Contract SPC 014058

Contract Order Number F61775-01-WE058

EOARD Liaison Officer : Dr Alex Glass

ITEM 004 - FOURTH AND FINAL REPORT covering period 10th June 2002 to 9th September 2002

Summary

The results of the previous photophysical studies have been used to tune the chemical structures of the π-conjugated silicon-containing polymers. Based on the Kerr and photorefractive properties reported previously, many new π-conjugated silicon-containing polymers with acetylene and arylene groups in the backbone have been synthesized in high yield and structurally characterized by standard techniques including IR and multinuclear NMR. The UV/visible spectra in solution have enabled the separation of the polymers into two groups - those likely to give high Kerr non-linearities around 1000 nm, and those for photorefraction at telecommunication wavelengths. The very interesting photorefractive properties of the polymers at 1500 nm are probably connected to the formation of nano-aggregates in the composite films through π-stacking. The π-stacking properties of the polymers have been investigated by studying the UV/visible spectra of colloids formed on addition of a non-solvent to the polymer solutions the colloids being models for the nano-aggregates in the films. The Kerr and photorefractive properties of the new polymers are being studied at present under the new contract. Electron microscopy and X-ray diffraction will be used to examine the composite films for the presence of nano-aggregates.

Introduction

In the first report we described the very high Kerr-type nonlinear optical properties of solutions and films of the novel organometallic polymers containing silicon or chromium or vanadium. The second and third reports concerned the new photorefractive properties of the silicon-containing polymers at 833 nm and 1500 nm, respectively. We found that (a) the polymers can be incorporated into composites showing photorefraction even in the absence of an applied electric field with no preliminary poling, and (b) they can be used as multifunctional materials for photorefraction at telecommunication wavelengths.

The results of these studies have been used to tune the chemical structures of the polymers. The present fourth report concerns this polymer synthesis done by the Chinese postdoctoral fellow Wenqing PENG in the Montpellier laboratory for 8 months from December 2001 to July 2002. He undertook the synthesis and structural characterization of many new silicon-containing polymers designed for high Kerr-type and photorefractive properties by fine-tuning the chemical structures of the polymers previously investigated. The structural characterization of the polymers was done by standard techniques including IR and multinuclear NMR. As described below the UV/visible spectra in solution have enabled us to separate the polymers into two groups - those likely to give high Kerr non-linearities around 1000 nm, and those for

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14. ABSTRACT

This report results from a contract tasking Universite de Montpellier II as follows: The contractor will investigate the nonlinear optical properties of a variety of organometallic polymer-based materials. Organic materials offer the potential for greatly increased non-linear interactions with intense laser light, enabling the construction of a wide variety of electro-optic components for laser systems.

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photorefraction at telecommunication wavelengths. The very interesting photorefractive properties of the polymers at 1500 nm are probably connected to the formation of nano-aggregates in the composite films through π-stacking. We have investigated the π-stacking properties of the polymers by studying the UV/visible spectra of colloids formed on addition of a non-solvent to the polymer solutions the colloids being models for the nano-aggregates in the films.

We now have a large number of specifically designed organometallic polymers for the Kerr and photorefractive optical studies which are at present proceeding under the new contract. The new project will involve essentially optical studies on these polymers, and it is not envisaged that further substantial chemical synthesis will be required.

POLYMER PREPARATION AND STRUCTURAL CHARACTERIZATION

The preparation and structural characterization of 38 new π-conjugated silicon-containing polymers with acetylene and arylene groups in the backbone are described in the experimental section below. The silicon atoms are tetra-, pent- or hexacoordinated, it being well known that the electronic properties are greatly influenced by silicon coordination number. Some contain the tetraphenylsilole group which, like hypercoordinate silicon, is an electron acceptor. Siloles possess low-lying LUMO energy levels associated with the σ*-π* conjugation arising from the interaction between the σ* orbital of two exocyclic σ-bonds on the ring silicon and the π* orbital of the butadiene moiety. As a result, siloles can serve as efficient electron-transport materials (J. Mater. Chem. (2001), **11**, 2974).

The results of our photophysical studies on analogous polymers (see previous reports) led us to introduce the various arylene groups into the polymers with a view to further improving the fast Kerr-type and photorefractive properties through chemical tuning.

The polymers were obtained in high yield, and were structurally characterized by standard methods. The spectra are consistent with the proposed structures, the IR absorbance around 2150 cm^{-1} arising from the disubstituted C≡C stretch for the acetylene groups in the polymer backbone. This band is shifted to lower energy for the anthracene-containing (e.g. 41) and terthiophene-containing polymers (e.g. 34), consistent with more extensive electron delocalization along the polymer backbone. Conversely, polymers with a donor-acceptor arylene group such as 02 and 32 show a C≡C stretch at higher energy. This is also so for the disulphide polymers such as 31, indicating that electron delocalization is not so extensive for these polymers.

The ^{1}H NMR spectra are consistent with the proposed structures. The ^{13}C NMR spectra show the expected two resonances for the acetylene carbons. In some cases (e.g. 30) four signals are observed. These may be the results of the formation of different conformations resulting from restricted bond rotation. The ^{29}Si NMR spectra show a single signal consistent with all the silicon atoms being equivalent. The chemical shift reflects essentially the coordination number of silicon; *ca*. -45 ppm for tetracoordinate silicon, *ca*. -54 ppm for pentacoordinate silicon, and *ca*. -61 ppm for hexacoordinate silicon. This is consistent with the large influence of coordination number on the electronic properties of silicon.

The multifunctional polymer exhibiting photorefraction at telecommunication wavelengths (described in the third report) contains tetracoordinate silicon and anthracene groups in the backbone. This polymer is active because of the long absorption tail stretching well into the IR in the case of the polymer films (but not solutions). As discussed below we ascribe this effect to π-stacking in the solid state, arising predominantly from the presence of anthracene groups for which this effect is well known. We have now synthesized other polymers of this type where extensive π-stacking might be expected, e.g. the bithiazolyl-containing polymers 06, 09, 28, and 33. (see Chem. Mater. (1997), 9, 1217 and J. Am. Chem. Soc. (1998), 120, 2047). Polymers 07, 08, and 16 contain both electron-poor bithiazolyl and electron-rich thiophene groups (terthiophene in the case of 16) this arrangement favouring along-chain conjugation.

Polymers 03, 19, 27 and 35 contain the 1,4-naphthalene group (two fused benzene rings) for comparison with the previously studied polymers containing 9,10-anthracene (three fused benzene rings). Polymers 04, 11, 20, 26 and 36 contain 2,6-naphthalene. In this case π-conjugation along the backbone must pass through both benzene rings.

Polymers 02, 18, 32, 38, 39 and 40 contain a benzonitrile CN group. These polymers are intended for blending with the chromium and vanadium-containing polyacrylonitrile materials developed in the Nizhny Novgorod laboratory. In addition, they contain donor-acceptor groups, as do polymers 01, 10, and 17, to enhance the second order nonlinear optical properties.

In some cases, long chains have been introduced into the polymers. For example, polymers 12, 21, and 34 contain terthiophene with two long chains, and polymer 41 contains 9,10-anthracene with two long chains. The effects of the long chains are threefold: 1) increased electron density on the arylene, 2) increased solubility and compatibility, and 3) change in the aggregation and π-stacking properties of the polymers (see below).

The binaphthalenyl polymers 22, 30 and 37 contain a chiral centre and may be obtained optically pure. Such chiral polymers should give nanostructured films formed by regular aggregation of the single-handed helical polymer chains giving rise to enhanced nonlinear optical properties.

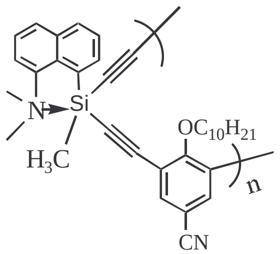
Polymers 15, 25 and 31 have a disulphide linkage in the backbone which should allow along-chain conjugation through the sulphur bonds involving the S d-orbitals.

