Precursor route to ethenyl-substituted polyacetylenes: synthesis of homopolymers of o-trimethylsilyl ethers of 1-alkyl and 1-aryl substituted but-3-yn-1-ols. Desilylation, dehydration and pyrolysis to conducting films

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Precursor route to ethenyl-substituted polyacetylenes: synthesis of homopolymers of o-trimethylsilyl-ethers of 1-alkyl and 1-aryl substituted but-3-yn-1-ols. Desilylation, dehydration and pyrolysis to conducting films

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Abstract

Poly(o-trimethylsilyl-but-3-yn-1-ols) were prepared from trimethylsilyl ethers of RCH(OH)CH$_2$CCH (R=H, Me, C$_6$H$_5$ or $\text{-CH=CHCH}_2$) via Ziegler-Natta polymerization (Fe(acac)$_3$/AlEt$_3$ in toluene, 20–35 °C) of the terminal triple bond. The polymers were obtained as yellow amorphous solids (10–23%, polymer with R=H was a viscous gum) with atactic microstructure ($^{13}$C NMR), soluble in apolar solvents. The polymer from the monomer with R = $\text{-CH=CHCH}_2$ could be desilylated quantitatively with potassium fluoride. Elimination of water at 200–250 °C from films of this deprotected polymer gave a semiconducting material ($10^{-4}$ S/cm) after activation with iodine. Heating the undoped film for 10–20 min at 650 °C in nitrogen atmosphere gave an intrinsically conducting brittle film ($10^{-2}$ S/cm) with silvery-black lustre. Activation with iodine enhanced the conductivity to $10^1$–$10^2$ S/cm. High conductivity was not persistent in ambient atmosphere.

Introduction

The homopolymer of acetylene is the most efficient synthetic metal known to date [1]. Poor mechanical properties and sensitivity toward autoxidation in ambient atmosphere have barred practical application. Attempts to stabilize the material by protecting the polyenic backbone with bulky substituents or by replacing olefinic units by phenyl, thienyl, etc., functions have invariably led to loss of conductivity. Ethynyl, carbonyl and amide moieties impair electron mobility in polymer chains to an even higher extent. Naturally, anti-aromatic units, such as cyclobutadienyl, benzocyclobutadienyl, fulvenyl groups, etc., lead in theory to narrow bandgap CH conductors. However, all these structures can be expected to be sensitive to oxygen. In the (n)-phenylene series (alternating annelated phenyl and cyclobutadiene units) the silylated pentamer was reported as a deep-red, extremely air-sensitive compound and the hexamer could not be prepared [2a]. Instability of polyacenes at the pentamer–hexamer level is well documented [2b]. The polyfulvene and polyvinylene fulvene, for which bandgaps of 0.87 and 0.96 eV were calculated [2c], are predestined to be air-sensitive. Thus, the
development of physical or chemical methods to stabilize synthetic CH metals is of prime importance. From a polymer synthetic point of view, the development of a fully interconnected non- or even anti-aromatic $sp^2$-polyenic 3-D net seem a viable answer to the problem [3a]. Stabilization of electronic properties can be envisioned to occur eventually by passivation via a protecting 'oxide' (cf. carbonylic) coating on the surface strands [3b].

In this perspective, the present study is focused on new polyacetylenes with small unsaturated side chains to (i) define the conditions for an optimal compromise between chemical stabilization with substituents and retention of electronic properties and (ii) develop precursor routes to essential polyenic 'knots' for a 3-D net, i.e., configurations of the type:

Grubbs and coworkers have recently demonstrated accessibility to structures with one side chain per eight carbon atom fragments by ring-opening metathesis polymerization of cyclooctetraene and several derivatives [4a]. Conductivity of soluble polymers was shifted to the metallic regime after doping with I$_2$; however, chemical stability was not improved [4b]. The concepts outlined here can be extended to this monomer. The possibility of incorporating one side chain per four $sp^2$-carbon atom fragments via 1,4-polymerization of conjugated monosubstituted enynes has scarcely been explored [5]. Russian workers have reported 1,4-addition polymerization of vinylacetylene and its 1- and 3-phenyl-substituted derivative and have claimed high conductivity after doping with FeCl$_3$ [6]. The initially formed polyallenic structure was assumed to isomerize to a polyacetylene*. Other workers reported vinylacetylene polymerization in the presence of excess butyllithium to a material in which triple bonds are intact [7]. The influence of triple bond substituents on polymerization modes and electronic properties has been evaluated in considerable detail. Cyanoacetylene and dicyanoacetylene were reported to give rise to conducting solids (10 S/cm) unaffected by dopants [1b]. Selective 1,2-polymerization of the terminal triple bond in butadiynyltriethylsilane gave a dark-brown solid after treatment with fluoride ion (80% desilylation, $10^{-8}$ S/cm undoped, with iodine $10^{-5}$ S/cm). An intrinsic conductivity of $7.8 \times 10^{-1}$ S/cm was observed after heat treatment of this polymer at 800 °C [8]. Anionic polymerization of but-3-en-1-ynyltrimethylsilane (monosilylated vinylacetylene) produced a non-conducting ethynyl-flanked polyethylene [9]. Silylated 1,1-diethynyl ethene was found to undergo rapid thermal polymerization

