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Polymerization of isomeric *N*-(4-substituted benzylidene)-4-ethynylanilines and 4-substituted *N*-(4-ethynylbenzylidene)anilines by transition metal catalysts: preparation and characterization of new substituted polyacetylenes with aromatic Schiff base type pendant groups

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Abstract

N-(4-substituted benzylidene)-4-ethynylanilines $R{-}C_6H_4{-}CH{=}N{-}C_6H_4{-}C{\equiv}CH$, where R = Me, *t*-Bu, F, Br, CN, NO_2, Me_2N and $-C{\equiv}C{-}SiMe_3$ and isomeric 4-substituted *N*-(4-ethynylbenzylidene)anilines $R{-}C_6H_4{-}N{=}CH{-}C_6H_4{-}C{\equiv}CH$, where R = Me, *t*-Bu, F, Br, I, CN, NO_2 and $-C{\equiv}C{-}SiMe_3$ were polymerized using (i) $[Rh(cod)OCH_3]_2$ [(cod) = η^4-cyclooctadiene] in THF, (ii) $Mo({=}CHCPhMe_2)({=}N{-}C_6H_3{-}i\text{Pr}_2\text{-}2,6)[O{-}CMe(CF_3)_2]_2$ in aromatics, (iii) $PdCl_2$ in DMF. All catalysts tested exhibited high tolerability towards $-CH = N-$ group (confirmed also by the in situ ^{1}H NMR study) providing polyacetylenes with aromatic Schiff base type pendant groups. Positive correlation between acidity of ethynyl group and monomer polymerizability was found for Rh catalyst. Depending on catalyst, molecular weight of polymers decreases in the series: Rh (M_w = 45 000–300 000) > Mo (M_w = 13 000–40 000) > Pd (M_w about 5000). The main chain *cis* double bond content and the microstructure uniformity of polymer were found to decrease in the same order. In THF, all polymers prepared exhibited fluorescence (λ_{max} = 500–550 nm) considerably red-shifted in comparison with their parent monomers. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Substituted polyacetylenes; Ethynylated aromatic Schiff bases polymerization; Transition metal catalysts

1. Introduction

Substituted polyacetylenes attract attention as materials with potential applications in micro- and optoelectronics and non-linear optics [1,2]. Unique properties of these polymers, such as photoconductivity, photo- and electroluminescence and non-linear optical effects, are a function of their molecular architecture. These properties can be tuned through both the main chain microstructure (*cis–trans* and head-to-tail isomerism) and the choice of pendant groups. Substituted polyacetylenes with widely conjugated substituents represent an interesting group of these polymers due to a combination of main chain and side groups conjugation effects. Several polymers of this type have been reported over the last few years, e.g. mono- and disubstituted polyacetylenes with condensed aromatic rings (e.g. naphthyl, anthryl, phenanthryl, etc.) [3,4]; or monosubstituted polyacetylenes with rod-like aryleneethynylene side chains of various length and end-capping groups (e.g. $-(C_6H_4{-}C{\equiv}C)_n{-}$ $Si{-}i\text{Pr}_3$, $-(C_6H_4{-}C{\equiv}C)_n{-}$Ferrocenyl) [5–7]. Another possibility for preparation of polyacetylenes with conjugated pendants is polymerization of ethynylated *N*-benzylideneanilines (aromatic Schiff bases), the first examples of which have been reported recently [8,9].

Although ethynylated *N*-benzylideneanilines are assumed to adopt a non-planar conformation in solution (i.e. with the twist angle between planes of the aniline ring and that of the azomethine fragment), spectroscopic observations have clearly proved that the conjugation between benzylidene and aniline rings occurs in a considerable extent [10]. Therefore, it can be assumed that the electronic effect of pendant imino groups (which can be tuned by substituents on both rings) may directly affect the electron density in the polyene main chain of the polymer. The dipole moment of

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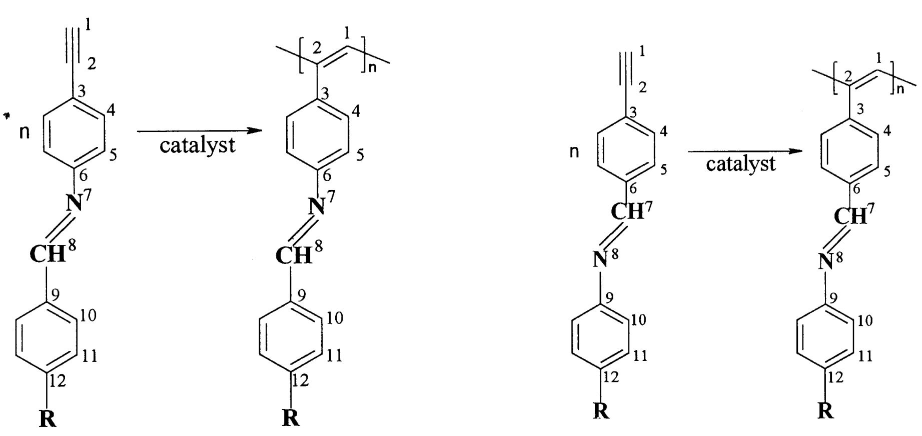

Compound	R
I-Me	CH_3
I-Bu	t-Bu
I-F	F
I-Br	Br
I-Si	$C^{13}\equiv C^{14}$-$SiMe_3$
I-CN	CN
I-NO_2	NO_2
I-NMe_2	NMe_2

Compound	R
II-Me	CH_3
II-Bu	t-Bu
II-F	F
II-Br	Br
II-I	I
II-Si	$C^{13}\equiv C^{14}$-$SiMe_3$
II-CN	CN
II-NO_2	NO_2

catalyst/solvent
1. $[Rh(cod)OCH_3]_2$/THF
2. Mo Schrock carbene/benzene or benzene/chlorbenzene (1:1)
3. $PdCl_2$/DMF

Scheme 1.

azomethine group and fluorescence activity of some Schiff base type monomers [10] should also be taken into consideration about expected properties of these polymers.

For polymerization of acetylenes carrying nitrogen-containing substituents, a proper choice of catalysts is of key importance. In the case of ethynylated aromatic Schiff bases, classical metathesis catalysts based on W- or Mo-chlorides are less suitable because of their low compatibility with such monomers. On the other hand, Rh(I) insertion catalysts proved highly efficient in polymerization of ring-substituted phenylacetylenes with a variety of substituents including those with basic nitrogen [11–13] and they were also found to initiate polymerization of some ethynylated Schiff bases monomers. Masuda and co-workers [9] used $[Rh(nbd)Cl]_2$ + Et_3N [(nbd) = η^4-norbornadiene] system for a polymerization of *N*-(3- or 4-ethynylbenzylidene)anilines and their derivatives bearing isopropyl and *n*-hexyl on the aniline ring. They obtained high molecular weight polymers with enhanced stability against oxidative degradation in solutions. In our previous study [8], we used $[Rh(cod)OCH_3]_2$ [(cod) = η^4-cyclooctadiene] in tetrahydrofuran (THF) for polymerization of a series of *N*-(4-substituted benzylidene)-4-ethynylanilines R–C_6H_4–CH=N–C_6H_4–C≡CH, where R = H, *t*-Bu, F, Br, CN, NO_2 and Me_2N. Monomers with R = H, *t*-Bu and F provided THF-soluble polymers of molecular weights M_w from 15 000 to 100 000. However, monomers with Br, CN, NO_2 and Me_2N substituents gave polymers insoluble in THF and in common organic solvents, which restricted a study of their properties. As limited polymer solubility is often observed for polymers prepared with Rh catalysts [14], additional catalysts should also be tested in polymerization of these monomers, in order to develop processable polymers. Successful applications of Schrock carbenes and $PdCl_2$ catalyst for polymerizations of ethynylazobenzenes [15] and nitrogen-containing propargylderivatives [16,17] suggest testing these catalysts for polymerizations of monomers with azomethine groups.

