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Novel carbonaceous coupling products containing sulphur

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Summary

The coupling of alkali ethynides with $CSCl_2$, $SOCl_2$, or SO_2Cl_2 results in new carbonaceous polymeric products; their structures were studied by FTIR and XPS spectra, and the assumptions on reaction mechanism were made with respect to the found elemental composition and model calculations. These macromolecular products, obtained in the yields of 80–92%, contain chlorine in the chain terminals, and alkyne sequences along with inserted C=S, S=O or SO_2 groups. These inserted sulphur groups contribute to the stability of alkyne sequences as evidenced by FTIR spectra. Soluble thioketone $iPr_3SiC{\equiv}C\text{-}CS\text{-}C{\equiv}CSiiPr_3$ (**2**) prepared by similar coupling of $iPr_3SiC{\equiv}CLi$ (**1**) with $CSCl_2$ in the yield of 72%, was considered as a support of the suggested coupling mechanism. Similarly monomolecular sulfoxide $iPr_3SiC{\equiv}C\text{-}SO\text{-}C{\equiv}CSiiPr_3$ (**3**) was prepared by coupling of $iPr_3SiC{\equiv}CLi$ (**1**) with $SOCl_2$ in the yield 75%.

Introduction

Walton and Johnson have started the polyyne stabilization by α,ω- silylation [1] of the alkyne chain. The polyyne terminals were capped by bulky groups, and Hirsch [2] et al. applied even 3,5-disubstituted diphenylether dendrimers in α,ω-positions of alkyne chain for an improved protection. Diederich and coworkers [3-5] suggested, moreover, an internal stabilization of the polyyne chain. They have introduced polymer coupling of bifunctional alkyne monomer containing arylene or hetarylene substituted by bulky groups. The other copolymerization reactions were a little more complex, since, moreover, the same bifunctional main monomer alkyne a minority monoprotected alkyne component was included [5]. The disproportionation reaction, at the substituted alkali monoalkynide and at the bare monoalkynide derivatives, proceeds quickly, relatively to other derivatization reactions. This feature decreases the efficiency of the Hay dimerization reaction, aimed at preparation of longer polyyne chains. A regular sequence of triple bonds conjugated in the polyyne chain is rather an ideal vision. The alkyne structure of the monomer is disturbed at its transfer into the resulting polymer chain by the course of side addition and casual crosslinkage reactions. Both mentioned side reactions affect the length of the carbon chain, the length of alkyne sequences, and the nature of the chain terminals.

We tried to carry out simple coupling reactions in order to obtain internally protected polyyne chains. The interaction of alkali alkynides with chlorinated compounds of sulfur, as $CSCl_2$, $SOCl_2$, and SO_2Cl_2, was selected in order to implement this idea. The reactivity of easily available dialkali alkynides is low perhaps due to their poor solubility, esp. at low temperature. On the other hand, an increased temperature (higher than –20°C) leads to the disproportionation course at monoprotected or monoderivatized alkali alkynides. According to Brandsma [6], at elevated temperatures dialkali ethynides are prepared. On the contrary, higher dialkali alkynides cannot be prepared by lithiation of bare alkynes, since instead of disproportionation reaction operating at ethyne, a polymerization occurs towards higher polymer alkali alkynides. That is why higher alkali alkynides (C_4 – C_6) were reliably generated by alkali dehydrochlorination of particular α,ω-di(chloromethyl)alkynes [7].

Experimental

Materials

Dilithium ethynide was prepared according to Brandsma [6], dipotassium ethynide in a similar way from t-BuOK. Dialkali hexatriynides were prepared from particular α,ω-di(chloromethyl)alkynes by dehydrochlorination with BuLi and with t-BuOK respectively, according to Brandsma procedure [6]. $CSCl_2$, $SOCl_2$, SO_2Cl_2, t-BuOK and $iPr_3SiC{\equiv}CH$ were delivered by Sigma-Aldrich, BuLi and 1,6-dichlorohexadiyne were prepared by the Brandsma procedures [6].

