COMPARATIVE STUDY OF POLYMERIZATION OF 2-, 3- AND 4-IODOPHENYLACETYLENES WITH Rh-, Mo- AND W-BASED CATALYSTS

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2-, 3- and 4-Iodophenylacetylenes (IPA) have been polymerized with $[Rh(cod)(OCH_3)]_2$ complex in THF (system Rh), $MoCl_5$ in benzene (Mo), $WOCl_4$ in benzene (WB) and $WOCl_4/Ph_4Sn$ in benzene–dioxane 1 : 1 (WD). All the systems provide poly(iodophenylacetylene)s (PIPA) and diverse amounts of oligomers (mostly cyclic trimers and tetramers) but the system 2-IPA/Rh that provides mostly dimers only. 2-IPA has also been polymerized with $MoOCl_4/Bu_4Sn/EtOH$ in toluene (Masuda's catalyst system), however, neither living nor pseudo-living polymerization has been observed. The ring-iodine steric effects control the polymerization activity of the Rh and WB systems and the oligomerization activity of the Mo system. The ring-iodine electronic effects are important for the oligomerization activity of the Rh and WB systems and both oligomerization and polymerization activity of the WD system. Both types of the ring-iodine effect are important for polymerization activity of the Mo system. Rh catalyst provides high-*cis*-transoid, head-to-tail (HT) 3-PIPA that slowly isomerizes in $CDCl_3$ solution to an insoluble trans-polymer. In the case of 4-PIPA, the isomerization is extremely fast upon polymer entering into contact with methanol. On the basis of spectral changes accompanying this isomerization, the Raman band at 1 338 cm^{-1} is assigned to the presence of HT sequences of both *cis*-transoid and *trans*-cisoid type. The other catalysts provide irregular PIPAs with content of both cis units and HT sequences decreasing in order Mo > WD > WB. Solubility of PIPA samples is shown as a result of complex interplay of the ring-iodine position and the polymer microstructure and molecular weight.

Key words: Iodophenylacetylene; Substituted polyacetylenes; Poly(phenylacetylene); Conjugated polymers; Metathesis polymerization; Tungsten; Molybdenum; Rhodium; Raman spectroscopy.

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Electric, photoelectric and nonlinear optical properties of conjugated polymers have brought about big promises for their utilization as materials for polymer conductors, solar cells and optical computing devices[1–5]. Although these polymers have not been developed on a level of large-scale production for the applications mentioned above (mostly because of their poor processability and low resistance to chemical corrosion[5–9]), they are already utilized commercially in electrochemical cells for energy storage applications. Recently, some of these polymers have been shown to exhibit strong electroluminescence phenomena, which boosted a new wave of increasing interest in basic and applied research of this group of materials[10,11].

Steadily increasing tendency to exploit polymers involving one-dimensional π-electron system in electronic and optoelectronic applications needs a deeper knowledge of the structure-to-physical-properties relations for π-conjugated polymers as well as attaining a better control of synthesis of polymers possessing a desired structure. It is the aim of the present paper to contribute to spreading knowledge in these fields. We report on polymerizations of ring-positional isomers of iodophenylacetylene (further denoted as 2-, 3- and 4-IPA) with Mo-, Rh- and W-based catalysts. Particular attention is paid to the influence of the ring iodine electronic and steric effects on the formation, microstructure and solubility of respective polymers (further denoted as 2-, 3- and 4-PIPA). Examples of controversial assignment of polymer microstructure on the basis of NMR and/or Raman spectra are shown and correction of rules for the interpretation of Raman spectra of substituted poly(phenylacetylene)s[12,13] is suggested.

EXPERIMENTAL

Chemicals

Benzene, toluene, 1,4-dioxane (all Lachema, Czech Republic), $WOCl_4$ (Aldrich) and tetraphenyltin (Ph_4Sn, Aldrich) were purified as described earlier[14,15]. $RhCl_3 \cdot 3\ H_2O$, cycloocta-1,5-diene, $MoCl_5$ and $MoOCl_4$ (all Aldrich) were used as supplied. Anhydrous ethanol (EtOH) was prepared by refluxing ethanol with metallic magnesium. Tetrabutyltin (Bu_4Sn, Koch-Light, pure) was distilled in vacuum. Tetrahydrofuran (THF, Riedel–DeHaen, purity 99.5%+, stabilized with 2,6-di-*tert*-butyl-4-methylphenol, 0.025% w/v) was distilled from CaH_2 and Cu_2Cl_2. Preparations of monomers (2-, 3- and 4-IPA) as well as their spectroscopic characteristics are described elsewhere[8,16]. Di-μ-methoxo-bis[(η^4-cycloocta-1,5-diene)rhodium], [Rh(cod)(OCH$_3$)]$_2$, was prepared from $RhCl_3 \cdot 3\ H_2O$ according to procedures used in syntheses of analogous norbornadiene complex[17–19].

Methods

NMR spectra were recorded on a Varian Unity 500 instrument operating at 499.843 MHz for ^{1}H, and 125.697 MHz for ^{13}C using the samples dissolved in $CDCl_3$ and hexamethyldisilane (1% v/v) for referencing [1]H (δ +0.04 ppm). The ^{13}C spectra were referenced to the solvent (δ +76.99 ppm). The relaxation delay was set to 5 s. Signals of protonated and non-protonated carbons were distinguished by the APT (Attached Proton Test) method with the *J*-modulation period minimized by ^{13}C and ^{1}H refocusing pulses.

IR spectra were measured by the diffuse reflectance technique with non diluted, powdered samples using FTIR Nicolet 210 and ATI Matson Genesis Series FTIR spectrometers (128 scans at resolution 4 cm^{-1}).

FT Raman spectra were acquired on a Bruker IFS 55/S Equinox spectrometer fitted with quartz beamsplitter and equipped with FRA 106/S FT-Raman module with a liquid nitrogen-cooled germanium detector. The defocused 1 064 nm line of an air-cooled, Nd/YAG near-IR laser (Coherent) was used to excite spectra. All samples were excited in 180° arrangement with the laser power at the sample less than 30 mW. The spectra were collected with resolution 4 cm^{-1}; 256 scans were co-added for one spectrum.

UV/VIS optical absorption spectra were recorded on a Hewlett–Packard 8452 diode-array spectrometer using quartz cuvettes (0.2 cm) and freshly distilled THF.

Size exclusion chromatography (SEC) analyses were made on a TSP (Thermo Separation Products) 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) and THF (flow rate 0.7 ml min^{-1}) were used. Molecular weight averages relative to polystyrene standards are reported.

Synthesis of Polymers

Polymerizations induced by $MoCl_5$, $[Rh(cod)(OCH_3)]_2$ and $WOCl_4$-based catalysts were performed at room temperature with the following initial concentrations: [catalyst] = 3.3 mmol l^{-1}, [monomer] = 170 mmol l^{-1}, polymerization induced by $MoOCl_4/Bu_4Sn/EtOH$ was performed at 30 °C with [catalyst] = 10 mmol l^{-1}, [monomer] = 170 mmol l^{-1}. For all polymerizations with W- and Mo-based catalysts, standard vacuum break-seal technique and benzene as the main solvent were used. Polymerizations induced by single-component $WOCl_4$ and $MoCl_5$ catalysts were simply started by mixing benzene solution (2 ml) of monomer (114 mg, 0.5 mmol) with the respective catalyst solution (1 ml, 10 mmol l^{-1}). Polymerization with $WOCl_4/2$ Ph_4Sn in benzene–dioxane was performed as follows: Solution of $WOCl_4$ (1 ml, 10 mmol l^{-1}) was first mixed with solid Ph_4Sn (molar ratio W/Sn = 1/2) and allowed to ripen for 15 min. Afterwards, dioxane (1.5 ml) was added, the formed blue solution stirred for another 15 min and then mixed with the particular monomer (0.5 mmol) dissolved in 0.5 ml of benzene. Polymerizations were quenched by excess of methanol, isolated polymers were washed with methanol, dried in vacuum at room temperature to constant weight and the polymer yields were determined gravimetrically. Conversions of monomers were determined by gas chromatography analysis of supernatants from isolation of polymers.

For the polymerization of 2-IPA with $MoOCl_4/Bu_4Sn/EtOH$, first $MoOCl_4$ (7.5 mg, 0.029 mmol) was mixed with Bu_4Sn (molar ratio Mo/Sn = 1/1) in 2 ml of toluene and the solution allowed to ripen for 15 min. Then EtOH (0.029 mmol) in 0.5 ml of benzene was added and, after another 15 min of ripening, the polymerization was started by adding 2-IPA (0.5 mmol) in 0.5 ml of benzene.