In the present paper, we report results on polymerization of two complementary series of substituted acetylenes: *N*-(4-substituted benzylidene)-4-ethynylanilines R–C_6H_4–CH=N–C_6H_4–C≡CH (monomers of the class **I**) and 4-substituted *N*-(4-ethynylbenzylidene)anilines R–C_6H_4–N=CH–C_6H_4–C≡CH (monomers of the class **II**) induced with three different catalysts: (i) $[Rh(cod)OCH_3]_2$ in THF, (ii) Mo(=$CHCPhMe_2$)(=N–C_6H_3–$i$$Pr_2$-2,6)[O–$CMe(CF_3)_2]_2$ (Schrock carbene) in benzene or benzene/

chlorobenzene (1:1 by vol.) mixture, (iii) $PdCl_2$ in dimethylformamide (DMF) (Scheme 1). Attention is mainly paid to the effect of (i) –N=CH– group orientation with respect to the triple bond, (ii) character of the substituent R and (iii) catalyst used on the course and character of polymerization, the yield of oligomeric side products and the yield, molecular weight characteristics and microstructure of formed polymers.

2. Experimental

2.1. Materials

The preparation and characterization of monomers ($R–C_6H_4–CH{=}N–C_6H_4–C{\equiv}CH$ and $R–C_6H_4–N{=}CH–C_6H_4–C{\equiv}CH$) except for **I**-Si and **II**-Si is described elsewhere [8,10]. Monomers **I**-Si and **II**-Si were prepared in a similar way by a condensation of 4-(trimethylsilylethynyl)benzaldehyde with 4-ethynylaniline and 4-(trimethylsilylethynyl) aniline with 4-ethynylbenzaldehyde, respectively.

2.1.1. N-(4-trimethylsilylethynylbenzylidene)-4-ethynylaniline (I-Si)

Yield 33%, m.p. 113–116°C. MS, *m/z*: 301 ($M^{+}\cdot$), 286 $(M–CH_3)^+$. IR (KBr) ν, cm^{-1}: 3300 (s, $\nu(\equiv C–H)$), 2150 (s, $\nu(C\equiv C)$), 2100 (vw, $\nu(\equiv C–H)$), 1613 (s, $\nu(N{=}C)$), 1250 (s, $\delta(Me_3Si)$), 840 (vs, $\nu(Si–C)$). ^1H NMR ($CDCl_3$), ppm: 0.27 s, 9H (CH_3); 3.11 s, 1H (H1); 7.16 d, $J = 8.4$, 2H (H5); 7.54 m, 4H (H4 + H11); 7.86 d, $J = 8.0$, 2H (H10); 8.41 s, 1H (H8). ^{13}C NMR ($CDCl_3$), ppm: −0.04 (CH_3), 77.43 (C1), 83.55 (C2), 97.25 + 104.54 (C13 + C14), 119.81 (C3), 120.90 (C5), 126.38 (C12), 135.73 (C9), 128.62 (C10), 132.29 + 133.09 (C4 + C11), 152.04 (C6), 159.72 (C8).

N-(4-ethynylbenzylidene)-4-trimethylsilylethynylaniline (**II**-Si)

Yield 48%, m.p. 107–110°C. MS, *m/z*: 301 ($M^{+}\cdot$), 286 $(M–CH_3)^+$. IR (KBr) ν, cm^{-1}: 3300 (s, $\nu(\equiv C–H)$), 2150 (s, $\nu(C\equiv C)$), 2100 (vw, $\nu(\equiv C–H)$), 1620 (s, $\nu(N{=}C)$), 1250 (s, $\delta(Me_3Si)$), 840 (vs, $\nu(Si–C)$). ^1H NMR ($CDCl_3$), ppm: 0.26 s, 9H (CH_3); 3.23 s, 1H (H1); 7.15 d, $J = 8.4$, 2H (H10); 7.50 d, $J = 8.4$, 2H (H11); 7.59 d, $J = 8.0$, 2H (H4); 7.86 d, $J = 8.0$, 2H (H5); 8.42 s, 1H (H7). ^{13}C NMR ($CDCl_3$), ppm: 0.05 (CH_3), 79.59 (C1), 83.17 (C2), 94.61 + 104.89 (C13 + C14), 120.84 (C10), 125.16 (C3), 128.63 (C5), 132.46 + 132.93 (C4 + C11), 136.07 (C6), 151.51 (C9), 159.44 (C7).

Di-μ-methoxo-bis(η^4-cycloocta-1,5-diene)dirhodium, $[Rh(cod)OCH_3]_2$ was prepared according to literature [18]. $PdCl_2$ (Aldrich, 99%) and 2,6-diisopropylimido neophylidenemolybdenum(VI) bis(hexafluoro-*t*-butoxide) $Mo({=}CHCPhMe_2)({=}N–C_6H_3–i\text{Pr}_2\text{-}2,6)[O–CMe(CF_3)_2]_2$ (Strem Chemicals) were used as obtained. THF (Riedel-DeHaen, 99.5% +) was distilled from CaH_2 and Cu_2Cl_2. DMF (Lachema, Czech Rep., purum) was dried with P_2O_5, distilled and degassed in vacuo. Benzene (Lachema, Czech Rep., purum) was predried with P_2O_5, and refluxed with NaH, distilled and degassed in vacuo. Chlorobenzene (Lachema, Czech Rep., purum) was purified with P_2O_5, distilled and degassed in vacuo.

2.2. Polymerization

Polymerizations induced with $[Rh(cod)OCH_3]_2$ were carried out under argon atmosphere at room temperature. They were started by mixing monomer (0.49 mmol in 1.5 ml of THF) and catalyst (9.8 μmol in 1.5 ml of THF) solutions in a vial provided with a magnetic stir bar. Monomers **I**-Me, **I**-Bu, **I**-F, **I**-Si, **II**-Me and **II**-Bu underwent solution polymerization with formation of soluble polymers. For other monomers, precipitation of polymers occurred during polymerizations. The time course of homogeneous polymerizations was monitored by SEC [8,14]. At a given time, a volume of 5 μl was sampled from the reaction mixture, diluted with 0.5 ml of THF and the resulting solution (20 μl) was injected into SEC column. Contents of unreacted monomer and formed oligomers and polymer were determined from relative areas of the corresponding SEC peaks (total area of the SEC record was remaining constant in the course of the reaction). Polymerization was quenched after 3 h by adding methanol (8 ml) to the reaction mixture. Isolated polymer was several times washed with methanol/THF (80/20 by vol.) mixture and dried in vacuo at room temperature to the constant weight to determine the polymer yield also gravimetrically. Gravimetric yields were found to be in a good agreement with the yields obtained from SEC records (±5%). In the case that polymer was precipitating during polymerization, termination and polymer isolation were the same as given above and the polymer yield was determined by gravimetry, the yield of oligomers as well as the content of unreacted monomer by the SEC analysis of the supernatant resulting from the polymer isolation.

Polymerizations induced with Schrock carbene and $PdCl_2$ were carried out using the standard vacuum break-seal technique [19]. A volume of 1 ml of 0.004 M solution of Schrock catalyst in benzene was, in vacuum, mixed with 0.2 mmol of monomer in 1 ml of benzene (or chlorobenzene) and resulting mixture was allowed to react for 3 h under stirring at room temperature. The reaction was quenched by adding 0.5 ml 0.1 vol.% benzaldehyde in THF and a formed polymer was precipitated by adding 10 ml of methanol. In the case of polymerizations induced with the $PdCl_2$ catalyst, a solution of $PdCl_2$ (2 mg in 1.5 ml DMF) was mixed with a monomer solution (0.5 mmol in 1.5 ml of DMF) and allowed to react for 24 h in a constant temperature bath (85°C). The reaction was quenched by pouring the reaction mixture in an excess of methanol. The polymer yield of methanol insoluble product was determined by the gravimetry and unreacted monomer and formed oligomers were followed by the SEC method.

2.3. Techniques

SEC analyses were made on a TSP (Thermo Separation Products, FL, USA) chromatograph fitted with a UV detector operating at 254 nm. A series of two PL-gel columns (Mixbed-B and Mixbed-C, Polymer Laboratories Bristol, UK) and THF (flow rate 0.7 ml min^{-1}) were used. Molecular weights (weight-average and number-average molecular weights, M_w and M_n, respectively, and molecular weight corresponding to the apex of SEC peak, MW) relative to polystyrene standards are reported.