*In our hands, polymerization of cyclohexenyl acetylene with Fe/Al catalyst or MoCl$_5$, did not proceed in a 1,4-addition mode.
exclusively via the double bond to a yellow non-conjugated material, dark-brown after desilylation (10⁻⁶ S/cm, I₂ dopant) [10a]. The polymerization mode of phenyl-, t-butyl analogue and of the unsubstituted 1,1-diethynyl ethene moiety is presently unknown [10a]; we assume the sp–sp² system to react via an inter- or intra(macro)molecular cycloaddition (enyne + ene), similar to the dimerization of fulvene [10b]. The homopolymer of isopropenylacetylene was obtained as an orange solid, poorly conducting (10⁻⁹ S/cm) after doping with FeCl₃ [11]. Polymerization of cyclohexenyl acetylene was described in a patent without experimental data of spectroscopical and/or electrical properties of the product* [12]. Polyacetylenes with sp² –CH=CH₂ substituents have not been reported.

In this communication we describe the syntheses of polyacetylenes with masked ethylenic side-chain substituents, to be unveiled via eliminative pyrolysis after processing into fibres or films. Specifically, we prepared homopolymers of o-silylated but-3-yn-1-ols and evaluated structural requirements for a desilylation–dehydration sequence:

\[
R₁CH=O + HC=CH₂Br \xrightarrow{1. \text{Zn, ultrasound}} \xrightarrow{2. \text{ClSiMe₃}} R₁CCH₂C=CH
\]

\[
\text{Fe(acac)}₃ \rightarrow \text{AlEt₃}
\]

\[2 \text{a-d}\]

\[3 \text{d}: R₁ = \text{CH}=\text{CHCH₃}; R₂ = \text{H} ; 4: R₁ = \text{-CH}=\text{CHCH₃}\]

Analogous to previously developed examples of precursor routes to polyacetylene and other conducting polymers [13], complete characterization of soluble intermediates prior to the conversion to intractable conducting materials was possible [13]. This strategy, in addition to being relevant for the design of synthesis of a 3-D polyenic net, has potential in lithographic etching of conducting tracks in cast films with laser irradiation [14] and covalent binding of carbon solids to pretreated glass or semiconductor supports [4b].

*In our hands, polymerization of cyclohexenyl acetylene with Fe/Al catalyst or MoCl₅, did not proceed in a 1,4-addition mode.
Experimental

Synthesis of monomers 1a–1d

O-Trimethylsilyl-but-3-yn-1-ols RCH(OSiMe₃)CH₂CCH₃, 1a (R = H) and 1b (R = CH₃), were prepared by o-silylation of commercial 1-pentyne-4-ol (racemic) and but-3-yn-1-ol with trimethylchlorosilane in dry ether with a 1.2 equivalent of pyridine for 3–4 h at ambient temperature according to literature procedures [15]. After neutral work-up, the monomers 1a and 1b were purified by distillation: 1a, b.p. 121–125 °C/760 mmHg, and 1b, b.p. 61–62 °C/22 mmHg.