Instruments

The FTIR spectra were recorded by the NICOLET apparatus Impact 41. The XPS measurements were carried out using ESCA 310 (Gammadata Scienta, Sweden) spectrometer equipped with monochromatized Al Kα X-ray source and hemispherical electron analyzer operated in the FAT (Fixed Analyzer Transmission) mode. The samples were spread on gold plates which were mounted on a sample probe by means of tantalum clips. The pressure of residual gases in the spectrometer chamber during spectra acquisition was below 10^{-7} Pa. The high resolution spectra of S 2p, Cl 2p, O 1s, and C 1s electrons were measured. The surface static charge was removed using Scienta flood gun. The spectra were fitted using a Gaussian-Lorentzian line shape, Shirley background [8] and a damped nonlinear least square procedure. Quantification of the surface concentrations of elements was accomplished by correcting the photoelectron peak areas for spectrometer transmission function and for their cross-sections [9]. The assignment of the peaks to particular chemical states of elements was based on comparison of the measured binding energies with values reported in the literature[10-11].

The general procedure for coupling thiophosgene and diakali alkynides

C_2Li_2 was prepared [6] from 100 mmol BuLi in 100ml THF under argon, before the subsequent conversion cooled down to –60°C. Solution of 5.5g $CSCl_2$ (50 mmol) in 30 ml THF was dropwise added to it under stirring and the temperature was kept low for 1.5 hours. Afterwards the cooling gradually ceased, so that the reaction mixture slowly warmed up to RT. The black polymeric product, which precipitated in it (neutral reaction), was filtered off and washed by hot distilled water under sonication. Finally it was washed by ethanol and dried at 40°C. The experiments, started from C_2K_2, proceeded analogously. HC_2Li /HC_2K prepared by Brandsma [6], were exploited in a similar way in a reaction with thiophosgene.

$iPr_3SiC{\equiv}C\text{-}CS\text{-}C{\equiv}CSiiPr_3$ (**2**) was prepared analogously, by coupling $iPr_3SiC{\equiv}CLi$ (**1**) with $CSCl_2$. Corresponding lithiumethynide **1** was prepared in 80ml THF from 50mmol $iPr_3SiC{\equiv}CH$ and 50mmol BuLi, and subsequently it was added to 25 mmol of $CSCl_2$ in 20 ml THF, which was stirred at -70°C under argon. The particular yellow-brown reaction mixture, was almost neutral. It was processed by addition of ether and cold brine. The separated organic phase was dried over anhydrous $CaCl_2$ and concentrated under vacuum of 3mm Hg at the temperature of -30°C. The remaining oil was subjected to column chromatography on 50g silicagel in n-hexane. An almost colorless oil was obtained as product **2** after concentration of particular fractions under low temperature and vacuum (similar as above) in the yield of 72%.

^{1}HNMR (400MHz, $CDCl_3$, δ in ppm): 1.07 (d, 2x18H, J=7 Hz,CH_3), 1.4 (sep.,2x3CH, J=7 Hz).

^{13}CNMR (150MHz,$CDCl_3$, δ in ppm) : 18.63, 87.72, 94.69, 111.75.

FTIR spectrum (liquid, in cm^{-1}):1200 (m,CS), 2034 (w,C_{sp}), 2090 (m, C_{sp}), 2880 (l, diffuse, C_{sp}) cm^{-1}. Elemental analysis : $C_{23}H_{42}Si_2S$ (406.81): calcd. C 67.90, H 10.40, S 7.88; found: C 67.70, H 10.61, S 7.65 %.

The record of LC-MS demonstrated the presence M^+ 406.8.

$iPr_3SiC{\equiv}C\text{-}SO\text{-}C{\equiv}CSiiPr_3$ (**3**) was prepared similarly as above thion **2** by treatment 50mmol $iPr_3SiC{\equiv}CLi$ with 25 mmol $SOCl_2$ in THF solution. Analogical processing and purification on silica column/hexane resulted in 7.5g of yellow oil product **3** in the yield 73%.

^{1}HNMR (400MHz, $CDCl_3$, δ in ppm): 1.05 (d, 2x18H, J=7 Hz,CH_3), 1.35 (sep.,2x3CH, J=7 Hz).