Polymerizations induced by Rh complex were started by mixing the catalyst solution in THF (1 ml, 10 mmol l^{-1}) with monomer solution (0.5 mmol in 2 ml THF) under argon atmosphere. The course of these reactions was monitored by SEC. At a given time, a volume of 5 µl was withdrawn from the reaction mixture, diluted with 1 ml of THF and the solution injected into SEC columns. The contents of non-reacted monomer and oligomers and polymers formed were estimated from relative areas of the corresponding SEC peaks.

RESULTS AND DISCUSSION

Polymerizations

Every monomer has been polymerized with four different catalyst systems. In the following text, the catalyst used in preparation is denoted as an extension of particular polymer acronym: /Rh for [Rh(cod)(OMe)]₂ complex in THF, /Mo for MoCl₅ in benzene, /WB for WOCl₄ in benzene and /WD for WOCl₄/2 Ph₄Sn in benzene–dioxane (1 : 1 by volume). The polymerization systems differ in: (i) homogeneity/heterogeneity (owing to diverse solubility of polymers formed), (ii) overall monomer conversion and (iii) distribution of products into oligomers and polymers. Characteristics of polymerization processes as well as basic data concerning the molecular weights and solubility of formed polymers are given in Table I.

Polymerizations Induced by [Rh(cod)(OMe)]₂ Catalyst in THF

Conversion curves for reactions of IPA monomers with [Rh(cod)(OMe)]₂ are shown in Fig. 1. First it is seen that the Rh complex does not polymerize 2-IPA at all, only oligomers being formed in this reaction. On the other hand, high polymer yields are attained with 3-IPA and 4-IPA. Thus, it is clear that the *ortho*-position of iodine is highly unfavorable for polymerization of IPA with [Rh(cod)(OMe)]₂. This can be due to purely steric reasons and/or due to a formation of some chelate-like structures involving both ethynyl group and *ortho*-iodine coordinated to the same Rh atom.

Examples of SEC records given in Fig. 2 show that oligomers formed on the Rh-based catalyst are not a continuous series of homologues but particular species are prevailing among them. According to SEC retention times, these species can be tentatively assigned as a mixture of trimers and tetramers in the case of 3-IPA (apparent MW = 660) and 4-IPA (MW = 820), but mainly dimers in the case of 2-IPA (MW = 380). Although we did not analyze the oligomers more in detail, those derived from 3-IPA
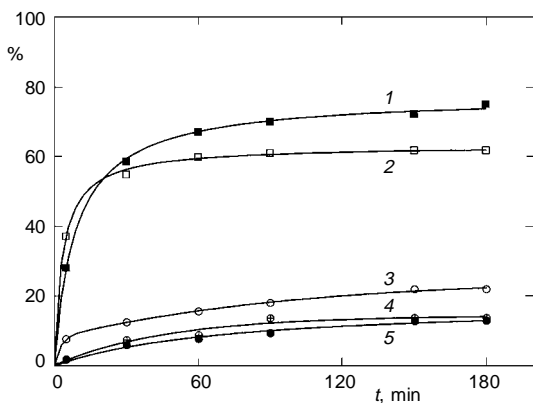

FIG. 1
Conversion curves of transformation of iodophenylacetylenes into polymers and oligomers with [Rh(cod)(OMe)]2 catalyst in THF at room temperature: *1* 4-PIPA, *2* 3-PIPA, *3* 3-IPA oligomers, *4* 2-IPA oligomers, *5* 4-IPA oligomers

TABLE I
Main characteristics of polymerization of 2-, 3- and 4-iodophenylacetylenes (initial concentrations: catalyst: 3.3 mmol l⁻¹ (MoOCl₄ 11 mmol l⁻¹), monomer: 170 mmol l⁻¹)

Monomer		Reaction mixture	Monomer conversion %	Oligomer yield %	Polymer yield %	$10^{-3}\langle M\rangle_w$	$10^{-3}\langle M\rangle_a$	Notes
			[Rh(cod)(OMe)]₂, THF, 3 h, room temperature					
1	2-IPA	homogeneous	13	13	0	–	–	16% of oligomers formed after 24 h
2	3-IPA	homogeneous	84	22	62	45	24	mostly insoluble upon isolation[a]
3	4-IPA	homogeneous	89	6	83	140	57	fraction soluble upon isolation
					7	9	5	
			MoCl₅, benzene, 24 h, room temperature					
4	2-IPA	homogeneous	27	3	24	46	25	
5	3-IPA	homogeneous	74	38	36	26	16	
6[b]	4-IPA	heterogenous	96	71	25	–	–	insoluble in benzene, THF, CHCl₃, DMF, DMSO, N-methylpyrrolidone
			MoOCl₄/Bu₄Sn/EtOH, toluene–benzene (2 : 1 by volume), 3 h, 30 °C					
7	2-IPA	mostly heterogeneous	85	5	80			
					23	30	14	fraction soluble in reaction mixture
					57	–	–	insoluble fraction (benzene, THF, CHCl₃, DMF, DMSO, N-methylpyrrolidone)

TABLE I
(*Continued*)

Monomer		Reaction mixture	Monomer conversion %	Oligomer yield %	Polymer yield %	$10^{-3} \langle M \rangle_w$	$10^{-3} \langle M \rangle_a$	Notes
		WOCl₄, benzene, 24 h, room temperature						
8	2-IPA	partly heterogeneous	38	6	32			
					30	53	34	fraction soluble in reaction mixture
					2			fraction insoluble in benzene and THF
9	3-IPA	mostly heterogeneous	>99	30	69			
					25	25	10	fraction soluble in reaction mixture
					44	51	20	fraction insoluble in reaction mixture
10[b]	4-IPA	heterogeneous	90	15	75	53	19	
		WOCl₄/2 Ph₄Sn, benzene–dioxane (1 : 1 by volume), 24 h, room temperature						
11	2-IPA	heterogeneous	>99	17	82			
					42	60	33	fraction soluble in THF
					40	–	–	insoluble fraction
12	3-IPA	homogeneous	>99	27	72	120	50	
13[b]	4-IPA	mostly heterogeneous	99	9	90			
					20	44	26	fraction soluble in reaction mixture
					70	190	110	fraction insoluble in reaction mixture

[a] Polymer becomes insoluble upon entering into contact with methanol; [b] polymerization data taken from ref.[8].

and 4-IPA can be considered to be predominantly of the cyclic type. It is namely clear that there is no principal constraint of the formation of linear chains of any length, including oligomeric ones, if reasonably long macromolecules are formed with these reaction systems. Thus, the gap existing between the trimers to tetramers and longer macromolecules should be ascribed to a particular structure of these oligomers. Cyclic structure affording an increased stability to oligomeric molecules comes first into consideration. It is after all well known that cyclotrimers (1,3,5- and 1,2,4-trisubstituted benzenes) are common byproducts of polymerizations of monosubstituted acetylenes[20,21].

The kinetic curves shown in Fig. 1 clearly demonstrate that the oligomers are formed in the course of the entire polymerization process, in the later reaction stage as fast as polymers. This can be a result of slowing down the propagation owing to a significant decrease in monomer concentration. If the propagation is slow the growing species have longer time between two consecutive additions of a monomer molecule, which increases the probability of their backbiting reactions leading to an elimination of cyclic oligomers. Another, equally probable explanation consists in spontaneous transformation of polymerization into the oligomerization centers, on which direct cyclooligomerization of IPA molecules takes place.

It is seen from both Fig. 1 and Table I that the highest oligomer yield is achieved with 3-IPA. The yield of 3-IPA oligomers is almost twice that of 4-IPA, despite higher steric hindrance to ring closure in the case of 4-IPA. This suggests that the iodine
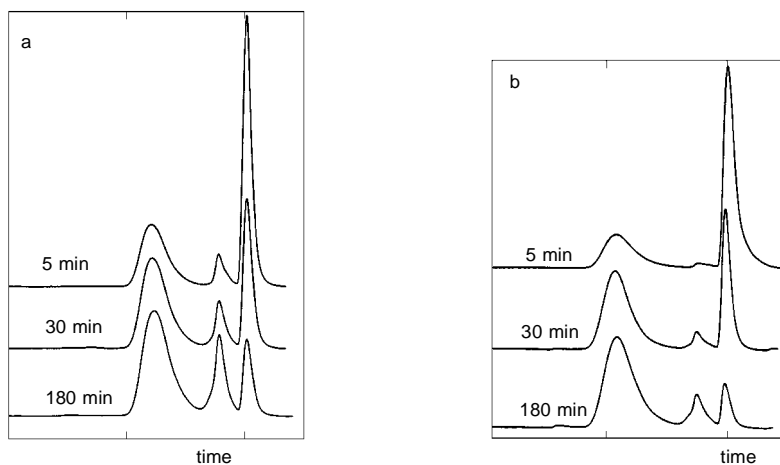

FIG. 2
SEC records of polymerization mixtures: **a** 3-IPA, **b** 4-IPA; polymerizations induced by [Rh(cod)(OMe)]$_2$ catalyst, sampling at indicated reaction times

electronic rather than steric effects are important for formation of cyclic oligomers on the [Rh(cod)(OMe)]$_2$ catalyst.