IR spectra were recorded on a Specord 75 IR spectrometer using KBr pellets. NMR spectra of monomers and catalysts were measured on a Varian GEMINI-200 spectrometer. In the case of Mo catalyst, sealed evacuated cuvettes were applied. Spectra were referenced to the solvent lines (7.26, 7.16 and 1.72 ppm for ^{1}H spectra and $CDCl_3$, C_6D_6 and THF-d_8, respectively, 76.99 ppm for ^{13}C and $CDCl_3$). NMR spectra of soluble polymers were recorded on a Varian UNITY-500 spectrometer. Hexamethyldisilane ($\delta = 0.04$) was added as an internal standard for ^{1}H spectra. ^{13}C NMR spectra were referenced to the solvent lines: 128,70 ppm for C_6D_6, 76.99 ppm for $CDCl_3$ and 39.7 ppm for DMSO-d_8. ^{13}C CP MAS NMR spectra of insoluble polymers were recorded on a Bruker Avance DSX 200 NMR spectrometer in a 4 mm probe with spinning speed about 4500 or 7500, sometimes both speeds were used for one sample. Details of CP MAS NMR measurements are given elsewhere [8].

UV–Vis absorption spectra were recorded on a Hewlett-Packard HP8950 spectrometer. Fluorescence emission spectra were recorded by using a laser kinetic spectrometer (Applied Photophysics). Transient species were generated by a Lambda Physic LPX 205 XeCl laser (excitation wavelength 308 nm, pulse length 20 ns, energy 10–20 mJ pulse^{-1}). Details are given elsewhere [8,20,21].

3. Results and discussion

3.1. Polymerizations induced with $[Rh(cod)OCH_3]_2$

Results of polymerizations of both series of monomers (**I** and **II**) induced with $[Rh(cod)OCH_3]_2$ catalyst in THF are summarized in Table 1. As can be seen, a high monomer conversion, mostly above 70%, as well as a high polymer yield is always achieved. In all cases, the formation of high molecular weight polymer is accompanied by the formation of methanol soluble oligomers (MW about 2000). Data from Table 1 together with IR and NMR spectra of polymers prepared (vide infra), clearly demonstrate catalyst tolerability with respect to the azomethine groups. The absence of $[Rh(cod)OCH_3]_2$ interaction with azomethine group was confirmed by the in situ ^{1}H NMR study of a mixture of this catalyst with *N*-benzylideneaniline in THF-d_8 solution (molar excess of *N*-benzylideneaniline = 2.5, catalyst concentration = 20 mmol l^{-1}). NMR spectrum of this mixture was repeatedly recorded during 7 days together with the spectrum of blank mixture (THF-d_8 solution of $[Rh(cod)OCH_3]_2$). Neither a shift nor a decrease in the intensity of the azomethine hydrogen signal at 8.48 ppm has been observed and *N*-benzylideneaniline was completely recovered from the mixture after 7 days. Also character of the ^{1}H NMR spectrum of $[Rh(cod)OCH_3]_2$ consisting of bands at 1.60 ppm (d, CH_2), 2.39 ppm (m, CH_2), 2.62 ppm (s, OCH_3) and 3.46 (s,=CH) has remained unchanged. Two new signals in aliphatic region (at 1.25 and at 2.55 ppm) have occurred in spectra of both mixtures, which indicates that these signals belong to the products of the slow catalyst interaction with THF. We did not isolate these products but we found that the signal at 1.25 ppm belongs to a non-volatile compound while that at 2.55 ppm to a compound of the volatility comparable to that of THF.

Polymerizations of monomers with additional triple bond **I**-Si and **II**-Si demonstrate high polymerization selectivity of Rh catalyst towards terminal triple bond. Although

Table 1
Results of polymerization of $R{-}C_6H_4CH{=}NC_6H_4C{\equiv}CH$ (**I**) and $RC_6H_4N{=}CHC_6H_4C{\equiv}CH$ (**II**) with $[Rh(cod)OCH_3]_2$ (polymerization conditions: $[C]_0$ = 3.3 mmol l^{-1}, $[M]_0/[C]_0$ = 50, THF, argon atmosphere, room temperature, reaction time 3 h, solution polymerizations followed by SEC)

No.	R	Conversion of monomer (%)		Yield of polymer (%)		Yield of oligomers in %		$M_w \times 10^{-3}$		Solubility in THF	
		I	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**
1	Me	75	100	52	92	23	8	60	240	Yes[a]	Yes
2	*t*-Bu	71	100	34	88	37	12	45	310	Yes	Yes
3	F	88	100	62	89[b]	26	11	100	–	Yes[c]	No
4	Br	96	100	70[b]	92[b]	26	8	–	–	No	No
5	CN	53	89	40[b]	58[b]	13	31	–	–	No	No
6	NO_2	97	100	89[b]	87[b]	8	13	–	–	No	No
7	Me_2N	64	–	61[b]	–	3	–	–	–	No	–
8	Me_3SiCC	71	99	45	89[b]	26	10	170	–	Yes	No

[a] Partly soluble after isolation.

[b] Determined gravimetrically.

[c] Insoluble after isolation.

for **II**-Si insoluble polymer resulted, spectroscopic characterization of both poly(**I**-Si) and poly(**II**-Si) (vide infra) confirmed the preservation of trimethylsilylethynyl groups in polymer pendants and formation of polyene main chain via polymerization of terminal ethynyl groups.

Results of experiments in Table 1 show that both the character of R-substituent and the –N=CH– group orientation with respect to the ring carrying triple bond (**I** vs. **II**), significantly influence a course of the polymerization. First, we shall discuss the effect of the R-substituent. It can be evaluated for monomers **I** only because the total conversion of **II** was achieved in almost all cases and the differences in yields of poly(**II**)s were negligible. It can be seen from Fig. 1, that the overall monomer conversion as well as the polymer yield increase with increasing value of the Hammett constants σ of R. The opposite trend, i.e. the decrease with increasing σ is observed for the yield of oligomers. The highest declinations from these trends are observed for **I**-CN and **I**-NMe$_2$. In both cases, the high ability of R-substituents to coordinate to the central Rh atom in catalytic species must be taken into account. Negative effect of the CN group on monomer polymerizability seen for both **I**-CN and **II**-CN may indicate the deactivation of polymerization species as a result of CN coordination. Contrary to this, as trisubstituted amines such as triethylamine and 4-(dimethylamino)pyridine are known to reduce catalyst side reactions and even to promote living polymerizations of terminal arylacetylenes with [Rh(cod)OCH$_3$]$_2$ [23,24], negligible formation of oligomers and relatively higher polymer yield observed for **I**-NMe$_2$ may be ascribed to the coordination of NMe$_2$ groups to the catalyst in a way reducing formation and/or activity of species responsible for oligomerization. Positive correlation between σ of R-substituent and the NMR chemical shifts of ethynyl hydrogen and C1 carbon atom for both **I** and **II** monomers has been recently demonstrated [10]. Presented results thus suggest positive influence of ethynyl acidity on the polymerizability of monomers studied.

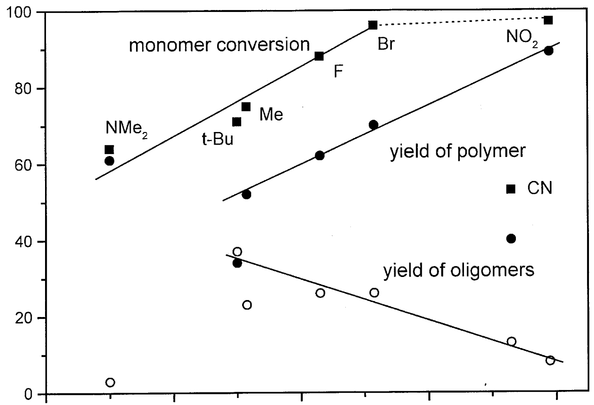

Fig. 1. Monomer consumption and yields of polymer and oligomers (%) achieved in polymerization of R–C$_6$H$_4$CH=NC$_6$H$_4$C≡CH (**I**) with [Rh(cod)OCH$_3$]$_2$ as a function of Hammett constant σ of substituent R. σ values taken from Ref. [22]. THF, room temperature, reaction time = 3 h, initial catalyst concentration = 3.3 mmol l^{-1}, initial monomer/catalyst mole ratio = 50.

