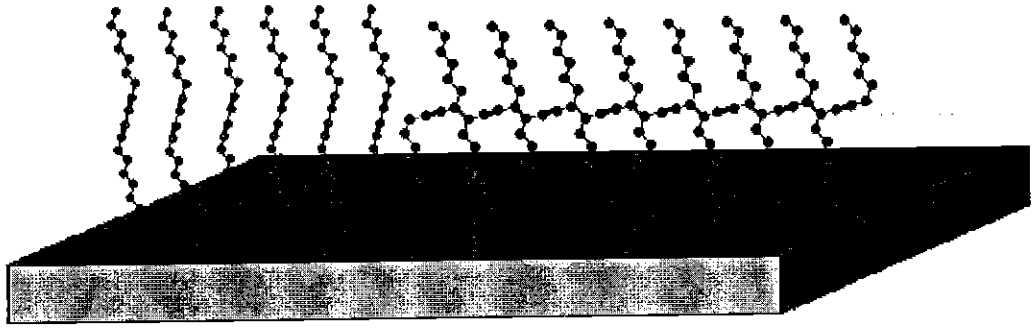
Building the molecular wire

Assembly of covalently bound diacetylene-containing monolayers on silicon surfaces



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Abstract

Formation of molecular wires through polymerisation of diacetelenic moieties in self-assembled monolayers on gold and silver surfaces, have been extensively studied. Molecular wires in covalently bound monolayers on silicon however, have not yet been reported. Established methods for monolayer assembly on silicon involve the use of high temperatures or UV-irradiaton, and are unsuitable for diacetylenic molecules. However, the recently in this laboratory developed vacuum method requires no light and can be performed at low temperatures. Therefore it is very mild and proves to be very promising.
Experiments with monolayers of newly synthesized diacetylenic compounds confirm the success of this new method. Strong interaction of the triple bonds with the surface however, disturbs regular monolayer formation and results in low quality monolayers. Furthermore this attachment of the diacetylene to the surface renders polymerisation, and the subsequent formation of a nanowire impossible. Other methods (thermal and visible light) are also tested and yield the same interaction. A solution to this problem has unfortunately not yet been found.

Contents

1 Introduction

General introduction

Silicon has been playing a large role in the recent history of electronics. Its semiconductor properties and its availability have turned this material in the substrate of choice in the microelectronics industry. Many electronic devices such as microchips and sensoring equipment are based on this material. For the last few decades these devices are getting smaller, almost by the day, and cheaper to manufacture. As a result computers are getting also smaller and faster and are often implemented in common household appliances. As the dimensions are getting smaller a size boundary is being met, it's impossible to build smaller structures with the regular techniques. Nanotechnology however, provides interesting opportunities for further miniaturization. In this field, functionality is expressed by small groups of molecules or even a single molecule. This takes electronics to the molecular level.

Attaching molecules to a surface can create a layer of molecular width. Such structure is called a monolayer and can be used for many purposes. It can act as an insulator to the surface or can be fitted with specific groups that act as a receptor for example. Passivation of these monolayers inhibits the oxidation of the surface. High quality monolayers are therefore very stable. However, polymerization of molecules within the layer provides for additional stability. Research has led to linear molecules that contain a group that can polymerize parallel to the surface without disturbing the monolayer too much. The reactive group consists of two closely positioned triple bonds, called a diacetylene. An example of the system is pictured in the schematic representation below.

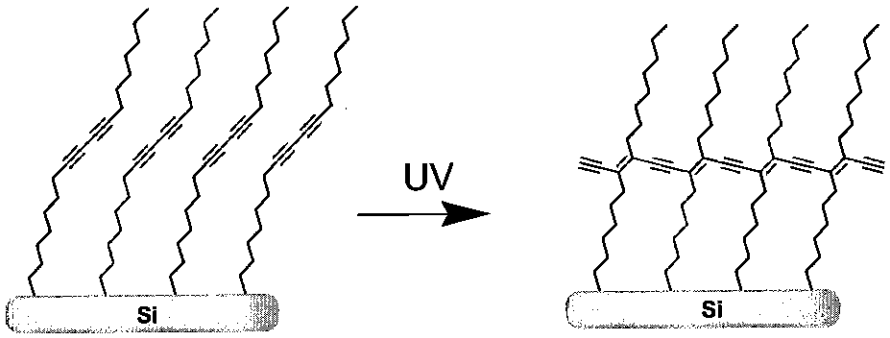

Fig. 1.1: Representation of a monolayer containing diacetylenes that can polymerize under influence of UV-irradiation.

The resulting polymer consists of a chain of alternating double and triple bonds. This structure is able to conduct electrons and forms a molecular wire parallel to the surface. The chains on both sides protect the polymer and surface and also act as insulators. The molecular wire may be used as a nano-scale conductor or the system can be used as a scaffold for sensoring groups.

Outline of this thesis

The process of creating a molecular wire can be roughly divided into three steps. First the diacetylene monomers need to be synthesized and purified. The second step is the formation of a monolayer, which is then followed by the third step, polymerization of the diacetylenes. For other substrates is reported in literature that spacer and tail length can influence the conjugation length of the molecular wire. This thesis will involve making a series of 3 compounds, monolayer formation onto a silicon surface, and the production and characterization of a molecular wire. A broad range of techniques will be used for characterization of the products of both the synthesis and the monolayer formation.

2 Theory and backgrounds

2.1 Semiconductors

The bandgap

Solid-state materials can be grouped into three classes on basis of their conductivity. In the first place there are the insulators, such as glass, which have a very low conductivity. Secondly there are the conductors, such as iron or copper, which have a high conductivity. And then there's a third group that is right in between, the semi-conductors. This group is rather special because the conductivity is sensitive to temperature, illumination, magnetic field and impurity.
In order to explain these phenomena it's important to look at the atomic model. For an isolated atom, its electrons can have only discrete energy levels. The lowest level being the ground level, and then the higher excited levels [1].

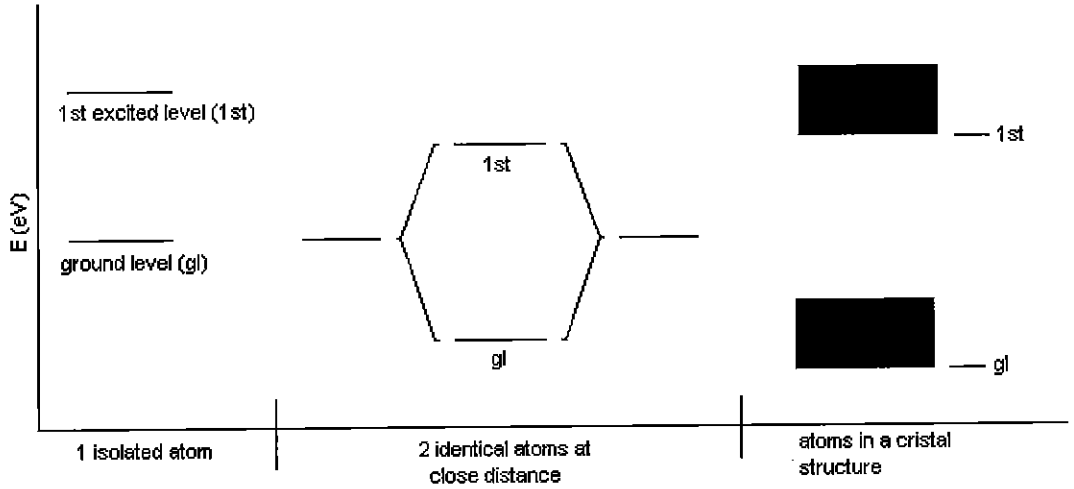

Fig. 2.1: Schematic representation of energy levels for: an isolated atom (1), identical atoms at close distance (2) and atoms in a crystal structure (3).

When two atoms approach each other they will split up the added energy levels because of the interaction between the atoms. The electrons will now take up the new levels, which are called molecular orbitals. This results in a bond when two electrons take up a same level that is lower than the initial energy level, a bonding orbital. The electrons can also take their position at a higher energy level, an anti-bonding orbital. In this state no bond is formed and the electrons are "free".
In a crystal structure even more atoms are close together and the energy levels split up in separate but closely spaced levels. These spaces are so close that all the levels together form a continuous band. The lower band is called the valence band, and the upper one is called the conduction band. The space in between is called the bandgap, which is a forbidden energy level, and cannot contain any electrons [1].

Conduction

Materials can express conduction when some of their electrons are in an excited state and are in the conduction band. For insulators, the bandgap is very wide, and it takes much energy to excite electrons into the conduction band. In the case of conductors, the conduction band can be partially filled in the ground state, or the bandgap can be absent, which is depicted in the picture below. When the two bands overlap, electrons jump between them without requiring excitation energy.

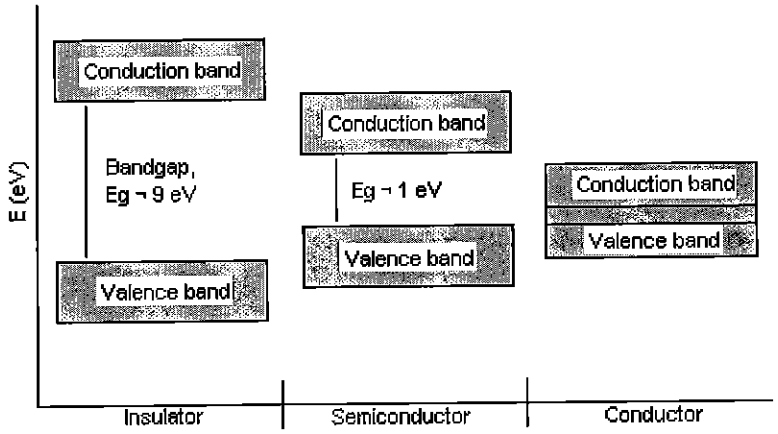

Fig. 2.2: Representation of conduction and valence bands for insulators, semiconductors and conductors. Redrawn from [1].

Semiconductors express themselves by having a relatively small bandgap, typically around 1 eV. This energy can be easily met by for example heating, or irradiating the material [1].

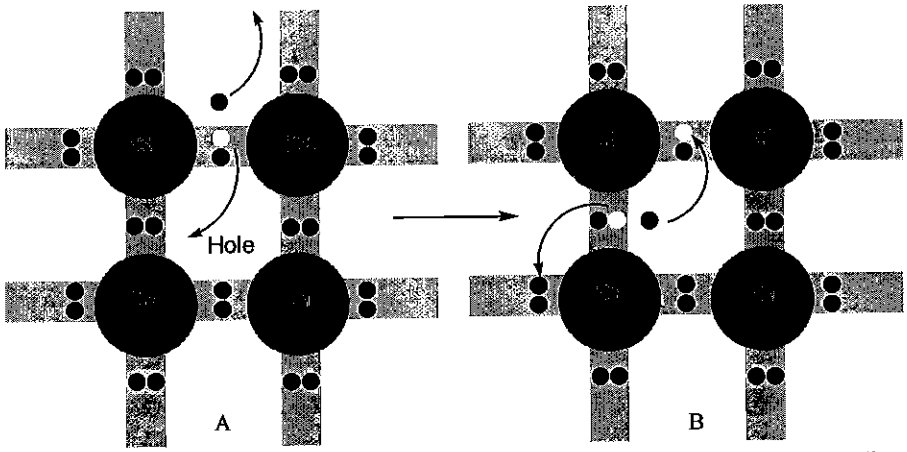

Fig. 2.3: Schematic for formations of holes upon excitation of electrons to the conductionband. [1]

When an electron moves to the conduction band, it leaves a positively charged hole (A). An electron from a neighbouring bond can fill this hole, and again a hole is created (B). Another way of decreasing the bandgap is to add impurities to the semiconductor material. In this process, which is called doping, either holes are created (positive, p-type) or electrons are donated (negative, n-type). For the positive doping these

impurities exist of atoms that are short of one electron and thus can only form three bonds instead of four. This leaves its neighbouring silicon atom one bond short, which becomes a hole. Negative doping involves adding atoms that have a surplus of one electron. They form four bonds and have one electron spare which contributes to the crystal [1].

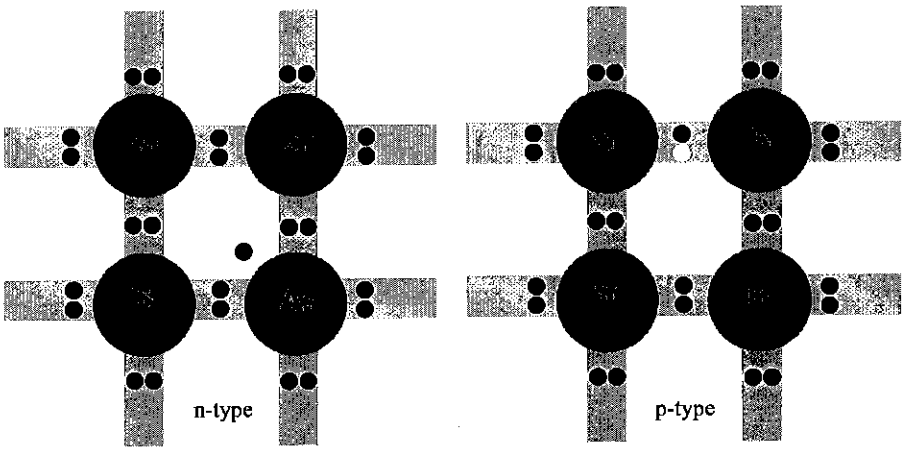

Fig.2.4: Representation of n-type and p-type silicon, the arsenic atom donates an electron, the boron atom 'steals' one from a neighbouring silicon atom.

Upon excitation electrons and holes are created in the bulk, which are separated by large electric fields. This results in an upward bandbending for n-type silicon and downward bending for p-type silicon [2]. This is represented in the picture below.