Particular attention should be paid to the polymerization of 4-IPA with [Rh(cod)(OMe)]$_2$ catalyst (Table I, entry 3, Fig. 2b). The reaction mixture is dark yellow and homogeneous throughout the entire polymerization such that it could readily be analyzed by SEC to determine the mixture composition as well as molecular weights of the polymer and oligomers. However, during quenching the polymerization, over-whelming majority (above 90%) of the formed polymer has instantaneously coagulated from the solution immediately after addition of only first several drops of methanol. The coagulated carmine-red polymer is insoluble in any tested solvent (see Table I) including THF in which it was well soluble until the onset of quenching. This polymer is further denoted as 4-PIPA/Rh(i). Ochre, well soluble low-MW fraction of 4-PIPA/Rh, further denoted as 4-PIPA/Rh(low-MW), has been isolated upon addition of further amount of methanol to the remaining solution (1 : 1 by volume). Oligomers and unreacted monomer have been isolated from the supernatant.

The described sudden and irreversible deep change in both the color and solubility of high-molecular-weight 4-PIPA/Rh upon a contact with a few drops of methanol is per-haps the most peculiar observation concerning this polymerization system. The X-ray analysis has shown that there is no crystallinity in 4-PIPA/Rh(i) such that some regular packing of 4-PIPA macromolecules into detectable crystallites was not confirmed. Therefore, some crosslinking of 4-PIPA macromolecules and/or their packing into sol-vent resistant, predominantly amorphous supramolecular structures can be assumed as a reason of insolubility of 4-PIPA/Rh(i).

Polymerizations Induced by MoCl$_5$ in Benzene

Important data concerning these polymerizations are given in Table I, entries 4 to 6. First, it is seen that MoCl$_5$, unlike the preceding Rh catalyst, polymerizes 2-IPA to a soluble polymer and that the amount of oligomers formed as side products is very low. Second, the yields of 2-PIPA, 3-PIPA and 4-PIPA polymers achieved with MoCl$_5$ under equal reaction conditions are comparable, whereas the yield of oligomers shows a re-markable, stepwise increase (steps of 35%) from 2-IPA to 4-IPA. This conclusively shows that the iodine steric effects have little influence on the polymerization activity of MoCl$_5$ whereas they virtually control the oligomerization activity of this catalyst.

As in the case of the Rh catalyst, the oligomers formed with the MoCl$_5$ catalyst obviously are mainly cyclotrimers and cyclotetramers. Accordingly, the observed growth of the MoCl$_5$ oligomerization activity when going from 2-IPA to 4-IPA can be rationally explained in terms of lowering the steric hindrances to the molecular ring closure. Enormous difference between yields of the 2-IPA and 4-IPA oligomers points to marginal (if any) importance of electronic effects for oligomerization of IPAs on species derived from the MoCl$_5$. (According to well-known and theoretically substan-tiated rules the electronic effects of *ortho-* and *para-*substituent should be approxi-

mately equal.) On the other hand, significantly higher yield of 3-PIPA as compared with 2-PIPA and 4-PIPA polymers (36% *vs ca* 25%) indicates that the lower electron withdrawing effect of *meta*-iodine supports the polymerization activity of MoCl$_5$.

Third, the heterogeneity of the reaction mixture increases from 2- to 4-IPA isomer. This means that the polymer solubility in benzene decreases from 2-PIPA to 4-PIPA, the latter being insoluble at all. The 4-PIPA/Mo sample has been analyzed by X-ray scattering method and no crystallinity has been detected[8]. This points to some cross-linking of 4-PIPA macromolecules and/or their strong packing into solvent resistant, predominantly amorphous supramolecular structures.

Polymerizations Induced by MoOCl$_4$/Bu$_4$Sn/EtOH Catalyst in Toluene

It is well known that the MoOCl$_4$/Bu$_4$Sn/EtOH catalyst system induces living polymerization of ring-substituted phenylacetylenes carrying bulky substituents in *ortho*-positions[7]. Therefore, we have examined this catalyst in polymerization of 2-IPA applying the conditions currently used by Masuda *et al.*[7] in these polymerizations (see Table I, entry 7). The reaction mixture is mostly heterogeneous during this polymerization and the formed 2-PIPA/MoO can readily be separated into two fractions: soluble and insoluble in the reaction mixture (and other solvents). The soluble fraction is of medium molecular weight and its polydispersity $\langle M \rangle_w / \langle M \rangle_n$, is about 2.15, which fairly exceeds the values typical of living or pseudo-living polymerizations (1.03–1.3). Thus, the polymerization of 2-IPA with MoOCl$_4$/Bu$_4$Sn/EtOH catalyst evidently is of the non-living type. Obviously, the iodine bulkiness is not high enough to provoke at least pseudo-living polymerization of 2-IPA. Nevertheless, it is clear that the MoOCl$_4$/Bu$_4$Sn/EtOH catalyst system is very active in the polymerization of 2-IPA and shows extremely low oligomerization activity with respect to this monomer.

Polymerizations Induced by WOCl$_4$ in Benzene

The WOCl$_4$ catalyst is remarkable in that respect that it polymerizes all three positional IPA isomers to high molecular weight polymers, which all are well soluble in low-polar solvents like THF, CHCl$_3$ and dioxane. 2-PIPA/WB and 3-PIPA/WB are even partly soluble in aromatic solvents (see Table I). According to attained polymer and oligomer yields, the polymerization activity of WOCl$_4$ follows the sequence: 2-IPA << 3-IPA < 4-IPA, whereas its oligomerization activity a different sequence: 2-IPA < 3-IPA > 4-IPA. This points to an importance of the iodine steric effects for the polymerization activity and the iodine electronic effects for the oligomerization activity of WOCl$_4$ catalyst.

Polymerizations Induced by WOCl$_4$/2 Ph$_4$Sn Catalyst in Benzene–Dioxane (1 : 1 by Volume)

This catalyst system (WD) had been chosen for present comparative study because it is well known to polymerize phenylacetylene and some its derivatives to well soluble, extremely high-molecular-weight polymers[6,8,23,24]. High yields of PPA are obtained

with WD catalyst even at the monomer-to-catalyst ratio values above 1 000. Dioxane, although being formally used as a co-solvent, actually acts as a component of the catalyst system. This solvent was shown to form defined coordination species with $WOCl_4$ (ref.[25]). Therefore, it is assumed to be rather strongly but reversibly (entering the competition with acetylenic monomer molecules) coordinated to oxotungsten growing species (and also their precursors[15]) providing them with increased resistance against termination[8,15].

As it is seen from Table I (entries 11–13), the above-mentioned advantages of the WD system come into play in polymerizations of IPA isomers. Virtually total monomer conversion, highest polymer yield (70 to 90%) and highest values of PIPA molecular weight have been achieved for all three positional isomers with the WD catalyst system. The amounts of oligomers of particular IPA isomer are comparable with those obtained with $WOCl_4$ single-component catalyst. Again, the highest oligomer yield is obtained for 3-IPA isomer. These observations point to a low importance of the ring-iodine steric effects for both the polymerization oligomerization activity of WD catalyst. Both types of the catalyst activity are rather controlled by the iodine electronic effects, which is in agreement with the idea that monomer molecules are in a strong competition with dioxane molecules about oxo-tungsten species.

Heterogeneity of the WD polymerization mixtures considerably differs from their counterparts involving $WOCl_4$ and benzene only (WB systems, see Table I, entries 8 to 10). The 2-IPA–WD system is almost purely heterogeneous whereas the 2-IPA–WB system only slightly heterogeneous. The THF-insoluble fraction of 2-PIPA/WD makes up about 50% (w/w) while that of 2-PIPA/WB only about 10% of the corresponding polymer. It shows a decreased solubility of 2-PIPA/WD polymer as compared to its WB counterpart. The 3-IPA–WD system is homogeneous throughout the entire polymerization, whereas the 3-IPA–WB system is mostly heterogeneous. The 4-IPA–WD system is mostly heterogeneous and the formed 4-PIPA/WD spontaneously separates into two fractions (soluble and insoluble in the reaction mixture) differing in molecular weight. On the other hand, the 4-IPA–WB system is almost purely heterogeneous, no polymer fractionation occurring. The observed solubility differences of polymers formed in the WD and WB systems evidently cannot be explained in terms of diverse solvent quality, only. Thus these differences point to a microstructure diversity of the same positional-type PIPA polymers formed in the WD and WB systems.