As concerns the difference in reactivity between monomers **I**, and corresponding monomers **II**, it is evident that under the same reaction conditions, the overall monomer conversion as well as the polymer yield and molecular weight is, in general, higher for **II** monomers compared to their **I** counterparts. Simultaneously, class **I** monomers mostly provide higher yield of oligomers than class **II** monomers. These findings correspond with the effect of –N=CH– group orientation on the acidity of terminal ethynyl. For monomers **II**, both chemical shifts of acetylenic hydrogen and C1 carbon are always higher than those of the corresponding **I** monomers, the differences being about 0.15 ppm (^{1}H) and about 2 ppm (^{13}C) fairly exceed any difference observed within each class of monomers [10]. Similarly to the effect of R-substituent, the higher ethynyl group acidity of monomers **II** corresponds with their higher polymerizability as compared to the monomers **I**.

In order to obtain a better insight into this reaction systems, time profiles of polymerization of both **I**-Me and **II**-Me performed as two-stage experiments (addition of the second portion of monomer during the polymerization) was followed by SEC (see Section 2). Results are shown in Fig. 2. In the first stage (i.e. before addition of second monomer dose), reactions are characterized as follows: (i) no observable induction period and rapid increase in polymer

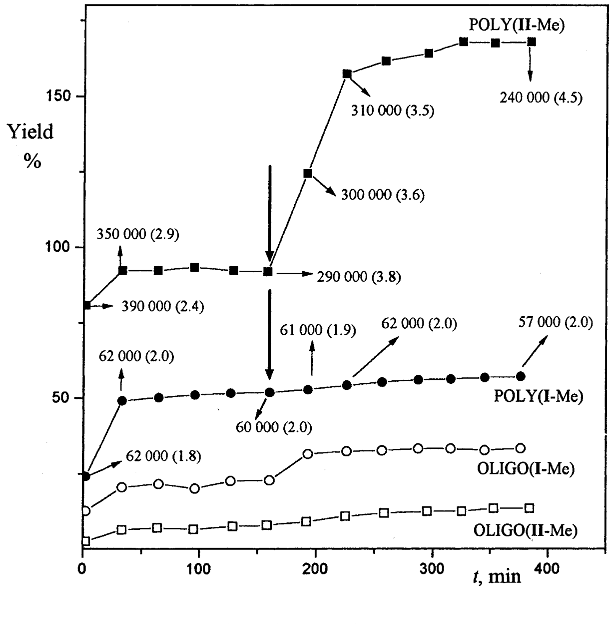

Fig. 2. Time course of polymerization of **I**-Me and **II**-Me with [Rh(cod)-OCH$_3$]$_2$ in two-stage experiments (the addition of the second monomer dose is marked by arrows). Numbers at experimental points show corresponding values of M_w and polydispersity index (M_w/M_n, in parenthesis). THF, room temperature, initial catalyst concentration = 3.3 mmol l^{-1}, initial monomer/catalyst mole ratio = 50. The second monomer dose (amount the same as for the initial one) diluted the reaction mixture by the factor 1.5.

yield for both **I**-Me and **II**-Me, (ii) strong decrease in polymerization rate after 0.5 h (at that reaction time, **II**-Me is almost totally consumed; however, about 30% of **I**-Me is still remaining in the reaction mixture), (iii) formation of oligomers (MW about 2000) from the onset of the reaction (oligo(**II**-Me) in nearly negligible amount, oligo(**I**-Me) in amounts considerably higher), (iv) polymer molecular weight of both poly(**I**-Me) and poly(**II**-Me) reaches its highest values at the beginning of the polymerization (2 min), its slight decrease accompanied by broadening of molecular weight distribution is observed at prolonged reaction times. The last fact is most probably contributed by: (a) formation of shorter polymer chains in the later stage of reaction due to the lack of monomer; (b) slow polymer degradation caused by traces of oxygen (auto-oxidative degradation is well known for monosubstituted polyacetylenes [25]). After addition of a new monomer portions (the second reaction stage), the behaviour of reaction mixture with **I**-Me and **II**-Me differed markedly. With **II**-Me, polymerization was re-started and about 80% of the re-submitted monomer were converted prevailingly into polymer within 3 h. However, the progress in polymerization was not accompanied by a rise in polymer molecular weight. With **I**-Me, only a small step increase in yield of oligo(**I**-Me) was induced by adding the second monomer dose, while the increase in poly(**I**-Me) yield was negligible. These experiments suggest a simultaneous presence of two different kinds of catalytic centres in the reaction mixture (active in polymerization and oligomerization, respectively). The irreversible decay of both these centres must be assumed to explain incomplete consumption of **I**-Me and the polymer molecular weight development during polymerization of both **I**-Me and **II**-Me. The revitalization of the system with **II**-Me after addition of a new portion of monomer indicates that the centres newly formed from intact catalyst are responsible for the second stage polymerization activity. The complete termination of catalytic species active in polymerization as well as the total consumption of intact catalyst during the first stage of polymerization explain the failure in renewal of polymerization activity in the system with **I**-Me monomer.

The above findings are supported by the in situ ^{1}H NMR study of mixtures of this catalyst with **I**-Me and **II**-Me monomers at the mole ratio 1:1 (THF-d_8, catalyst concentration = 20 mmol l^{-1}, room temperature). As can be seen from Fig. 3a and b, the acetylenic hydrogen signals (3.51 ppm for **I**-Me and 3.72 ppm for **II**-Me) gradually disappear upon mixing monomer with the catalyst. Faster consumption of **II**-Me in comparison to **I**-Me is clearly seen. Simultaneously, new signals at 6.04 and 5.5 ppm occur, the signal of azomethine hydrogen is upfield shifted from 8.5 to 8.1 ppm and signals of aromatic protons are significantly broadened compared to those observed for monomers. The signal at 6.04 ppm is typical of olefinic hydrogens in poly(**I**-Me) and poly(**II**-Me) and signal at 5.5 ppm can be assigned to CH_2= end groups of oligomers. There are also new signals in aliphatic region in ^{1}H NMR spectra of reaction mixtures, which should be assigned to methanol (3.00 and 3.26 ppm) liberated during the initiation and to the products of a slow reaction of catalyst with THF that was discussed above. These spectral changes prove that the oligomerization/polymerization takes place in the studied mixtures. The presence of unreacted $[Rh(cod)OCH_3]_2$ clearly shows that only a part of the fed catalyst had undergone a transformation to the active species. Even after consumption of two additional equivalents of monomers (under formation of polymers of MW about 10 000 and oligomers of MW about 2000, polymer/oligomers 30/70 (w/w) for **I**-Me and 50/50 (w/w) for **II**-Me), a high amount of untransformed catalyst was still visible in both reaction mixtures. It clearly indicates a slow initiation step is followed by a rapid propagation of the polymer chains. The low initiation efficiency, simultaneous formation of polymer and oligomers and faster polymerization/oligomerization of **II**-Me compared to **I**-Me are in a good agreement with the results of experiments performed at the monomer/catalyst mole ratio = 50 (Table 1, Fig. 2).

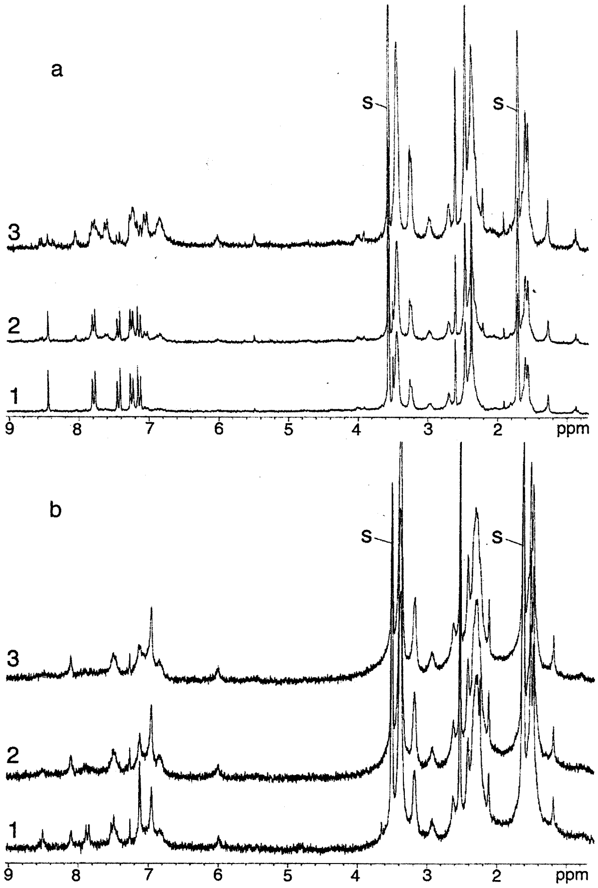

Fig. 3. ^{1}H NMR spectra of mixture of $[Rh(cod)OCH_3]_2$ with **I**-Me (a) and of $[Rh(cod)OCH_3]_2$ with **II**-Me (b) in THF-d_8. Initial catalyst concentration = initial monomer concentration = 20 mmol l^{-1}, room temperature, reaction time (*t*): 5 min (1), 15 min (2), 30 min (3).