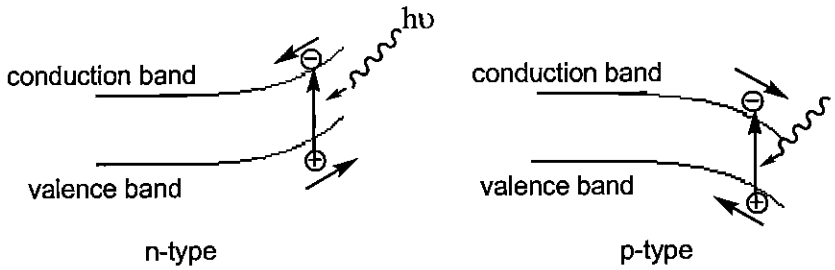

Fig. 2.5: Representation of bending of energy bands in n-type and p-type silicon [2].

In n-type silicon the electrons tend to move to the bulk and the holes move to the surface. These positively charged holes can be targeted by nucleophiles, and thus chemistry can be conducted at the surface [3]. For p-type doping it's the other way around, the holes move to the bulk and the electrons move to the surface.

2.2 Monolayer formation on silicon surfaces

The silicon surface

Silicon exists in a crystal structure and can be cleaved or cut into thin wafers that are used in the electronics industry. Dependent on the plane that is used for cleavage of the crystal, different surfaces can be obtained. If the cut is made at the 100-plane of silicon, Si-100 is obtained, which, after etching with HF, has two hydrogen atoms per silicon at the surface. The Si-111 surface, after etching with NH_4F, consists of 1 hydrogen atom per silicon, which angle is perpendicular to the surface.

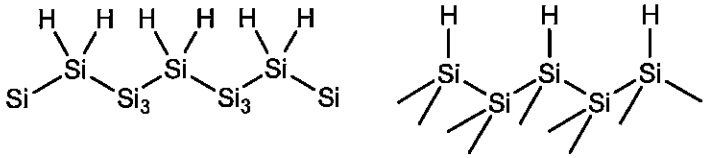

Fig. 2.5: Schematic representation of hydrogen-terminated Si(100) (left) and Si(111) (right) surfaces [4].

These surfaces can be functionalized by covalently binding molecules that subsequently form a monolayer. Many techniques for formation of monolayers are reported in literature. Among them are for example: nucleophilic substitution on halide-terminated surfaces, electrochemical grafting [5], thermally- and UV-induced hydrosilylation [4, 6] and visible light induced hydrosilylation [7]. In this thesis the focus will be on a very mild technique that is derived from thermally induced and photochemically induced hydrosilylation. To introduce this technique it's important to first understand the mechanisms of the thermal and the photochemical methods.

Thermally- and UV-induced hydrosilylation

These methods are based on the formation of a silicon radical at the surface, through the radical chain mechanism as proposed by Linford [6].

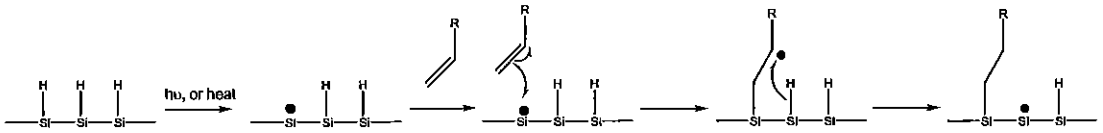

Fig. 2.6: Representation of the proposed radical chain mechanism on a Si(111) surface [6].

Firstly a silicon radical is formed as a result of heating (> 200°C) [6], or UV-irradiation [3], as depicted in the picture above. An approaching alkene will then donate one electron to pair with the radical on the surface and a bond is formed. The remaining electron forms a carbon radical that is protonated upon cleavage of the neighbouring Si-H bond. This leaves another Si-radical on the surface, which subsequently causes propagation of the mechanism.

Hydrosilylation induced by visible light

Sun [3] and De Smet [7] published a milder method for fabrication of monolayers. They used visible light to induce hydrosilylation at the surface. The character of the reaction mechanism is still not clear. In n-type silicon, at room temperature, many electrons are already in the conduction band. Band-bending causes these electrons to move to the bulk, and the holes towards the surface, which becomes positively charged.

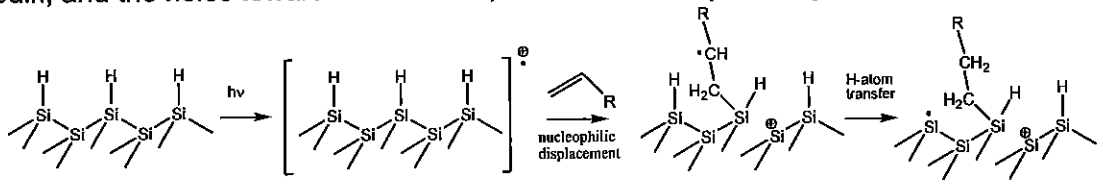

Fig. 2.7: Proposed mechanism for the initiation of the light-induced reaction [3].

The delocalised radical cations at the silicon surface are susceptible to nucleophilic attack (initiation). This may result in a Si-C bond, and the formed radical can pick up a H-atom, leaving a silicon radical at the surface (propagation). The chain reaction that is set in motion is similar to the mechanism proposed by Linford [6].

Monolayer formation at low temperatures: The vacuum-method

The most promising method however uses very mild temperatures and an argonflow at low pressure. Studies, at this moment still unpublished, show that monolayer formation is possible at room temperature in normal daylight. At temperatures over 50^{O}C, these reactions are successful in the dark and result in contact angles of 109-110^{O}. At lower temperatures, daylight is of significant influence. Experiments performed in the dark will be slower. The mechanism is thought to be similar to that of the visible light method, as explained earlier. The reduced pressure (10 mbar) and the argonflow are necessary to flush oxygen away, which would otherwise react with the surface and disturb the reaction.

Characterization of monolayers

Upon formation of the monolayer, the alkyl tails will 'stick' together, due to the Van der Waals interaction, which will stabilize the monolayer. A well-defined monolayer expresses a dense packing of these tails and a high crystallinity.

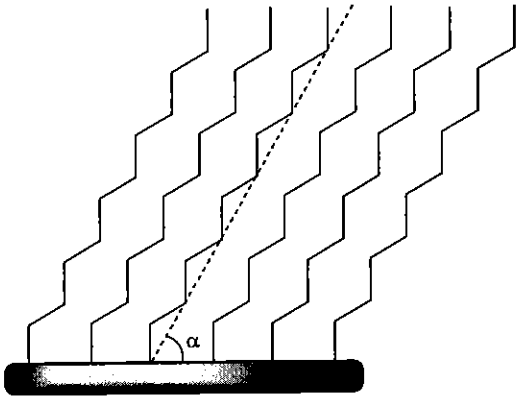

Fig. 2.8: Schematic representation of a well-packed monolayer, and the tilt angle (α).

The alkyl-tails in the monolayer are not perpendicular to the surface, but rather at an angle. This angle is not exclusively determined by the angle of the Si-C bond but also by the packing of the layer itself. The transition to a higher crystallinity can put this bond under stress, and change it. For well-packed alkyl monolayers tilt angels of 18-39° were reported in literature [8].
The hydrophobicity of the modified surface, which can be determined through static water contact angle measurements, is also an indication for the quality of the obtained layer. The contact angle will increase with better packing, resulting in contact angles up to 109° for high quality monolayers [4].

The properties of monolayers can be determined by a range of powerful (optical) techniques. In this the thesis the following methods were used:

- Static contact angle measurements, for quantifying the hydrophobicity of the surface. This is related to the surface coverage and homogeneity of the monolayer.
- Attenuated total reflection (ATR) infrared spectroscopy, for characterization of the Si-C and the C≡C bonds and determining the degree of order within the layer.
- Ellipsometry, for determining the layer thickness.

These techniques will be discussed more extensively in the experimental section in chapter 4.

2.3 Polymerization of diacetylenes

Introduction

Diacetylenes are very susceptible to polymerisation when their geometrical criteria are met. An enyne-type polymer is then formed through a 1,4-topochemical reaction. A schematic representation of this reaction and its parameters are depicted below.

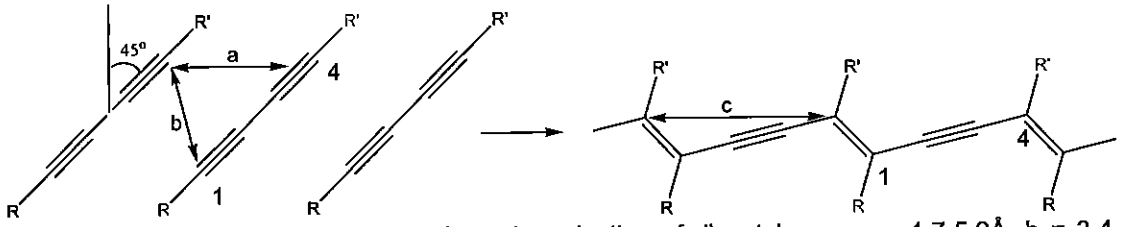

Fig 2.9: Geometric requirements for the polymerisation of diacetylenes: a = 4.7-5.2Å, b = 3.4-4.0Å, c = 4.9Å and $\lambda \approx 45^{O}$ [9].

The polymerisation can be induced by heat, irradiation and mechanical stress. The degree of polymerisation depends on the packing of the crystalline structure. From the figure above it becomes clear that polymerisation changes the distance between monomers (if a is slightly larger or smaller than c). The reaction may be terminated as a result of the molecules shifting out of the geometrical boundaries.

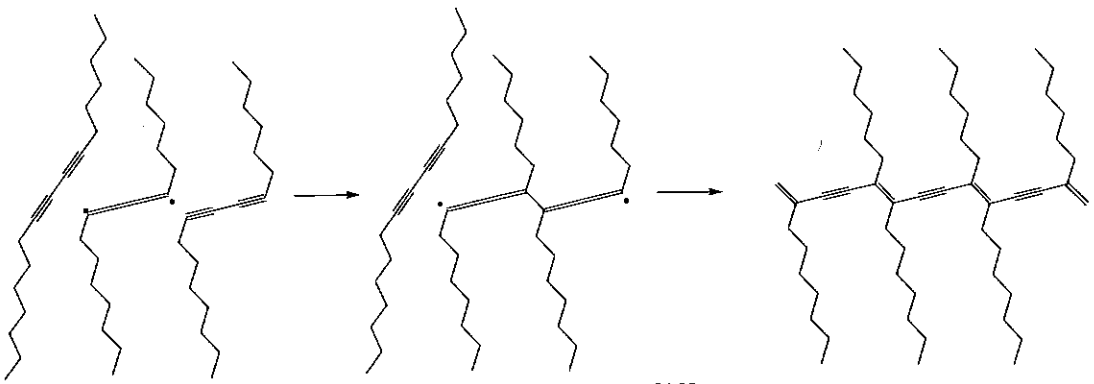

Fig 2.10: Proposed mechanism for photopolymerization [10].

The mechanism for photopolymerisation proposed by Okawa consists of the formation of a diradical upon excitation by photoadsorption. Due to thermal vibration, a neighbouring molecule can approach and an addition will occur. The product is a dimer, which is still a diradical and able to propagate the polymersation [10].

Extensive studies of polydiacetylenes in self-assembling monolayers (SAMs) on gold [11-18] and silver [19, 20] showed that the conjugation length of these polymers is depended on the length of the polymer chain, the conformation of the chain and the stress on the polymer backbone. The chromatic phase transition from blue to red is a good indication of the polymerization process [17].

The above-mentioned studies showed, that polymerization in monolayer depends on several factors, such as length of both spacer and tail and an odd/even effect in the spacer. In this thesis however another factor is introduced by using a silicon surface instead of a gold surface. The molecules will be covalently bound to the silicon in contrast to the semi-covalent bonds that are present on gold.

Influence of the substrate

In paragraph 2.2 two characteristic silicon surfaces were introduced: Si(111) which has one Si-H perpendicular to the surface and Si(100) with two Si-H bonds that are at approximately 35° to the surface. In the picture below, a schematic drawing shows that the orientation of the silicon atom affects the tilt angle.

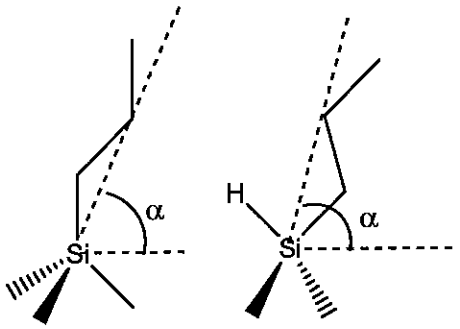

Fig. 2.11: Schematic representation of the tilt angle as a result of the orientation of the silicon atoms at the surface.

A characteristic difference between the two surfaces is the surface roughness. Si(100) expresses a higher surface roughness which doesn't necessarily affect the monolayer formation [21], but will move the diacetylenes out of the geometrical boundaries. Si(111) on the other hand is atomically flat.
Furthermore the Si-C bond resembles the Au-S bond found in SAMs, with respect to its perpendicular orientation to the surface normal. Therefore the Si(111) surface will be the substrate of choice in this thesis.

The odd/even effect

In SAMs on gold, the odd even effect is expressed by the change of the hybridization of the sulphur atom, which binds to the gold surface.

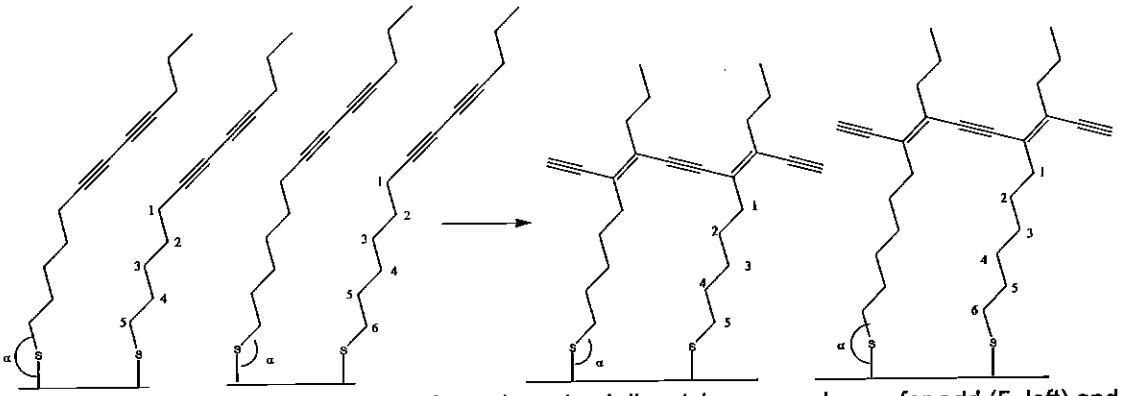

Fig. 2.12: Schematic representation of unpolymerized diacetylene monolayers for odd (5, left) and even (6, right) numbered spacers on the left side of the arrow. On the right side is the representation of polymerized diacetylene monolayers for comparable numbered spacers [17].