Characterization of Polymers by NMR and IR Spectroscopy

NMR Spectra of 2-PIPA and 4-PIPA Polymers

NMR spectra of 4-PIPA have already been discussed[8]. They have merely shown that 4-PIPA polymers prepared by $WOCl_4$- and $MoCl_5$-based catalysts are irregular, however, they do not provide more detailed information about the configurational structure

of these polymers due to low spectral resolution. The obtained NMR spectra of soluble 2-PIPA samples prepared with $MoCl_5$ (2-PIPA/Mo) and $WOCl_4$ (2-PIPA/WB) have also been poorly resolved. Nevertheless, minor differences showing a structure diversity of these samples have been apparent.

The ^{1}H NMR spectrum of 2-PIPA/Mo involves a broad band at 3.6 ppm (width 1 ppm) suggesting the presence of cyclohexadiene sequences[26] and a very broad band (5 to 8.5 ppm) with shoulders at 6 ppm (H8) and 6.6 ppm (H6) suggesting the presence of small amounts of cis units in this polymer[26–28]. The ^{13}C NMR spectrum of 2-PIPA/Mo consists of band at 101 ppm (C2-I), merged bands at 127 ppm (C4, C5, C6) and 131 ppm (C8), and a broad band with a flat maximum between 137 and 141 ppm (C1, C3, C7).

In the ^{1}H NMR spectrum of 2-PIPA/WB, the signal at 3.6 ppm is virtually absent, which points to absence of cyclohexadiene units in this polymer. Broad band between 5 and 8.5 ppm does not involve shoulders observed in the Mo-type polymer, which suggests absence of cis units in 2-PIPA/WB. In the ^{13}C NMR spectrum of 2-PIPA/WB, the shoulder at 131 ppm is absent and also signal at 141 ppm is considerably weaker compared with that of the Mo-type polymer.

It can be, therefore, summarized on the basis of NMR spectra that both the discussed polymers are strongly irregular and: (i) 2-PIPA/Mo is the medium-cis polymer including cyclohexadiene sequences, whereas (ii) 2-PIPA/WB is rather high-trans polymer that is virtually free of cyclohexadiene sequences.

NMR Spectra of 3-PIPA Polymers

NMR spectra of three 3-PIPA/Rh, -/Mo and -/WB are shown in Figs 3 and 4. The spectra of 3-PIPA/Rh stand out by a high resolution which proves a high stereoregularity of this polymer[27–29]. The signal assignment for these spectra has been done on the basis of: (i) spectra of poly(phenylacetylene), PPA, prepared on the same catalyst; (ii) calculations based on the monomer spectrum; (iii) changes accompanying the transformation of phenylacetylene into PPA and (iv) the selective decoupling measurements. (For numbering the atoms see Scheme 1.) ^{1}H NMR, ppm: 5.76 s (H8); 6.61 d (H6, coupled to H5, 5.9 Hz); 6.78 t (H5, coupled to H5 and H8, 7.1 Hz and 7.3 Hz); 7.07 s (H2); 7.48 d (H4, coupled to H5, 7.6 Hz). ^{13}C NMR, ppm: 94.69 (C3-I), 126.79 (C6), 129.97 (C5), 131.83 (C8), 135.86 (C4), 136.66 (C2), 138.64 (C1) and 143.96 (C7). According to these spectral features, 3-PIPA/Rh can be regarded as the virtually all-*cis*-
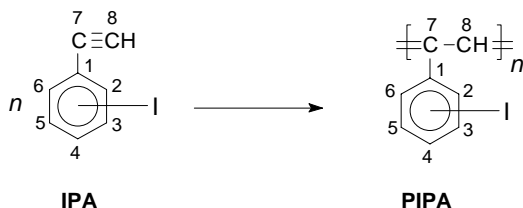
SCHEME 1

transoid, head-to-tail (HT) polymer (for characteristic features of the NMR spectra of poly(phenylacetylene)s of this structure type see, *e.g.*, refs[12,13,18,22,26–29]).

Storage of a fresh 3-PIPA/Rh solution in CDCl₃ under argon (one day at room temperature during an unsuccessful attempt to measure HETCOR and then for two weeks in refrigerator at –15 °C) has resulted in significant changes in the polymer ¹H NMR spectrum. First, all NMR signals broadened most of them merged into one band with residues of original lines (Fig. 3b), which proves the loss of polymer regularity and the
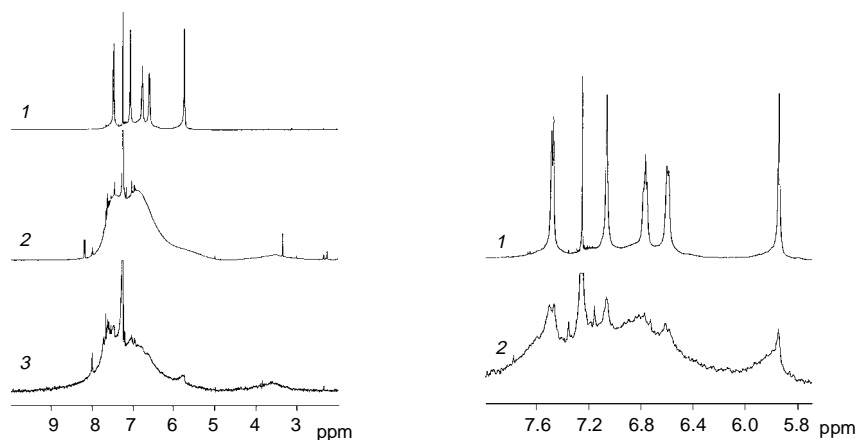
Fɪɢ. 3

a ¹H NMR spectra of 3-PIPA samples prepared with indicated catalysts: *1* 3-PIPA/Rh, *2* 3-PIPA/WB, *3* 3-PIPA/Mo. **b** Detail of ¹H NMR spectra of 3-PIPA/Rh samples: *1* fresh sample, *2* sample aged in CDCl₃ solution for 14 days
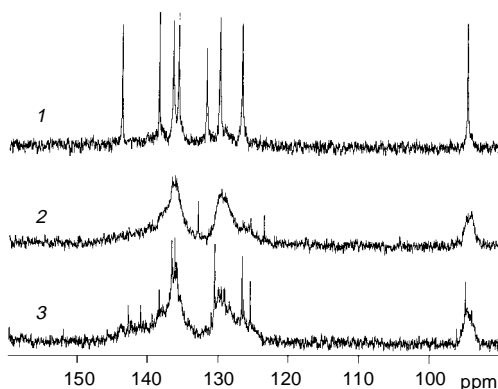
Fɪɢ. 4

¹³C NMR spectra of 3-PIPA samples prepared by indicated catalysts: *1* 3-PIPA/Rh, *2* 3-PIPA/WB, *3* 3-PIPA/Mo

decay of cis units, *i.e.*, the significant *cis*-to-*trans* isomerization of 3-PIPA/Rh in CDCl$_3$ solution. Second, a week band at 3.6 ppm occurred (not shown in Fig. 3) indicating the presence of cyclohexadiene sequences[21] in the isomerized 3-PIPA/Rh sample.

Aging of 3-PIPA/Rh in CDCl$_3$ is accompanied by a change of the polymer color from yellow to orange and by the polymer coagulation. After 50 days of standing of the solution, about 80% of 3-PIPA/Rh changed to an insoluble orange solid (further denoted as 3-PIPA/Rh(i)) for which, as in the above cases, no crystallinity has been detected by X-ray diffraction. The remaining 20% of polymer has been isolated from the rest solution as a soluble ochre powder with $\langle M \rangle_n = 2\ 800$ and $\langle M \rangle_w = 6\ 700$ (further denoted as 3-PIPA/Rh(s)).

The change in polymer color is consistent with the suggested *cis*-to-*trans* isomerization. It is namely known that cis units effectively act as weak defects deteriorating the extent of π-conjugation[5,30,31]. Thus the *cis*-to-*trans* isomerization should increase the effective conjugation length of polymer main chains and cause a bathochromic shift of the polymer optical absorption. If the *cis*-to-*trans* isomerization proceeds *via* free spin (radical) migration along the main chain, the crosslinking as well as intramolecular cyclization (formation of cyclohexadiene sequences) of macromolecules can occur by means of the intermolecular and intramolecular recombination of free spins. The presence of free spin in PPA and its derivatives was evidenced many times by EPR spectroscopy, see, *e.g.*, refs[12,13,22,28,32].