Although Rh(I) diene complexes are well known to

Table 2

Results of polymerization of $R{-}C_6H_4CH{=}NC_6H_4C{\equiv}CH$ (**I**) with $Mo({=}CHCPhMe_2)({=}N{-}C_6H_3{-}i\mathrm{Pr}_2\text{-}2,6)[O{-}CMe(CF_3)_2]_2$ (polymerization conditions: $[C]_0 = 2\ \mathrm{mmol\ l^{-1}}$, vacuum, room temperature, reaction time 3 h)

No.	R	$[M]_0/[C]_0$	Solvent[a]	Character of polymerization	Yield of polymer (%)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
1	Me	20	B	Solution	100	13.0	6.6	1.97
2	Me	50	B	Solution	79	19.5	10.0	1.95
3	Br	50	B/C	Solution	93	21.3	10.2	2.09
4	Me_3SiCC	50	B	Solution	75	31.5	17.6	1.79
5	CN	50	B/C	Precipitation	9	14.5	7.3	1.99
6	Me_2N	50	B/C	Precipitation	6	THF insoluble		

[a] B: benzene; B/C: benzene/chlorobenzene (1:1 by vol.).

polymerize terminal acetylenes via insertion mode [23] details concerning the initiation and insertion mechanism have not been elucidated completely. An open question concerns the role of acetylenic hydrogen and the importance of its acidity. Ogawa and co-workers [26] reported that proper acidity of ethynyl hydrogen is essential for the successful polymerization of terminal acetylenes with these catalysts. On this basis, they designed a model of polymerization assuming hydrogen transfer in each propagation step. However, the isolation of living polyphenylacetylene chains with σ-bonded active Rh-containing ends accomplished later [24] seems to contradict this model. For $[Rh(cod)OCH_3]_2$, the initiation is nowadays considered [24] as a multistep process induced by reaction of $[Rh(cod)\text{-}OCH_3]_2$ with ethynyl hydrogen under formation of methanol and mononuclear rhodium species. Following steps involving additional molecules of monomers are assumed to lead to rhodium hydride species, on which propagation is started by monomer insertion into Rh–H bond. For oligomerization of alkylacetylenes, formation of alkynylrhodium hydride complex has also been suggested as the initiation step [27]. Thus, in the initiation, the acetylenic hydrogen is assumed to play an essential role. Our results: (i) high selectivity towards the terminal triple bond in polymerization of trimethylsilylethynyl substituted monomers and (ii) positive correlation between monomer acidity and reactivity in polymerization experiments and especially the higher molecular weight of poly(**II**) in comparison with poly(**I**) suggest the acetylenic hydrogen plays a substantial role also in the propagation. More subtle experiments, however, are needed for revealing further details.

3.2. Polymerization with Mo catalyst

Tables 2 and 3 give results (gravimetric yield of polymers and their molecular weight characteristics) for polymerization of monomers **I** and **II** with the Schrock carbene complex $Mo({=}CHCPhMe_2)({=}N{-}C_6H_3{-}i\mathrm{Pr}_2\text{-}2,6)[O{-}CMe(CF_3)_2]_2$ in benzene or in benzene/chlorobenzene (v/v = 1/1) mixture. **I**-Me and **II**-Me reacted quantitatively giving high yield of polymers together with some amount of oligomers (MW about 2000). More precise SEC quantification and characterization of oligomers were, however, impossible due to a non-baseline separation of oligomers and strongly UV-absorbing catalyst residua in SEC records of supernatants (see Section 2). Compared to the polymerizations with Rh catalyst, poly(**I**-Me) and poly(**II**-Me) prepared with Mo-carbene are of lower molecular weights with M_n indicating a high initiation efficiency. This is in agreement with reported ability of well-defined Schrock catalysts to induce living or living-like metathesis polymerization of selected cycloolefines and acetylenes [28]. However, a detailed inspection of results achieved for various ratios **I**-Me (**II**-Me) to the catalyst (Tables 2 and 3) reveals that the polymerization with these monomers is not of the living character: (i) M_n values are not fully proportional to the consumed monomer, (ii) molecular weight distributions

Table 3

Results of polymerization of $R{-}C_6H_4N{=}CHC_6H_4C{\equiv}CH$ (**II**) with $Mo({=}CHCPhMe_2)({=}N{-}C_6H_3{-}i\mathrm{Pr}_2\text{-}2,6)[O{-}CMe(CF_3)_2]_2$ (polymerization conditions: $[C]_0 = 2\ \mathrm{mmol\ l^{-1}}$, vacuum, room temperature, reaction time 3 h)

No.	R	$[M]_0/[C]_0$	Solvent[a]	Character of polymerization	Yield of polymer (%)	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
1	Me	30	B	Solution	90	13.4	8.6	1.56
2	Me	50	B	Solution	96	16.0	9.8	1.63
3	F	50	B	Solution	95	19.8	11.5	1.72
4	Br	50	B	Precipitation	93	18.3	11.3	1.62
5	Me_3SiCC	50	B	Solution	89	40.4	22.3	1.81
6	I	50	B/C	Precipitation	95	15.7	10.9	1.44
7	CN	50	B	–	0	–	–	–
8	NO_2	50	B/C	Precipitation	80	THF insoluble		

[a] B: benzene; B/C: benzene/chlorobenzene (1:1 by vol.).

are broader ($M_w/M_n = 1.5–2.0$) than expected for living course of polymerization.

The in situ ^{1}H NMR investigation of Mo(=CHCPhMe$_2$)(=N–C_6H_3–*i*Pr$_2$-2,6)[O–CMe(CF_3)$_2$]$_2$ mixed with fivefold molar excess of *N*-benzylideneaniline in C_6D_6 (catalyst concentration = 3 mmol l^{-1}) proved no interaction between catalyst and azomethine group. Only unchanged signals of original components (for catalyst: 12.11 ppm, s, 1H, Mo=CH; 6.94–7.20 ppm, aromatic; 3.56 ppm, hept., 2H, C*H*Me$_2$; 1.51 ppm, s, 6H, OC*Me*(CF_3)$_2$; 1.18 ppm, s, 6H, CHC*Me*$_2$Ph; 1.14 ppm, 12H, CH*Me*$_2$ and for *N*-benzylideneaniline: 8.12 ppm, s, 1H, CH=N; 7.80 ppm, dd, 2H, aromatic; 7.10–7.20 ppm, aromatic) were observed in the spectrum during a day at room temperature. A similar study of mixture of **II**-Me with Mo(=CHCPhMe$_2$)(=N–C_6H_3–*i*Pr$_2$-2,6)[O–CMe(CF_3)$_2$]$_2$ in C_6D_6 (mole ratio **II**-Me/catalyst = 3 and catalyst concentration, $c = 3$ mmol l^{-1}) showed that 12 min after component mixing all monomer was consumed (as indicated by complete disappearance of C≡CH signal at 2.78 ppm) and transformed into product characterized by broad bands in aromatic region and at 2.1 ppm and having MW = 3000 according to SEC. However, besides these signals, only signals of the original catalyst were observed in the spectrum. Evidently, only a minor part of Schrock carbene reacts with **II**-Me and converts the residual monomer very fast into polymer (similarly as for 1-octyne and Schrock catalyst [29]). The absence of additional signals in alkylidene region may suggest that α-insertion of monomer into carbene bond occurs. Higher reactivity of second insertion product in comparison with the first one (slower initiation comparing to the propagation) may be the reason for observed non-proportionality in M_n and monomer consumption and for broadening of molecular weight distribution.