INVESTIGATIONS OF OPTICAL PROPERTIES IN UV/VIS AND NIR SPECTRAL REGIONS

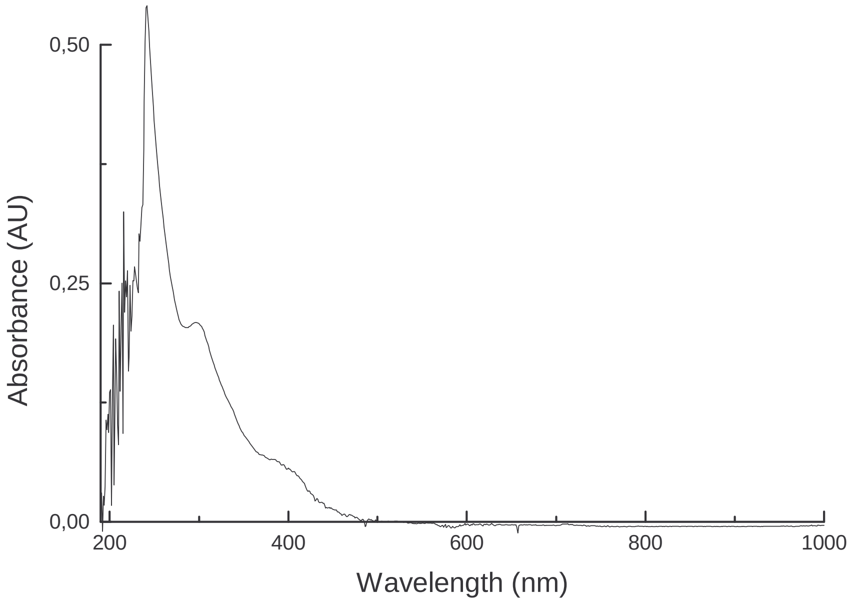
(a) SILICON-CONTAINING POLYMERS

The spectral results have enabled us to select two main groups of polymers.

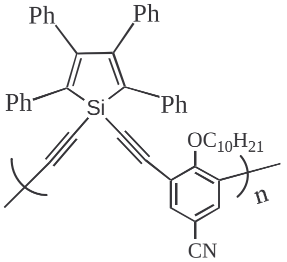
(1) The first group consists of new candidates for Kerr investigations in the non-resonant region around 1000 nm. These show UV absorptions below 450 nm thus avoiding resonant phenomena in the wavelength region used for the Kerr measurements. As was described in the first report, one of the polymers with the highest Kerr nonlinearity was that containing pentacoordinate silicon together with an amide acceptor group on the backbone benzene ring. We designed polymer 32 to also contain pentacoordinate silicon but in this case we incorporated the considerably stronger CN acceptor group together with an alkoxy $OC_{10}H_{21}$ strong donor group in the para postion.



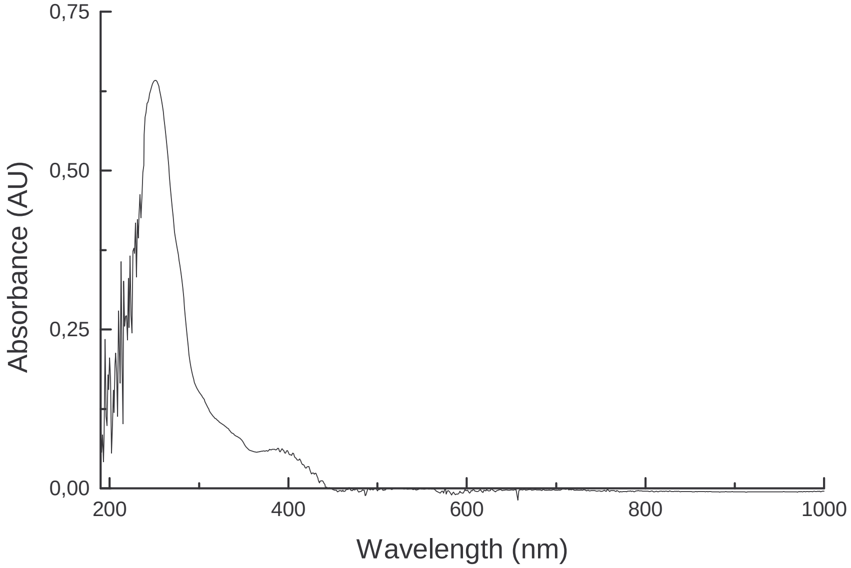
This donor-acceptor arylene is intended to enhance the second order nonlinear optical response. Since the polymer exhibits UV absorption below 450 nm it should also exhibit a high non-resonant third order nonlinearity:



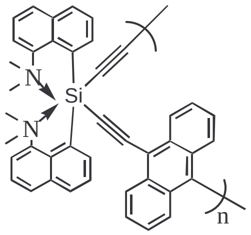
The analogous polymer 39 has the same donor-acceptor arylene but a tetraphenylsilole group in place of the pentacoordinate silicon.

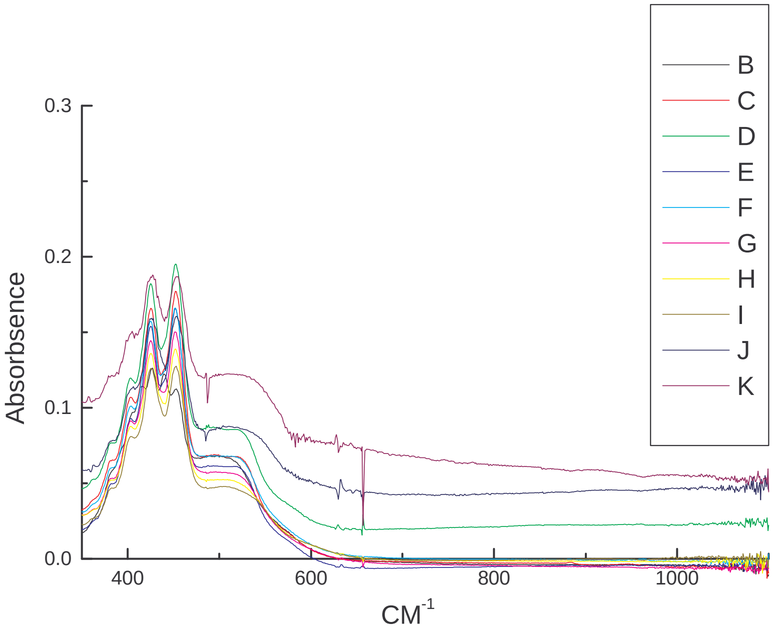


We have found that pentacoordinate silicon favours high Kerr nonlinearities, probably because of the electron deficient nature of the silicon. The silole ring, like pentacoordinate silicon, acts as an electron acceptor (J. Amer. Chem. Soc., (1998), 120, 4552) and so polymer 39 containing silole groups should show high Kerr nonlinearities in the 1000 nm region there being no absorption above 450 nm:



(2) The second group of polymers consists of those designed for photorefraction in the NIR region. The multifunctional polymer exhibiting photorefraction at telecommunication wavelengths described previously (third report) contains tetracoordinate silicon and anthracene groups in the backbone. This polymer is active because of the long absorption tail stretching well into the IR in the case of the polymer films (but not solutions). We ascribe this effect to π-stacking in the solid state, arising predominantly from the presence of anthracene groups for which this effect is well known. Such π-stacking is considered to result in larger optical third-order nonlinear susceptibilities (Chem. Mater. (1997), **9**, 1217). We are investigating the π-stacking effect by addition of methanol non-solvent to the solution thus forming a colloid which mimics the aggregation occurring in the film. This method (JACS, (1998), **120**, 2047) enables us to screen polymers for potential photorefractive activity in the NIR region. For example, the spectra below show the effect of addition of increasing amounts of methanol non-solvent (ranging from B [no methanol] to K [90% methanol]) for the polymer containing hexacoordinate silicon and anthracene.