The spectra of the other two 3-PIPA samples are poorly resolved, which proves their microstructure non-homogeneity[27]. The ^{1}H NMR spectrum of 3-PIPA/Mo consists of a broad band at 3.6 ppm proving the presence of cyclohexadiene sequences and a broad band ranging from 5 to 9 ppm with shoulders resembling all the signals observed for the high-cis Rh-type polymer (see the preceding paragraph). Other low-intensity signals on the broad band can be attributed to oligomers occluded in the measured sample. The ^{13}C NMR spectrum of 3-PIPA/Mo consists of signal at 94.5 ppm (C5-I) and two broad bands with maxima at 129 and 136 ppm also possessing shoulders at positions characteristic of the high-cis 3-PIPA/Rh polymer.

The ^{1}H NMR spectrum of 3-PIPA/WB, unlike that of the *ortho*-isomer, exhibits signal at 3.5 ppm which can be ascribed to the presence of cyclohexadiene sequences. The main broad band of this spectrum shows two maxima. As to the shape, this band resembles that of the corresponding band of the partly isomerized (still soluble) 3-PIPA/Rh, but it clearly differs from that observed for 3-PIPA/Mo. Furthermore, this band does not show the shoulders corresponding to signals of the high-cis Rh-type polymer. Small differences between the ^{13}C NMR spectra of 3-PIPA/Mo and 3-PIPA/WB samples are also seen from Fig. 4 but they can hardly be discussed more in detail. It can be concluded that both Mo- and WB-type polymers are highly irregular, comprise cyclohexadiene sequences and that the main chain double bonds of
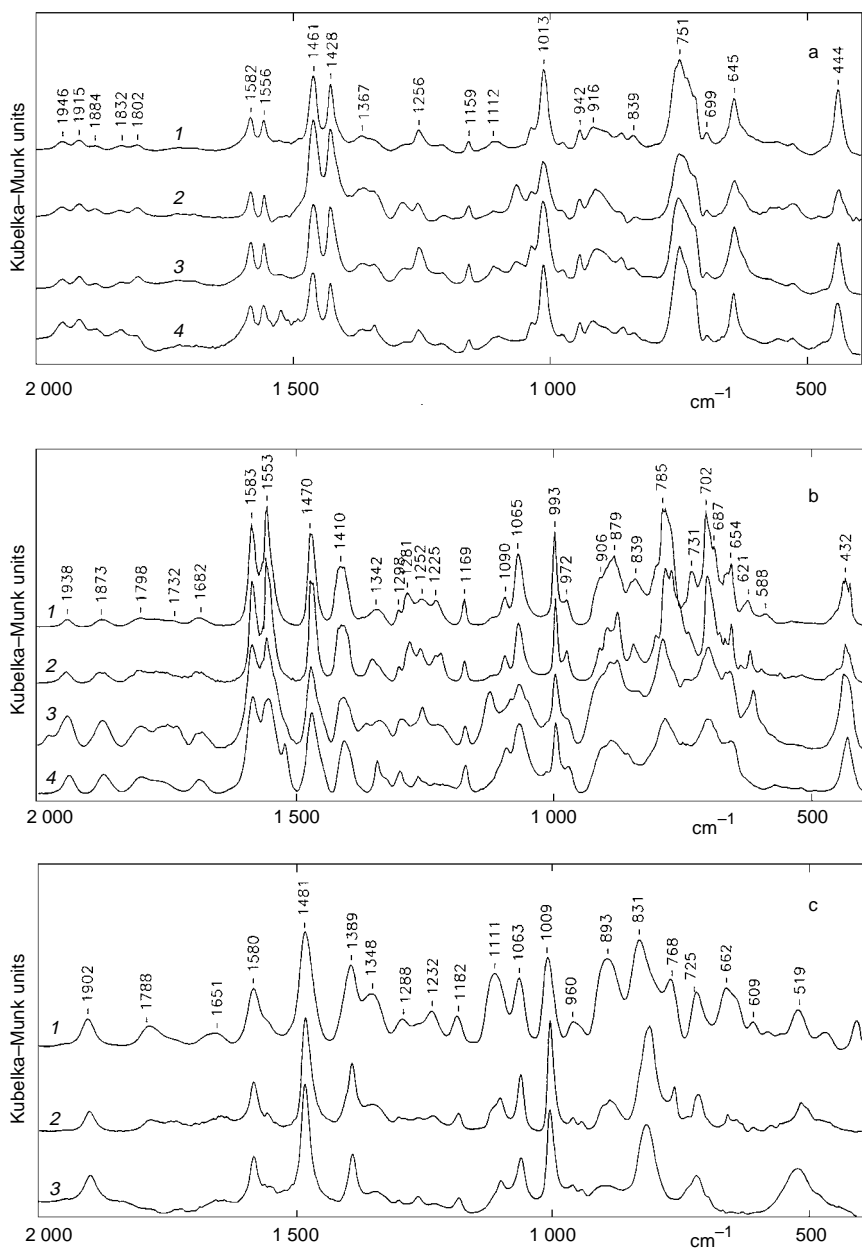
FIG. 5

Diffuse reflectance IR spectra of selected PIPA polymers: a *1* 2-PIPA/Mo, *2* 2-PIPA/WD (insol.), *3* 2-PIPA/WD (sol.), *4* 2-PIPA/WB; b *1* 3-PIPA/Rh, *2* 3-PIPA/Rh (i), *3* 3-PIPA/WD, *4* 3-PIPA/WB; c *1* 4-PIPA/Rh (i), *2* 4-PIPA/Mo, *3* 4-PIPA/WB

3-PIPA/Mo are of the both *cis*- and *trans*-configuration while those of 3-PIPA/WB are predominantly of *trans*-configuration.

IR Spectra

The diffuse reflectance IR spectra of all the prepared polymers are free of bands most characteristic of triple bonds: $\nu(H–C\equiv)$ in the region from 3 260 to 3 290 cm^{-1} and $\nu(C\equiv C)$ in the region from 2 101 to 2 108 cm^{-1}. This demonstrates vanishing of triple bonds during the polymerization. The most important parts of IR spectra of selected PIPA samples are compared in Figs 5a to 5c. The spectra exhibit minor differences proving a structure variety of polymers of the given ring-substitution type. However, they lack bands that might be generally assigned to a particular main-chain microstructure feature independently of the ring-substitution type.

There are at least two reasons for the above observation. First it is the fact that the bands of the main-chain $\nu(C=C)$ stretching mode as well as bands of the $\nu(H–C)$, $\delta_{ip}(H–C)$ and $\delta_{oop}(H–C)$ vibrational modes of main-chain hydrogens interfere with the corresponding bands of phenyl rings and the ratio of main-chain to ring hydrogens is equal to 1 : 4. Second, these IR bands are generally weak in the pristine conjugated polymers; they are strong in the doped polymers, only[31,32]. Therefore, we can only conclude that IR spectra of PIPA by itself do not provide a conclusive evidence for the presence of a particular main chain microstructure.

Characterization of Polymers by Off-Resonance FT Raman Spectroscopy

The most important parts of the off-resonance Raman spectra of PIPA polymers, which were obtained in a good and/or acceptable quality, are shown in Figs 6 to 8. (A complete series was obtained for 3-PIPA samples only.) In every figure, the spectra are normalized to the height of the band at about 1 585 cm^{-1}, which belongs to the $\nu(C=C)$ stretching mode of phenyl rings. In addition, it should be noted that the Raman band most characteristic of triple bonds, $\nu(C\equiv CH)$ at 2 113 (s) cm^{-1}, is absent in all these spectra (this wavelength region is not shown in the figures).

As it is seen, the transformation of IPA monomers into PIPA polymers is always accompanied by an occurrence of new bands in the region: (i) from 1 570 to 1 450 cm^{-1}, typical of the skeletal $\nu(C=C)$ stretching mode[30,31]; (ii) at about 1 338 cm^{-1}, attributed to $\nu(C–CPh)$ mode of the bond linking the main chain and pendant phenyl ring[12,33,34] and (iii) from 1 200 to 1 250 cm^{-1}, characteristic of $\delta_{ip}(C–H)$ modes. An enhancement of bands in the region of $\delta_{oop}(C–H)$ modes, from *ca* 930 to 800 cm^{-1}, is apparent, too. As can be seen from a comparison of the shown Raman spectra, the intensity and/or position of the mentioned bands show systematic course with the catalysts used in the polymer preparation independently of the iodine position on the phenyl ring. This indicates that parameters of these bands might be correlated with the microstructure of

these polymers. This suits well the concept that the polymer microstructure should be controlled by the catalyst species in the first place.