It is clear that before polymerization the odd/even effect is quite large. For the odd numbered spacer (5) a bond angle of nearly 180° is found. This corresponds with a sp2 hybridization of the sulphur. The sulphur in the even numbered spacer (6) on the other hand, resides in a more favourable angle close to 109°, required for sp3 hybridization. However, from the figure above it becomes also clear that upon polymerization (right part), the sulphur changes its hybridization to accommodate for the change of tilt, for both even and odd numbered spacers. This results in a bond angle of almost 180° for the even numbered spacer and a bond angle of almost 109° for the odd one. Apparently an even numbered spacer is favourable for monolayer formation but an odd numbered spacer can accommodate better for the required tilt angle after polymerization [17].
For silicon surfaces the story is quite different because the carbon bound to the substrate in monolayers on silicon is not able to change its hybridization from sp3 to sp2 or vice versa. The bond angle of Si-C-C is approximately 109° according to its sp3 hybridization. This means that the even numbered spacer would result in a well packed monolayer but that it would be less able to compensate for the geometrical shift upon polymerization. The Si-C-C bond would be under some stress in a monolayer, which could be relieved by polymerization. As mentioned before, the choice of substrate determines the position of the Si-C bond. The odd/even effect can be studied by attaching the same molecule on Si(111) and Si(100).

Spacer length and the influence of alkyl tails (on gold)

In the beginning of this paragraph it was mentioned that polymerization of the diacetylene units causes a geometrical shift. The change of hybridization from sp to sp2 in the polymer causes a shift in the vertical direction. This strain is likely to be translated into the alkyl chains that support the polymer. This may induce twisting and tilting of these chains. The spacer is on one side attached to the surface, and will have difficulty in compensating for this strain. A greater degree of freedom, which will reduce the stress, can be obtained by introducing a longer spacer. A red shift for decreasing spacer length was reported on gold surfaces in literature [22].

The tail region expresses a greater degree of freedom since the tails are only constrained on one side. The order in the tail region increases with increasing length, and even high crystallinity is observed. Though this increase in order does not release the backbone of the stress. Apparently order in the tail region facilitates the relaxation of the backbone. High crystallinity however inhibits this relaxation because of the preservation of the high order [22].

Inducing controlled polymerization

Assuming that a monolayer of sufficient quality is obtained, and that the diacetylenes are in the right geometrical position, the next step will be controlled polymerization. As was mentioned before, the chromatic phase is an indicator for the conjugation length. The exposure time of UV for UV-induced polymerisation has been extensively studied for SAMs on gold [12] and silver [20]. Both studies report a relation between the ratio of red/blue phase polymer and the exposure time. They find that with increasing exposure time, the yield of blue phase increases until an optimum (7 min.) is reached. For longer exposure time a decrease in blue phase is found. The explanation is given by the hybridization shift from sp to sp2 that induces strain to the spacer and tail region. Due to prolonged exposure to UV, this strain can build up until the spacer region cannot compensate anymore because it is covalently bound to the surface. The strain is then transferred to the polymer backbone, which leads to a decreasing conjugation length.

2.4 Synthesis of diacetylenes

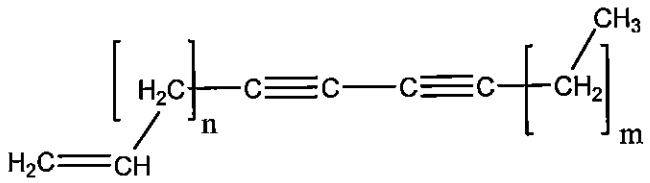

Fig. 2.13: Schematic drawing of a diacetylene unit between a variable spacer (n) and tail (m).

The synthesis of the compounds as pictured above can be performed in two steps. The first step is to create an intermediate, which consists of a diacetylene unit with an alkyl tail (m). In the second step the spacer (n) and the surface reactive group are attached as a whole.

First step: cleavage and alkylation

The starting compound is 1,4-bis(trimethylsilyl)-1,3-butadiyne, which is purchased. It consists of a diacetylene unit (1,3 butadiyne) protected by a TMS-group on each side. Firstly on one side, the TMS-group is cleaved by methyl-Lithium, and an acetylide anion is formed.

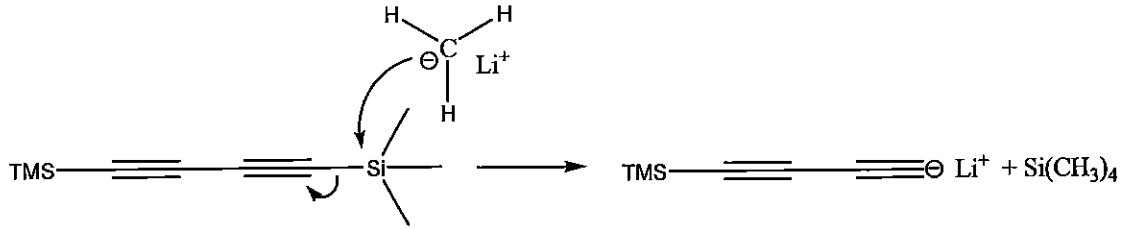

Fig. 2.14: Cleavage of a TMS-group by methyl-lithium.

This anion is stabilized by the sp-hybridization of the carbon. In an sp-hybridization, the electrons are closer to the positive core, and the positive charge can more easily stabilize for the negative charge. The positively charged Lithium-ion also stabilizes the carbanion. However the acetylide anion is strongly nucleophilic because of its unshared electron pair, and can react with an alkyl halide because the bromide ion forms a good leaving group In this case, the anion is alkylated with 1-Bromo-dodecane (m = 11) or 1-Bromo-hexane (m = 5) in an S_N2-type reaction[23].

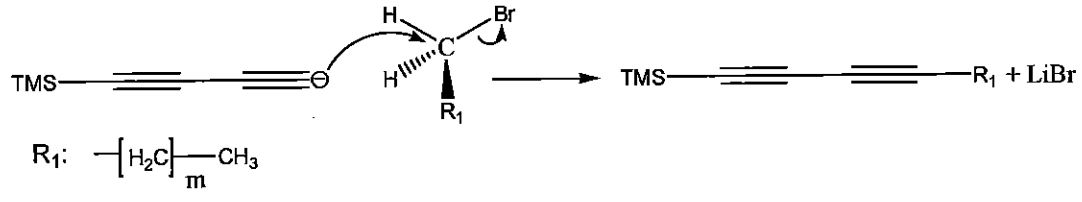

Fig. 2.15: Alkylation of the acetylide anion with a Bromo-alkane, m = 5 or m = 11.

The nucleophile attacks the primary carbon. In the following transition state, it shares its electron pair with the carbon atom and, simultaneously one shared electron pair shifts to form a bromide ion.

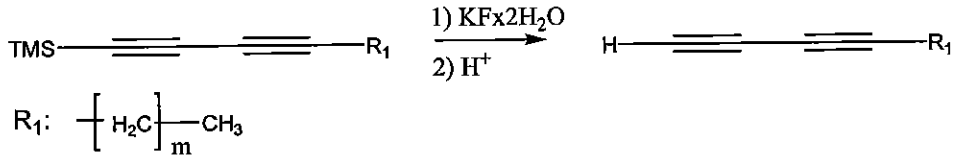

Fig. 2.16: Cleavage of the remaining TMS-group.

The remaining TMS-group is removed by adding a base, and again an acetylide anion is formed. The anion reacts with the added Hydrochloric acid, and 1,3-Hexadecadiyne (n=11) or 1,3-Decadiyne (n=5) is formed. After purification the compound is then used in the second step.

Second step: attaching the alkyl spacer

The addition of the alkene spacer is very similar to the alkylation in the first step of the synthesis. Instead of MethylLithium, the more reactive n-ButylLithium is used to form an acetylide anion. This anion is then alkylated by either 11-Bromo-1-undecene (n = 9) or 7-Bromo-1-heptene (n = 5) in an S_N2 reaction, and thus an alkendiyne is formed.

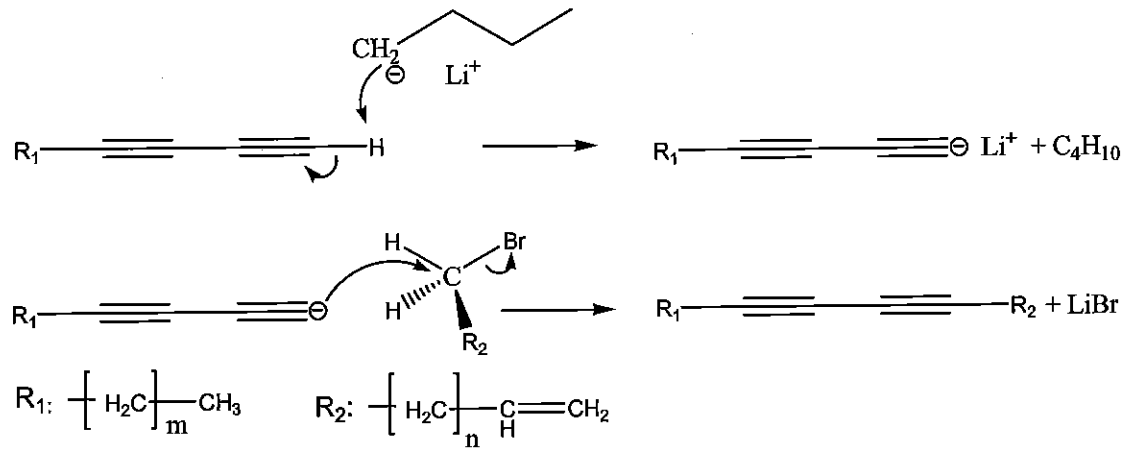

Fig. 2.17: Formation of an acetylide anion with butyl-lithium and the subsequent alkylation by a Bromo-alkene, n = 5 or n = 9.

3 Results and discussion

3.1 Synthesis of C_{27} and finding the right conditions for a monolayer

Synthesis and characteristics of C_{27}

The fabrication of a well-defined monolayer and the strict geometrical requirements for polymerization of diacetylenes were already discussed in chapter two. A brief analysis of the available literature resulted in the choice for C_{27}, a diacetylene with n=9 and m=11.

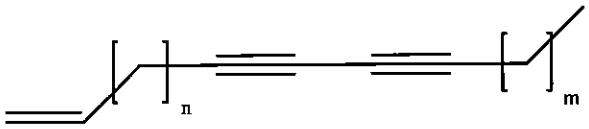

Fig 3.1: Schematic representation of a diacetylene with variable spacer (n) and tail (m) length.

The C_{12} tail (m=11) should be sufficiently long to achieve a good ordering in the monolayer but also be able to reduce stress on the polymer backbone upon polymerization. A spacer length of C_{11} (n=9) is chosen for because of its odd number and the length. The length should facilitate a well packing of the monolayer and enough flexibility for the geometrical shift. The odd numbering also contributes to the requirements for polymerization.
The synthesis was successful and yielded a clear slightly yellow coloured liquid. The procedure of the synthesis and purification will be discussed in the experimental section in chapter 4. Storage of the compound proved to be a bit trickier however. The compound was known to be sensitive to polymerization induced by light and heat, and was thus stored in hexane solution at –15°C. Under these conditions polymerization still occurred, possibly due to aggregation because of decreased solubility, which yielded a bright red coloured 'blob'. When the solution was stored at 5°C, no polymerization was observed.

Fabrication of the monolayer, finding the right conditions

Initial experiments were performed to determine the ideal reaction conditions for the vacuum method. These experiments yielded contact angles of 90° and 97° after respectively 8 hours at 20°C and 4 hours at 60°C. To investigate the gain in contact angle for increasing temperature longer and higher temperatures were used. This yielded a contact angle of 103° after 4 hours at 80°C. In the figure below, the reaction conditions are plotted against the resulting contact angle. The used procedure will be discussed in chapter 4.

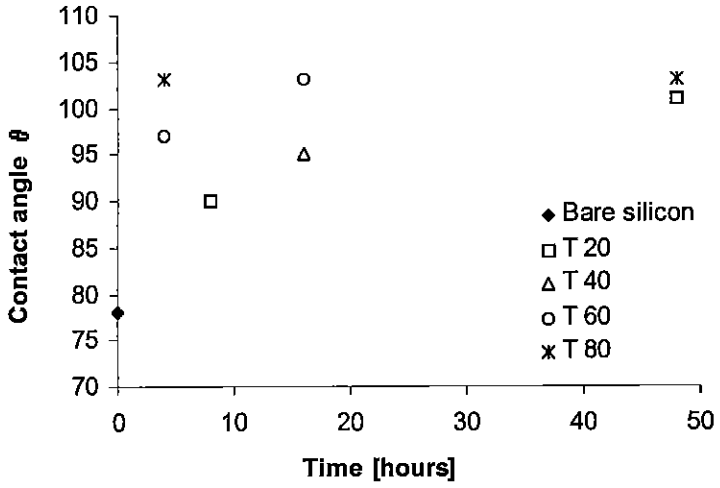

Fig. 3.2: Contact angles found for monolayers of C_{27} on n-Si(111), for different temperatures and reaction times.