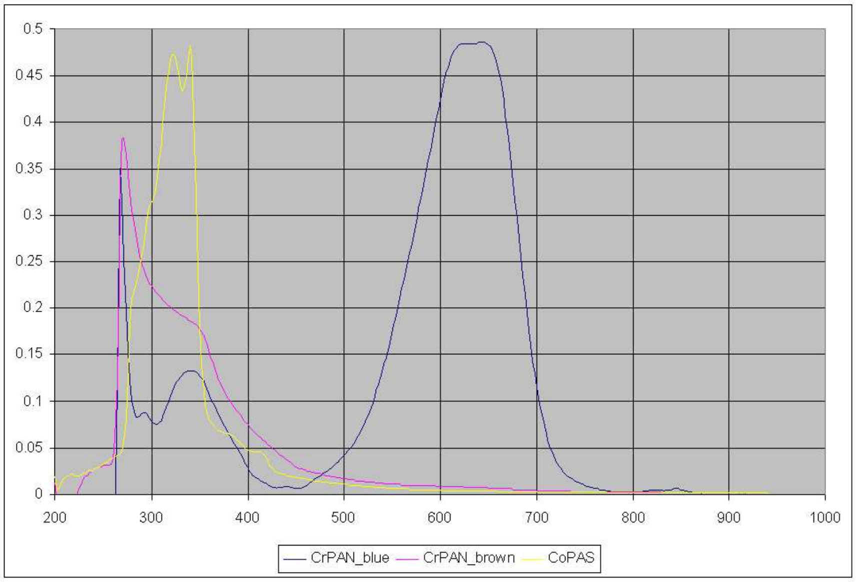




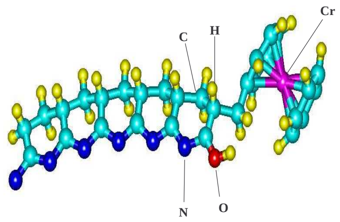
This polymer is a very promising candidate as a charge generator in the NIR region in photorefractive compositions - its properties are being studied at present. Possibly the photorefractive effects we have observed in the NIR are the result of nanoparticle aggregates of π-stacked polymer chains similar to the colloidal particles produced by addition of the methanol non-solvent to the polymer solution. We will use electron microscopy and X-ray diffraction to examine the composite films for the presence of such nanostructures.

(b) TRANSITION METAL -CONTAINING POLYMERS

The UV/visible spectra of the chromium-containing polyacrylonitrile and cobalt carbonyl-containing polymers in solution are shown below.

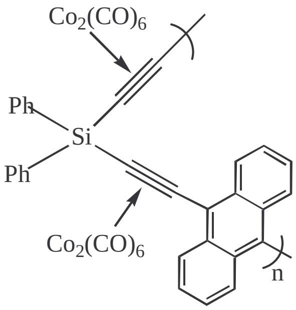


CrPAN_brown consists of a (bis-benzene)chromium sandwich bonded to a polynaphthyridine chain:



CrPAN_blue is the blue charge-transfer material formed by chromium-containing polyacrylonitrile in the presence of the strong electron-acceptor tetracyanoethylene (TCNE).

CoPAS is the following cobalt-containing polymer:

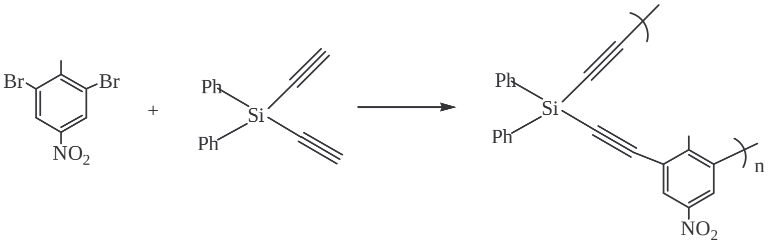


The formation of the CrPAN charge transfer complex with TCNE has a dramatic effect on the UV/visible spectrum, the maximum being shifted from 350 nm (pink line) to 630 nm (purple line). This is very promising for the photorefractive properties of composite films containing the CrPAN_blue material - these are being investigated at present.

Although incorporation of cobalt into the silicon-containing polymer has little effect on the position of maximum absorbance (yellow line), the tail extends considerably further towards the IR. It is expected that in the films this effect will be enhanced giving rise to improved photorefraction properties at telecommunication wavelengths. This effect is being investigated at present.

EXPERIMENTAL SECTION (Polymer Preparation)

Polymer-01



1,3-Dibromo-2-methyl-5-nitro-benzene(0.37g, 1.25mmol), diphenyldiethynylsilane (0.29g, 1.25mmol), $Pd(Ph_3P)_2Cl_2$ (3.2mg, 4.56×10^{-3}mmol), CuI (5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 12 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.44 g brown solid was obtained (96%).

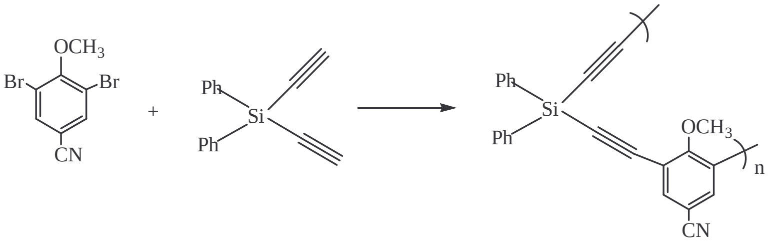
IR: 2158 cm^{-1}

^{1}HNMR($CDCl_3$): 7.3-8.5(12H), 2.56(3H)

^{13}CNMR: 104.9, 95.3

^{29}SiNMR: -47.16

Polymer-02



3,5-Dibromo-4-methoxy-benzonitrile(0.36g, 1.25mmol), diphenyldiethynylsilane(0.29g, 1.25mmol), $Pd(Ph_3P)_2Cl_2$(3.2mg, 4.56×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 36 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.27 g yellow solid was obtained (60%).

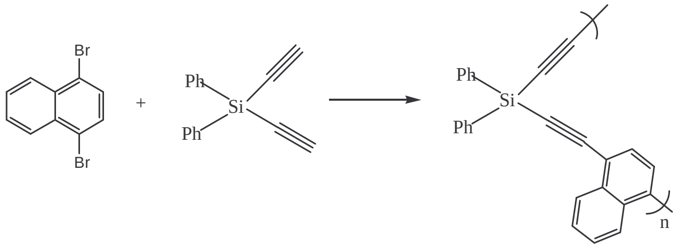
IR: 2166 cm^{-1}

^{1}HNMR($CDCl_3$): 7-8 (12H), 4.2 (3H)

^{13}CNMR: 107.7, 95.4

^{29}SiNMR: -47.18

Polymer-03



1,4-Dibromo-naphthalene (0.36g, 1.25mmol), diphenyldiethynylsilane(0.29g, 1.25mmol), $Pd(Ph_3P)_2Cl_2$(3.2mg, 4.56×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.35 g brown solid was obtained (80%).

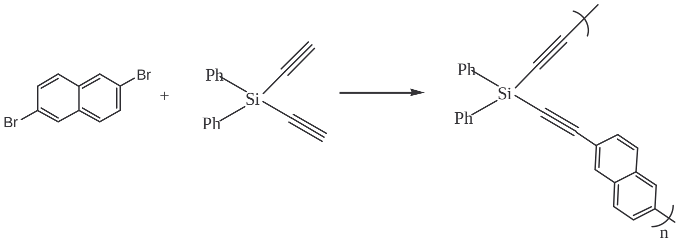
IR: 2152 cm^{-1}

^{1}HNMR($CDCl_3$): 7.3-8.5

^{13}CNMR: 107.1, 95.5

^{29}SiNMR: -47.4

Polymer-04



2,6-Dibromo-naphthalene (0.36g, 1.25mmol), diphenyldiethynylsilane(0.29g, 1.25mmol), $Pd(Ph_3P)_2Cl_2$(3.2mg, 4.56×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 85° for 3 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.42 g pale yellow solid was obtained (94%).