It has been shown that relevant features of Raman spectra of conjugated polymers are always related to the skeletal vibrational mode that can be described as the stretching of double bonds and contraction of single bonds[5,30]. Only this skeletal mode and the modes that are in-line with it are highly active in Raman spectra of conjugated polymers. As a result, the intensity and often also frequency of the Raman band of an active mode is a function of the effective π-conjugation length: the longer is the effective conjugation length the higher is the band intensity and the lower is the band frequency. This phenomenon is generally referred to as the intensity and frequency dispersion of Raman bands with the effective conjugation length[5,30,31] and it must be taken into account in any interpretation of Raman spectra of conjugated polymers.

According to UV/VIS spectra, the extent of conjugation of all types of soluble PIPA polymers generally increases in the following sample-type sequence: PIPA/Mo < PIPA/Rh << PIPA/WB $\cong$ PIPA/WD. The long-wavelength UV-absorption maxima are found at wavelengths from 350 nm (for Rh- and Mo-type samples) to 450 nm (WB and WD samples). The absorption reaches zero value at 500 to 650 nm. According to the change in polymer color from yellow to orange (3-PIPA/Rh(i)) or carmine-red (4-PIPA/Rh(i)), the extent of π-conjugation of original 3- and 4-PIPA/Rh samples significantly increased upon their isomerization.
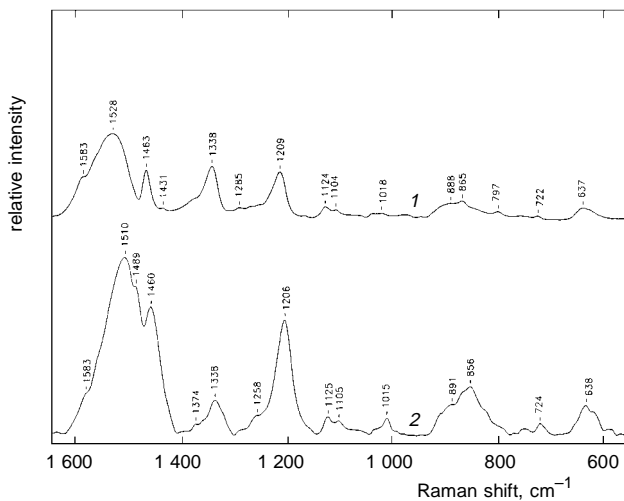

Fig. 6

Off-resonance FT Raman spectra of 2-PIPA/WD (*1*) and 2-PIPA/WB (*2*) samples. The spectra are normalized to the height of the 1 583 cm^{-1} band (phenyl ν(C=C) mode)

Raman Spectra and Structure of 3-PIPA

Looking at complete series of Raman spectra of 3-PIPA samples (Fig. 7), it is apparent that the overall intensity of the band of the ν(C=C) stretching mode increases in the sequence: Mo < Rh(i) $\cong$ Rh < WB < WD that is identical with that derived from UV/VIS spectra. Further, it is seen that the wavenumber of this band apex increases along somewhat different sequence: Rh $\cong$ Rh(i) < Mo < WB < WD, which also fits the intensity of δ_{ip}(C–H) mode band at 1 225 cm^{-1}. However, the intensity of ν(C–CPh) mode band at 1 338 cm^{-1} rises in a substantially different sample-type sequence: WB < Mo $\cong$ WD $\cong$ Rh < Rh(i). Taking the effects of intensity and frequency dispersion into account, the discussed 3-PIPA samples can be characterized in the following way:
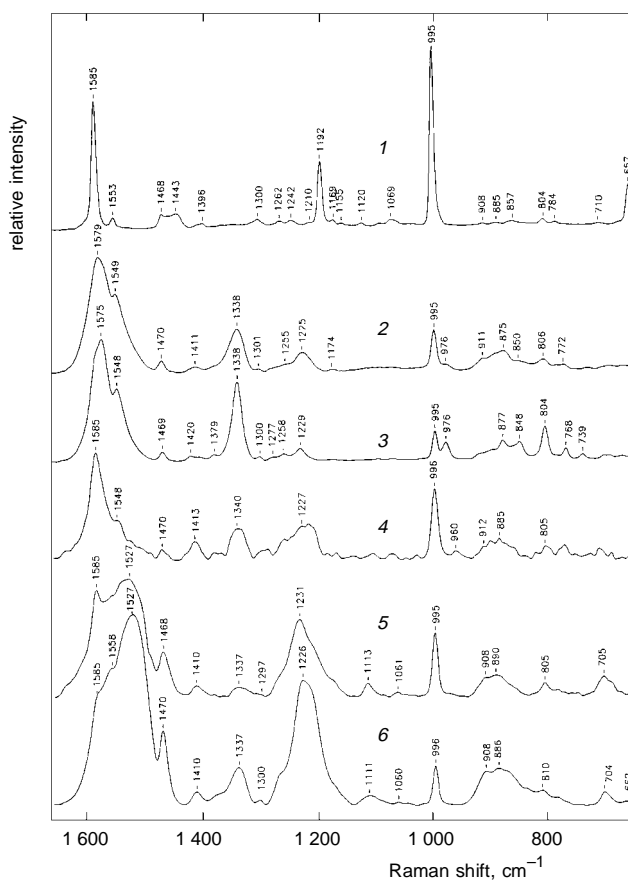
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Off-resonance FT Raman spectra of 3-IPA (*1*) and complete series of 3-PIPA (*2* 3-PIPA/Rh, *3* 3-PIPA/Ph(i), *4* 3-PIPA/Mo, *5* 3-PIPA/WB, *6* 3-PIPA/WD) samples. Spectra of polymers are normalized to the height of the 1 585 cm^{-1} band (phenyl ν(C=C) mode)

a) The 3-PIPA/Mo sample contains low concentration of conjugated sequences of low to medium extent of conjugation. This is in accord with relatively low molecular weight and rather high concentration of cyclohexadiene sequences (see NMR spectra) found for this sample.

b) Original 3-PIPA/Rh as well as isomerized 3-PIPA/Rh(i) sample contains high concentrations of sequences of lower to medium extent of conjugation.

c) The samples 3-PIPA/WB and 3-PIPA/WD contain high concentrations of long conjugated sequences. The observed differences in the band intensity and frequency can be ascribed to lower concentration of conjugation defects in 3-PIPA/WD sample.

According to the literature, the presence of intensive Raman bands of the ν(C=C) and δ_{ip}(C–H) modes and shift of the ν(C=C) band towards lower frequencies are typical of high-trans PPA and its analogues[12,13,22]. On the other hand, the presence of the intensive ν(C–CPh)-mode band and low intensity of the δ_{ip}(C–H)-mode band are typical features of polymers prepared with Rh(diene) complexes, which are assumed to be of high-cis HT structure[18,19,22,27,28,34]. The ν(C–CPh)-mode band is usually weak or almost absent in the Raman spectra of high-trans polymers prepared with W-based catalysts.
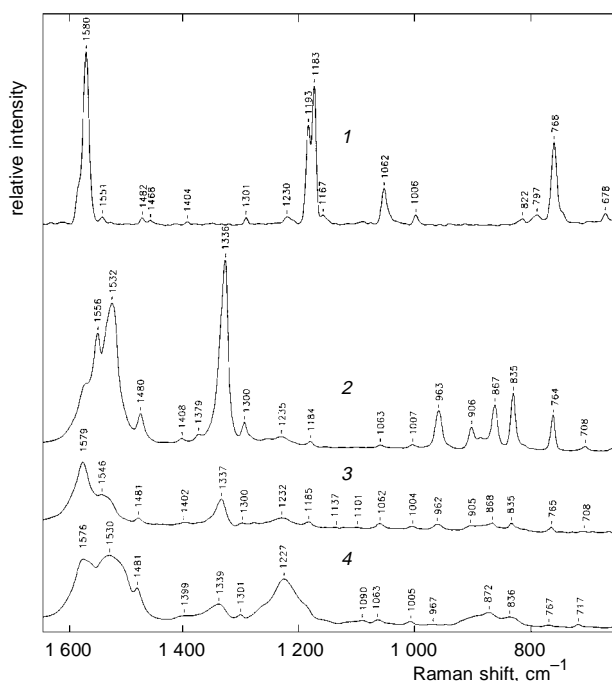

Fig. 8

Off-resonance FT Raman spectra of 4-IPA (*1*) and indicated 4-PIPA (*2* 4-PIPA/Rh(i), *3* 4-PIPA/Rh (low-Mw), *4* 4-PIPA/WD) samples. Spectra of polymers are normalized to the height of the 1 579 cm^{-1} band (phenyl ν(C=C) mode)

Following the outlined Raman band assignment, the 3-PIPA/WB sample can be as-signed as high-trans polymer, because it shows strong bands of the ν(C=C) and δ_{ip}(C–H) modes and the band of the ν(C–CPh) mode is entirely absent. The 3-PIPA/WD sample is of the high-trans–low-cis structure because it exhibits a not negligible band at 1 338 cm^{-1} in addition to intensive bands of the ν(C=C) and δ_{ip}(C–H) modes. Analogously, the 3-PIPA/Mo sample contains medium amounts of both trans and cis units.