Halogen substituted monomers **I**-Br, **II**-F, **II**-Br and **II**-I (mole ratio monomer/catalyst = 50) polymerize with 100% monomer conversion and more than 90% polymer yield. Small amounts of oligomers (MW up to 2000) were detected in supernatant after polymer isolation. Contrary to the polymers prepared with Rh catalyst, all polymers with halogen substituted pendants prepared with Mo catalyst were completely soluble in THF, aromatics and $CHCl_3$. Trimethylsilyethynyl substituted **I**-Si and **II**-Si provide also high yields of polymers completely soluble in solvent mentioned above. Oligomers (MW = 1000–3000) and small amount of unreacted monomers were observed in supernatants. Their SEC quantification, however, was not possible for the reasons given in the foregoing paragraph. Spectroscopic characterization confirmed preservation of internal triple bonds in polymers. **II**-NO_2 polymerizes with 80% polymer yield. In supernatant, oligomers (MW = 1400) and small amount of unidentified low molecular weight product were found by SEC. The polymer, however, is completely soluble only in strongly polar organic solvents such as dimethyl sulfoxide (DMSO).

With monomers having Me$_2$N and CN substituents (**I**-CN, **I**-NMe$_2$, **II**-CN) poor polymerization results were gained. Monomer conversion of about 50% was achieved only, moreover, majority of converted monomer formed methanol-soluble oligomers (MW = 1000–2000) while yields of methanol-insoluble polymers were up to 9% only. These findings testify to the low compatibility of Schrock carbene complex with Me$_2$N and CN groups in monomers.

3.3. Polymerization with Pd catalyst

Results of polymerization of **I** and **II** with $PdCl_2$ in DMF are summarized in Table 4. Reaction conditions different from those used in polymerizations with Rh and Mo catalysts were adopted (elevated temperature, prolonged reaction time), according to our experiences in $PdCl_2$ catalysed polymerizations of other substituted acetylenes [16]. $PdCl_2$ in DMF was found to be active in polymerization of monomers of both series **I** and **II** with non-polar (Me) as well as with polar (Br, CN) substituents. However, only moderate yields of methanol-insoluble polymers were achieved. Polymers prepared are of low molecular weight (M_w about 4000; $M_w/M_n = 1.6–2.0$), and are soluble in common organic solvents. Significant fraction of monomers (mostly 40–50%) was found to be transformed into methanol-soluble oligomers (MW about 1000) in the course of polymerization.

$PdCl_2$ is a known insertion catalyst for polymerization of various unsaturated hydrocarbons [30]. Dissolution of $PdCl_2$ in DMF results in formation of various Pd-complexes with DMF ligands [31,32]. However, the exact composition of the catalytically active species is not known. The results reported here indicate high tolerance of this catalyst to various heteroatom-containing groups of monomers (–CH=N–, CN, Br). On the other hand, the efficiency of $PdCl_2$ in polymerization of **I** and **II** (polymer yield

Table 4
Results of polymerization of R–C_6H_4CH=NC_6H_4C≡CH (**I**) and R–C_6H_4N=CHC_6H_4C≡CH (**II**) with $PdCl_2$ (polymerization conditions: $[C]_0 = 3.3$ mmol l^{-1}, $[M]_0/[C]_0 = 50$, DMF, vacuum, 85°C, reaction time 24 h)

No.	R	Conversion of monomer (%)		Yield of polymer (%)		$M_w \times 10^{-3}$		$M_n \times 10^{-3}$		M_w/M_n	
		I	**II**	**I**	**II**	**I**	**II**	**I**	**II**	**I**	**II**
1	Me	83	92	27	57	3.7	4.3	2.1	2.5	1.76	1.72
2	Br	–	71	–	59	–	4.2	–	2.2	–	1.91
3	CN	94	–	50	–	4.0	–	2.6	–	1.54	–

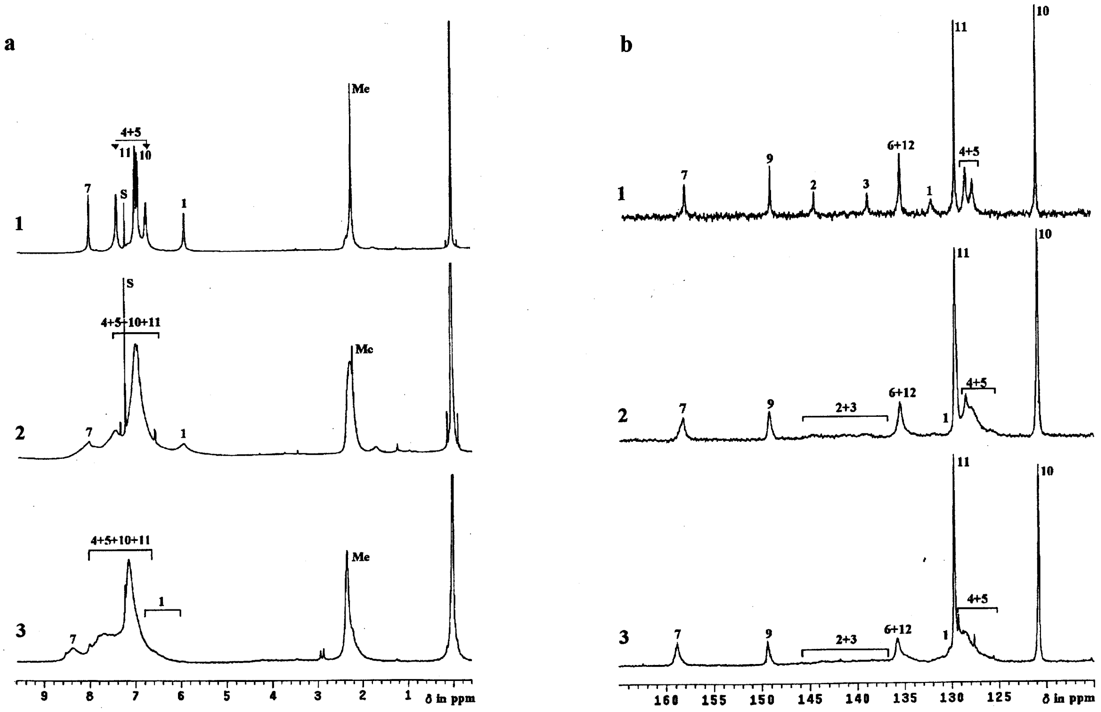

Fig. 4. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of poly(**II**-Me) prepared with Rh (1), Mo (2) and Pd (3) catalysts. CDCl$_3$, numbers at signals correspond to the atom numbers in Scheme 1.

and molecular weight) is evidently worse as compared with Rh and Mo catalysts tested.

3.4. Spectroscopic characterization of polymers

Polymers prepared are coloured solids (yellow, orange, brown), fairly stable in air. IR, NMR and UV–Vis spectra fully confirmed polyacetylene structure of polymers consisting from conjugated polyene main chain and aromatic Schiff base pendants. In IR spectra, no absorption band due to the acetylene C–H stretching and bending vibrations (at 3233–3300 and 619–666 cm^{-1}, respectively) was detected. On the other hand, all spectra exhibited band of CH=N stretching vibration (at about 1620 cm^{-1}) and of other vibrations characteristic for substituted *N*-benzylideneanilines. Spectra of poly(**I**-Si) and poly(**II**-Si) clearly showed strong bands corresponding to the internal triple bond stretching vibration at 2150 cm^{-1} and to vibrations of Me$_3$Si-group at 1250 and 840 cm^{-1}.

