL microwave tube. Dry and degassed acetonitril (2mL) was submitted to the tube via syringe, 13mg $Pd(PPh_3)_4$ (0.06eq, 0.011mmol) and 165µL (6eq, 1.09mmol) 1,8-diazabicyclo-[5.4.0]undec-7-ene were added immeditely followed by addition of 50µL (15eq, 2.78mmol) distilled water. The sealed tube was heated in the microwave for 30 minutes at 60°C. The obtained clear orange solution was dropped in 100mL ice cold diethylether, the precipitated, green-brown polymer redissolved in dichloromethane and passed through a short column of silica gel. A second precipitation in a mixture of 3mL cold diethylether and 1mL cold hexane yielded 23mg (35%) of a dirty white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 295K): δ 8.17 (s, 2H, Ar-H), 7.89 (s, 1H, Ar-H), 5.84-5.78 (m, 1H, H_{vinyl}), 5.43-5.32 (m, 2H, H_{vinyl}), 4.38 (bs, 2H, CH_2), 4.18 (bs, 1H, CH), 3.75-3.47 (m, 12H, OCH_2), 3.31 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.78, 138.33, 134.84, 132.84, 131.21, 123.66, 119.27, 89.05, 79.08, 71.92, 70.67, 70.52, 68.50, 67.02, 58.97; Anal. C: 66.40 H: 5.79 (calcd. for $(C_{20}H_{24}O_6)_n$ C: 66.65 H: 6.71); IR (KBr) 3429, 3260, 3067, 2918, 2868, 2592, 2217, 1724, 1643, 1595, 1450, 1384, 1351, 1323, 1296, 1235, 1201, 1109, 1023, 996, 933, 893, 849, 787, 766, 677, 603, 581, 533cm^{-1}; SEC (THF, 30°C): M_w = 61495 g/mol, M_n = 29230 g/mol, PDI (M_w/M_n) = 2.10; UV/ vis ($CHCl_3$, 25°C) λ_{max} (abs/conc): 290nm, 305nm shoulder (1.05/ 9.6 ± 1.6mg/L), using the M_n determined by SEC this gives an average extinction coefficient per repeat unit ε_{ru} ~ 487 ± 70M^{-1}cm^{-1}; UV/ vis (CH_3CN, 25°C) λ_{max} (abs/conc): 289nm (0.52/ 9.6 ± 1.6mg/L), ε_{ru} ~ 240 ± 35M^{-1}cm^{-1}.

Synthesis of nitril-compounds

4-Cyano-3,5-diiodo-ethyl benzoat 65



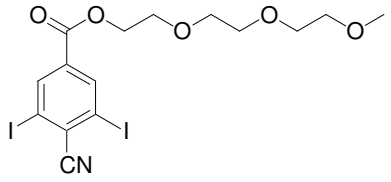
To a solution of 0.5g $NaNO_2$ in 3mL water (7.2mmol, 2.5N) were added carfully, within 15min, 4.5mL (~40mmol, 50%) H_2SO_4 at -5°C. The blue solution was added to a suspension of 3g (7.2mmol) 3,5-diiodo-4-amino-benzoic acid **34** in a 3mL acetic acid within 10min at 0°C, to provide the yellow diazonium compound. The mixture was stirred for one hour at 5°C, the excess NO_2^- destroyed with $CO(NH_2)_2$ (controled with KI-paper), and poured stepwise, within 30min, to a mixture of 2g