^{13}CNMR (150MHz,$CDCl_3$, δ in ppm) : 11.04, 18.43, 100.01,106.4.

FTIR spectrum (liquid, in cm^{-1}):1220 (m,SO), 2030 (w,C_{sp}), 2060 (m, C_{sp}), 2100 (m, C_{sp}) 2860 (l, diffuse, C_{sp}) cm^{-1}. Elemental analysis : $C_{22}H_{42}Si_2SO$ (410.81): calcd. C 64.32, H 10.30, S 7.80; found: C 64.26, H 10.38, S 7.86 %.

LC-MS spectrum confirmed the M^+ 410.6.

The general procedure for coupling sulfurylchloride and alkali ethynides

The initial C_2Li_2 (prepared from 100 mmol BuLi) in 100 ml THF was stirred under argon at –60°C. The solution of 6.8 g SO_2Cl_2 (50mmol) in 20 ml THF was dropwise added to it. This reaction mixture was stirred at the low temperature for the next 2 hours and then allowed to warm up to room temperature. The yellow-brown reaction mixture, of weak acidic reaction, after its cooling was precipitated with 50 ml Et_2O. The filtered off brown precipitate is soluble in THF, AcOEt, EtOH and also in water. It was dissolved in distilled water and the LiCl contained was eliminated by dialysis against distilled water by means of tubing manufactured by Medicell Int.Ltd.. The remaining aqueous solution of the polymer product was concentrated by vacuum evaporator. The remainder was a brown-yellowish solid product, nonmelting till 250°C. The treatment of sulfuryl chloride with C_2K_2 proceeded analogously, giving a polymeric product of similar nature.

The coupling of C_2K_2 with thionyl chloride

yielded a product limited soluble in methanol, whereas that of C_2Li_2 resulted, under identical conditions, in an insoluble polymer. Thus 50 mmol C_2K_2 prepared in THF (as above) reacted with 5.5 g $SOCl_2$ (50mmol) in THF in the similar procedure. To the yellow-brown reaction mixture were added 40 ml ether and 50 ml of saturated brine. The separated organic phase was washed several times with brine and distilled water, dried over anhydrous $CaCl_2$ and concentrated, to yield a greasy solid product. The reaction mixture, after C_2Li_2 / $SOCl_2$ treatment, contained a brown suspension of an insoluble polymer, which was separated and washed with distilled water under sonication. The remaining solid was suspended in ethanol, filtered off and dried at 40°C. The obtained coupling products were studied by FTIR (KBr technique) and XPS spectra, and their elemental composition was determined. The modification of the coupling products formed from thiophosgene was performed by treatment with BuLi /t-BuOK. Thus 1g of the coupling product (C_2Li_2 + $CSCl_2$) was suspended in 80 ml THF, cooled down under stirring to –70°C in argon.

75 mmol BuLi was dropwise added and the low temperature maintained for 2 hours. Than the cooling was gradually stopped. The liquid mixture of alkaline reaction was after further 3 hours acidified by 3M HCl under cooling and filtered off. The filtrate was extracted by 35ml ether and the organic phase separated. The collected ethereal extracts washed by distilled water and dried over anhydrous $CaCl_2$, were concentrated by vacuum evaporator. Finally a yellow-brown solid remained soluble in methanol or THF. The products of similar treatment, carried out by t-BuOK, were processed as insoluble brown-black solids. The couplings of the alkali hexatriynides with chlorinated sulfur compounds were carried out in a similar way as that of the alkali ethynides, and the yielded products were processed in the air by careful washing and sonication.

Results and discussion

The elemental composition of the coupling products formed from the mentioned chlorinated sulfur compounds and the alkali ethynides are summarised in Tables 1 and 2. We assume the formation of the primary polymer structure demonstrated by formula $ClSC\text{-}[C{\equiv}C\text{-}CS]_n\text{-}Cl$ after the interaction of C_2Li_2 with $CSCl_2$ according to the scheme 1.

$$n\,LiC{\equiv}CLi + (n+1)\,CSCl_2 \longrightarrow ClSC\text{-}[C{\equiv}C\text{-}CS]_{n-1}\text{-}C{\equiv}C\text{-}CSCl + 2n\,LiCl \qquad (1)$$