Difficulties arise in attempts to assign the 3-PIPA/Rh and Rh(i) samples. The former might be assigned the high-cis polymer because it shows: (i) only a weak band of the δ_{ip}(C–H) mode at 1 225 cm^{-1}, (ii) a medium intensive band of the ν(C–CPh) mode at 1 338 cm^{-1} and (iii) a medium intensity doublet at higher frequencies of the ν(C=C) mode region, which well corresponds with the known fact that cis units act as weak conjugation defects[5,30]. However, it must be recognized that none of these features of the 3-PIPA/Rh Raman spectrum is as clear as those observed for other high-cis HT polymers of related structure[12,13,18,19,22,27,28,34]. Therefore, the structure assignment of 3-PIPA/Rh on the basis of its Raman spectrum is fairly not as conclusive as the assign-ment resulting from uniquely resolved NMR spectra of this polymer. Nevertheless, the information following from the Raman and NMR spectra is not controversial in the case of original, non-isomerized 3-PIPA/Rh sample.

The structure assignment of the 3-PIPA/Rh(i) sample is difficult. According to the outlined rules concerning Raman spectra, this polymer should comprise even more cis units than its precursor. The 3-PIPA/Rh(i) sample namely shows the ν(C–CPh) band at 1 338 cm^{-1} of double intensity compared with its pristine precursor. However, accord-ing to changes in ^{1}H NMR spectrum accompanying isomerization of 3-PIPA/Rh (Fig. 3), the 3-PIPA/Rh(i) sample is irregular and contains cyclohexadiene sequences and higher amount of trans units. This controversy suggests that the above outlined assignment of the ν(C–CPh) Raman band at 1 338 cm^{-1} to the presence of cis units is incorrect. There-fore, this band should be ascribed to another structural feature of substituted PPAs. The original assignment of this band was introduced on the basis of Raman spectra of highly regular, high-cis HT PPAs. Therefore, it is rational to assign this band to the presence of long, regularly arranged HT sequences of both *cis*-transoid and *trans*-cisoid type (see Fig. 9). Within such sequences, the ν(C–CPh) modes of neighbouring phenyls can be in-line (oscillating in phase) giving rise to a strong Raman band of this mode.

Raman Spectra and Structure of 4-PIPA

The outlined controversy in the interpretation of band at 1 338 cm^{-1} is also seen from the Raman spectra of 4-PIPA samples (Fig. 8). According to the interpretation used in the literature, the carmine-red 4-PIPA/Rh(i) sample can be assigned the high-cis (or even all-cis) polymer, if the almost absence of δ_{ip}(C–H) band at 1 230 cm^{-1} and the presence of extremely strong ν(C–CPh) band at 1 338 cm^{-1} are only taken into account. However, this polymer also shows very strong absorption at 1 532 cm^{-1} (band of the ν(C=C) skeletal mode), according to which it can be assigned an extensively conju-

gated high-trans polymer. The failure of the existing interpretation rules is evident. This controversy disappears if the band at 1 338 cm^{-1} is ascribed to the presence of longer HT sequences of both *cis*-transoid and *trans*-cisoid type in which individual C–CPh bonds can oscillate in phase. Then the 4-PIPA/Rh(i) can be conclusively assigned the high-trans low-cis all-HT polymer (presence of cis units is indicated by occurrence of high-frequency secondary maximum of the ν(C=C) band at 1 556 cm^{-1}).

This interpretation is supported by the observed sudden change of yellow soluble 4-PIPA/Rh to bright carmine-red insoluble 4-PIPA/Rh(i) upon contact with methanol. This indicates that the original polymer has undergone a fast extensive isomerization increasing the effective conjugation length of its macromolecules. Literature data show that PPA as well as numerous ring-substituted PPAs prepared with Rh[I](diene) catalysts has high-*cis*-transoid structure[12,13,18–20,22,27,28,34]. Therefore, the discussed fast change can be regarded as the transformation of original *cis*-transoid polymer into thermodynamically more stable[5] high-*trans* isomer, most probably of the *trans*-cisoid type because there is no time for an extensive conformational transitions needed for attaining the *trans*-transoid configuration during the isomerization process. Besides, an increased rigidity of better-conjugated macromolecules will facilitate packing of 4-PIPA/Rh(i) macromolecules into solvent resistant supramolecular structures, which can explain insolubility of this polymer.

The differences between Raman spectra of the 3- and 4-PIPA/Rh(i) samples can be explained in terms of higher bulkiness (width) of 3-substituted phenyls due to which they cannot be arranged in regular HT sequences as easily as 4-substituted phenyls. This hindrance lead to distortion of the main chain which brings about lowering of the effective conjugation length and, through the intensity dispersion effect, also lowering the intensity of the ν(C–CPh)-mode band at 1 338 cm^{-1}.

According to Raman spectrum, the 4-PIPA/WD sample is a typical high-trans low-cis polymer containing some amounts of longer HT sequences.
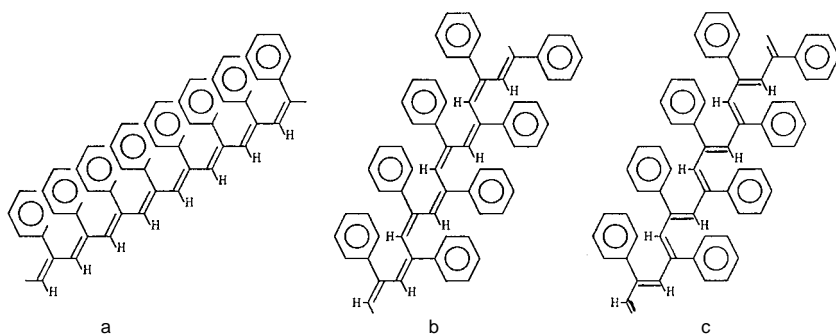

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Planar projections of main configurations of PPA chains: **a** HT *trans*-transoid, **b** HT *cis*-transoid, **c** HT *trans*-cisoid

Raman Spectra and Structure of 2-PIPA Polymers

Unlike the 3-PIPA samples, 2-PIPA/WB exhibits a much higher intensity of both the ν(C=C) and δ_{ip}(C–H) bands compared with the 2-PIPA/WD (Fig. 6). Actually, the 2-PIPA/WB sample shows the highest intensity of the skeletal ν(C=C) band (relative to the ν(C=C) band of phenyls) and the highest shift of this band towards lower frequencies from all prepared PIPA samples (this band has maximum at 1 510 cm^{-1}!). These characteristics prove to an extremely high effective conjugation length in macromolecules of 2-PIPA/WB. High extent of conjugation in this sample is further confirmed by the high intensity of the δ_{ip}(C–H) band at 1 204 cm^{-1}. A not negligible intensity of the ν(C–CPh) band at 1 338 cm^{-1} can be explained by a high contribution of the intensity dispersion with the conjugation length. In summary, 2-PIPA/WB can be regarded as high-trans polymer with low content of longer HT sequences.

Also 2-PIPA/WD exhibits strong ν(C=C)-mode and δ_{ip}(C–H)-mode bands although they are not as strong as those ones of the WB sample. In contrast, the ν(C–CPh) band at 1 338 cm^{-1} is evidently more intensive for the WD- than for the WB-type sample, which indicates a higher content of HT sequences in the 2-PIPA/WD sample.

CONCLUSIONS

A survey of activities of various catalyst systems and solubility of synthesized polymers as functions of ring-iodine position and polymer configurational and sequential microstructure as functions of the catalyst system is given in Table II. As can be seen, the ring-iodine electronic effects mostly control the oligomerization activity of tested catalyst systems. Highest amount of oligomers is formed from 3-IPA, which means that increased electron density in the monomer triple bond supports a formation of oligomers. Only exception is the MoCl$_5$ catalyst for which, obviously, a steric hindrance to ring closing is of key importance. Most probably, this is an intrinsic feature of molybdenum active species because the steric hindrance by itself is virtually given by the monomer structure.