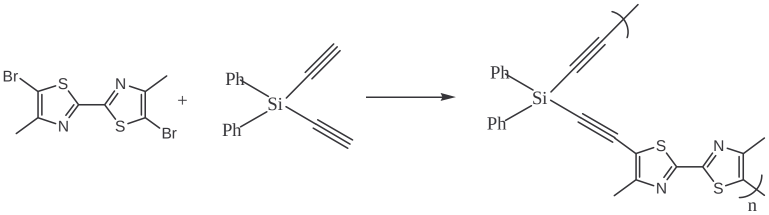
IR: 2152 cm^{-1}

^{1}HNMR($CDCl_3$): 7.3-8.0

^{13}CNMR: 109.3-89.5

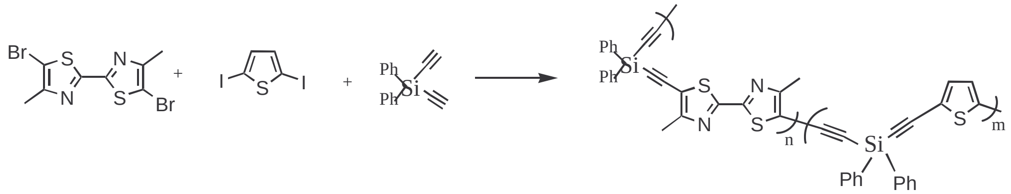
^{29}SiNMR: -47.68

Polymer-06



5,5'-Dibromo-4,4'-dimethyl-[2,2']bithiazolyl (0.354g, 1mmol), diphenyldiethynylsilane(0.232 g, 1mmol), $Pd(Ph_3P)_2Cl_2$(3.2mg, 4.56×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 85° for 3 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.41g yellow solid was obtained (97%).
IR: 2147 cm^{-1}
^{1}HNMR($CDCl_3$): 7.87 (4H), 7.44(6H), 2.64 (6H)
^{13}CNMR: 114.0, 97.6
^{29}SiNMR: -47.35

Polymer-07

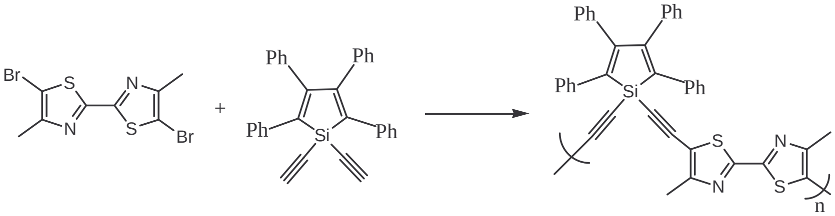


5,5'-Dibromo-4,4'-dimethyl-[2,2']bithiazolyl (0.177g, 0.5mmol), 2, 5-diiodothiophene (0.167g, 0.5mmol), diphenyldiethynylsilane(0.232 g, 1mmol), $Pd(Ph_3P)_2Cl_2$(3.2mg, 4.56×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.30g brown solid was obtained (81%).
IR: 2147 cm^{-1}
^{1}HNMR($CDCl_3$): 7.86-7.27 (11H), 2.63 (3H)
^{13}CNMR: 114.3, 99.6, 97.6, 92.4
^{29}SiNMR: -47.33

Polymer-08

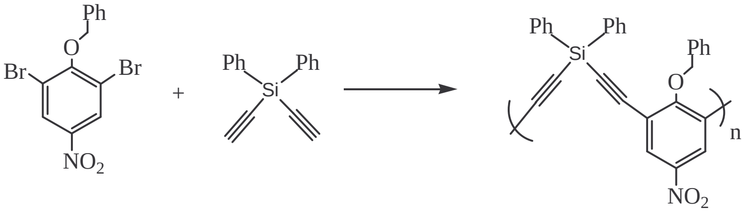
2, 5-diiodothiophene (0.167g, 0.5mmol), diphenyldiethynylsilane(0.232 g, 1mmol), $Pd(Ph_3P)_2Cl_2$(3.6mg, 5.13×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 4h. Then 5,5'-Dibromo-4,4'-dimethyl-[2,2']bithiazolyl (0.177g, 0.5mmol) was added. The reaction mixture was heated for another 12h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.32g red solid was obtained (86%).
IR: 2147 cm^{-1}
^{1}HNMR($CDCl_3$): 7.2-8.1 (11H), 2.63(3H)
^{13}CNMR: 115.1, 99.5, 97.6, 92.4
^{29}SiNMR: -47.35

Polymer-09



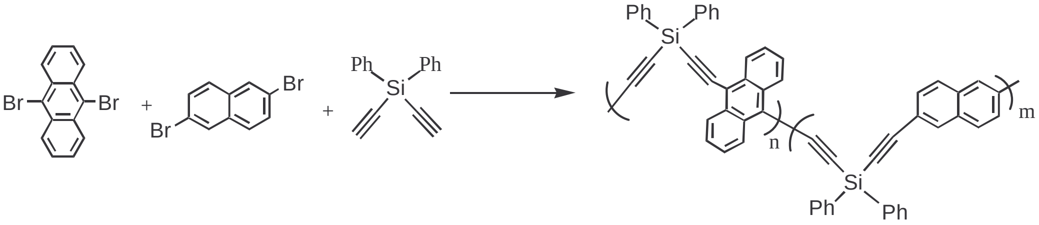
5,5'-Dibromo-4,4'-dimethyl-[2,2']bithiazolyl (0.354g, 1mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.435g, 1mmol), Pd(Ph_3P)$_2$$Cl_2$(3.6mg, 5.13×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 85° for 4 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.61g orange solid was obtained (97%).
IR: 2144 cm^{-1}
^{1}HNMR($CDCl_3$): 6.5-7.5 (10H), 2.63 (3H), 2.46 (3H)
^{13}CNMR: 99.2, 97.1, 90.0, 88.0
^{29}SiNMR: -45.50

Polymer-10



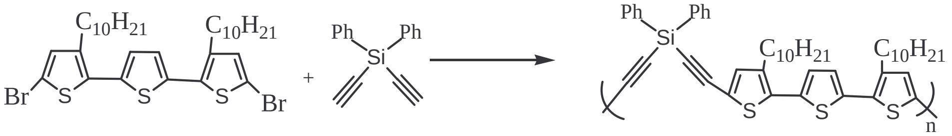
1,3-Dibromo-2-benzyloxy-5-nitro-benzene (0.48g, 1mmol), diphenyldiethynylsilane(0.232 g, 1mmol), Pd(Ph_3P)$_2$$Cl_2$(3.6mg, 5.13×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 24 h. Most of polymer precipitated from solution. After removing solvent, the residue was taken up with THF and then filtered. Filtrate was concentrated and added pentane to precipitate polymer. 0.25g brown solid was obtained (54%).
IR: 2164 cm^{-1}
^{1}HNMR($CDCl_3$): 6.8-8.5 (17H), 4.64 (2H)
^{13}CNMR: 117.4, 88.3
^{29}SiNMR:

Polymer-11



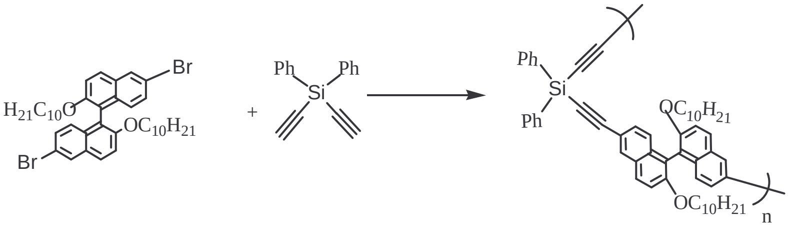
9,10-dibromo-anthracene (0.168g, 0.5mmol), 2,6-dibromo-naphthalene (0.143g, 0.5mmol), diphenyldiethynylsilane (0.232g, 1mmol), Pd($Ph_3P)_2Cl_2$(2.6mg, 3.70×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 4h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.35 g red solid was obtained (94%).
IR: 2156 cm^{-1}, 2130 cm^{-1}
^{1}HNMR($CDCl_3$): 7.4-9.0
^{13}CNMR: 109.4, 109.3, 105.8, 105.7, 102.2, 89.5
^{29}SiNMR: -47.16, -47.55. –47.64

Polymer-12



5,5''-Dibromo-3,3''-bis-decyl-[2,2';5',2'']terthiophene (0.343g, 0.5mmol), diphenyldiethynyl silane (0.166g, 0.5mmol), Pd($Ph_3P)_2Cl_2$(6.5mg, 9.26×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 3.5h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.29 g red solid was obtained (76%).
IR: 2144 cm^{-1}
^{1}HNMR($CDCl_3$): 7.91-7.46(10H), 7.30-6.99(4H), 2.83(4H), 1.69(4H), 1.32(28H), 0.93(6H)
^{13}CNMR: 102.0, 93.4
^{29}SiNMR: -47.72