Table 1 The coupling of alkali ethynides with $CSCl_2$

Nr.	Ethynide applied	Coupling products					
		%C	%H	%Cl	%S	yield %	υ C_{sp} [cm^{-1}]
1	C_2Li_2	44.84	0.74	3.14	41.75	83.0	2050,2170
1[a]	C_2Li_2	59.81	7.50	2.07	19.39	85.0	2050,2150
2	HC_2Li	43.46	1.52	4.77	44.20	87.5	2030,2100
2[a]	HC_2Li	59.32	6.50	3.54	23.57	84.0	2040
3	HC_2K	45.80	1.40	1.63	41.02	83.5	2020,2150
3[b]	HC_2K	46.40	1.96	1.72	36.92	88.5	2020

[a] treatment with BuLi [b] treatment with t-BuOK

The content of chlorine in the range 1.5-4.5 % in the insoluble polymer products (prepared from thiophosgene) and the corresponding XPS [10] (cf. Table 3) and FTIR spectra (KBr, 1120cm^{-1}(s, CSCl)) confirm the presence of chlorosulfenic CSCl groups at the terminals. The XPS independent spectral results support it clearly. Even if we can not exclude partial hydrolysis of these groups during the LiCl/KCl washing, the CSCl groups are not easily accessible and can survive due to the steric assembling of the polymer chain. The mechanism of coupling of dialkali ethynide with thiophosgene assumes the occurrence of $-[C\equiv C\text{-}CS]_n-$ internal segments (m.w. $[68.09]_n$) containing the thioketo group. The elemental composition of this theoretical unit corresponds to 52.9% C and 47.0% S.

The sulfur content found in the composition of our coupling products in the average value of 41 –44% is near to it. But the presence of oxygen in the amount till 12% derives from the ideal elemental composition and XPS [11] and FTIR spectra display it as well. It is the consequence of the reactivity of the primary poly(ethynethione) product, which is insoluble and must be thoroughly washed from the alkali chloride (LiCl, or KCl). This processing, including the hot water treatment and the sonication in the air at elevated temperature, deteriorates the primary coupling structure $ClSC\text{-}[C\equiv C\text{-}CS]_n\text{-}C\equiv C\text{-}CSCl$, by water addition. This conclusion is confirmed by the XPS [10-11] spectra of selected polymer products (cf. Table 3 item 1/1), indicating CS group in the structure as well as presence of -CO, and CSCl. These groups were simultaneously indicated in the FTIR spectrum (KBr; 1180 (m,CS), 1100 (m,CSCl), 1710 (l, CO) cm^{-1}). When we consider the structure of real washed coupling product, some -C(OH)=CH-CS- or rather tautomeric $-CO\text{-}CH_2\text{-}CS-$ sequences must be included. Thus a model coupling product, which contains in the structure $ClSC\text{-}[C\equiv C\text{-}CS]_n\text{-}C\equiv C\text{-}CSCl$ for n=18 eight of the above presented saturated carbonyl sequences, has the m.w. 1552.98. The corresponding calculated elemental composition for $C_{58}H_{16}S_{20}O_8Cl_2$ is 44.85% C, 41.29%S, 1.09%H, 4.56% Cl and 8.24%O. The comparison with the found elemental data (cf.Table 1) demonstrates, that our structural explanations are justified. The sulfur bound in the thioketone structure was partly eliminated by subsequent treatment of the coupling product with BuLi or t-BuOK. The resulted elemental composition of polymer products are summarized in Table 1 as well (items 1^a, 2^a, 3^b). BuLi is more efficient agent than t-BuOK. The resulting products after treatment with BuLi were soluble in methanol, containing approx. half of the original sulfur content, about 20% (cf. Table 1), the chlorine content decreases very little. Model calculations for product with eliminated sulfur was performed, considering for n= 18 twelve eliminated sulfur in sequences (substituted by 12 mols of water) and including 4 water moles added after product washing. For $C_{57}H_{32}S_8O_{16}Cl_2$ (m.w.1300.34) is elemental composition 52.65 %C, 19.72% S, 2.48% H, 19.68% O, 5.45% Cl, which suits the experimental values. Other attempts to eliminate sulfur by BuLi treatment from coupling products, generated from alkali ethynides and $SOCl_2$ or SO_2Cl_2, were unsuccessful. This fact confirms the presence of sulfur bound in the thion (splittable off) and supports the course of the assumed primary coupling mechanism (2).