(2eq, 14.5mmol) K_2CO_3, 0.82g (1.25eq, 9.2mmol) CuCN and 1.85g (5.25eq, 37.8mmol) NaCN in 10mL water, maintaining the temperature below 5°C and pH >10 by stepwise addition of solid K_2CO_3. The pale brown mixture was stirred for 20min, three times extracted with 25mL toluene, the combined organic phases dried over $MgSO_4$, the solvent evaporated at low pressure and the crude product purified by column chromatography (ethyl acetate, R_f: 0.59) and recrystallization from ethyl acetate to yield 1.3g (42%) of colourless crystalls: m.p. 163.5-164.5°C. ^{1}H NMR (500 MHz, $CDCl_3$, 296±2K): δ 8.45 (s, 2H, Ar-H), 4.38 (dd, $^3J_{HH}$ = 7.1 Hz, 2H, CH_2), 1.38 (t, $^3J_{HH}$ = 7.1 Hz, 3H, CH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 296±2K): δ 162.37, 139.44, 135.12, 130.76, 119.88, 98.72, 62.49, 14.16; MS (EI, 80eV, 90°C): *m/z* (%) = 427 (100) [M = $C_{10}H_7I_2NO_2]^+$, 399 (42) $[C_8H_3I_2NO_2]^+$, 382 (53) $[C_8H_2I_2NO]^+$, 354 (19) $[C_7H_2I_2N]^+$, 127 (8) $[I]^+$, 128 (9) $[HI]^{\cdot+}$, 73 (14) $[C_3H_5O_2]^+$, 45 (21) $[C_2H_5O]^+$; HRMS (EI, 80eV, 90°C): *m/z* = 426.85669 (calcd. 426.85638 for $[C_{10}H_7I_2NO_2]^+$); Anal. C: 28.17 H: 1.57 N: 3.34 (calcd. C: 28.13 H: 1.65 N: 3.28); HPLC (Varian Microsorb-μ 100-5 C18, 80% MeOH/ H_2O, 1ml/ min, 190bar): 97.5% in the peak area.

byproduct

3,5-Diiodo ethyl benzoat **10** (deamination), column chromatography (ethyl acetate, R_f: 0.71), ^{1}H NMR (250.13 MHz, $CDCl_3$, 296±2K): δ 8.25 (d, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 8.15 (d, $^4J_{HH}$ = 1.5 Hz, 1H, Ar-H), 4.33 (dd, J_{HH} = 14.3 Hz, 7 Hz, 2H, OCH_2), 1.35 (t, $^3J_{HH}$ = 7 Hz, 3H, CH_3); MS (EI, 80eV, 60°C): *m/z* (%) = 402 (100) [M = $C_9H_8I_2O_2]^+$, 357 (54) $[C_7H_3I_2O]^+$, 329 (20) $[C_6H_3I_2]^{\cdot+}$, 127 (5) $[I]^{\cdot+}$.

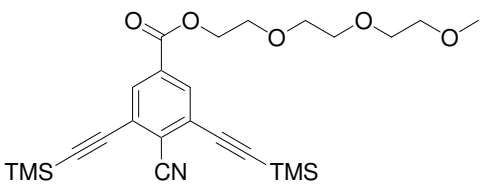
2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-cyano-3,5-diiodo-benzoate 66



1.15g (2.7mmol) 4-Cyano-3,5-diiodo-ethyl benzoate **65**, 2.12g (5eq, 13.5mmol) triglyme and 0.075g (0.2eq, 0.4mmol) K_2CO_3 were mixed and stirred at low pressure at 65°C for 90 minutes. The crude product was purified by gradient column chromatography (hexane/ ethyl acetate 4:1 to ethyl acetate, R_f: 0.32), and recrystallization from hexane to yield 1.02g (69%) of a cotton like white solid: m.p. 90-91°C. ^{1}H NMR (500 MHz, $CDCl_3$, 295K): δ 8.47 (s, 2H, Ar-H), 3.80-3.79 (m, 2H, OCH_2), 3.68-3.66 (m, 2H, OCH_2), 3.66-3.60 (m, 6H, OCH_2), 3.52-3.50 (m, 2H, OCH_2), 3.34 (s, 3H, OCH_3); ^{13}C NMR (125 MHz, $CDCl_3$, 296K): δ 162.42, 139.52, 134.78, 130.90, 119.88, 98.72, 71.87, 70.58, 70.56, 68.78, 65.32, 59.02; MS (EI, 80eV, 120°C): *m/z* (%) = 545 (1) [M = $C_{15}H_{17}I_2NO_5]^+$, 426 (100) $[C_{10}H_6I_2NO_2]^+$, 59 (12) $[C_3H_7O]^+$, 486 (0.5) $[C_{12}H_{10}I_2NO_4]^+$, 470 (0.5)

$[C_{12}H_{10}I_2NO_3]^+$, 382 (40) $[C_8H_2I_2NO]^+$; HRMS (EI, 80eV, 120°C): *m/z* = 544.91986 (calcd. 544.91937 for $[C_{15}H_{17}I_2NO_5]^+$); Anal. C: 33.10 H: 2.96 N: 2.54 (calcd. C: 33.05 H: 3.14 N: 2.57); HPLC (Varian Microsorb-µ 100-5 C18, 90% MeOH/ H_2O, 1ml/ min, 190bar): 97.1% in the peak area; IR (KBr) 3433, 3105, 3068, 2988, 2959, 2912, 2878, 2831, 2725, 2227, 1805, 1730, 1685, 1667, 1526, 1495, 1485, 1465, 1453, 1448, 1420, 1395, 1389, 1367, 1328, 1269, 1260, 1206, 1199, 1186, 1138, 1114, 1099, 1077, 1053, 1040, 1010, 905, 889, 871, 843, 762, 715, 607, 598, 549, 449cm^{-1}.