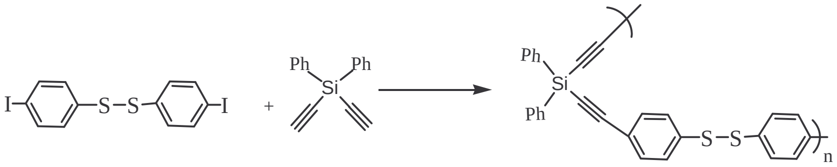
Polymer-14



6,6'-Dibromo-2,2'-didecyloxy-[1,1']binaphthalenyl (0.726g, 1mmol), diphenyldiethynyl silane (0.232g, 1mmol), Pd($Ph_3P)_2Cl_2$(5.9mg, 8.40×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 4h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.52 g red solid was obtained (65%).
IR: 2153 cm^{-1}

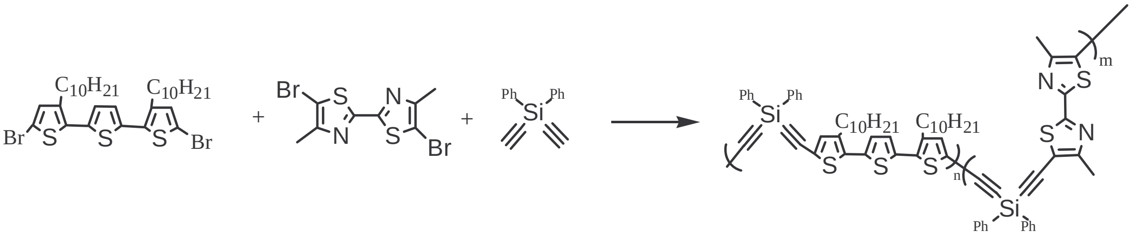
^{1}HNMR($CDCl_3$): 8.13-7.05(20H), 3.91(4H), 1.32-0.85(38H)
^{13}CNMR: 110.0, 87.7
^{29}SiNMR: -47.92

Polymer-15



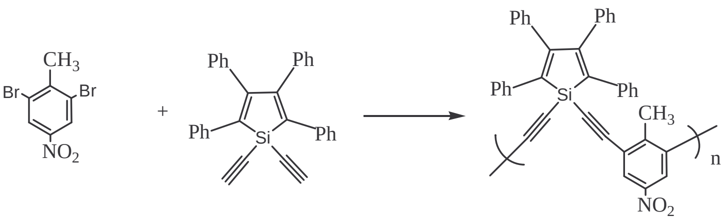
4,4'- (0.47g, 1mmol), diphenyldiethynylsilane (0.232g, 1mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.43 g red solid was obtained (96%).
IR: 2160 cm^{-1}
^{1}HNMR($CDCl_3$): 7.0-7.9
^{13}CNMR: 97.7, 93.1, 89.2, 84.3
^{29}SiNMR: -47.80

Polymer-16



5,5''-Dibromo-3,3''-bis-decyl-[2,2';5',2'']terthiophene(0.344g, 0.5mmol), 5,5'-Dibromo-4,4'-dimethyl-[2,2']bithiazolyl(0.177g, 0.5mmol), diphenyldiethynylsilane (0.232g, 1mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 24 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.15 g red solid was obtained (25%).
IR: 2146 cm^{-1}
^{1}HNMR($CDCl_3$): 7-8 (14H), 2.79(2H), 2.65(3H), 1.69(2H), 1.31(14H), 0.92(3H)
^{13}CNMR: 115.14, 98.55
^{29}SiNMR: -47.26, -47.33

Polymer-17



2,6-dibromo-1-methyl-4-nitro-benzene(0.295g, 1mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.435g, 1mmol), $Pd(Ph_3P)_2CI_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 6 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.40g yellow solid was obtained (70%).

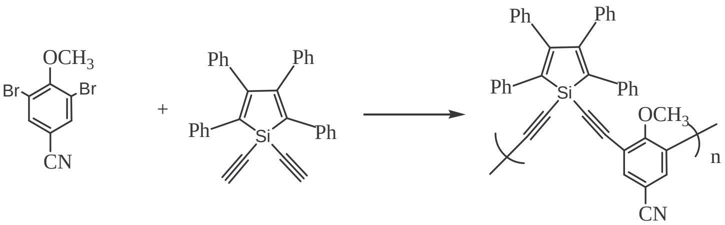
IR: 2157 cm^{-1}

^{1}HNMR($CDCl_3$): 6.5-8.5(22H), 2.42(3H)

^{13}CNMR: 103.8, 100.0, 95.7, 91.6

^{29}SiNMR: -45.30

Polymer-18



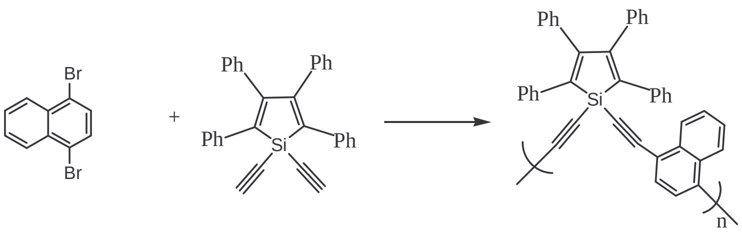
3,5-Dibromo-4-methoxy-benzonitrile(0.276g, 0.95mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.414g, 0.95mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 24 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.40g yellow solid was obtained (74%).

^{1}HNMR($CDCl_3$): 6.5-8.0(22H), 4.00(3H)

^{13}CNMR: 99.7, 97.4, 90.2, 84.6

^{29}SiNMR: -45.55

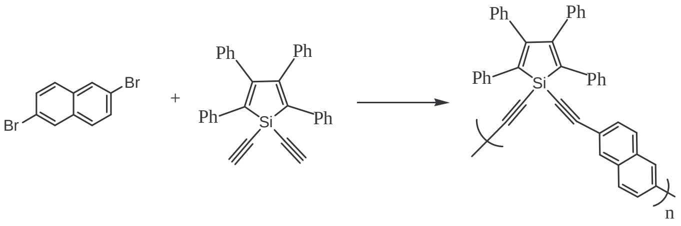
Polymer-19



1,4-dibromo-naphthalene(0.286g, 1mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.435g, 1mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 4 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.43g yellow solid was obtained (77%).

IR: 2147cm^{-1}
^{1}HNMR($CDCl_3$): 6.5-8.5
^{13}CNMR: 107.1, 93.4
^{29}SiNMR: -45.11

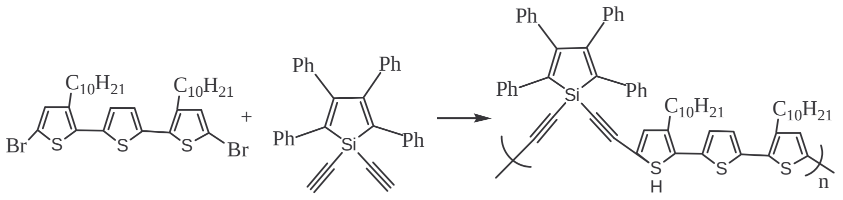
Polymer-20



2,6-dibromo-naphthalene(0.286g, 1mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.435g, 1mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 4 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.47g orange solid was obtained (84%).

IR: 2147cm^{-1}
^{1}HNMR($CDCl_3$): 6.5-8.0
^{13}CNMR: 109.2, 87.4
^{29}SiNMR: -45.50

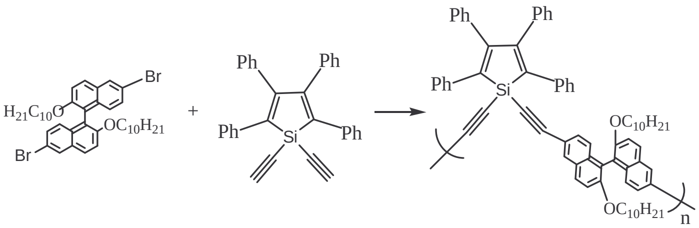
Polymer-21



5,5''-Dibromo-3,3''-bis-decyl-[2,2';5',2'']terthiophene (0.343g, 0.5mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.218g, 0.5mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.40g red solid was obtained (95%).