$$n\ LiC\equiv CLi + n\ CSCl_2 \longrightarrow -[C\equiv C\text{-}CS]_n- \quad + 2\ n\ LiCl \qquad (2)$$

Unfortunately, the terminal chlorosulfenic groups in polymer chains, oxygen and water added during the product processing, cause that the final structure differs from the ideal elemental composition, what XPS and FTIR spectra indicate and confirm. The FTIR spectra of products of the coupling with thiophosgene (after LiCl extraction) exhibit distinct low diffuse C_{sp} band at 2100 cm^{-1} (cf.Fig.1). The assumed reaction mechanism is also supported by the preparation of thioketone 2 as a model compound. As demonstrated, the product of this structure was prepared from TIPS (triisopropylsilyl) protected lithium ethynide and thiophosgene. The FTIR and NMR spectra, the elemental analysis and LC-MS (cf.experim.part) confirmed its structure. This clear course of preparation of monomeric thioketone 2 contributes to the validity of the above mechanism suggested for the polymeric primary thioketone products generated from the "bifunctional" dialkaline ethynides. The coupling products prepared from $CSCl_2$ and monometallic ethynides have similar nature, due to the course of disproportionation reaction [7].

The reaction of RC≡CLi with $SOCl_2$ resulting in monomeric RC≡C-SO-C≡CR is described by Brandsma [6]. The couplings of bifunctional dialkali ethynide and thionyl chloride yield products characterised by the elemental composition in Table 2. The primary coupling structure could look like $ClOS\text{-}[C{\equiv}C\text{-}SO]_n\text{-}C{\equiv}C\text{-}SOCl$, containing the internal segments generated by the reaction (**3**).

$$n\ LiC{\equiv}CLi + n\ SOCl_2 \longrightarrow -[C{\equiv}C\text{-}SO]_n- \qquad + 2n\ LiCl \qquad (3)$$

Potassium ethynide gives limited soluble polymer, whereas lithium ethynide the insoluble one. This difference can be associated with various volume, solvation and reactivity of applied alkali alkynides. The content of chlorine in both polymer products is almost equal, bound likely in the sulfinylchloride terminal groups SOCl, whereas the content of sulfur is different. The SOCl groups can be protected against hydrolysis (on the base of the chain assembling) during the product processing, but their partial hydrolysis can not be excluded. The limited soluble (in methanol) coupling product prepared from potassium ethynide contains only 19 % sulfur and 43 % carbon. On the contrary, the insoluble product yielded from lithium ethynide has 34% S and about 45% C.

Table 2 The coupling of alkali ethynides and $SOCl_2$ or SO_2Cl_2

Nr.	Ethynide applied	Coupling products					
		%C	%H	%Cl	%S	yield %	υ C_{sp} [cm^{-1}]
1	C_2K_2 / $SOCl_2$	43.13	4.11	4.19	19.15	91.0	2170 dif.
2	C_2Li_2 / $SOCl_2$	45.06	1.58	3.97	34.68	88.5	2100 dif.
3	C_2K_2 /SO_2Cl_2	36.12	3.10	2.99	18.55	74.5	2070, 2200 dif.
4	C_2Li_2 /SO_2Cl_2	30.16	2.10	1.46	22.13	78.0	2120 dif.

When we consider $-[C{\equiv}C\text{-}SO]_n-$ (m.w. $[72.07]_n$) as internal repeating unit in the primary coupling product, the theoretical composition is equivalent to 33.3% C and 44.4 % S. For the insoluble product obtained from dilithium ethynide, the composition with sequences $-[C{\equiv}C\text{-}C{\equiv}C\text{-}SO]_n-$ (m.w. 96.09, formed by possible dimerisation [7] under our experience) corresponding to 49% C and 33.3% S, is more probable (cf.Tab.2). The FTIR spectra of coupling products formed from $SOCl_2$ exhibit diffusive band of the alkyne vibrations, and bands 1060 (m, SO), 1100 (s, SOCl), and 1720 (m, CO) cm^{-1}.The independent XPS spectrum [10-11] of the corresponding coupling product indicates the content of SO and SO_2 groups (cf. Table 3, item 2/2).

