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Study of molecular weight and configurational stability of substituted polyacetylenes

Ph.D. Thesis

Supervisor: Doc. RNDr. Jan Sedláček, Dr.

Prague, 2013

DECLARATION

I hereby declare that this submission is my own work and that, to the best of my knowledge and belief, it contains neither material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the University or other Institute of higher education, except for the already published results, which are included in the list of references.

Prague
10. 7. 2013

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Signature

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ABSTRACT

Complexes [Rh(cycloolefin)(acac)] (cycloolefin = norborna-2,5-diene, cycloocta-1,5-diene and cyclooctatetraene) were investigated as catalysts of polymerization of monosubstituted acetylenes into stereoregular *cis-transoid* polyacetylenes. All complexes were highly active in arylacetylenes polymerizations in both coordinating and non-coordinating solvents. Selection of solvent and cycloolefin ligand of the catalyst allowed the control over polymer MW. The onset of initiation in the [Rh(cycloolefin)(acac)]/monomer systems proceeded as the proton transfer from the monomer molecule to the acac ligand under the release of acetylacetone and coordination of -C≡CR ligand to Rh(cycloolefin) moiety.

C*is-transoid* poly(phenylacetylene) and poly[(2,4-difluorophenyl)acetylene]s with required initial MW were prepared with these catalysts and submitted to the long-term ageing in which the polymers were exposed to the atmosphere and diffuse daylight either dissolved in tetrahydrofuran or in the solid state. Tightly connected processes of *cis*-to-*trans* isomerization of the polymer main-chains double bonds and oxidative degradation were found to proceed during polymers ageing in the solution. Besides, the formation of corresponding cyclotrimers accompanied the polymers ageing. However, the cyclotrimers amount was too low for explaining the degradation and isomerization of polymers in terms of intramolecular cyclization mechanism of Percec et al.

The mechanism was proposed that assumes the *cis*-to-*trans* isomerization of a particular macromolecule to be affected by a “domino effect” that results in the deep isomerization of this macromolecule. As experimentally verified, the isomerized macromolecules were enriched with unpaired electrons and thus they were significantly more prone to the oxidative degradation than the non-isomerized ones that were also present in the partly aged sample. The different degradation rates of isomerized and non-isomerized macromolecules explain the experimentally observed non-uniform distribution of these two kinds of macromolecules along the MW distribution of partly aged samples. The proposed mechanism is consistent with the experimental finding that the increase in configurational stability (resulting either from reduction of polymer MW or from a change in the covalent structure) is simultaneously accompanied by an increase in the MW stability of the polymer.

1. INTRODUCTION

1.1. Substituted polyacetylenes

Study of π-conjugated polymers is the subject of permanent interest in the last few decades. Large spectrum of potential applications of these polymers has been shown to range from the field of electronics, photonics, nonlinear optics and sensor constructions to gas separation and storage. [1-15]

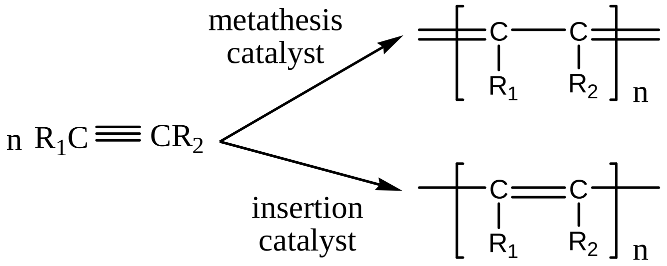
Various classifications of π-conjugated polymers have been applied in the literature. If we adopt the source-based classification we can delimit an important subclass of π-conjugated polymers derived from acetylene-type monomers. In dependence on the synthetic path, following main types of π-conjugated polymers can be obtained from acetylenes: (i) poly(aryleneethynylene)s and poly(arylenebutadiynylene)s [12;16-22], (ii) polycyclotrimers [12;23-25] and (iii) polyacetylenes (polyvinylenes) [12;26-31]. The last mentioned group, polyacetylenes, is probably the largest group of π-conjugated polymers as the diversity of chemical composition and structure are concerned. The conjugation of polyacetylenes is given by the character of the polymer main chains in which double and single carbon-carbon bonds are alternating. In dependence on the configurational structure and on the character of substituents the partial overlapping of π orbitals on the main chains is achieved. Moreover, the main-chain conjugation can be combined, in some cases, with the conjugation of substituents or pendant groups.