From the figure above it becomes clear that the maximum contact angle is 103°. After monolayer formation however, the colour of the compound had changed to a darker yellow. This can be contributed to a degree of polymerization of the compound, which is also depended on temperature and reaction time. The optimum for minimal change of colour and the highest maximum contact angle was found for 60°C. Reaction times at this temperature and resulting angles are depicted in the figure below.

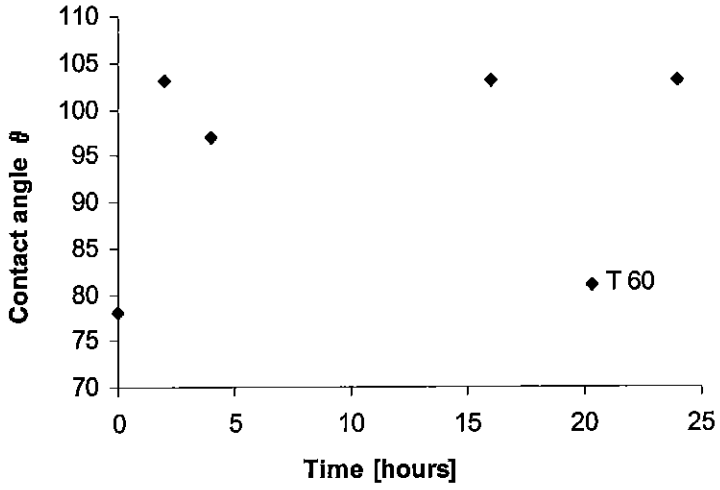

Fig. 3.3: Contact angles obtained for monolayers of C_{27} on n-Si(111) for different reaction times at 60°C, and the contact angle for bare silicon (t=0).

The maximum contact angle is already obtained after 2 hours. The lower value at 4h is probably an artifact but it could also be that the value at 2h is too high. More measurements are needed to be sure.

Characterization of the monolayer

The increase in contact angle is an indication that there are molecules on the surface. In literature contact angles of 109-110^0 are indicative of high crystalline monolayers. The obtained maximum angle of 103° is much lower. This can be contributed to a less dense packing of the monolayer.
The layer thickness of the samples with contact angles of 103°, determined with ellipsometry, turned out to be ~10Å. This is less than can be expected for a monolayer of C_{27} molecules. It's possible to make an estimation using the calculated length of the molecule and the range of tilt angles, 18°-30°, found in literature (chapter 2). This is represented in the figure below.

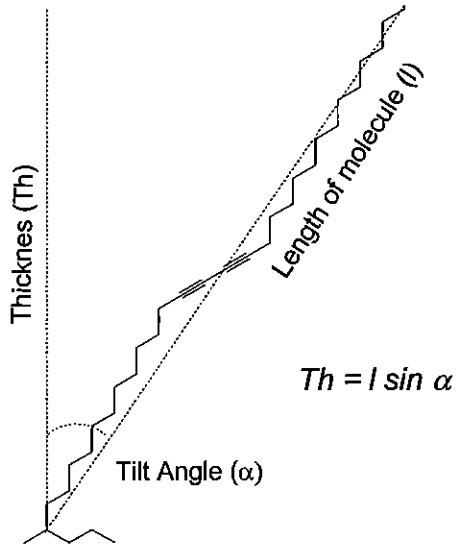

Fig. 3.4: Estimation of layer thickness, with the estimated bond lengths from ChemDraw and the expected tilt angles (from literature, chapter 2).

The length of the molecule was calculated in Chem3D Pro (MOPAC, PM3, closed shell restriction) [7], for C_{27} this gave 30Å. Using the equation in the figure above a thickness of 25 to 29Å is found. This is in sharp contrast with the measured value of 10Å. The thickness was also measured after sonication for 10 min. in petroleum ether (40/60) and remained the same. Only a little decrease in the water contact was measured. Perhaps some material was physisorbed but most of the material is covalently bound to the surface.

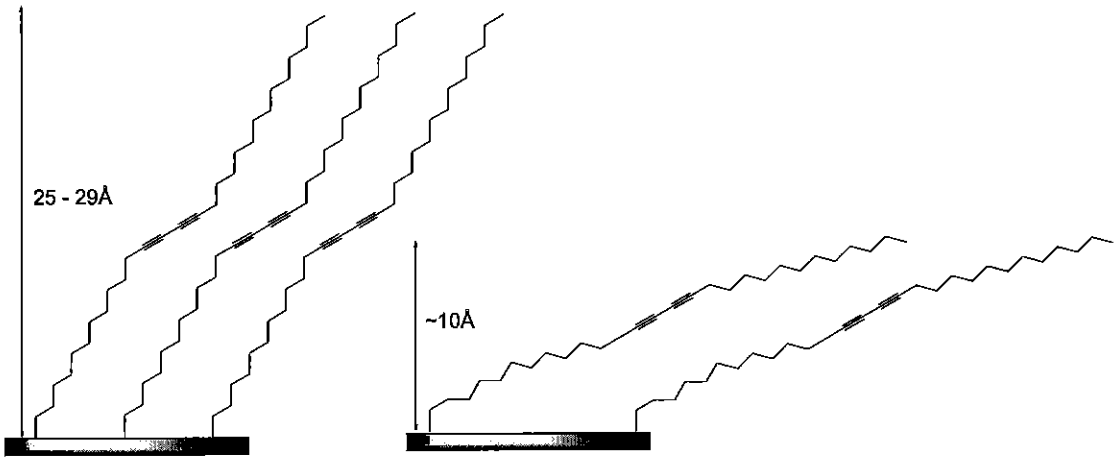

Fig. 3.5: Representation of a well-defined monolayer (left) in contrast to a layer with a low surface coverage (right).

An explanation can be given by the fact that upon formation of the Si-C bond, the molecules will orientate themselves close to the surface, or even lie flat. Which is depicted in the picture above. In this way, the surface will be less accessible and the monolayer formation is disturbed. Certain surface coverage is still achieved, which accounts for the water contact angle of 103° and the obtained layer thickness of 10Å.

3.2 Introduction of a shorter spacer and tail: Synthesis of C_{17}

The key to the formation of a molecular wire is a well-packed monolayer. Another reason for the low quality of the monolayers may be the length of the molecule. Upon formation of monolayers, molecules will lose a lot of freedom and the entropy will decrease. This is compensated by the Van der Waals interaction between the molecules, which causes them to pack together and will lower the free energy. Calculations show that the energy decreases linearly to the amount of carbon atoms in an alkyl tail (up to 18) [24]. Longer molecules are likely to lose more entropy and eventually the Van der Waals interaction cannot account for it anymore. Apparently the maximum length of molecules on gold is 22 carbon atoms. The solution may lie in a shorter molecule. For this purpose C_{17}, with n = 5 and m = 5, was synthesized.

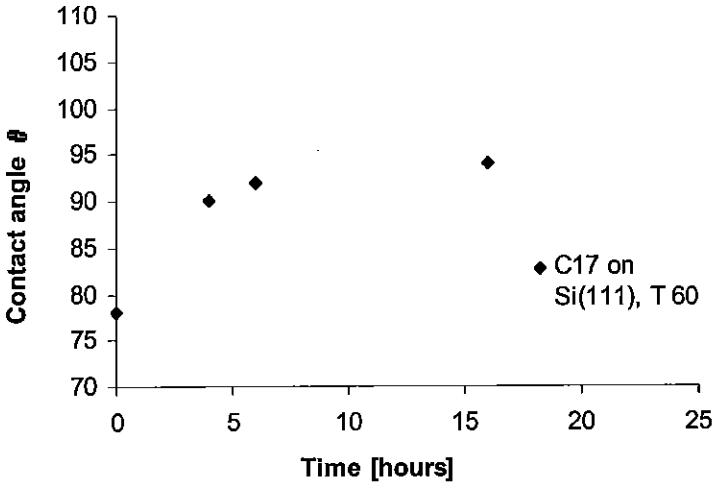

Fig. 3.6: Contact angles obtained for monolayers of C_{17} on Si(111) for different reaction times at 60°.

Water contact angles for C^{17} on Si(111) showed a very inhomogeneous and less hydrophilic surface. As can be seen in the picture above, a maximum contact angle of 94° was found. Ellipsometry showed a layer thickness of 7 to 9Å, which is significantly less than the calculated range for this molecule of 17 to 19Å. After sonication for 10 min. in petroleum ether (40/60) of the samples, the contact angle would decrease to 90°, but the layer thickness would remain the same.
A change of substrate, Si(100), which would have a different orientation of the Si-C bond, yielded the same maximum contact angle of 94 and a thickness of 9Å.
The low contact angle and the thin layer suggest that there is material on the surface but that it is not the quality of a monolayer that is expected.

3.3 Interaction of the diacetylenic moiety with the surface

At this moment another explanation comes into view, and that's the interaction of the diacetylenic moiety with the surface. Until now it was thought that the diacetylene would not interact with the surface due to steric hindrance and it would rather form aggregates due to pi stacking. A simple method to investigate this interaction is through synthesis of a diacetylenic compound without a terminated alkene. For this purpose two C_{12} tails (m=11) were successfully attached to the diacetylene to form C_{28}.
Monolayer formation resulted in contact angles of 105° for reactions of 4 hours at 40°C and 60°C. After sonication in petroleum ether (40/60) the contact angle decreased slightly to 104°. The layer thickness was measured at 10Å, which is the same for C_{27} from the first paragraph. This is also close to the calculated value of 13 to 14Å for this molecule (see fig. 3.7). From these results can be concluded that the diacetylenic moiety is very reactive with the surface. The increased contact angle indicates a higher ordering of molecules on the surface. The interaction of the originally used diacetylenes (C_{17} and C_{27}) to the surface is represented in the picture below.

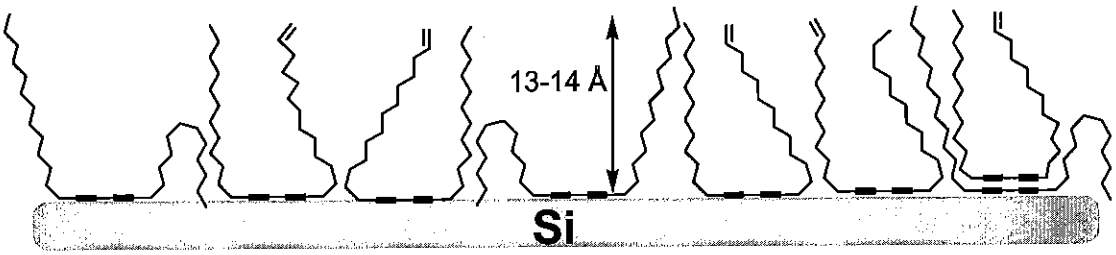

Fig. 3.7: Schematic representation of diacetylene interaction with the silicon surface.

Huang proposed two possible structures as products of binding of diacetylene (HC≡C-C≡CH) to silicon surfaces [25, 26]. They used silicon surface with dangling bonds acquired by sputtering of the surface. The proposed structures are translated to the diacetylenic molecules used in this thesis and depicted in the figure below.

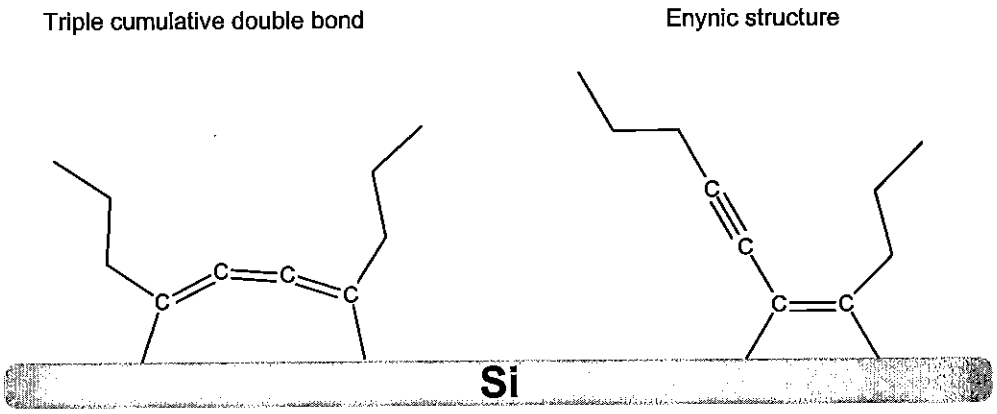

Fig. 3.8: Two possible structures of diacetylenes on a silicon surface [25, 26].

Further experiments were performed to investigate the diacetylenic interaction with the surface with IRRAS and ATR. Unfortunately the intensities of the vibrations were too low to obtain clear bands for double or triple bonds. Without this evidence it's difficult to determine the precise mechanism for attachment.

3.4 Can other methods inhibit the diacetylene from binding to the surface?

In chapter two, several methods for the fabrication of monolayers were discussed. Only one method was thought to be mild enough to avoid early polymerization. Perhaps the method reduces the reactivity of the alkene with respect to the diacetylene moiety, or even enhances the reactivity of the latter one. So far the vacuum method was only performed with pure compound. In this way the surface is already filled with molecules in all possible orientations, including orientations with the diacetylene moiety close to the surface. Using a solution of the compound in mesitylene, a solvent often used in the thermal method [21], the molecules have a greater freedom. Also the mesitylene can have stacking interactions with the diacetylene, which would reduce the reactivity due to sterical hindrance.

Method	Before sonication		After sonication	
	Contact angle	Thickness (Å)	Contact angle	Thickness (Å)
C_{27}, 4h	98	8-9	94	8-9
C_{27}, 8h	94	9-10	91	10
C_{28}, 4h	103-104	10	101	10
C_{27}, 2h	103-104	-	-	-
C_{28}, 4h	105	11	104	11

Table 3.1: Obtained values for the water contact angle and layer thickness of monolayers of C_{27} and C_{28} on n-Si(111) for the vacuum method with refluxing mesitylene (0.4M solution in mesitylene at 60°C), compared to the regular vacuum method (lower part: 60°C, pure).