Racemic but-3-yn-1-ols R*CH(OH)CH₂CCH₃, 1c (R = C₆H₅) and 1d (R = –CH=CHCH₃), were prepared from benzaldehyde, respectively crotonaldehyde and propargyl bromide, via a Reformatsky reaction in tetrahydrofuran stimulated with ultrasound [16]. In a well-ventilated hood, equivalent amounts of carbonyl compound and the bromide (50 mmol scale at maximum) were dissolved in tetrahydrofuran (200 ml, p.a., undistilled) in a three-necked flask with magnetic stirrer, immersed in an ultrasound bath filled with water at 20 °C (Bransonic 12, 30 W output at 48 kHz, cleaning bath). Unactivated Zn dust (100 mmol) was added and disappearance of the colour of a few dissolved iodine crystals indicated the start of the reaction when the stirrer and ultrasound bath were switched on. Stirring and ultrasound stimulation were maintained for 1–2 h, during which time the temperature rose to 45–50 °C. Consumption of the aldehyde was monitored by ¹H NMR. The mixture was poured on ice, extracted with ether and extracts were washed with water to neutrality; solvents were removed and the tertiary alcohol was submitted to vacuum distillation, the 1-phenylbut-3-yn-1-ol at 87–89 °C/0.3 mmHg (precursor for 1c) and b.p. for hept-5-en-1-yn-4-ol 70–72 °C/16 mmHg (precursor for 1d). A 2–7% contamination of allenic material (NMR multiplet at 4.8–5.2 ppm) could be removed by column chromatography (silica gel, eluent hexane/ethylacetate 4:1 vol./vol.), monitored by analytical thin layer chromatography and NMR as a slightly less polar component. Treatment with trimethylchlorosilane in ether in the presence of pyridine [15] at room temperature for 20 h afforded the monomers, 1c and 1d, as distillable liquids, 1c, b.p. 53–55 °C/0.04 mmHg (58%) and 1d, 63–65 °C/15 mmHg (52%). Structure and purity of all monomers were monitored by 400.13 MHz ¹H and 100.61 MHz ¹³C FT NMR and elemental analyses.

Synthesis of homopolymers 2a–2d

Polymerization the monomers of 1a–1d was carried out with a Ziegler–Natta catalyst derived from Fe(acac)₃ and AlEt₃ (Fe/Al ratio 1:4, Fe/monomer ratio 1:20) under nitrogen in dry toluene at 20–35 °C [14]. Conditions, molecular weight yield and melting behaviour are listed in Table 1.

The polymerization was terminated by pouring the brown–black reaction mixture in excess methanol. Stirring was continued for 20 h at 20 °C until complete trituration of the crude product. The polymers were purified by
### TABLE 1

Homopolymers of o-silylated but-3-yne-1-ols 2a–2d

<table>
<thead>
<tr>
<th>Polymer</th>
<th>T (°C)</th>
<th>Time (h)</th>
<th>Yield (%)</th>
<th>M.p. (°C)</th>
<th>M.W. (10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a, R = H</td>
<td>40–45</td>
<td>1</td>
<td>&gt; 95</td>
<td>syrup</td>
<td></td>
</tr>
<tr>
<td>2b, R = CH₃</td>
<td>18–20</td>
<td>12</td>
<td>24</td>
<td>185</td>
<td>80</td>
</tr>
<tr>
<td>2c, R = C₆H₅</td>
<td>18–20</td>
<td>20</td>
<td>15</td>
<td>175</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>250 (dec.)</td>
<td></td>
</tr>
<tr>
<td>2d, R = –CH=CHCH₃</td>
<td>18–20</td>
<td>20</td>
<td>19</td>
<td>250</td>
<td>148</td>
</tr>
</tbody>
</table>

*aTypical run: 1 mmol Fe(acac)₃ (recr.) was dissolved in 8 ml dry degassed toluene under nitrogen; 4 mmol of Al(Et)₃, 2 ml of a commercial 2 M stock solution in toluene, were added with a syringe. The resulting brown-black mixture was stirred and heated at 35 °C for 1–2 min and the catalyst allowed to age at ambient temperature for 30 min. The 20–30 mmol of the monomer was added without cooling or heating.*

*bRecorded on a Perkin–Elmer automated DSC, indium standard.

*cGel-permeation chromatography, calibrated with polystyrene, tetrahydrofuran solvent.

*dExothermic reaction.

*ePhase transition.

Soxhlet extraction with chloroform and reprecipitation in methanol. The polymers were stored under nitrogen in the dark in a refrigerator. FT NMR spectroscopy was performed on a Bruker AM-400 instrument operating at 400.13 MHz for ¹H and 100.61 MHz for ¹³C with a relaxation delay of 7.5 s and 5–6000 cumulative scans for the polymers in CD₂Cl₂.

**Desilylation**

Desilylation was carried out in a deoxygenated well-stirred two-phase system of dilute aqueous HCl/methanol (10:1)/KF and CHCl₃ with a catalytic amount 18-crown-6 at ambient temperature, monitoring the decrease of –OSiMe₃ signal in ¹H NMR. Thermogravimetric analyses were performed on a Perkin-Elmer automated TGA-7 apparatus.