Both chlorine and -CO groups were found as well. When we consider model structure $ClOS\text{-}[C{\equiv}C\text{-}C{\equiv}C\text{-}SO]_n\text{-}C{\equiv}C\text{-}SOCl$ for n=14, including four added water molecules

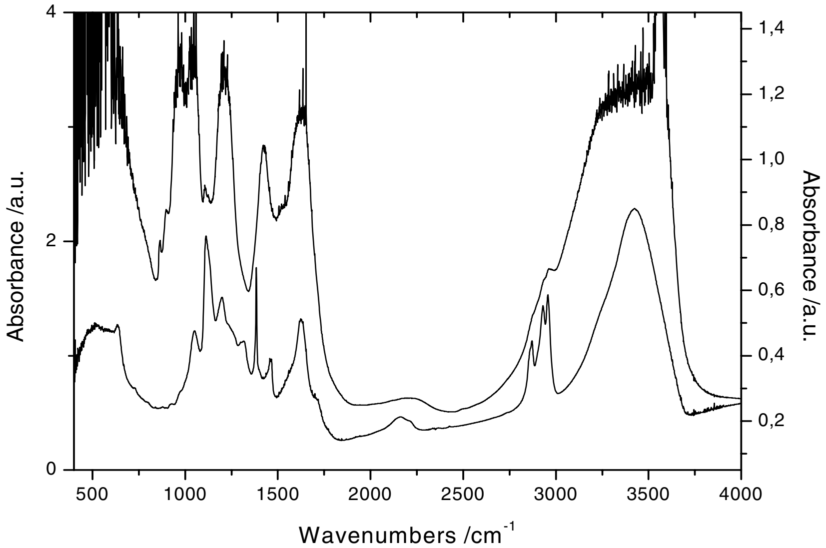

Fig.1 FTIR spectra of the products generated from $CSCl_2$: top with C_2Li_2, bottom with C_6Li_2

Table 3 The XPS spectra of the representative samples of coupling products

Table/item	C_2Li_2+ sulfur reag.	Surface stoichiometry *					
		-CS-	-SO-	$-SO_2-$	-CO	-COOH	CCl
1/1	$CSCl_2$	0.375	-	-	0.09	0.06	0.17
2/2	$SOCl_2$	-	0.039	0.036	0.29	0.07	0.04
2/4	SO_2Cl_2	-	0.042	0.063	0.45	0.08	0.01

*Calculated from the integral intensities of the photoemission lines S_{2p}, C_{1s}, O_{1s}, Cl_{2p} related to the integral carbon concentration. Binding energy E_B (eV): CS 163.6, SO 166.7, SO_2 168.5, CO 531.8, COOH 533.4, CCl 200.3.

(as a consequence of real processing), we obtain m.w.1608.51 for $C_{58}H_8S_{16}O_{20}Cl_2$. The corresponding calculated elemental composition is 43.3%C, 0.5%H, 31.89%S, 19.89%O and 4.4%Cl. The comparison with the composition found for the real coupling product (cf.Table 2) indicates the correctness of the structural considerations. Model substance $iPr_3SiC{\equiv}C\text{-}SO\text{-}C{\equiv}CSiiPr_3$ (**3**) was prepared for the support of the reaction mechanism and composition of products containing SO groups. The structure of **3** was evidenced by NMR, FTIR and LC-MS as well as by elemental analysis.