2-(2-(2-Methoxyethoxy)ethoxy)ethyl 4-cyano-3,5-bis(2-(trimethylsilyl)ethynyl)benzoate 67



To a solution of 1.97g (3.6mmol) 2-(2-(2-methoxy-ethoxy)ethoxy)ethyl 4-cyano-3,5-diiodo-benzoate **66** in 5mL degassed toluene and 20mL dry degased NEt_3 were added 0.14g (0.02eq, 0.07mmol) CuI, 0.125g (0.03eq, 0.11mmol) $Pd(PPh_3)_4$ and 2mL trimethylsilylacetylene (4.1eq, 29.5mmol) under a nitrogen atmosphere. The mixture was stirred half an hour at room temperature (white precipitate) and at 50°C for one hour. Reaction control showed incomplete conversion to the monosubstituted compound. The mixture was stirred at 65°C over night to complete the reaction, the solvent evaporated at low pressure and 30mL toluene added. The insoluble part was removed by filtration, the solvent evaporated and the orange-brown crude product purified by column chromatography (ethyl acetate/ hexane 1:1, R_f: 0.33; ethyl acetate, R_f: 0.51) to yield 1.3g (74%) of a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$, 291K): δ 8.06 (s, 2H, Ar-H), 4.47-4.45 (m, 2H, OCH_2), 3.81-3.79 (m, 2H, OCH_2), 3.68-3.66 (m, 2H, OCH_2), 3.65-3.60 (m, 4H, OCH_2), 3.51-3.49 (m, 2H, OCH_2), 3.33 (s, 3H, OCH_3), 0.26 (s, 18H, TMS); ^{13}C NMR (125 MHz, $CDCl_3$, 291K): δ 163.93, 133.19, 132.24, 127.79, 122.06, 115.21, 104.00, 99.43, 71.84, 70.56, 68.87, 64.95, 59.00, -0.50; MS (EI, 80eV, 140°C): *m/z* (%) = 45 (40) $[C_2H_5O]^+$, 59 (59) $[C_3H_7O]^+$, 73 (51) $[C_3H_9Si]^+$, 89 (28) $[C_4H_9O_2]^+$, 103 (7) $[C_5H_{11}O_2]^+$, 322 (25) $[C_{18}H_{20}NOSi_2]^+$, 338 (24) $[C_{18}H_{20}NO_2Si_2]^+$, 339 (15) $[C_{19}H_{17}NO_5]^+$, 366 (48) $[C_{20}H_{24}NO_2Si_2]^+$, 382 (53) $[C_{20}H_{24}NO_3Si_2]^+$, 396 (7) $[C_{21}H_{26}NO_3Si_2]^+$, 412 (9) $[C_{22}H_{26}NO_5Si]^+$, 440 (17) $[C_{23}H_{30}NO_4Si_2]^+$, 485 (18) $[M]^+$; HRMS (EI, 80eV, 140°C): *m/z* = 485.20622 (calcd. 485.20538 for $[C_{25}H_{35}O_5Si_2N]^+$); HPLC (Varian Microsorb-µ 100-5 C18, 90% MeOH/ H_2O, 1ml/ min, 105bar): 99.3% in the peak area; Anal. C: 61.76 H: 7.25 N: 2.90 (calcd. C: 61.82 H: 7.26 N: 2.88); IR (KBr) 3444, 3076, 2960, 2899, 2823, 2720, 2231, 2162, 1731, 1685, 1559, 1453, 1432, 1411, 1376, 1365, 1353, 1319, 1280, 1251, 1229, 1201, 1182,