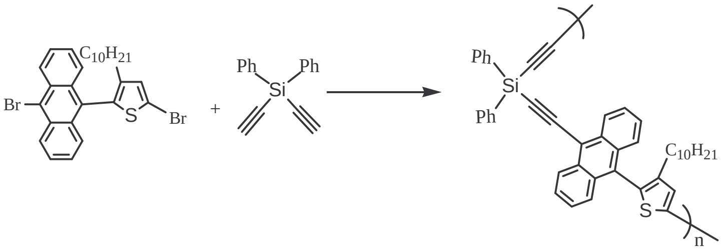
IR: 2142cm^{-1}
^{1}HNMR($CDCl_3$): 6.5-7.5(24H), 3.78(4H), 1.68(4H), 1.32(28H), 0.93(6H)
^{29}SiNMR: -45.93

Polymer-22



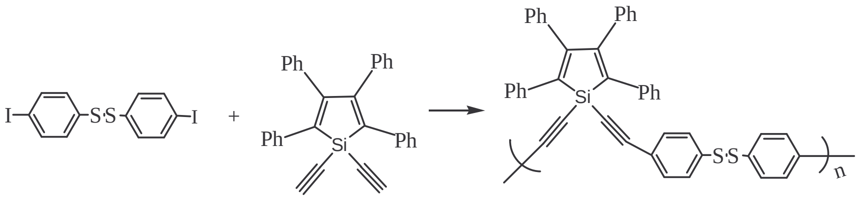
6,6'-Dibromo-2,2'-didecyloxy-[1,1']binaphthalenyl (0.363g, 0.5mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.218g, 0.5mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 12h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.40g red solid was obtained (95%).
IR: 2151cm^{-1}
^{1}HNMR($CDCl_3$): 6.5-8.2(30H), 3.99(4H), 0.9-1.47(38H)
^{13}CNMR: 109.9, 85.9
^{29}SiNMR: -45.51

Polymer-23



5-Bromo-2-(10-bromo-anthracen-9-yl)-3-methyl-thiophene(0.35g, 0.62mmol), diphenyl diethynylsilane (0.145g, 0.62mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.25 g yellow solid was obtained (64%).
IR: 2146 cm^{-1}
^{1}HNMR($CDCl_3$): 6.5-8.9(19H), 2.19(2H), 0.89-1.20(19H)
^{13}CNMR: 106.2, 102.1, 101.1, 93.4
^{29}SiNMR: -47.32

Polymer-25



4-iodophenyl-disulfide (0.24g, 0.5mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.22g, 0.5mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5.0×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.28g yellow solid was obtained (85%).

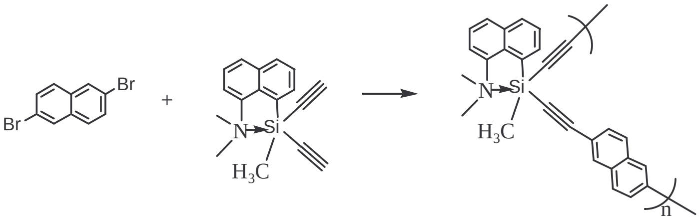
IR: 2158cm^{-1}

^{1}HNMR($CDCl_3$): 6.7-7.8

^{13}CNMR: 117.4, 108.3, 93.14, 87.35

^{29}SiNMR: -45.69

Polymer-26



2,6-dibromo-naphthalene(0.286g, 1mmol), [8-(Diethynyl-methyl-silanyl)-naphthalen-1-yl]-dimethyl-amine(0.263g, 1mmol), $Pd(Ph_3P)_2Cl_2$(4.2mg, 5.98×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.37g beige solid was obtained (95%).

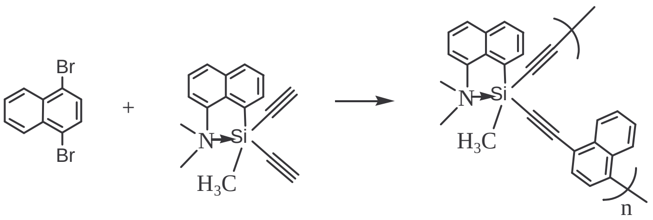
IR: 2155cm^{-1}

^{1}HNMR($CDCl_3$): 7.4-8.8(12H), 2.80(6H), 0.85(3H)

^{13}CNMR: 105.0, 104.7, 97.0, 93.2

^{29}SiNMR: -54.53, -55.51

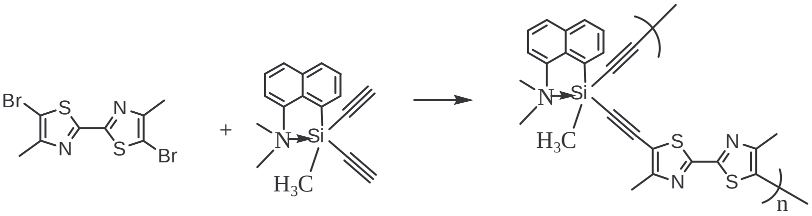
Polymer-27



1,4-dibromo-naphthalene(0.286g, 1mmol), [8-(Diethynyl-methyl-silanyl)-naphthalen-1-yl]-dimethyl-amine(0.263g, 1mmol), $Pd(Ph_3P)_2Cl_2$(4.2mg, 5.98×10^{-3}mmol),

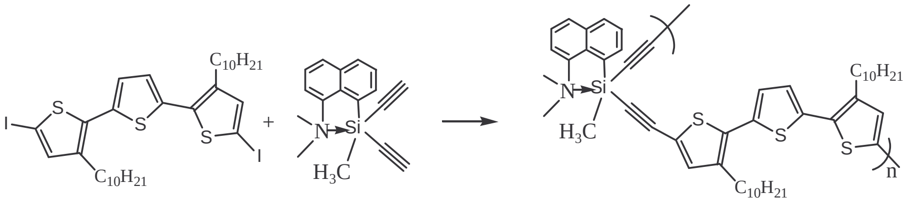
CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.21g yellow solid was obtained (54%).
^{1}HNMR($CDCl_3$): 7.0-8.9(12H), 2.87(6H), 0.96(3H)
^{13}CNMR: 103.3, 103.1, 93.2, 91.8
^{29}SiNMR: -54.79

Polymer-28



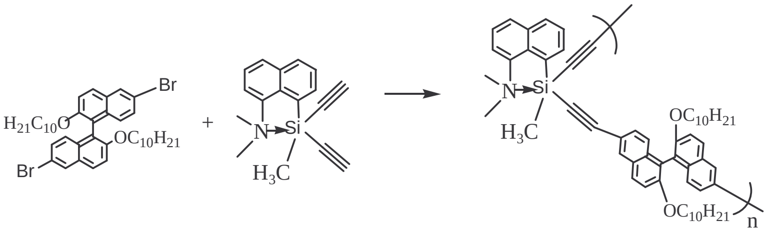
5,5'-Dibromo-4,4'-dimethyl-[2,2']bithiazolyl (0.354g, 1mmol), [8-(Diethynyl-methyl-silanyl)-naphthalen-1-yl]-dimethyl-amine(0.263g, 1mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.26g orange solid was obtained (57%).
IR: 2145cm^{-1}
^{1}HNMR($CDCl_3$):7.0-8.5(6H), 2.41-2.74(12H), 0.75(3H)
^{13}CNMR: 107.3, 94.5, 89.9, 87.8
^{29}SiNMR: -55.97