The couplings of alkali ethynides with sulfuryl chloride give mainly polymer products soluble in water, having presumably the primary structure like $ClO_2S\text{-}[C{\equiv}C\text{-}SO_2]_n\text{-}C{\equiv}C\text{-}SO_2Cl$, based on the internal segments formed in the reaction (4). The solubility in water originates undoubtedly from the high content of oxygen retained in the polar sulfon groups of the resulting product. For this case terminal SO_2Cl groups will be likely strongly restricted (hydrolysed) and partially converted due to the washing treatment. Moreover obtained products follow less the suggested structure. We assume the product containing in ideal case the $\text{-}[C{\equiv}C\text{-}SO_2]_n\text{-}$ (m.w. 88.07) primary internal segments corresponding to 24.2% C and 36.4% S theoretically. The sulfur contents in both coupling products are in fact lower, amounting to 18 – 22 %. There is

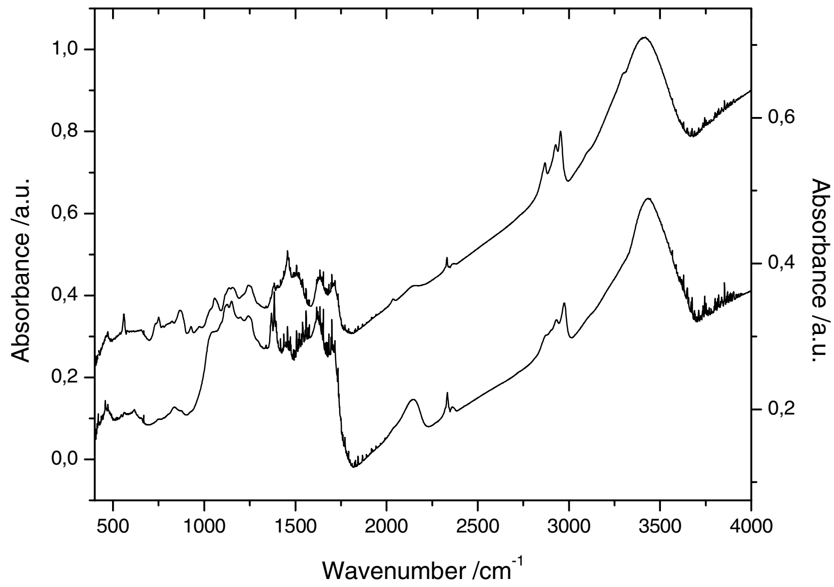

Fig.2 FTIR spectra of the products generated from SO_2Cl_2 : top with C_2Li_2, bottom with C_6Li_2

a distinct difference in the carbon contents, namely 30.1% in the product from dilithium ethynide, and 36.1% C in that prepared from potassium ethynide.

$$n\ LiC{\equiv}CLi + n\ SO_2Cl_2 \longrightarrow -[C{\equiv}C\text{-}SO_2]_n- \quad + 2n\ LiCl \qquad (4)$$

The oxygen content is proportional. Calculation of the model polymer structure including SO_2 groups indicates, that the dimerisation of two ethynyl groups -C≡C-C≡C-SO_2- likely prefers in the primary sequence.

Thus $ClO_2S\text{-}[C{\equiv}C\text{-}C{\equiv}C\text{-}SO_2]_n\text{-}C{\equiv}C\text{-}SO_2Cl$ is the model structure respecting this fact. Considering this structure for n =18, including 10 C_4SO_2 and 8 C_2SO_2 segments, and taking into account the real processing – the addition of ten molecules of water, we can calculate the m.w.2220.99 for $C_{58}H_{20}S_{20}O_{50}Cl_2$. The corresponding calculated elemental composition of the model is 31.36%C, 0.90%H, 28.87%S, 36.0%O, and 3.19% Cl. Its comparison with data from Table 2 indicates how could look the real structure of the coupling product generated with SO_2Cl_2.The content of SO_2 groups was evidenced by the XPS [11] in the selected sample of the particular coupling products (cf.Table 3, item 2/4). This spectrum revealed SO, CO and COOH groups present as well, what indicates subsequent course of intermolecular interactions and addition of water during the product processing. The FTIR spectra (KBr) of both products indicate alkyne structure characterised by the intensive diffusive C_{sp} bands (cf. Table 2, Fig.2) and bands 1200 (w, SO_2), 1390(w, SO_2Cl) cm^{-1}.The preferred occurrence of butadiynyl segments over ethynyl ones appears in the composition of the coupling products prepared both from $SOCl_2$ and SO_2Cl_2. The reason can be in slower rate of combination of ethynyl with SO or SO_2 groups in comparison with the simultaneous offer of ethynyl dimerisation.