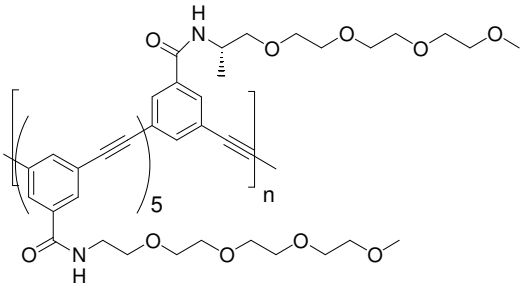
1135, 1111, 1096, 1029, 1009, 966, 910, 848, 764, 747, 733, 717, 704, 650, 522, 496, 462, 451cm^{-1}.

byproduct

(mono substituition) column chromatography (ethyl acetate, R_f: 0.42), ^{1}H NMR (250.13 MHz, $CDCl_3$, 296±2K): δ 8.38 (s, 1H, Ar-H), 8.26 (s, 1H, Ar-H), 4.45-4.42 (m, 2H, OCH_2), 3.78-3.75 (m, 2H, OCH_2), 3.62-3.56 (m, 6H, OCH_2), 3.48-3.45 (m, 2H, OCH_2), 3.29 (s, 3H, OCH_3), 0.23 (s, 9H, TMS).

Synthesis of amid-copolymers

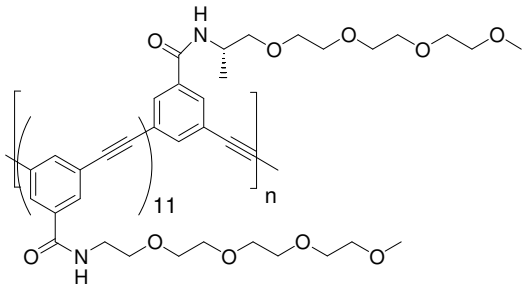
Poly(*m*-aryleneethynylene) P15



58mg (0.107mmol) 3-Iodo-*N*-(3,6,9,12-tetraoxa-tridec-1-yl)-5-[(trimethylsilyl)ethynyl]benzamide **31**, 12mg (0.17eq, 0.021mmol) 3-Iodo-*N*-[(1*S*)-1-methyl-3,6,9,12tetraoxatridec-1-yl]-5-[(trimethyl-silyl)ethynyl]-benzamide **29**, and 2mg CuI (0.12eq, 0.01mmol) were loaded under argon in a 25mL microwave tube. Dry and degassed acetonitril (0.25mL) was submitted to the tube via syringe, 7mg $Pd(PPh_3)_4$ (0.07eq, 0.007mmol) and 115µL 1,8-diazabicyclo-[5.4.0]undec-7-ene (7eq, 0.75mmol) were added immeditely followed by addition of 29µL distilled water (15eq, 1.6mmol). The sealed tube was heated in the microwave for 80 minutes at 60°C. The obtained clear yellow solution was dropped in 100mL ice cold diethylether, the precipitated, slightly yellow-green polymer redissolved in dichloromethane and passed through a short column of silica gel. A second precipitation in 10mL cold diethylether yielded 30mg (70%) of a brownish solid. ^{1}H NMR (500 MHz, $CDCl_3$, 297K): δ 9.03 (broad, Ar-H), 6.50 (bs, 1H, NH), 3.75 (broad, 14H, OCH_2), 3.40 (bs, 3H, OCH_3), 1.40 (bs, 3H, CH_3); ^{1}H NMR (500 MHz, $CDCl_3$, containing 5% trifluorethanol, 299K): δ 7.90 (bs, 2H, Ar-H), 7.80 (bs, 1H, Ar-H), 7.56 (bs, 1H, NH), 3.65-3.54 (m, 14H, OCH_2), 3.46 (bs, 2H, OCH_2), 3.27 (s, 3H, OCH_3), 1.27 (d, $^3J_{(HH)}$ = 5.8Hz, 3H, CH_3); Anal. C 60.86 H 6.58 N 3.80 (calcd. for $(C_{109}H_{141}N_6O_{30})_n$ C: 64.96 H: 7.05 N: 4.17); IR (KBr) 3264, 3066, 2914, 2868, 2815, 1634, 1586, 1539, 1450, 1348, 1323, 1274, 1251, 1199, 1092, 1026, 941, 912, 881, 848, 763, 724, 677, 540cm^{-1}; SEC (THF, 30°C): M_w = 10580 g/mol, M_n = 8420 g/mol, PDI (M_w/M_n) = 1.26; UV-visible absorption spectra under identical conditions (THF, 30°C) indicate, that the majority of the polymer is adopting folded, helical conformations and therefore SEC presumably underestimates the molecular weight due to