Polymer-29



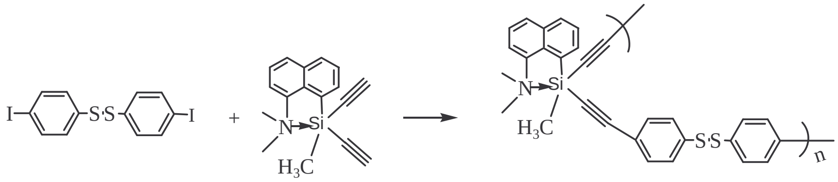
3,3''-Bis-decyl-5,5''-diiodo-[2,2';5',2'']terthiophene (0.450g, 0.57mmol), [8-(Diethynyl-methyl-silanyl)-naphthalen-1-yl]-dimethyl-amine(0.151g, 0.57mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.34g solid was obtained (79%).
IR: 2144cm^{-1}
^{1}HNMR($CDCl_3$): 7.0-8.6(10H), 2.82(10H), 1.69(4H), 1.33(32H), 0.95(6H)
^{13}CNMR: 101.3, 97.6
^{29}SiNMR: -54.77

Polymer-30



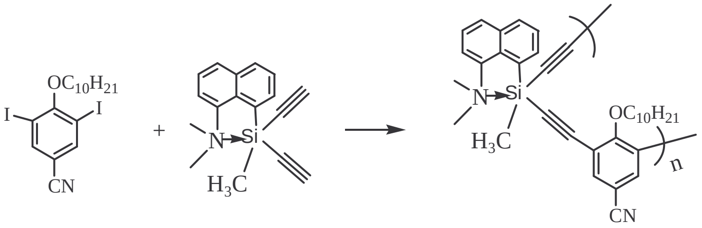
6,6'-Dibromo-2,2'-bis-decyloxy-[1,1']binaphthalenyl (0.400g, 0.55mmol), [8-(Diethynyl-methyl-silanyl)-naphthalen-1-yl]-dimethyl-amine(0.145g, 0.55mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 7h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.31g light brown solid was obtained (67%).
IR: 2153cm^{-1}
^{1}HNMR($CDCl_3$): 7.0-8.7(16H), 3.97(4H), 2.80(6H), 1.27-0.78(38H)
^{13}CNMR: 105.4, 95.2, 90.3, 85.1
^{29}SiNMR: -53.95

Polymer-31



4-aminophenyl-disulfide(0.396g, 0.84mmol), [8-(Diethynyl-methyl-silanyl)-naphthalen-1-yl]-dimethyl-amine(0.222g, 0.84mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 20h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.32g beige solid was obtained (67%).
IR: 2160cm^{-1}
^{1}HNMR($CDCl_3$): 7.0-8.6(13H), 2.77(6H), 0.76(3H)
^{13}CNMR: 104.0, 97.1
^{29}SiNMR: -54.68

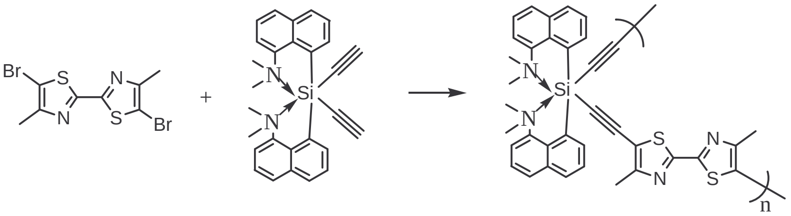
Polymer-32



4-Decyloxy-3,5-diiodo-benzonitrile(0.400g, 0.55mmol), [8-(Diethynyl-methyl-silanyl)-naphthalen-1-yl]-dimethyl-amine(0.145g, 0.55mmol), Pd(Ph_3P)$_2$$Cl_2$(5.0mg, 7.12×$10^{-3}$mmol), CuI(5.3mg, 2.56×$10^{-2}$mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 7h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.31g light brown solid was obtained (67%).

IR: 2161cm^{-1}

Polymer-33



5,5'-Dibromo-4,4'-dimethyl-[2,2']bithiazolyl(0.354g, 1mmol), di(8-dimethylamino-1-naphthyl)-diethynylsilane(0.419g, 1mmol), Pd(Ph_3P)$_2$$Cl_2$(5.0mg, 7.12×$10^{-3}$mmol), CuI(5.3mg, 2.56×$10^{-2}$mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 60h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.54g brown solid was obtained (89%).

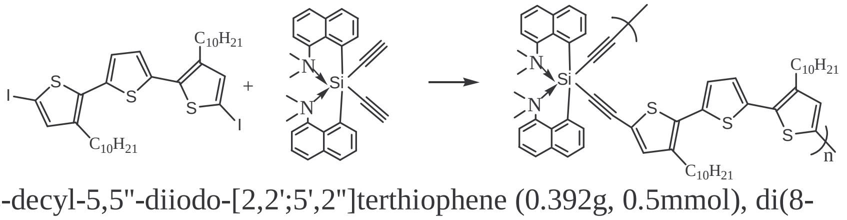
IR: 2145cm^{-1}

^{1}HNMR($CDCl_3$): 7.2-8.9(12H), 2.69(6H), 2.43(6H), 1.40(6H)

^{13}CNMR: 110.8, 107.7, 95.2, 94.1

^{29}SiNMR: -63.29

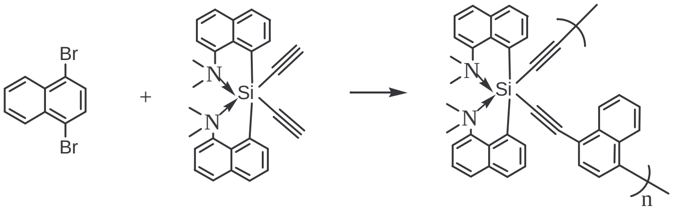
Polymer-34



3,3''-Bis-decyl-5,5''-diiodo-[2,2';5',2'']terthiophene (0.392g, 0.5mmol), di(8-dimethylamino-1-naphthyl)-diethynylsilane(0.210g, 0.5mmol), Pd(Ph_3P)$_2$$Cl_2$(6.0mg, 8.55×$10^{-3}$mmol), CuI(5.3mg, 2.56×$10^{-2}$mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were

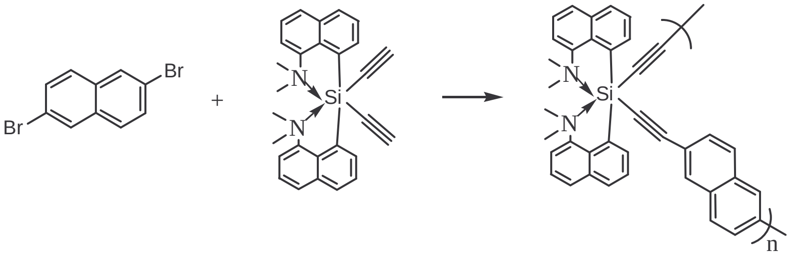
put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 60h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.35g yellow solid was obtained (74%).
IR: 2143cm^{-1}
^{1}HNMR($CDCl_3$): 7.0-8.8(16H), 2.71(10H), 0.9-1.64(44)
^{13}CNMR: 104.8, 98.2
^{29}SiNMR: -61.98

Polymer-35



1,4-dibromo-naphthalene(0.286g, 1mmol), di(8-dimethylamino-1-naphthyl)-diethynylsilane(0.419g, 1mmol), $Pd(Ph_3P)_2Cl_2$(10.0mg, 1.42×10^{-2}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 20h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.52g yellow solid was obtained (96%).
IR: 2148cm^{-1}
^{1}HNMR($CDCl_3$): 7.1-9.1(18H), 2.72(6H), 1.44(6H)
^{13}CNMR: 106.7, 103.8
^{29}SiNMR: -61.54

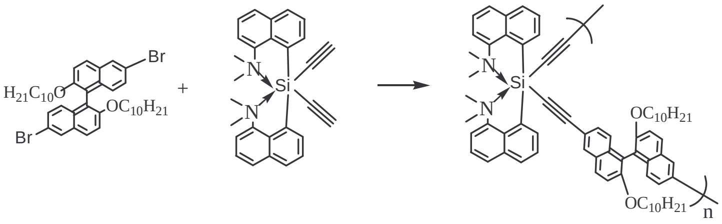
Polymer-36



2,6-dibromo-naphthalene(0.286g, 1mmol), di(8-dimethylamino-1-naphthyl)-diethynylsilane(0.419g, 1mmol), $Pd(Ph_3P)_2Cl_2$(10.0mg, 1.42×10^{-2}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 5h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.51g off white solid was obtained (94%).
IR: 2151cm^{-1}

^{1}HNMR($CDCl_3$): 9.02-7.29(18H), 2.71(6H), 1.35(6H)
^{13}CNMR: 105.7, 100.2
^{29}SiNMR: -61.07

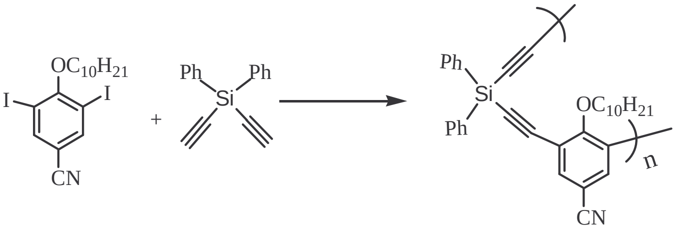
Polymer-37



6,6'-Dibromo-2,2'-bis-decyloxy-[1,1']binaphthalenyl(0.726g, 1mmol), di(8-dimethylamino-1-naphthyl)-diethynylsilane(0.419g, 1mmol), $Pd(Ph_3P)_2Cl_2$(10.0mg, 1.42×10^{-2}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.92g light yellow solid was obtained (94%).