All soluble polymers were characterized with ^{1}H and ^{13}C NMR, the insoluble ones by ^{13}C CP MAS NMR. The absence of signals of monomer C≡CH group was confirmed in spectra of all polymers. ^{1}H NMR spectra of poly(**II**-Me) prepared with Rh, Mo and Pd catalysts are shown in Fig. 4a (for atom numbering, see Scheme 1). In very well-resolved spectrum of polymer prepared with Rh catalyst, the signal of *cis*-olefinic hydrogen is well evident at 5.93 ppm and from its area 90% *cis* double bond content in the main chain was estimated according to Ref. [33]. Singlets at 6.77 and 7.42 ppm are due to the aromatic hydrogen atoms of the benzylidene rings 4 and 5, doublets at 6.96 and 7.02 ppm were ascribed to the aniline ring hydrogen 10 and 11 using HETCOR. Azomethine hydrogen signal is well evident at $\delta = 8.03$ and is shifted about 0.4 ppm upfield in comparison with monomer. Spectrum of poly(**II**-Me) prepared with Mo catalyst shows broad and not completely separated signal of *cis*-olefinic proton, from which 60% *cis* double bond content was roughly estimated. The signals of aromatic protons are overlapped giving two broad bands at 7.00 and 7.45 ppm. Azomethine proton signal has its maximum at 8.04 and it is broadened downfield up to 8.5 ppm. Spectrum of poly(**II**-Me) prepared with Pd catalyst does not show any signal of *cis*-olefinic hydrogen. Broad signal of azomethine hydrogen has its maximum at 8.40 ppm. Comparison of spectra in Fig. 4a shows (i) a strong decrease in spectral resolution in the series Rh > Mo > Pd indicating decrease in microstructure uniformity and (ii) decrease in *cis* double bond content in the same order. This decrease is accompanied by broadening and downfield shift of the azomethine signal and by downfield shift of the CH$_3$ group signal from 2.2 to 2.4 ppm. The same trends were also observed from ^{1}H NMR spectra of poly(**I**-Me)s and of other soluble samples of poly(**I**)s and poly(**II**)s as evident from Table 5. This finding is in accordance with high *cis*-transoidal, head-to-tail type of microstructure published for polyphenylacetylenes, (PPhA)s, prepared with Rh catalysts [14,24,34], and with high *trans* character of (PPhA)s produced with Pd catalysts [35]. ^{13}C NMR spectra of poly(**II**-Me)s prepared with Rh, Mo and Pd catalysts are shown in Fig. 4b. Decrease in spectral resolution similar to that in proton spectra is

Table 5
^{1}H NMR chemical shifts of hydrogens 1, 4, 5, 7 (8), 10, 11 in poly(**I**)s and poly(**II**)s prepared with various catalysts. For atom numbering, see Scheme 1 (n.o.: not observed; p: broad peak involving more than one signal)

Polymer	Catalyst	1 (*cis*)	4	5	7 (8)	10	11	R
Poly(**I**-Me)	Rh	5.96	6.81p	6.81p	7.96	7.55	7.03	2.23
Poly(**I**-Me)	Mo	6.0	7.0p	7.0p	7.9	7.6	7.0	2.3
Poly(**I**-Me)	Pd	n.o.	6.0–7.6	6.0–7.6	8.0–8.6	7.8	6.0–7.6	2.4
Poly(**II**-Me)	Rh	5.93	6.77	7.42	8.03	6.96	7.02	2.24
Poly(**II**-Me)	Mo	6.0	7.0p	7.5	8.0	7.0p	7.0p	2.3
Poly(**II**-Me)	Pd	n.o.	7.7	7.2p	8.4	7.2p	7.2p	2.4
Poly(**I**-Bu)[a]	Rh	6.3	7.2p	7.2p	8.2	7.9	7.2p	1.1
Poly(**II**-Bu)[a]	Rh	6.22	6.96	7.75	8.14	7.21p	7.21p	1.18
Poly(**II**-Br)	Mo	6.0	6.9p	7.4p	8.0	6.9p, 7.4p	6.9p, 7.4p	
Poly(**II**-Br)	Pd	n.o.	7.1p	7.5p	8.3	7.1p, 7.5p	7.1p, 7.5p	
Poly(**I**-CN)	Pd	n.o.	7.2p	7.2p	8.4	7.7, 8.0	7.7, 8.0	
Poly(**I**-Si)	Rh	5.94	6.78p	6.78p	7.93	7.37, 7.55	7.37, 7.55	0.26
Poly(**II**-Si)	Mo	6.0	7.0p	7.4p	8.0	7.0p	7.4p	0.26
Poly(**II**-F)	Mo	6.0	7.0p	7.5	8.0	7.0p	7.0p	
Poly(**II**-I)	Mo	6.0	6.7p	7.5p	8.0	6.7p	7.5p	
Poly(**II**-NO_2)[b]	Mo	n.o.	7.1p	7.1p	7.9p	7.1p	7.9p	

[a] Measured in C_6D_6 instead of $CDCl_3$.

[b] Measured in DMSO-d_6 instead of $CDCl_3$.

evident. Signal assignment (numbers correspond to the carbon atoms in Scheme 1) was made on the basis of spectra of monomers [10] and the literature data for (PPhA) [34,35]. Signal for CH_3 group was found at 20.95 ppm for all three polymers. Signals of carbons 1 and 2 at 132.1 and 144.6 ppm, respectively, are seen as sharp only in the spectrum of polymer prepared with Rh catalyst; in both remaining spectra, the signals of backbone and of benzylidene ring are strongly broadened due to the loss of polymer microstructure uniformity. In Tables 6 and 7, carbon chemical shifts for poly(**I**)s and poly(**II**)s, respectively, are listed. It is apparent that for the carbons of ring directly adjacent to the polymer backbone, the differences between chemical shifts of individual polymers in the same series [poly(**I**) and poly(**II**), respectively] are very small. On the other hand, the chemical shifts of the distant ring carbons are governed predominantly by substituents R and are close to the values for corresponding monomers.

UV–Vis spectra of monomer **II**-Me and corresponding poly(**II**-Me) prepared with Rh, Mo and Pd catalysts are given in Fig. 5. The polymer spectra band tailing in the region from 350 to 600 nm is due to the double bond conjugation of the main chain. However, the shape and the intensity of these band tails suggest the effective conjugation length is rather low. The reduced effective conjugation length is probably connected with prevailing *cis*-transoidal conformation of polymer main chains, which is believed to restrict the double bond coplanarity. Although polymers prepared with Pd catalyst are of low *cis* double bond content, the relatively low length of polymer chains prevents the occurrence of longer sequences with perfect conjugation and therefore the spectrum does not exhibit any important difference in comparison with spectra of polymers prepared with Rh and Mo catalysts. UV–Vis spectra of other soluble poly(**II**)s are very close to the spectra shown in Fig. 5. UV–Vis spectra of soluble poly(**I**)s indicate the extent of effective conjugation similar to that of poly(**II**)s.

All soluble poly(**I**)s and poly(**II**)s prepared exhibit fluorescence in THF. Poly(**I**-Me), poly(**I**-Bu), poly(**I**-Br) and poly(**I**-Si) were found to emit green light of λ_{max} between 540 and 570 nm, which is 40–70 nm higher than the fluorescence maxima of the corresponding monomers [10]. Poly(**II**-Me), poly(**II**-Bu), poly(**II**-F), poly(**II**-Br), poly(**II**-I) and poly(**II**-Si) emit in the same region (λ_{max} about 550 nm) exhibiting even larger red shift from the fluorescence maxima of their parent monomers (about 150 nm) [10]. In Fig. 6, fluorescence spectra of samples of poly(**I**)s and poly(**II**)s prepared with Mo catalysts are compared. It is seen that (i) the intensity of fluorescence is significantly

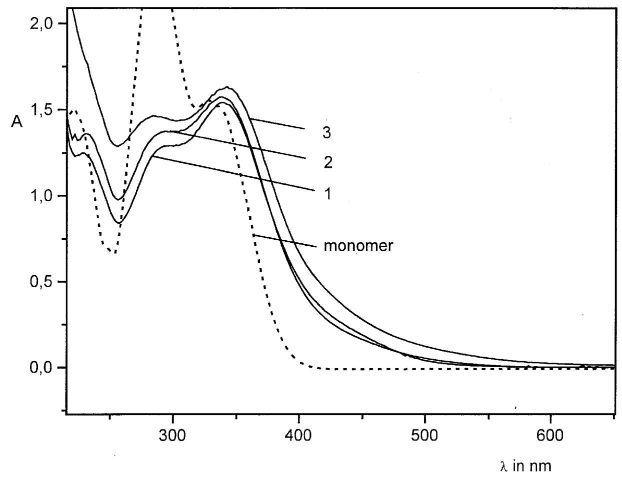

Fig. 5. UV–Vis spectra of **II**-Me and poly(**II**-Me)s prepared with Rh (1), Mo (2) and Pd (3) catalysts. THF, $c = 0.2$ mg ml^{-1}, $l = 0.1$ cm.