When the results from the mesitylene experiment are compared to the experiments with pure compound, it becomes clear that the monolayer formation is disturbed. The contact angles are lower, but the layer thickness is in the same order. The disturbing of the monolayer formation didn't prevent the diacetylene interaction.
Though at first discarded as not preferable, the other methods: thermal and visible light, were easily available and also tested for their influence on the reactivity of the diacetylene. The reaction conditions and the resulting contact angles and layer thicknesses are depicted in the table below.

Method	Before sonication		After sonication	
	Contact angle	Thickness (Å)	Contact angle	Thickness (Å)
Thermal method	100	10	95	10
Visible-light method	92	8-9	90	8-9
Vacuum method	103-104	10	101	10

Table 3.2: Values for the water contact angle and layer thickness of monolayers of C_{27} on n-Si(111) obtained with the Thermal method (2h in refluxing mesitylene at 166°C, 0.4M), the Visible light method (15h in mesitylene, 0.4M) and the regular vacuum method (2h, 60°C, pure).

From the results in table 3.2 it becomes clear that both the contact angles and the layer thicknesses are still too low. This means that also harsher conditions are not able to inhibit the diacetylene interaction. Again the formation of the monolayer is somehow disturbed in these experiments. This could indicate that the diacetylene interaction has also decreased.

Unfortunately these were the last experiments that were performed. ATR and IRRAS experiments were not successful and no additional information was obtained.

4 Conclusion and recommendations

In the introduction was stated that this project can be roughly divided into three successive stages: synthesis, monolayer formation and assembly of a molecular wire. The synthesis part proved to be successful and resulted in three well-characterized and pure compounds. Additional experiments with respect to the sensitivity of these compounds to polymerisation lead to methods for storage and recycling.

Producing a monolayer by attaching the compounds to a silicon surface proved to be more challenging. Unfortunately no high-quality monolayer was obtained, though contact angle measurements and layer thickness showed that some material was attached to the surface. Experiments with a diacetylene derivative without an alkene tail, showed that the diacetylenic group interacts with the surface. Subsequently, regular assembly of a monolayer was not possible, and the molecular wire could not be investigated. The vacuum method for monolayer formation however proved to be very successful for covalently attaching molecules to the surface. The reaction conditions were much milder than the established methods ad the resulting monolayers were of at least equal quality. Infrared measurements at the surface (IRRAS and ATR) were also unsuccessful and yielded no information about double and triple bonds at all.

Further studies on the formation of covalently bound diacetylenic monolayers on silicon are necessary before characterization of a molecular wire is possible. Some interesting alternatives for the fabrication of monolayers can be found in literature. The key to success may lie in using a technique, which inhibits the interaction of the diacetylene with the surface. Basically two pathways are possible for avoiding this interaction.

The first strategy is creating a monolayer from molecules already containing the diacetylene but shielding it from the surface. A possibility may be adding solvents (other than mesitylene) that have a stacking interaction with the diacetylene; its reactivity may be decreased enough. Another possibility may lie in the use of a masking material adsorbed to the surface, which then is exchanged by diacetylenes at a slow rate. The surface is shielded and during the exchange, the adsorbed material may also work as a template.
More rigorous changes would involve the synthesis of new molecules. By adding a polar group to the molecule, in an apolar solvent micelles are formed. The alkene-terminated tails will point out and are able to attach to the surface. Procedures of similar synthesis are well reported in literature.

The second strategy would involve making a monolayer without the diacetylene, but terminated with functional groups. The second step will then consist of attaching the diacetylenic group to the scaffold before polymerization can be induced. However making this connection may be a problem since it would take up quite a lot of space in the monolayer.

Without the necessary information obtained from infrared spectroscopy it's difficult to characterize monolayers. More experiments are needed to investigate if the double and triple bonds can be detected in a monolayer.
STM (scanning tunneling microscopy) measurements can be recommended for investigating the surface more closely. This technique may give a more detailed view of the surface coverage and the orientation of molecules at the surface.

5 Materials and method

5.1 Chemicals

Reagents: All reagents were obtained from Aldrich, except for HCl, which was obtained from Fischer scientific: 1,4-Bis(trimethylsilyl)-1,3-butadiyne, 98%;1-Bromo-dodecane; 1-Bromo-hexane; 7-Bromo-1-heptene, 97+%; 11-Bromo-1-undecene, 95%; Potassium fluoride (KF), 98%; Potassium fluoride dihydrate ($KF{\cdot}2H_2O$), 98%; Methyllithium-Lithiumbromide complex 1.5M solution in diethyl ether; n-Butyllithium 1.6M solution in hexane

Solvents and other chemicals: The used solvents were obtained from several suppliers: Acetone p.a., Riedel de haen; Acetonitrile p.a., Acros; Dichloromethane; DMF, Fluka; 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), >97%, Aldrich; Ethanol, Merck; Hexamethylphosphoramide (HMPA), Aldrich; Hexane, Prolabo; Mesitylene, Fluka >99%; Pentane, Fisher scientific; Petroleum ether 40-60; Tetrahydrofuran (THF), Acros. Column-chromatography was performed on Si-60 230-400 mesh obtained from Aldrich and Si-100 C_{18}-reversed phase obtained from Fluka. Substrates: Si(111) was obtained from Addison engineering (n-typ1, phosphorous, 1.0-5.0 Ωcm) and Si(100) from Mitshubishi silicon (n-type, phosphorous, 1.0-2.0 Ωcm).

Preparation of reagents and solvents: Due to the sensitive nature of the monolayer formation and the synthesis, drying and extra purification of some chemicals was needed. Extra pure (double deionised) water was obtained from a Seralpur C90. THF was freshly distilled from sodium/benzophenone, HMPA and DMPU were dried over molecular sieves (4Å). All remaining solvents, except for DMF, were also distilled before use (mesitylene was two times distilled). The starting products are put under vacuum and then flushed with Argon.

5.2 Equipment

Equipment for characterisation of synthesized compounds

All NMR spectra were recorded as solutions in $CDCl_3$ at room temperature on a Bruker AC200 FT-NMR spectrometer. Mass spectra were recorded via direct probe measurement on a high resolution quadrupole time-of-flight mass spectrometer. UV-spectra were recorded as solutions in hexane on a Varian Cary 50 scan UV-VIS spectrophotometer. FT-IR spectra were recorded as solutions in CCl_4 at room temperature on a Bruker Vector 22 spectrometer. Surface samples were cleaned in a Harrick plasmacleaner/sterilizer Model PDC-002.

Ellipsometry

Ellipsometry is a well-established optical technique for studying surfaces and thin films. It is based on the theory that the polarization of light will shift upon reflection on a surface. Light is usually unpolarized, which means that the electric components are orientated in

all directions perpendicular to the direction of travel. If the electric field is oriented in one way, the light is linearly polarized. This polarization can be obtained by using special light sources, or optical elements that are called polarizers.
Linearly polarized light can be split into two perpendicular components that have the same direction of travel and are in phase with each other. By delaying one of these components, they can be shifted out of phase, which results in elliptically polarized light.

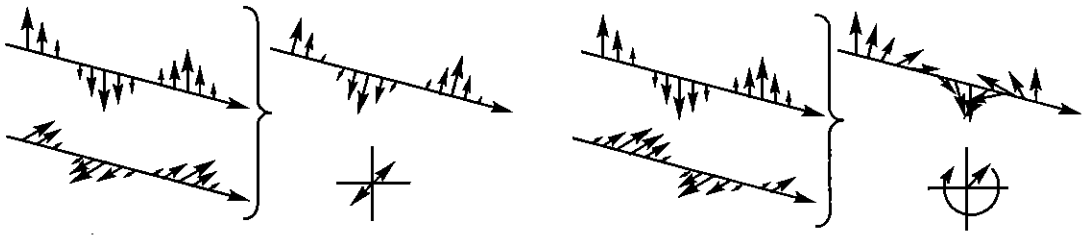

Fig. 5.1: Representation of linearly polarized light (left) and elliptically polarized light (right).

In ellipsometry this elliptically polarized light is directed at a surface and its reflection is analysed by a second polarizer and detector.

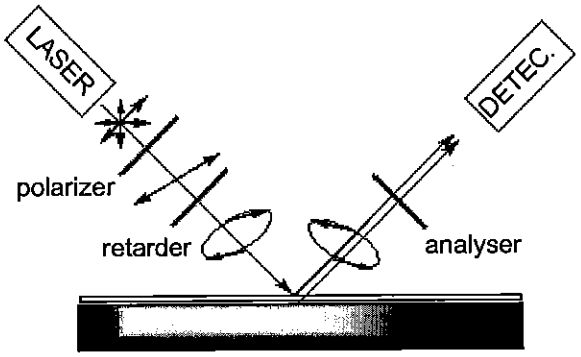

Fig 5.2: Ellipsometry set-up, as used for determining the thickness of monolayers on a silicon surface.

An ellipsometer measures the quantities Δ and Ψ, also referred to as Del and Psi. Del is the change in phase difference that occurs upon reflection and Psi is related to the ratio of the magnitudes of the total reflection coefficients. These values are then put in a model, which correlates them to the layer thickness and the refractive index of the monolayer.

Layer thicknesses were measured on an ellipsometer from Sentech Instruments GmbH at a wavelength of 632.8 nm and an angle of 70°.

Static contact angle measurement

Measurement of contact angles is a technique based on the concept of adhesional wetting of a solid substrate. Upon contact, a liquid droplet will adhere to a surface. The

affinity for the surface will determine the spread of the liquid. The free energy of adhesion is given by the Young-Dupré equation (5.1):

$$W_a = \gamma_{LG}(1+\cos\theta) \quad (5.1)$$

In this equation γ_{LG} is the surface tension of the liquid-gas interface and θ is the contact angle of the droplet of liquid on the solid surface.

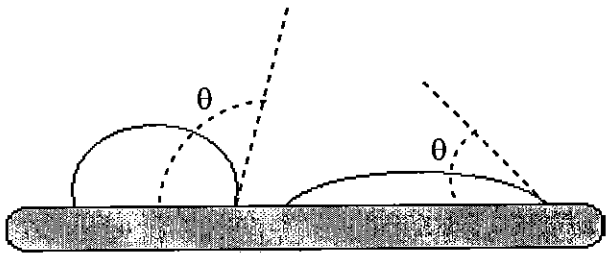

Fig. 5.3: Representation of the contact angle θ of a droplet of water on a hydrophobic (left) and a more hydrophilic (right) surface.

The contact angle is thus a measure for the adhesion to the surface, resulting in a zero contact angle for complete wetting. For partially wetting the contact angle will increase to a maximum of ~110° for the monolayer system used in this project [27]. The static water contact angles were measured on a Krüss G1, with an error of ±1°. Droplets were made from 3.5 μL ultra pure water.

Attenuated total reflection (ATR) infrared spectroscopy

Infrared spectroscopy can also be performed on surfaces. Because the infrared beam cannot transmit through the used surfaces, reflection is used. The IR-beam reflects from a surface and is then analysed. For thin layers and characterization of specific groups within those layers one reflection yields a very weak signal. The signal can be attenuated, by adding more reflections. To achieve this, a special double polished crystal prism is used as substrate. The prism expresses a Si-H surface and is transparent for IR-wavelengths and a monolayer is formed on both sides of the crystal [28].

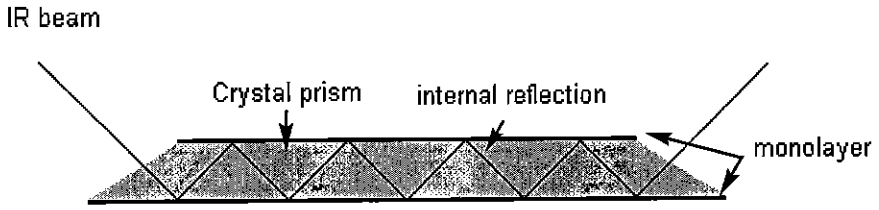

Fig. 5.4: Representation of the internal reflection of an IR beam in the ATR-crystal with attached monolayer [28].

The infrared beam enters the crystal and is then internally reflected. At each reflection, the electric vector of the IR radiation samples the attached monolayer. The weak signals of the layer are now enhanced, and should be clearer in the spectrum.

5.3 Synthesis

The crucial steps in the synthesis are the formation of acetylide anions and the alkylation steps. Some of the reagents used and of course the acetylide anion, are strong nucleophiles, which can react with water, if present. It's important that the reaction environment is water free. In order to obtain such environment, all glassware is dried in an oven to remove all traces of water. Just before the reaction, the set-up is put together. It is then alternately put under vacuum and flushed with Argon. The reaction itself takes place under an overflow of Argon.

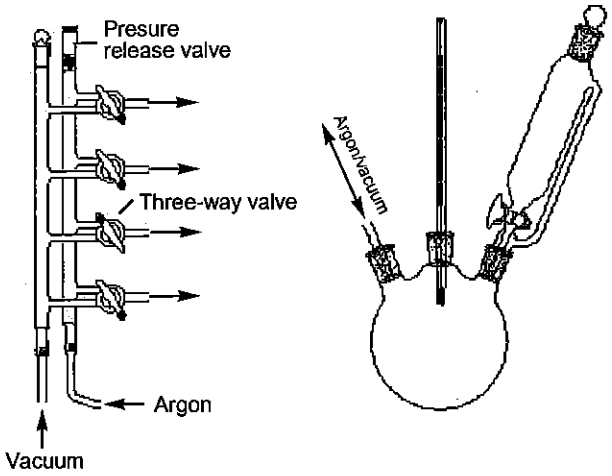

Fig. 5.5: Schenkline [29] (left) for switching between vacuum and argon, and the reaction set-up (right) used for synthesis of polydiacetylenes.

A so-called Schlenkline is used for switching between argon an vacuum. This set-up allows working with reactive chemicals under a protective atmosphere. Reagents can be added through the funnel, while maintaining the argonflow.
Some parts of the reaction need to take place at very low temperatures. By adding dry ice to acetone, temperatures as low as –78°C can be reached.
The compounds contain a diacetylene-unit, which can be subject to polymerisation under influence of light. Therefore it is important that brown coloured glassware is used for both in the formation and storage of the compounds. The compounds are also diluted in hexane and kept in the fridge at 5°C.