comparision of the samples` hydrodynamic volume with that of randomly coiled, extended polystyrene standards; UV/ vis ($CHCl_3$, 25°C) λ_{max} (abs/conc): 278.5nm (1.05/ 20 ± 1mg/L), using the M_n determined by SEC this gives an average extinction coefficient per repeat unit ε_{ru} ~ 699 ± 33$M^{-1}cm^{-1}$; UV/ vis ($CHCl_3$, 4% trifluorethanol, 25°C) λ_{max} (abs/conc): 290nm, 306.5nm shoulder (1.19/ 19.2 ± 1mg/L), ε_{ru} ~ 844 ± 36$M^{-1}cm^{-1}$.

Poly(*m*-aryleneethynylene) P16



59mg (0.11mmol) 3-iodo-*N*-(3,6,9,12-tetraoxa-tridec-1-yl)-5-[(trimethylsilyl)ethynyl]benzamide **31**, 5.7mg (0.085eq, 0.01mmol) 3-Iodo-*N*-[(1*S*)-1-methyl-3,6,9,12-tetraoxatridec-1-yl]-5-[(trimethyl-silyl)ethynyl]-benzamide **29**, and 2mg CuI (0.12eq, 0.01mmol) were loaded under argon in a 25mL microwave tube. Dry and degassed acetonitril (2mL) was submitted to the tube via syringe, 9mg $Pd(PPh_3)_4$ (0.07eq, 0.008mmol) and 109µL 1,8-diazabicyclo-[5.4.0]undec-7-ene (6.6eq, 0.73mmol) were added immeditely followed by addition of 22µL distilled water (11eq, 1.2mmol). The sealed tube was heated in the microwave for 25 minutes at 60°C. The obtained clear yellow solution was dropped in 50mL ice cold diethylether, the precipitated, slightly yellow polymer redissolved in dichloromethane and passed through a short column of silica gel. A second precipitation in 10mL cold diethylether yielded 18mg (45%) of a yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 298K): δ 9.02 (broad, Ar-H), 6.60 (bs, 1H, NH), 4.00-3.30 (broad, 14H, OCH_2), 3.28 (bs, 3H, OCH_3), 1.23 (bs, 3H, CH_3); ^{1}H NMR (500 MHz, $CDCl_3$ containing 4% trifluorethanol, 295K): δ 7.92 (bs, 2H, Ar-H), 7.79 (bs, 1H, Ar-H), 7.58 (bs, 1H, NH), 3.64-3.52 (m, 14H, OCH_2), 3.43 (bs, 2H, OCH_2), 3.25 (s, 3H, OCH_3), 1.27 (d, $^3J_{(HH)}$ = 6.6 Hz, 3H, CH_3); IR (KBr) 3498, 3281, 3067, 2914, 2868, 2820, 1637, 1589, 1537, 1448, 1349, 1318, 1277, 1251, 1199, 1090, 1025, 940, 882, 847, 762, 729, 679, 601cm^{-1}; SEC (THF, 30°C): M_w = 14060 g/mol, M_n = 11540 g/mol, PDI (M_w/M_n) = 1.22; UV-visible absorption spectra under identical conditions (THF, 30°C) indicate, that the majority of the polymer is adopting folded, helical conformations and therefore SEC presumably underestimates the molecular weight due to comparision of the samples` hydrodynamic volume with that of randomly coiled, extended polystyrene standards; UV/ vis ($CHCl_3$, 25°C) λ_{max} (abs/conc): 281nm (1.03/ 16 ± 1.3mg/L), using the M_n determined by SEC this gives an average extinction coefficient per repeat unit ε_{ru} ~ 619 ±

$45M^{-1}cm^{-1}$; UV/ vis ($CHCl_3$, 4% TFE, 25°C) λ_{max} (abs/conc): 290nm, 306.5nm shoulder (1.17/ 15.4 ± 1.3mg/L), ε_{ru} ~ 730 ± $50M^{-1}cm^{-1}$.

6.4 Literatur

[1] S. Hecht, A. Khan, *Angewandte Chemie, International Edition* **2003**, *42*, 6021.
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