IR: 2151cm^{-1}
^{1}HNMR($CDCl_3$): 9.10-7.03(22H), 3.94(4H), 2.75(6H), 1.40-0.89(44H)
^{13}CNMR: 106.2, 98.6
^{29}SiNMR: -60.12

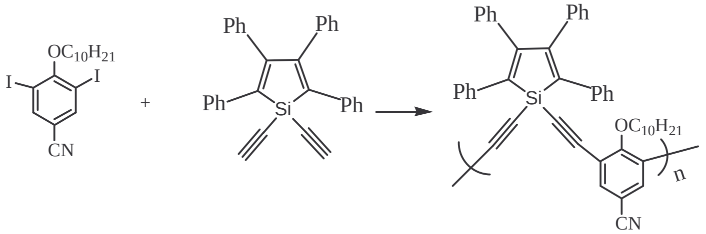
Polymer-38



4-Decyloxy-3,5-diiodo-benzonitrile (0.512g, 1mmol), diphenyldiethynylsilane(0.232g, 1mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 72h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.41g pink solid was obtained (84%).

IR: 2165cm^{-1}
^{1}HNMR($CDCl_3$): 7.77-7.44(12H), 4.32(2H), 1.60-1.12(19H)
^{13}CNMR: 107.2, 102.7, 98.0, 95.3
^{29}SiNMR: -47.42

Polymer-39



4-Decyloxy-3,5-diiodo-benzonitrile (0.512g, 1mmol), 1,1-Diethynyl-2,3,4,5-tetraphenyl-1H-silole (0.435g, 1mmol), $Pd(Ph_3P)_2Cl_2$(5.0mg, 7.12×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 36h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.51g yellow solid was obtained (94%).

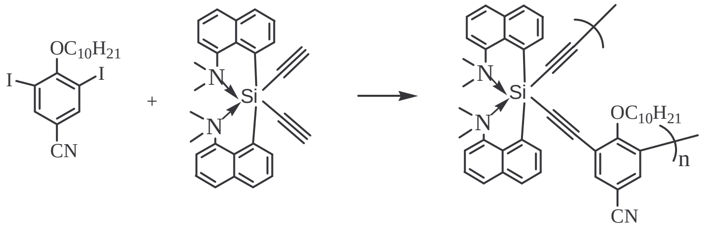
IR: 2151cm^{-1}

^{1}HNMR($CDCl_3$): 7.69-6.69(22H), 4.52-4.20(2H), 1.87-0.88(19H)

^{13}CNMR: 102.6, 93.2

^{29}SiNMR: -45.79

Polymer-40



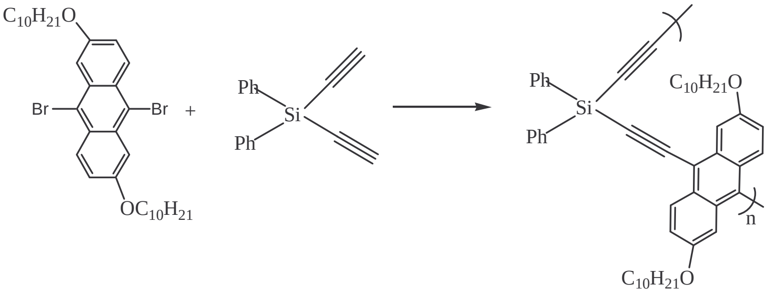
4-Decyloxy-3,5-diiodo-benzonitrile (0.512g, 1mmol), di(8-dimethylamino-1-naphthyl)-diethynylsilane(0.419g, 1mmol), $Pd(Ph_3P)_2Cl_2$(10.0mg, 1.42×10^{-2}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2}mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 72h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.42g offwhite solid was obtained (62%).

IR: 2160 cm^{-1}

^{1}HNMR($CDCl_3$): 8.86-7.29(14H), 4.10(2H), 2.69(6H), 1.34(19H), 0.96(6H)

^{13}CNMR: 106.26, 93.98

Polymer-41



9,10-Dibromo-2,6-bis-decyloxy-anthracene (0.324g, 0.5mmol), diphenyldiethynylsilane (0.116 g, 0.5mmol), Pd(Ph_3P)$_2$Cl$_2$(3.2mg, 4.56×10^{-3}mmol), CuI(5.3mg, 2.56×10^{-2}mmol) and Ph_3P (13.2mg, 5×10^{-2} mmol) were put into a degassed solution of 5ml toluene and 1ml triethylamine. The reaction mixture was heated to 90° for 16 h. After the reaction was cooled to r.t., the precipitate was filtered off and the solvent was removed under vacuum. The residue was taken up with CH_2Cl_2 and then precipitated from methanol. 0.31g dark red solid was obtained (84%).
IR: 2142 cm^{-1}
^{1}HNMR($CDCl_3$): 8.63-7.29(16H), 3.91(4H), 1.93-0.90(38H)
^{13}CNMR: 106.64, 104.38
^{29}SiNMR: -47.46

CONCLUSIONS

In the first report we described the very high Kerr-type nonlinear optical properties of solutions and films of the novel organometallic polymers containing silicon or chromium or vanadium. The second and third reports concerned the new photorefractive properties of the silicon-containing polymers at 833 nm and 1500 nm, respectively. It was found that (a) the polymers can be incorporated into composites showing photorefraction even in the absence of an applied electric field with no preliminary poling, and (b) they can be used as multifunctional materials for photorefraction at telecommunication wavelengths giving a net gain up to 10 cm^{-1}.

The results of these studies have been used to tune the chemical structures of the polymers. A large number of specifically designed tailor-made organometallic polymers for the ongoing Kerr and photorefractive optical studies has been synthesized and structurally characterized. The UV/visible spectra in solution have enabled the separation of the polymers into two groups - those likely to give high Kerr non-linearities around 1000 nm, and those for photorefraction at telecommunication wavelengths. The very interesting photorefractive properties of the polymers at 1500 nm are probably connected to the formation of nano-aggregates in the composite films through π-stacking. Indeed, such π-stacking favours larger optical third-order nonlinear susceptibilities. The π-stacking properties of the polymers have been investigated by studying the UV/visible spectra of colloids formed on addition of a non-solvent to the polymer solutions the colloids being models for the nano-aggregates in the films. The Kerr and photorefractive properties of the new polymers are being studied at present under the new contract. Electron microscopy and X-ray diffraction will be used to examine the composite films for the presence of nano-aggregates. The new project involves essentially optical studies on these polymers, and it is not envisaged that a further substantial chemical synthetic effort will be required.

The Contractor, Universite Montpellier II,, hereby delcares that, to the best of its knowledge and belief, the technical data delivered herewith under Contract No. F61775-01-WE058 is complete, accurate, and complies with all requirements of the contract.

DATE: **13 September 2002**

Name and Title of Authorized Official: **Dr. W.E. DOUGLAS** W. E. D

I certify that there were no subject inventions to declare as defined in FAR 52.227-13, during the performance of this contract.

DATE: **13 September 2002**

Name and Title of Authorized Official: **Dr. W.E. DOUGLAS** W. E. D