Preparation of 1,3-Hexadecadiyne (1a) and 1,3-Decadiyne (1b)

An amount of 1,4-bis (trimethylsilyl)-1,3-butadiyne was dissolved in dried THF (2.0 mL $mmol^{-1}$) and cooled down to –78°C. Under stirring, 1 equivalent of methyl lithium (1.5M in

Et_2O) was added dropwise. After adding, the dry-ice/acetone bath was removed and the mixture was maintained under stirring and under Argon flow at room temperature for 3.5 hours. A sample was taken and checked with GC-MS for the rate of conversion. Then a solution of 120% of 1-Bromododecane (a) or 1-Bromohexane (b) in HMPA (2.0 mL $mmol^{-1}$ of butadiyne) was added dropwise at –78°C. After adding the mixture was maintained under stirring for 30 minutes at room temperature. The mixture was cooled in an ice bath, neutralized with 0.3M HCl and then extracted with hexane. The solvents of the combined organic layers were removed under vacuum at room temperature. A slurry of $KF{\cdot}2H_2O$ (200 mol%) in DMF (2.0 mL $mmol^{-1}$ of butadiyne) was added to the residue, and the mixture was stirred for 30 minutes at room temperature. After this period a sample was checked with GC-MS for the presence of unreacted TMS. In the case of TMS still present, more $KF{\cdot}2H_2O$ was added and the mixture was stirred for another 30 minutes. Then the solution was cooled in an ice bath and under stirring refrigerated 3M HCl (1.5mL $mmol^{-1}$ of butadiyne) was added. The layers were isolated and the aqueous layer was extracted with hexane. The combined organic layers were washed with 3.0M HCL, saturated $NaHCO_3$, saturated NaCl, and dried over anhydrous Na_2SO_4. After filtration the solvent was removed under vacuum at room temperature and the residue was diluted in hexane for storage. Purification: The crude compound was purified with column chromatography by using Si-60 and eluding with hexane. Before combining the fractions, TLC and GC-MS were used to check for compound and impurity. The combined fractions were then checked for purity with GC-MS. After removing the solvent under vacuum at room temperature, the yield was determined and the residue was dissolved in hexane for storage.

1,3-Hexadecadiyne (1a) : Yield: 51%; ^{1}H-NMR: ($CDCl_3$) δ 2.28 (t, 2 H, $CH_2{\equiv}C$), 1.98 (s, 1 H, $HC{\equiv}C$), 1.28-1.56 (m, 20 H, $(CH_2)_{10}$), 0.90 (t, 3 H, ω-CH_3); ^{13}C-NMR: ($CDCl_3$) δ 78.62 ($C{\equiv}C$ –CH_2), 68.52 ($HC{\equiv}C$), 64.62 ($HC{\equiv}C$), 64.41 ($HC{\equiv}C$-$C{\equiv}C$), 31.91, 29.63, 29.62, 29.58, 29.45, 29.34, 29.05, 28.82, 28.00, 22.69, 19.03 ($C{\equiv}C$ –CH_2), 14.11 (ω-CH_3); UV: 218.0 nm, 225.1 nm, 232.9 nm, 252.1 nm; IR ν_{MAX} cm^{-1}: 3314, 2928, 2856, 2227, 1466.

1,3-Decadiyne (1b): Yield: 72%; ^{1}H-NMR: ($CDCl_3$) δ 2.28 (t, 2 H, $CH_2{\equiv}C$), 1.98 (s, 1 H, $HC{\equiv}C$), 1.22-1.56 (m,8 H, $(CH_2)_4$), 0.92 (t, 3 H, ω-CH_3); MS m/z (%): 133 ($[M\text{-}H]^+$, 2.6), 119 ($[M\text{-}CH_3]^+$, 20), 105 (83), 91 (100), 78 (42), 63 (31), 43 (30), 41 (36). Mass calc. for $C_{10}H_{13}$: 133.1017 $[M\text{-}H]^+$, measured: 133.1020 amu; UV,IR and ^{13}C-NMR spectra were not recorded.

Preparation of heptacosa-1-en-12,14-diyne (2a) and Heptadeca-1-en-8,10-diyne (2b)

To a solution of 1,3-Hexadecadiyne (1a) in THF (2 mL $mmol^{-1}$) at -23°C, was added dropwise 120 mol% of n-BuLi. The reaction mixture was kept stirring under Argon, at –23°C for 1 hour. Then a solution of 120 mol% of 11-Bromo-1-undecene (2a) in HMPA (2mL $mmol^{-1}$) was added dropwise. The mixture was kept at –23°C for 30 minutes, and then at room temperature for 2 hours. The pH was adjusted to pH 6 with 0,6M HCl, and the mixture was extracted with hexane. The combined organic layer was washed with saturated $NaHCO_3$, saturated NaCl, and dried over Na_2SO_4. After filtration, the solvent was removed in vacuum. The residue was diluted in hexane for storage. Purification: The obtained compounds were purified with column chromatography by using Si-60 and eluding with hexane. Before combining the fractions, TLC and GC-MS were used to check for compound and impurity. The combined fractions were then checked for purity

with GC-MS. After removing the solvent under vacuum at room temperature, the yield was determined.

Heptacosa-1-en-12,14-diyne (2a): Yield: 77%; ^{1}H-NMR: ($CDCl_3$) δ 5.82 (m, 1 H, C=CH-), 5.04-4.97 (m, 2 H, H_2C=C), 2.26 (t, 4 H, CH_2-C≡C), 2.05 (m, 2 H, =CH_2-CH_2-), 1.28-1.56 (m, 34 H, $(CH_2)_{17}$), 0.90 (t, 3 H, ω-CH_3); ^{13}C-NMR: ($CDCl_3$) δ 139.24 (H_2C=C), 114.11 (H_2C=C), 77.58 & 77.54 (CH_2-C≡C), 65.25 & 65.23 (C≡C-C≡C), 33.80, 31.92, 29.65, 29.63, 29.61, 29.48, 29.41 (2x), 29.35, 29.10 (2x), 29.07, 28.92, 28.86, 28.83, 28.35 (2x), 22.69, 19.21 (2x), 14.12 (ω-CH_3); MS m/z (%): 370 ([M]$^+$, 5), 216 (32), 201 (32), 147 (48), 145 (42), 133 (68), 119 (71), 105 (74), 91 (100), 81 (75), 79 (66), 67 (74), 55 (83). Mass calc. for $C_{27}H_{46}$: 370.3600 amu [M]$^+$, measured: 370.3606 amu; UV: 253.0 nm, 237.9 nm, 226.0 nm, 216.0 nm; IR ν_{MAX} cm^{-1}: 3079, 2829, 2257, 1640, 1466, 993, 912.

Heptadeca-1-en-8,10-diyne (2b): Yield: 64%;^{1}H-NMR: ($CDCl_3$) δ 5.82 (m, 1 H, C=CH-), 5.04-4.98 (m, 2 H, H_2C=C), 2.27 (t, 4 H, CH_2-C≡C), 2.07 (m, 2 H, =CH_2-CH_2-), 1.31-1.56 (m, 14 H, $(CH_2)_7$), 0.91 (t, 3 H, ω-CH_3); ^{13}C-NMR: ($CDCl_3$) δ 138.83 (H_2C=C), 114.39 (H_2C=C), 77.61 & 77.38 (CH_2-C≡C), 65.33 & 65.22 (C≡C-C≡C), 33.58, 31.30, 28.53, 28.37, 28.31 (2X), 28.20, 22.51, 19.21, 19.17, 14.03 (ω-CH_3); MS m/z (%): 230 ([M]$^+$, 4), 173 (28), 159 (39), 145 (64), 131 (66), 117 (65), 105 (62), 91 (100), 79 (53). Mass calc. for $C_{17}H_{26}$: 230.2035 amu [M]$^+$, measured: 230.2022 amu; UV: 253.0 nm, 237.9 nm, 226.0 nm, 216.0 nm; IR ν_{MAX} cm^{-1}: 3079, 2934, 2860, 2251, 1640, 1464, 996, 915.

Preparation of octacosa-13,15-diyne(3)

To a solution of 1,4-bis (trimethylsilyl)-1,3-butadiyne in THF (20 mmol in 40 mL) under Argon flow, was added dropwise 240mol% methylltihium-lithiumbromide complex in diethyl ether at –78°C. The mixture was kept under stirring for half an hour at –78°C and then was warmed up to –23°C and kept stirring at this temperature for 3 hours. After cooling down to –50°C, a solution of 240 mol% of 12-Bromoundecane in40 mL DMPU was added dropwise, and the system was maintained for 1 hour at –50°C. The system was then gradually warmed up to room temperature and kept stirring over night. Purification: The obtained compounds were first purified with column chromatography (Si-60/hexane) and then reversed phase chromatography (Si-100, C-18 reversed phase).

Octacosa-13,15-diyne(3): Yield: 56%;^{1}H-NMR: ($CDCl_3$) δ 2.26 (t, 4 H, CH_2-C≡C), 1.28-1.55 (m, 40 H, $(CH_2)_{20}$), 0.90 (t, 6 H, ω-CH_3); ^{13}C-NMR: ($CDCl_3$) δ 77.58 (CH_2-C≡C), 65.25 (C≡C-C≡C), 31.92, 29.65, 29.63, 29.61, 29.48, 29.35, 29.10, 28.86, 28.36, 22.69, 19.21, 14.12 (ω-CH_3);UV: 253.0 nm, 237.9 nm, 226.0 nm, 216.0 nm; IR ν_{MAX} cm^{-1}: 2928, 2856, 1465.

5.4 Formation of monolayers

Cleaning of the substrates

The samples were cleaned by sonication for at least 10 minutes in acetone. After drying with nitrogen they were treated for 3 minutes in oxygen plasma (plasmacleaner/sterilizer at high setting). Then for the Si(111) samples, the oxide-layer was removed by etching for 13 minutes in a 40%(v/v) NH_4F solution which was deoxygenated with argon for 30 minutes. The Si(100) samples were etched for 3 minutes in a 2.5%(v/v) HF solution. After quickly rinsing (only Si(111) !) with water (extra pure) and drying with nitrogen, the samples were immediately transferred to the reaction flask.

After the reaction the samples were cleaned with petroleum ether 40-60, ethanol, dichloromethane and dried with nitrogen. This step was repeated before every measurement. For storage the sample was flushed with nitrogen and packed under vacuum, either in plastic or a vacuum excicator.

Fabrication of monolayers

Thermal method: A 0,4 M solution of the used compound in mesitylene was transferred into a small three-necked flask fitted with a argon inlet, a reflux condenser with a $CaCl_2$ tube and was heated to 166°C. After heating and flushing with argon, the sample was added, and the monolayer was formed under refluxing mesitylene, for 2 hours.

Visible light method: A 0,4 M solution of the used compound in mesitylene was transferred into a special flask with a rectangular bottom and was flushed with argon for 30 minutes. After the wafer was added, the solution was flushed again with argon before the light was turned on. The reaction was performed with monochromatic 447 nm light obtained form a phosphor-coated pen lamp (Jelight Company, model 84-247-2, 32 nm bandwidth, ~3 mW/cm^2 intensity at 2 cm) at a distance of 0.5 cm, for 15 h under argon atmosphere [7].

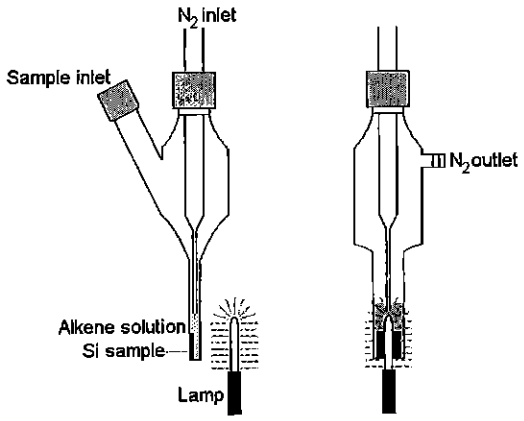

Fig. 5.6: Schematic representation of the set-up used for the visible light method [7].

Mild method: This method was performed by using either pure compound or a 0.4 M solution in mesitylene. The compound (1 g pure) was transferred into a special flask with

a flat bottom, a regular cooler was mounted and the system was heated to the desired temperature and put under vacuum. The liquid was flushed with argon through a capillary for at least 15 minutes, before the sample was added. After placing the sample the system was put under vacuum, and the capillary was retracted a few centimetres to leave the liquid interface undisturbed while still flushing with argon. The method for the reaction with mesitylene differed in such manner that a specially devised cooler was used to reflux the mesitylene. In order to cool down to a lower temperature, this cooler could be filled with ice and water. Instead of 1g of pure compound, 10 mL of a 0.4M solution in mesitylene was used.

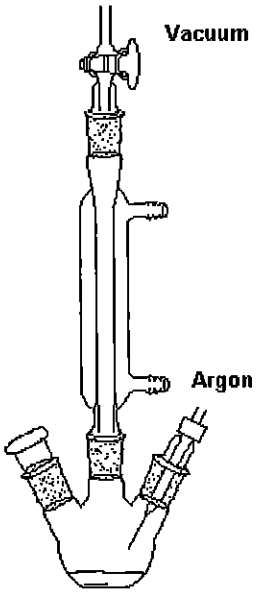

Fig. 5.7: Representation of the set-up used for the mild attachment method.

Recycling of used compounds

The formation of monolayers requires large quantities of compound that turn yellow when exposed to temperatures above room temperature. This colouring may be caused by polymerization of the diacetylenes. However the used compounds can be recycled by 'filtration' over silica gel. For this purpose a small column (ϕ ~2 cm) was packed with 3 to 4 cm of Si-60. The crude product was loaded pure or in a hexane solution and was eluded with hexane. The yellow substance that consists of short polymers (di-mers, tri-mers, etc.) stayed in the top cm of the gel. The 'filtrate' yielded slightly yellow coloured compound after evaporation of the solvents.