The polymerization activity of tested catalyst systems is a result of complex interplay of the steric and electronic effects of ring-iodine as well as the constitution of catalyst species. The steric effects are evidently crucial for the Rh system and important for the WB system, mainly in the case of ortho monomer. On the other hand, the electronic effects apparently control the polymerization activity of the Mo and WD systems: the increased electron density in triple bonds formally supports the polymerization activity of the Mo system but reduces that of the WD system. However, the observed orders of polymerization activities of Mo and WD systems can be as well explained by increased formation of 4-IPA oligomers in the case of the Mo system (steric control) and 3-IPA oligomers in the case of the WD system (electronic control). Therefore, the factor governing the polymerization activity of the Mo catalyst system is remaining uncertain.

TABLE II
Polymerization, oligomerization and overall activity of various catalyst systems and the polymer solubility as functions of the ring-iodine position (o, m and p denotes the position 2, 3 and 4, respectively) and polymer microstructure as a function of the catalyst system

Catalyst system	Oligomerization activity (prevailing control)	Polymerization activity (prevailing control)	Overall activity	Polymer solubility in aromatic and low-polarity solvents	Polymer microstructure
Rh ([Rh(cod)(OMe)]$_2$)	$o < m > p$ (electronic)	$o\,(= 0) \ll m < p$ (steric)	$o \ll m \lesssim p$	$(m \gg p)^a$	cis-transoid^a HT
Mo (MoCl$_5$)	$o \ll m \ll p$ (steric)	$o < m > p$ (??)	$o \ll m < p$	$o \cong m > p$ (insol.)	medium cis medium HT^b
WB (WOCl$_4$)	$o < m > p$ (electronic)	$o \ll m \lesssim p$ (steric)	$o \ll m \gtrsim\!\cong p$	$o \gtrsim m > p$	high trans very low HT^b
WD (WOCl$_4$/2 Ph$_4$Sn, diox.)	$o < m > p$ (electronic)	$o > m < p$ (electronic)	$o \cong m \cong p^c$	$o \ll m > p$	high trans, low cis low HT^{b,d}

^{a} Original soluble cis-transoidal polymers easily isomerize to insoluble trans-rich polymers; ^{b} it relates to a presence of longer head-to-tail sequences; ^{c} virtually total monomer conversion achieved for all three IPA isomers; ^{d} except for 2-PIPA/WD ($ortho$ isomer).

The overall activity of the Rh, Mo and WB catalyst systems (measured as a monomer overall conversion) is primarily controlled by steric effects and only secondarily by electronic effects of the iodine. The overall activity of the WD system seems to be independent of the ring-iodine position. Stabilization of active species by dioxane is perhaps the most important factor for the activity of this catalyst system.

Data summarized in Table II together with a spontaneous fractionation of soluble polymers during their preparation (see Table I) clearly indicate that solubility of PIPAs is a result of complex interplay of the ring-iodine position, polymer microstructure and polymer molecular weight. Other factors like crosslinking of macromolecules and/or their packing into tiny crystallites come as well into consideration in the case of insoluble polymers. Detailed discussion of PIPA solubility is beyond a scope of the present paper. Nevertheless, the acquired data show that: (i) 4-PIPA is mostly least soluble from PIPAs prepared by a given catalyst system and (ii) a presence of longer HT-trans sequences lead to lower solubility or even insolubility of PIPA.

REFERENCES

1. Skotheim T. A. (Ed.): *Handbook of Conducting Polymers*. Dekker, New York 1986.
2. Kiess G. H. (Ed.): *Conjugated Conducting Polymers*. Springer, Berlin 1992.
3. Prasad P. N., Ulrich D. R. (Eds): *Nonlinear Optical and Electroactive Polymers*. Plenum, New York 1988.
4. Nalwa H. S. (Ed.): *Handbook of Organic Conductive Molecules and Polymers*. Wiley, New York 1996.
5. Chien J. C. W.: *Polyacetylene – Chemistry, Physics and Material Science*. Academic Press, New York 1984.
6. Vohlidal J., Radrova D., Pacovska M., Sedlacek J.: *Collect. Czech. Chem. Commun*. **1993**, *58*, 2651.
7. Shirakawa H., Masuda T., Takeda K. in: *The Chemistry of Triple-Bonded Functional Groups* (S. Patai, Ed.), Suppl. C2, Chap. 17, p. 945. Wiley, New York 1994.
8. Vohlidal J., Sedlacek J., Pacovska M., Lavastre O., Dixneuf P. H., Balcar H., Pfleger J.: *Polymer* **1997**, *38*, 3359.
9. Sedlacek J., Pacovska M., Etrych T., Dlouhy M., Patev N., Cabioch S., Lavastre O., Balcar H., Æigon M., Vohlidal J.: *Polym. Mater. Sci. Eng.* **1997**, *77*, 52.
10. Bradley D. D. C., Tsutsui T. (Eds): *Organic Electroluminescence*. Cambridge University Press, Cambridge 1995.
11. Sariciftci N. S., Heeger A. J. in: *Handbook of Conducting Molecules and Polymers*, Vol. 1. Wiley, New York 1997.

12. Tabata M., Tanaka Y., Sadahiro Y., Sone T., Yokota K., Miura I.: *Macromolecules* **1997**, *30*, 5200.

13. Tabata M., Namioka M., Yokota K., Minakawa H.: *Polymer* **1998**, *37*, 1959.

14. Vohlidal J., Holander A., Jancalkova M., Sedlacek J., Sargankova I.: *Collect. Czech. Chem. Commun.* **1991**, *56*, 351.

15. Sedlacek J., Vohlidal J., Kares J., Pacovska M., Maca B.: *Collect. Czech. Chem. Commun.* **1994**, *59*, 2454.

16. Lavastre O., Cabioch S., Dixneuf P. H., Vohlidal J.: *Tetrahedron* **1997**, *53*, 7595.

17. Chatt J., Venanzi L. M.: *J. Chem. Soc.* **1957**, 4735.

18. Kishimoto I., Eckerle P., Miyatake T., Ikariya T., Noyori R.: *J. Am. Chem. Soc.* **1994**, *119*, 12131.

19. Connelly N. G., Loyns A. C., Fernandez M. J., Modrego J., Oro L. A.: *J. Chem. Soc., Dalton Trans.* **1989**, 683.

20. Ivin K. J., Mol J. C.: *Olefin Metathesis and Metathesis Polymerization*, Chap. 10, p. 190. Academic Press, London 1997.

21. Stepnicka P., Cisarova I., Sedlacek J., Vohlidal J., Polasek M.: *Collect. Czech. Chem. Commun.* **1997**, *62*, 1577.

22. Tabata M., Kobayashi S., Sadahiro Y., Nazaki Y., Yokota K., Yang W.: *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 641.

23. Sedlacek J., Vohlidal J., Grubisic-Gallot Z.: *Makromol. Chem., Rapid Commun.* **1993**, *14*, 51.

24. Sedlacek J., Pacovska M., Vohlidal J., Grubisic-Gallot Z., Zigon M.: *Macromol. Chem. Phys.* **1995**, *196*, 1705.

25. Fowles G. W. A., Frost J. L.: *J. Chem. Soc. A* **1967**, 671.

26. Percec V.: *Polym. Bull. (Berlin)* **1983**, *10*, 1.

27. Furlani A., Napoletano C., Russo M.V., Feast J. W.: *Polym. Bull. (Berlin)* **1986**, *16*, 311.

28. Tabata M., Yang W., Yokota K.: *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 1113.

29. Percec V., Rinaldi P. L.: *Polym. Bull. (Berlin)* **1983**, *9*, 548.

30. Gussoni M., Castiglioni C., Zebri G. in: *Spectroscopy of Advanced Materials* (R. J. H. Clark and R. E. Hester, Eds), Chap. 5, p. 251. Wiley, New York 1991.

31. Zebri G., Gussoni M., Castiglioni C. in: *Conjugated Polymers* (J. L. Bredas and R. Silbey, Eds), p. 435. Kluwer Academic Publishers, Dordrecht 1991.

32. Vohlidal J., Redrova D., Pacovska M., Sedlacek J.: *Collect. Czech. Chem. Commun.* **1993**, *58*, 2651.

33. Lefrant S., Lichtman L. S., Temkin H., Fitchen D. B., Miller D. C., Whitwell G. E., Burlitch J. M.: *Solid State Commun.* **1979**, *29*, 191.

34. Tabata M., Nozaki Y., Yokota K.: *J. Photopolym. Sci. Technol.* **1993**, *6*, 1.