**Dehydration and pyrolysis**

Pyrolyses of glass-supported films were carried out under nitrogen flow in a quartz or Pyrex tube in a cylindrical oven thermostat controlled by an Fe–CuNi or Rh–Pt thermocouple.

D.c. conductivities of the glass-supported films were measured by the two-point probe method, using copper wire contacts connected with colloidal Ag–epoxy glue, either in ambient atmosphere or under nitrogen in a Schlenck vessel with iodine crystals. Specific conductivity was calculated after removal of the films from the glass support, estimating the density of the material to be approximately 1.9 g/cm³, the value of commercial carbon fibre (PAN-based, d.c. conductivity 10¹ S/cm, unaffected by doping with iodine). Conductivities fluctuating within 0.5–1 order of magnitude between 17–22 °C are reported in integer powers of ten.
Results and discussion

Polymerization of o-trimethylsilyl ethers of but-3-yn-1-ols 1a–1d monitored by FT NMR took place selectively via the terminal triple bond. Sharp acetylenic signals of the monomers at 69.9 and 81.1 ppm reappeared as a multiplet in the olefinic region at 125–128 ppm. The signals of the $-\text{CH}_2\text{CRH}($OSiMe$_3$) side chain manifested as multiplets at 42–46 ppm ($-\text{CH}_2-$), 74–76 ppm ($-\text{CHRO}-$) and 0.2–0.4 ppm ($-\text{OSi(CH}_3)_3$) (see Fig. 1) with R = $-\text{CH}=\text{CHCH}_3$. Sharp $^{13}$C signals at 34.2 and 129.9 ppm were assigned to small amounts of trimer. The broad signal of the vinylic region clearly indicates atactic microstructures for all polymers [17, 18]. FT-IR spectroscopy (KBr pellets) proved the absence of carbonylic impurities (1705 cm$^{-1}$) [17]. The highest yield was realized in the case of the unsubstituted o-silylated but-3-yn-1-ol, 1a. A 7 g quantity of monomer was consumed within

![Fig. 1. $^{13}$C NMR spectra of 1d and 2d, for R = $-\text{CH}=\text{CHCH}_3$ (a) in CDCl$_3$; (b) polymer in CD$_2$Cl$_2$. Solvent at 77.0 and 53.8 ppm, respectively.](image)
30–60 min in an exothermic reaction 30–40 °C. The polymer 2a was obtained as an orange–yellow gum, completely soluble in chloroform. The polymers 2b–2d were isolated after Soxhlet extraction/reprecipitation in moderate yields (10–23%) and obtained as yellow solids (combustion analyses within 2% from theoretical values).

Polymer 2a (R=H) could be desilylated readily (20–30 min) to give a greenish gum (cf. oily polymers from propargyl alcohol [11]). Dehydration experiments with the desilylated 3a gave rise to incoherent black powders and this polymer was not studied in detail. The polymer 2b (R=Me) could be deprotected only up to 55–60% (2–3 days); 2c (R=phenyl) resisted desilylation completely under the given conditions. Treatment of 2d (R = crotyl, –CH=CHCH3) with potassium fluoride for 12–16 h gave rise to a yellow solid, insoluble in water, chloroform and methanol. This polymer could be reprecipitated from pyridine solution in methanol (dec. > 250 °C) and was characterized as the desilylated polymer 3d by FT-IR (broad intense absorption around 3406 cm⁻¹) and combustion analysis; yield 86%. Anal. Calc. for C₇H₁₀O: C, 76.4; H, 9.1%. Found: C, 72.61; H, 8.44%. ¹H NMR (in pyridine-d₅) proved >99% desilylation with an accuracy of 1%. ¹³C NMR gave a sharp signal at 18 ppm for the CH₃-group, broad signals at 70–74 ppm for –CHROH and 43–47 ppm for the –CH₂CHROR. The vinylic region was obscured by small amounts of H-pyridine after 30 000 cumulative scans. TGA analysis of 3d (see Fig. 2) showed that a distinct fragment corresponding to a weight loss of an equivalent of water was expelled at 200–222 °C under nitrogen flow.