Acknowledgements

Reflecting back on the past eighteen weeks, I can't help thinking that time went by very fast. A little bit too fast if think about the ideas that are still spinning in my head. On the other hand, I'm also happy that I almost completed this thesis. This wouldn't have been possible without the help of some people who I would like to thank.

First of all I would like to thank Luc Scheres, for being my supervisor and showing me around in the lab. I liked the way you guided me through my first experiments, and got me started out.

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During my experimental work I was bound to a tight time schedule and I would like to thank the following people for helping me out:
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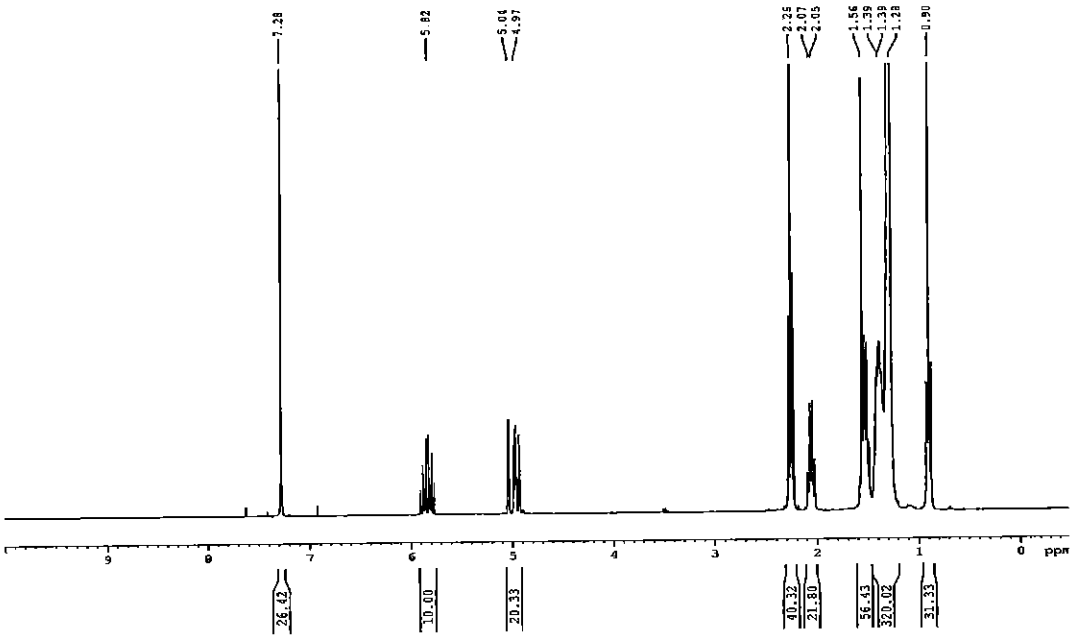
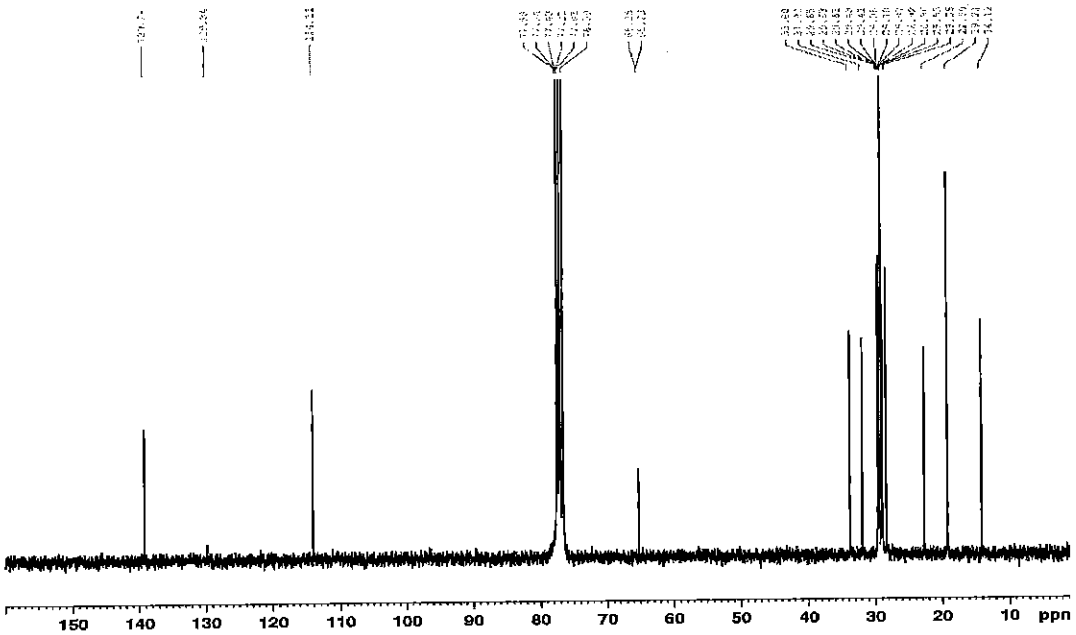
Appendix

NMR, FT-IR and UV-VIS spectra

Heptacosa-1-en-12,14-diyne (2a)-C27





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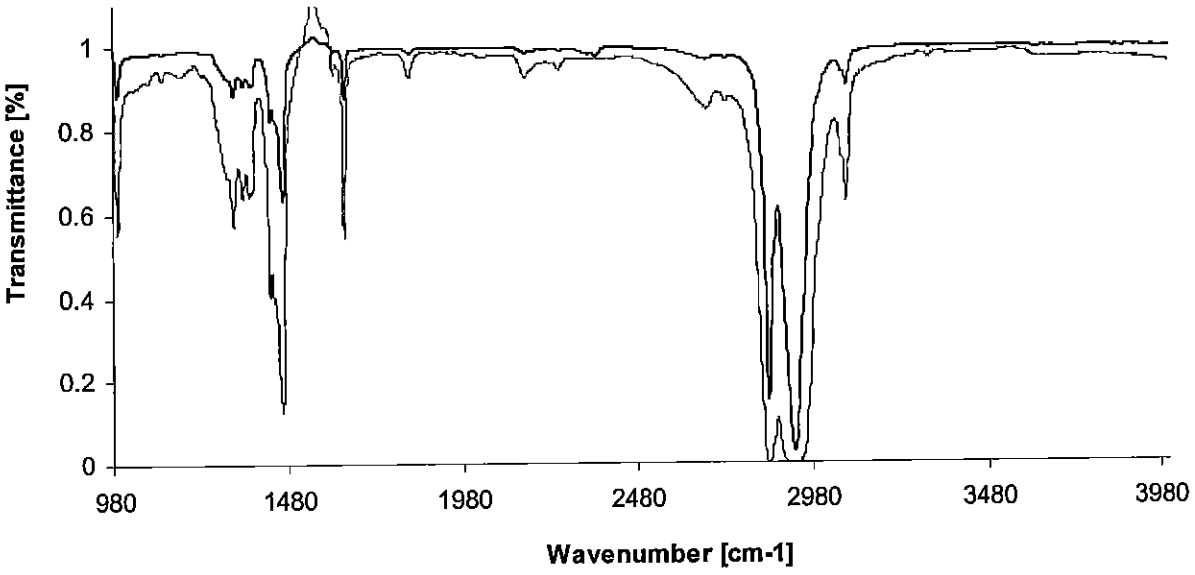
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2480
2980
3480
3980
Wavenumber [cm-1]

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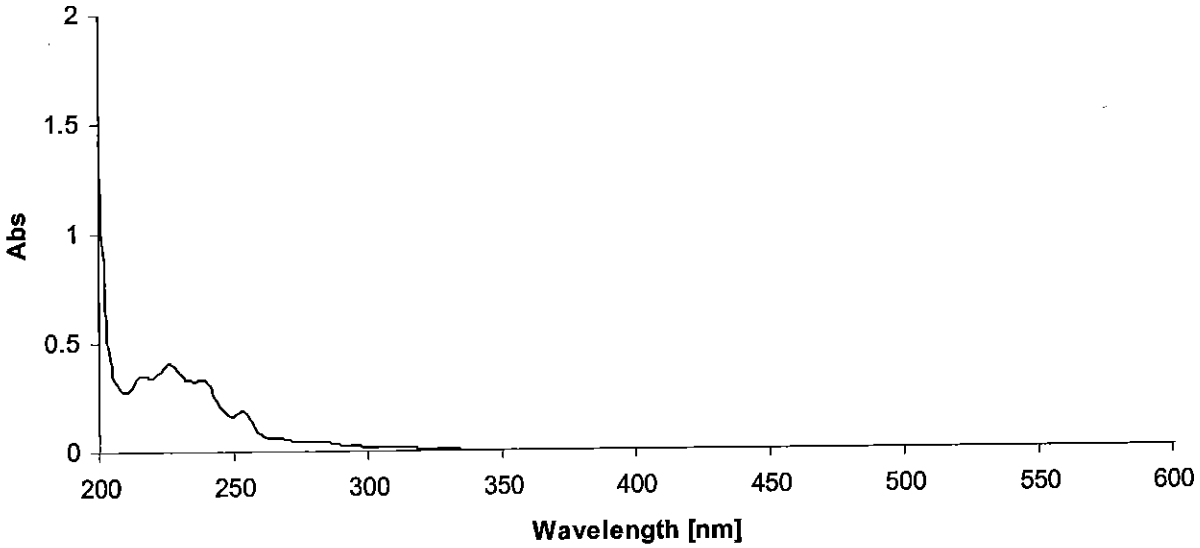
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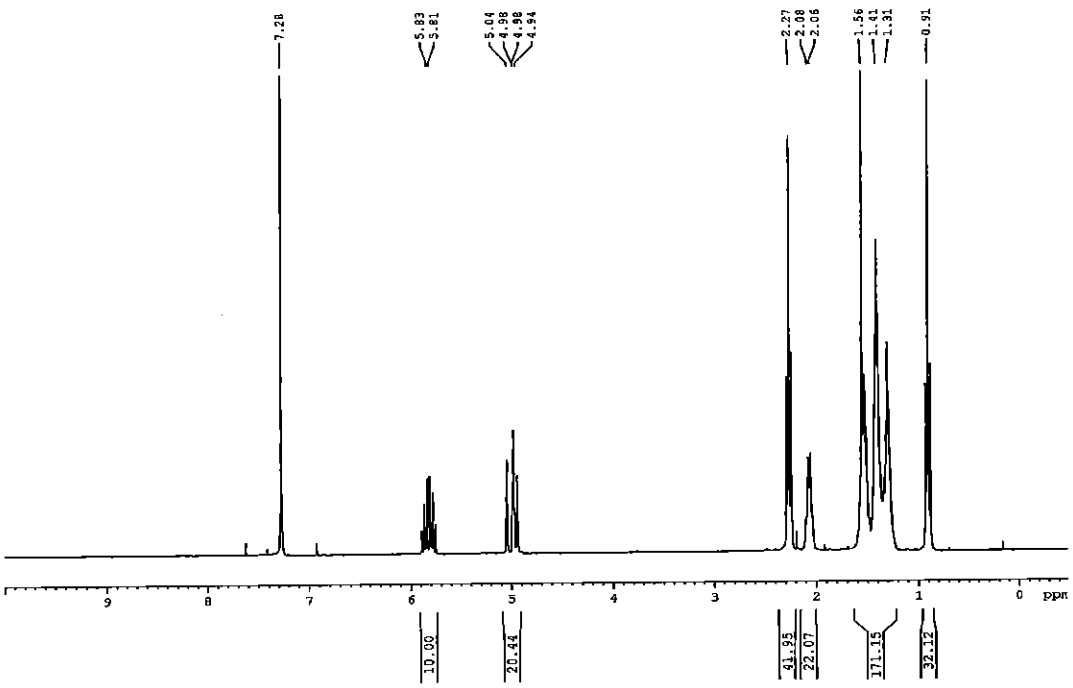
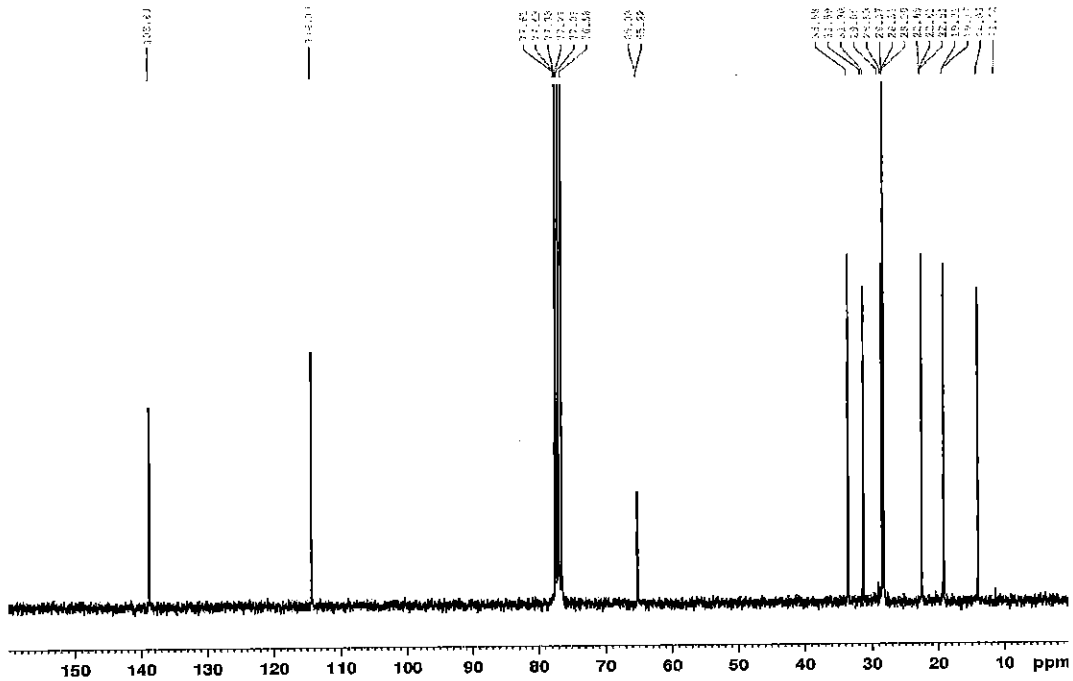
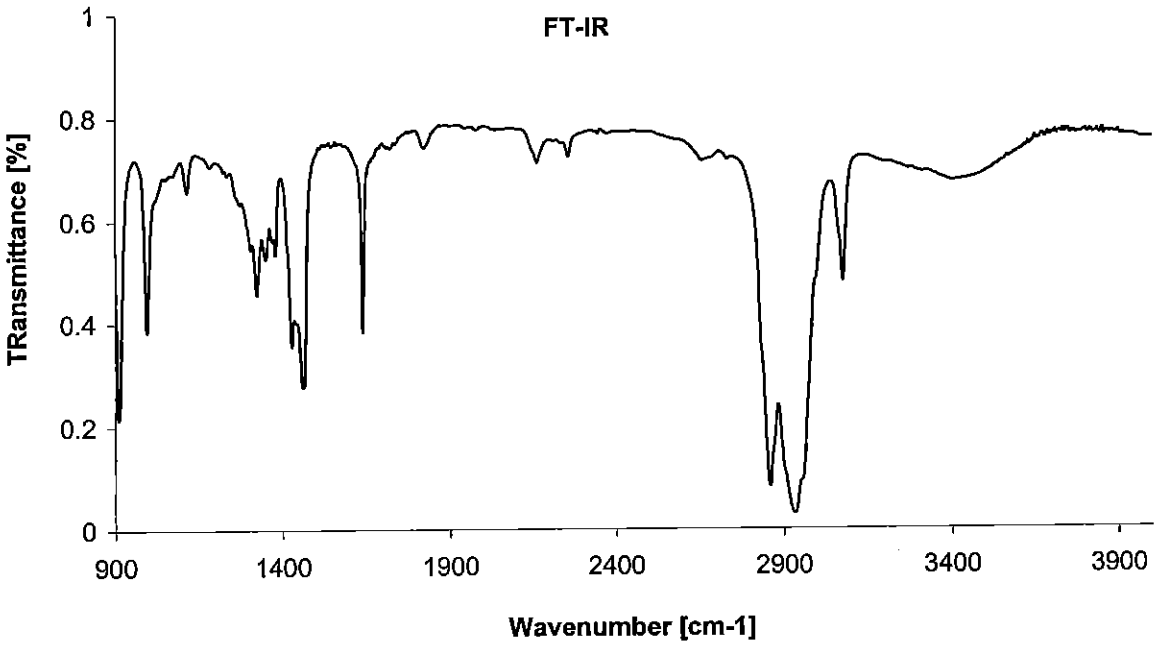
Wavelength [nm]