Table 6

^{13}C NMR chemical shifts of poly(**I**)s prepared with various catalysts. For atom numbering, see Scheme 1 (SS: solid state measurement by CP MAS NMR; n.o.: not observed; p: broad peak involving more than one signal; s: shoulder)

Polymer	Catalyst	1	2	3	4	5	6	8	9	10	11	12	R	Solvent
Poly(**I**-Me)	Rh	131.3	139.0, 140.6	139.0, 140.6	128.6	120.6	150.94	159.47	133.74	128.27, 128.83	128.27, 128.73	141.21	21.45	$CDCl_3$
Poly(**I**-Me)	Mo	n.o.	135–142	135–142	n.o.	120.6	149–151	159.5	133.80	128.84, 128.27	128.84, 128.27	141.2	21.5	$CDCl_3$
Poly(**I**-Me)	Pd	131	n.o.	n.o.	127	121	n.o.	160	134.0	128.7, 129.5	128.7, 129.5	141	21.6	$CDCl_3$
Poly(**I**-Bu)	Rh	132	137–143	137–143	n.o.	122	153	160.4	135.4	126.55, 129.98	126.55, 129.98	154.8	31.96 + 35.56	C_6D_6
Poly(**I**-F)	Rh	130p	140p	140p	130p	116p	151	157	130p	130p	116p	n.o.		SS
Poly(**I**-Br)	Rh	130p	141p	141p	130p	120s	150	157	130p	130p	130p	130p		SS
Poly(**I**-Si)	Rh	131.4	141.8, 138.7	141.8, 138.7	n.o.	120.7	150.36	158.42	135.79	128.54p, 132.29	128.54p, 132.29	125.84	−0.03 + 96.79 + 104.71	$CDCl_3$
Poly(**I**-CN)	Rh	130p	139p	139p	130p	120s	145–160	145–160	139p	130p	130p	120s	120s	SS
Poly(**I**-CN)	Pd	130–131	n.o.	n.o.	127–129	121	150	158	139.8	129.0, 132.5	129.0, 132.5	114.5	118.3	$CDCl_3$
Poly(**I**-NO_2)	Rh	129p	141p	141p	129p	124p	149p	155s	141p	129p	124p	149p		SS
Poly(**I**-NMe_2)	Rh	130p	140p	140p	130p	130p	145–165	145–165	130p	130p	111	145–165	40	SS

Table 7

^{13}C NMR chemical shifts of poly(**II**)s prepared with various catalysts. For atom numbering, see Scheme 1 (SS: solid state measurement by CP MAS NMR; n.o.: not observed; p: broad peak involving more than one signal; s: shoulder)

Polymer	Catalyst	1	2	3	4	5	6	7	9	10	11	12	R	Solvent
Poly(**II**-Me)	Rh	132.1	144.63	138.96	127.8, 128.5	127.8, 128.5	135.51p	158.35	149.26	120.91	129.63	135.51p	20.92	$CDCl_3$
Poly(**II**-Me)	Pd	n.o.	137–145	137–145	125–130	125–130	134–136	158.9	149.4	120.84	129.73	134–136	20.98	$CDCl_3$
Poly(**II**-Me)	Mo	n.o.	137–145	137–145	125–130	126–130	135.6p	158.3	149.2	120.92	129.65	135.6p	20.96	$CDCl_3$
Poly(**II**-Bu)	Rh	133.3	145.8	140.2	129–130	129–130	137.25	159.32	150.90, 149.42	122.03	127.00	150.90, 149.42	32.26 + 35.17	C_6D_6
Poly(**II**-F)	Rh	128p	140, 147p	140, 147p	128p	128p	135	157	147p	122	116	n.o.		SS
Poly(**II**-F)	Mo	n.o.	139–146	139–146	126–130	126–130	135.4	158.6	147.52	122.29	115.90	161.24		$CDCl_3$
Poly(**II**-Br)	Pd	n.o.	136–145	136–145	126–132	126–132	135	160	151	122.61	132.22	119.5		$CDCl_3$
Poly(**II**-Br)	Rh	131p	140p, 145s	140p, 145s	131p	131p	135	159	145s	123p	131p	123p		SS
Poly(**II**-Br)	Mo	n.o.	136–145	136–145	126–130	126–130	135	159.0	150.3	122.55	132.28	119.7		$CDCl_3$
Poly(**II**-Si)	Mo	n.o.	137–146	137–146	126–130	126–130	135.2	159.2	151.3	120.92	132.99	n.o.	0.04 + 94.59 + 104.97	$CDCl_3$
Poly(**II**-Si)	Rh	n.o.	145s	145s	129p	129p	135s	158	150	121p	133	121p	0 + 94 + 105	SS
Poly(**II**-NO_2)	Rh	134p	144p	144p	126p	126p	134p	158p	158p	115s	126p	144p		SS
Poly(**II**-NO_2)	Mo	n.o.	n.o.	n.o.	126–130	126–130	134	163	157	121.8	124.8	145		DMSO-d_6
Poly(**II**-CN)	Rh	133p	140s, 146s	140s, 146s	129p	129p	133p	150–165	150–165	122p	133p	109	122p	SS
Poly(**II**-I)	Mo	n.o.	140–146	140–146	126–130	126–130	135	159.0	150.9	122.94	138.28	90.9		$CDCl_3$

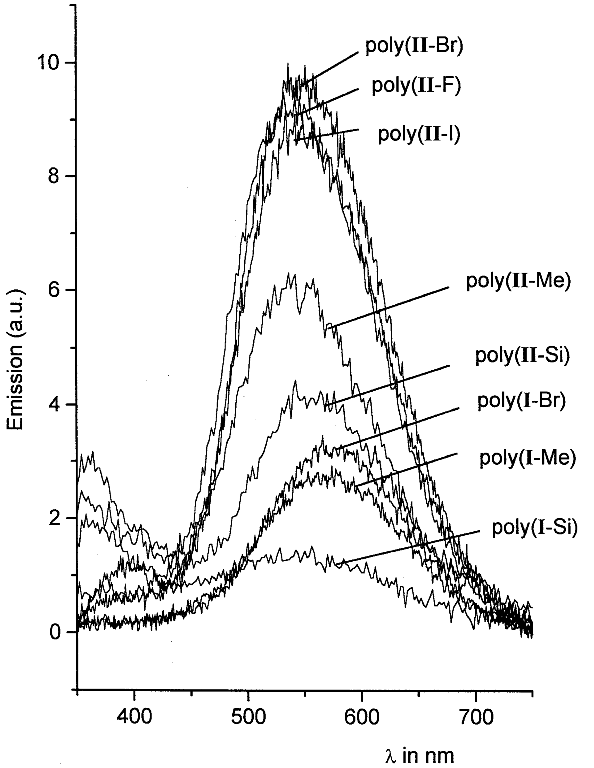

Fig. 6. Fluorescence spectra of poly(**I**-Me), poly(**I**-Br), poly(**I**-Si), poly(**II**-Me), poly(**II**-F), poly(**II**-Br), poly(**II**-I) and poly(**II**-Si) prepared with Mo catalyst. THF, $c = 0.066\,\mathrm{mg\,ml^{-1}}$.

higher for poly(**II**)s than for poly(**I**)s, (ii) the character of R-substituent has only marginal effect on the wavelength of the emitted light, (iii) R has significant influence on the intensity of emission (halogen substituted polymers exhibit higher intensity than polymers with methyl or trimethylsilylethynyl substituents). The changes in polymer molecular weight and polymer microstructure exerted no significant effect on $\lambda_{\max}$, e.g. spectra of poly(**II**-Me)s prepared with Rh, Mo and Pd catalysts, respectively, exhibited the same spectral profile with $\lambda_{\max}$ about 550 nm.

Intense emission of blue or green light has been observed for a number of disubstituted polyacetylenes [36]. Contrary to this, monosubstituted polyacetylenes have been reported to exhibit marginal fluorescence [36,37]. Only very recently, a strong blue fluorescence from poly(1-alkynes) containing biphenylyl type chromophores was described [38] and theoretical calculations showed that functional pendants could modify the band states of monosubstituted polyacetylenes substantially so that strong fluorescence occurs [39]. Attachment of coumarinyl chromophore to the polyacetylene main chain was found to lead to the fluorescence-active polymer with emission considerably red-shifted in comparison with parent monomer [40]. This red shift was assumed to be a result of a strong pendant–pendant intramolecular interaction and/or interaction of pendants and the polyene main chain. Since for poly(**I**)s and poly(**II**)s the spectral profile does not depend on changes in polymer microstructure and since the distance between pendants in uniform head-to-tail *cis*-transoidal polymer chain is rather high, the green fluorescence of these polymers probably results from electronic junction between aromatic Schiff base pendants and the polyene main chain.

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