The coupling products generated from higher alkali alkynides, hexatriynides are demonstrated in Table 4. These products are solid, powderlike insoluble substances exhibiting strong intensive alkyne bands in the FTIR spectrum (cf. Fig. 1 and 2). Due to high reactivity of hexatriyne segments the formed polymers exhibit more structure defects and irregularities especially after washing treatment. That is why the following structure interpretation has only limited value. They have hexatriyne sequences retained in some extent, and corresponding chlorine groups, (bands in FTIR spectrum) according to the starting sulfur reagent (cf. the above paragraphs), terminating the macromolecular chains. Unfortunately, the coupling products prepared from $CSCl_2$ contain 15 –16 % oxygen in the elemental composition, in consequence of the purification treatment. These coupling products containing C_6 conjugated sequences exhibit higher reactivity towards water and oxygen. For this reason the ideal composition $[-C_6-CS-]_n$ (m.w. 116.13) can not be found. The stoichiometric composition of $[-C_6-SO-]_n$ gives 13% O. In the particular product (cf. Table 3) we have found about 30% oxygen. The content of sulfur in this product is less than the stoichiometry indicates.

Table 4 The coupling of alkali hexatriynides and $CSCl_2$, $SOCl_2$, or SO_2Cl_2

Nr.	Hexatriynide applied/sulfur cmpd.	Coupling products					
		%C	%H	%Cl	%S	% yield	ν_{sp} [cm^{-1}]
1	$HC_6K/CSCl_2$	55.85	1.54	3.27	25.26	88.5	2155,broad
2	$C_6Li_2/CSCl_2$	66.04	3.53	4.12	12.02	91.0	2150,broad
3	$C_6Li_2/CSCl_2$	65.32	3.30	2.84	13.99	91.5	2131-2160
4	$C_6K_2/SOCl_2$	52.83	2.14	2.17	13.63	89.0	2140,broad
5	C_6Li_2/SO_2Cl_2	60.66	4.75	3.82	7.57	92.5	2160,broad

The products of interaction of hexatriynide with SO_2Cl_2 assume for the ideal composition $[-C_6-SO_2-]_n$ the content of 53% C, 23.6 %S and 23.6% O. The elemental analysis (cf. Table 4) indicates 60% C, 23.5%O and only 7.5% S. This discrepancy can be explained again by the treatment of the reactive product in air during its purification (an additional content of hydrogen). Higher carbon content in the product suggests a casual coupling of some bare hexatriyne units after the alkali metal elimination by SO_2Cl_2. This dimerisation forms C_{12} sequences in the coupling chain and diminishes the content of sulfur. Both hydrogen and oxygen contained in the elemental composition origin from added water.

Conclusions

We can conclude, that the kind of the sulfur group inserted in the macromolecular chain of the coupling product distinctly affects both its solubility and the efficiency of the C_{sp} bond protection. The occurrence of the bulky sulfonic polar group in the coupling products from ethynides brings their solubility in water along with the intensive C_{sp} bands in the FTIR spectrum. After the comparison of calculated model of polymers including SO and SO_2 groups with the corresponding real coupling products characterized by spectra and elemental composition their structures were suggested. The C=S group is in the coupling products, which are insoluble both in the water and in the organic solvents. Their structure, supported by model calculations and prepared monomeric thioketone 2, was interpreted and mechanism their generation suggested. The valuable independent XPS spectra results complete and confirm data from FTIR spectra and elemental composition. The hexatriynide coupling products demonstrate the most thorough alkyne protection, evident from the most intensive diffusive C_{sp} bands in the FTIR spectra. The suggested structure of these products suffers from defects and irregularities due to their increased reactivity and is of limited value.

Despite the partial deterioration of the primary coupling product structure, novel valuable sulfur containing polymers were prepared. Since the polyyne preparation is an important and uneasy task, this present investigation demonstrates a new feasible way, which can stimulate as a challenge some top equipped researcher to proceed with an improved or alternative solution.

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