Heptadeca-1-en-8,10-diyne (2b)-C17



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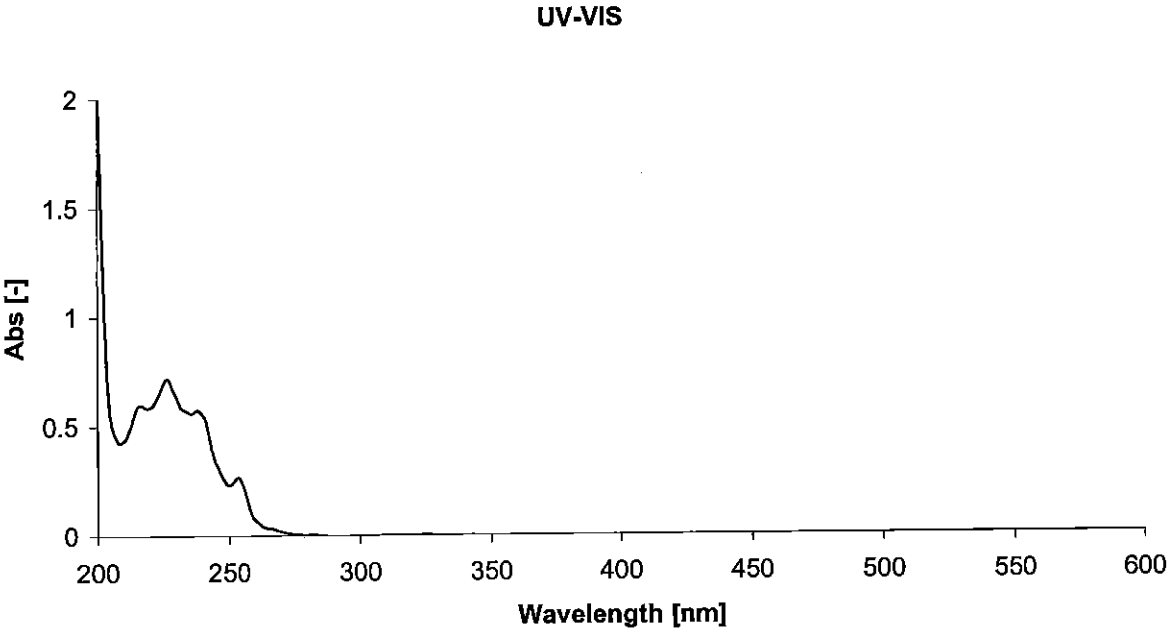
3900
Wavenumber [cm-1]


UV-VIS
Abs [-]
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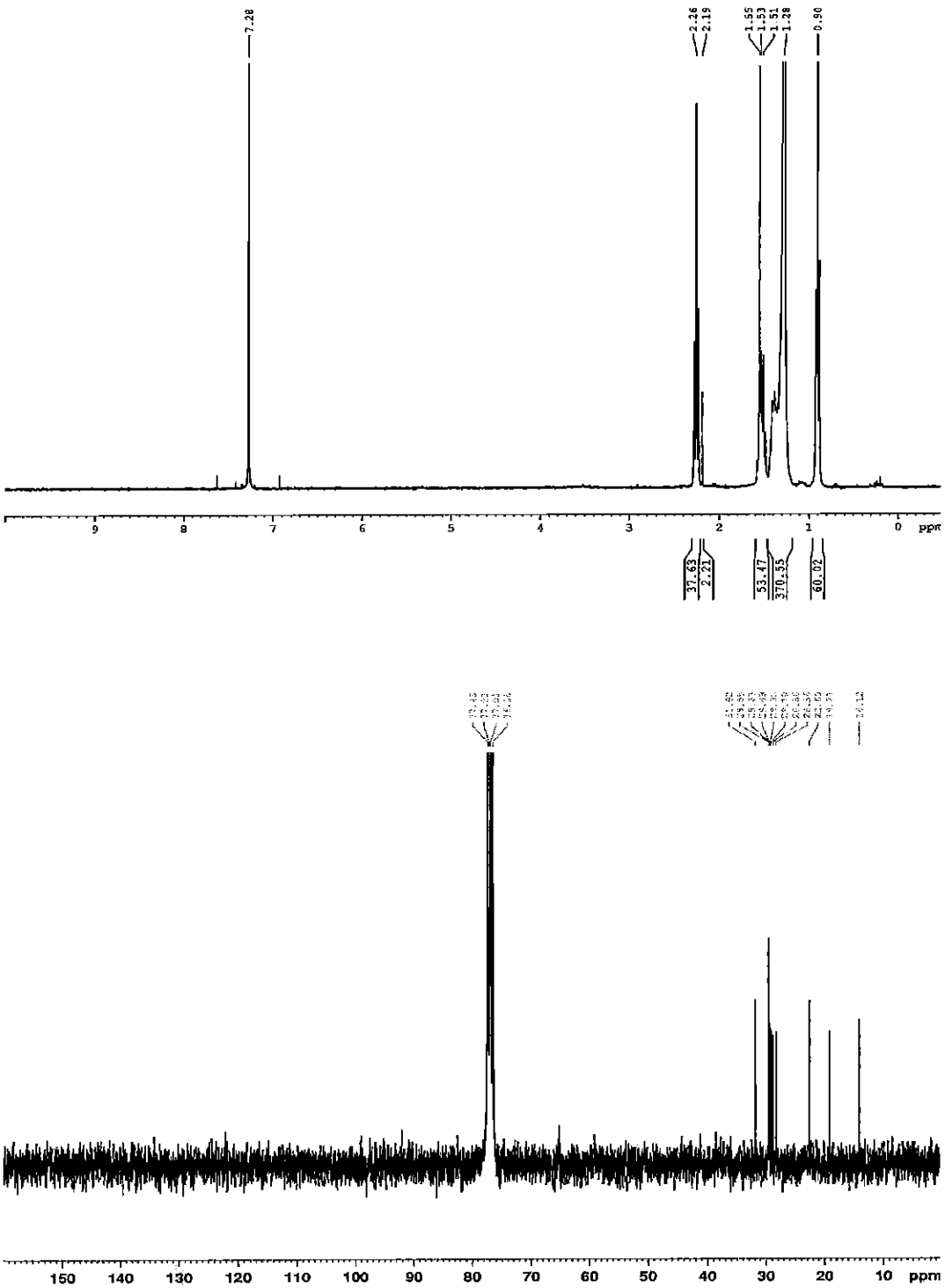
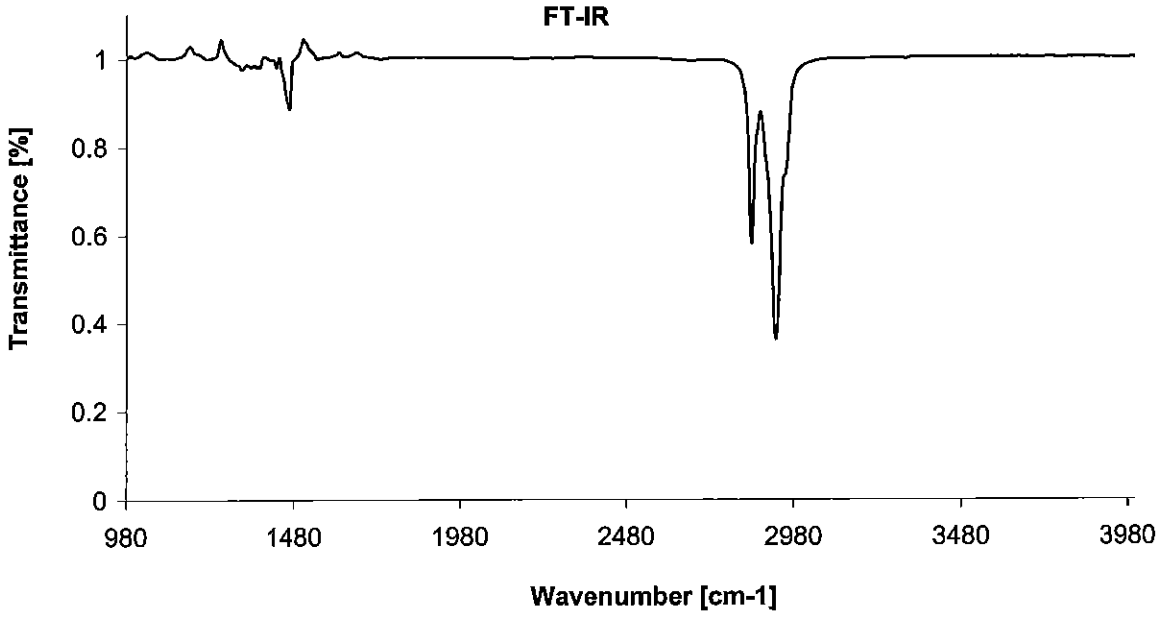
Wavelength [nm]

Octacosa-13,15-diyne (3)-C_{28}




FT-IR
Transmittance [%]
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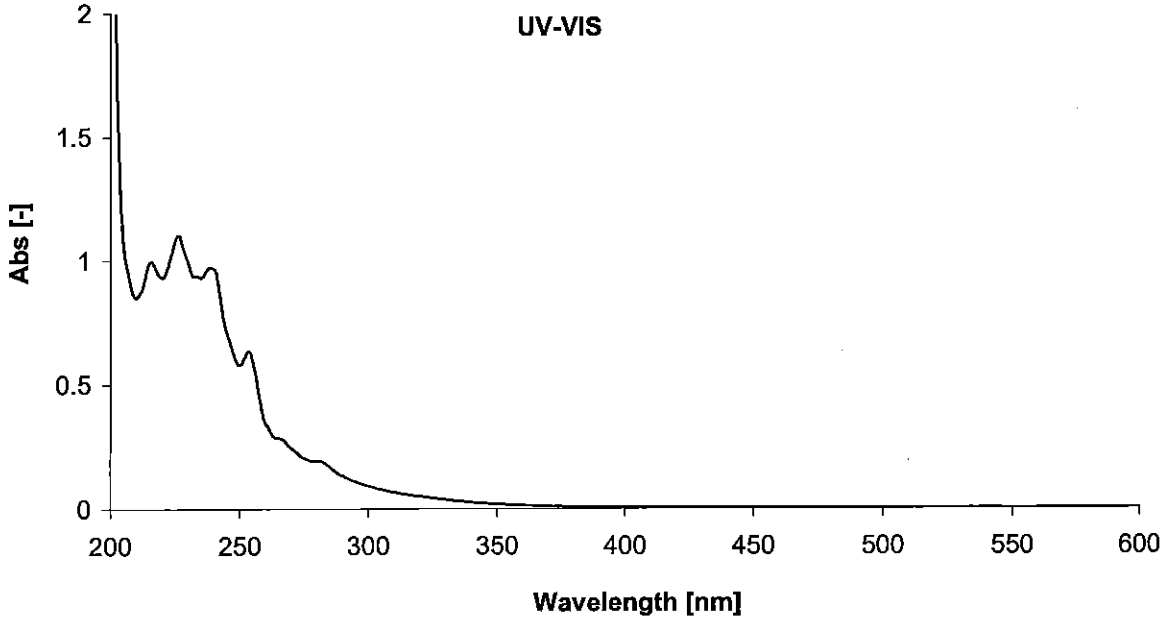
980
1480
1980
2480
2980
3480
3980
Wavenumber [cm-1]


UV-VIS
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Wavelength [nm]