Thermolysis of glass-supported films cast from pyridine solution (15–20 mg/cm²) of 3d below 260 °C (1–2 h) gave rise to an insoluble transparent

![Fig. 2. Thermogravimetric diagram of dehydration of polymer 3d.](image-url)
yellow-brown film, dehydrated and partially annealed as demonstrated by the change in IR spectrum (Fig. 3). This material had an intrinsic conductivity of $10^{-8} - 10^{-7}$ S/cm. Activation in iodine atmosphere raised this level to $10^{-3} - 10^{-4}$ S/cm within 5–6 h. We conclude that ethenyl sp$^2$-CH substituents flanking the polyene in alternating 1,3-fashion do not conjugate with the polyene backbone and impair planarity of the polyene backbone as well. However, in the case of 1d–2d–3d with $R_1 = -$CH=CHCH$_3$, a complete polymerization–desilylation–dehydration sequence to an idealized structure

![Fig. 3. IR spectra (KBr) of 3d (a) before and (b) after heat treatment at 200 °C for 2 h.](image)
4 is tractable and can be applied to other monomers [2]. Anal. Calc. for C\textsubscript{7}H\textsubscript{8}: C, 91.3\%; H, 8.7\%. Found: C, 88.2\%; H, 6.5\%.

Prompted by three reports of enhanced conductivity in carbon solids obtained after heat treatment of polymers at elevated temperature, i.e., laser irradiation of imide films [19] and thermal treatment of oxidatively coupled divinylbenzene-type polymers (all sp\textsuperscript{2}-carbon electrodes) [20], and the results of Khemani and Wudl with the pyrolysis of polyketene giving rise to an O-containing annelated network with an intrinsic conductivity higher than that of graphite [21], we decided to study the properties of the films of 3d after pyrolysis at elevated temperatures. TGA analysis indicated a gradual weight loss over the 250–600 °C region. Heat treatment of the glass-supported film at 650 °C for 10–15 min gave a 50–60\% yield of interconnected pieces of a silvery black lustrous material (FT-IR: broad undefined bands). Intrinsic conductivity in air was determined to be 10\textsuperscript{-2} S/cm. When impended in iodine atmosphere, the brittle films were rapidly activated (5–6 h) to a conductivity of 10\textsuperscript{1}–10\textsuperscript{2} S/cm, one power of ten above the commercial PAN-based carbon fibre we used as reference in d.c. conductivity measurements. We assume some graphitization has taken place during heat treatment. The highest conductivity of doped films of pyrolysed 3d was not persistent in ambient atmosphere (two powers of ten decrease in 2–3 days), indicative of partial retention of the polyenic character of the material. Heat treatment and doping of silylated polymers 2a, 2b and 2c produced films with inferior conductivity.

Conclusions

A route to polyacetylenes via polymerization of monomers RCH(OSiMe\textsubscript{3})CH\textsubscript{2}CCH gave rise to a moderately conducting glass-supported film after desilylation, dehydration at 200–250 °C and doping with iodine in the case of R=crotyl, --CH=CHCH\textsubscript{3}. An intrinsic conductivity 10\textsuperscript{-2} S/cm was achieved after heat treatment of the undoped film at 650 °C for 10–20 min. Doping with iodine activated the material up to 10\textsuperscript{2} S/cm. This level of conductivity was not persistent in ambient atmosphere. At present, the structural requirements for a successful precursor route to an ethenyl-substituted polyacetylene are defined. R in 2a–2d should be small and unsaturated to allow a tractable desilylation and dehydration sequence. With
the possibility of selective polymerization in a choice of monomers accessible from acetylene, vinylacetylene, cyclooctatetraene, etc., coupled with the facile hydrolysis of O–Si and Si–C bonds and the possibility of thermal crosslinking at moderate temperatures [10a] via eneyne, diethynylethene, fulvene, etc., unmasked side chains, a rich synthetic repertoire to 3-D polyenic nets is now available.

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References

3 (a) An idealized non-graphitic 3-D network of sp²-carbons was predicted to be metallic: R. Hoffmann, T. Balaban, M. Kertesz and P. Bird, J. Am. Chem. Soc., 106 (1987) 6742. "If one could only think of a way to synthesize such a compound".
4 (a) S. R. Marder, J. W. Perry, F. L. Klavetter and R. H. Grubbs, Chem. Mater., 1 (1989) 171; (b) Spin-coating of this polymer on n-silicon gave rise to efficient (1–5%) solar cells: (photo)conductivity was reported to be sensitive for oxygen in ambient atmosphere. M. J. Sailor, E. J. Ginsburg, C. B. Gorman, A. Kumar, R. H. Grubbs and N. S. Lewis, Science, 249 (1990) 1146.