The non-substituted polyacetylene, $[-HC=CH-]_n$, is one of the first reported π-conjugated polymer. [32] Polyacetylene exhibits high electrical conductivity after a proper doping and interesting optoelectronic properties [33-35], however, it is insoluble, infusible and highly unstable by exposure to air. In the last three decades, many groups (e.g. Masuda et al., [36;37] Tang et al., [38-41] and also our laboratory [42-45]) have synthesized various series of monosubstituted and disubstituted polyacetylene derivatives, $[-RC=CH-]_n$ and $[-R_1C=CR_2-]_n$, respectively. The synthesis of hydrocarbon and also many heteroatom-containing polyacetylenes has been mastered. Substituted polyacetylenes are more stable in air as compared to non-substituted polyacetylene and they are mostly soluble in common organic solvents that facilitate their processing. The electrical conductivity of substituted polyacetylenes is not as high as that of non-substituted polyacetylene. On the other hand, the introduction of substituents on the polyacetylene chains often gave rise to interesting functional properties of these materials: mainly photoluminescence and electroluminescence, photoconductivity, non-linear optical properties, chirality and microporosity in the solid state. [26]

1.1.1. Preparation of substituted polyacetylenes by coordination polymerization

Substituted polyacetylenes are mostly synthesized by chain-growth polymerization of respective mono- and disubstituted acetylenes. However, the standard methods of radical and ionic polymerizations exhibit only a low efficiency in this case. This reflects a decrease in reactivity of the radical or ionic active centres due to their delocalization along the growing conjugated oligomer/polymer chains.

The most effective tool for the preparation of well-defined high-molecular-weight substituted polyacetylenes is the chain-growth coordination polymerization of corresponding acetylenic monomers. [29;46-48] There are two possible modes of propagation of coordination polymerizations of acetylenes (Scheme 1): (i) metathesis mode in which two π bonds are cleaved in the monomer molecule [29] and (ii) insertion mode in which only one π bond is cleaved in the monomer molecule. [49;50]

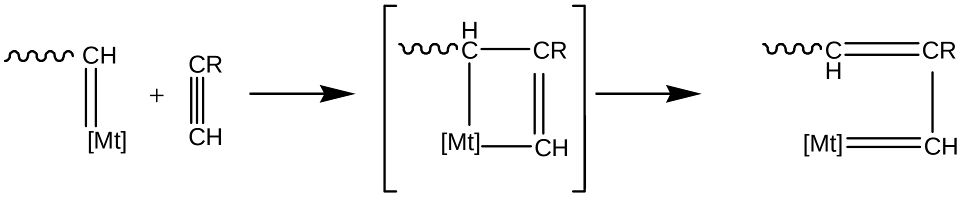


Scheme 1: Metathesis and insertion polymerization of substituted acetylenes.

The active catalysts for these polymerizations are various complexes and compounds of following transition metals Ti, Fe, Ta, Nb, Mo, W and Rh. [27;47] Complexes and compounds of W, Mo, Ta and Nb are used for metathesis coordination polymerization. Ta and Nb based catalysts are active in the polymerization of disubstituted monomers with bulky substituents, W based catalysts polymerize less bulky disubstituted monomers. Compounds and complexes of W and Mo are also active in the polymerization of monosubstituted monomers. For the insertion coordination polymerization, complexes of Ti, Fe, Ni, Ru, Pd and mainly Rh are used. Only monosubstituted acetylenes are polymerized with these catalysts. [29;30;47;48;51-56]

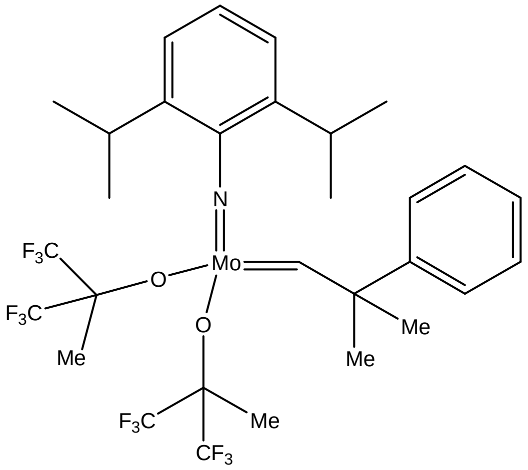
1.1.1.1.Mechanism of metathesis polymerization of substituted acetylenes

The metallacarbene mechanism of propagation has been proven for the metathesis polymerization of substituted acetylenes (Scheme 2). [57-61]



Scheme 2: The propagation mechanism of metathesis polymerization of substituted polyacetylenes.

The transition metal carbene complex is the catalytically active centre to which the monomer molecule is coordinated in the first reaction step. Subsequently, the transient metallacyclobutene species is formed. This species is unstable and due to its decomposition the monomer is inbuilt in the polymer chain as a new monomeric unit and the metallacarbene active centre is recovered in each propagation step. The primary metallacarbene initiating the polymerization reaction is either in the structure of the catalyst or it is arising in the reaction of the catalyst complex with cocatalyst or monomer. Scheme 3 shows an example of the Mo metallacarbene catalyst labelled, according to its author, as the Schrock carbene. [62] Example of the metallacarbene formation by the reaction of the WCl_6 catalyst with $(CH_3)_4Sn$ cocatalyst is summarized in Equations 1 and 2. [63-65]



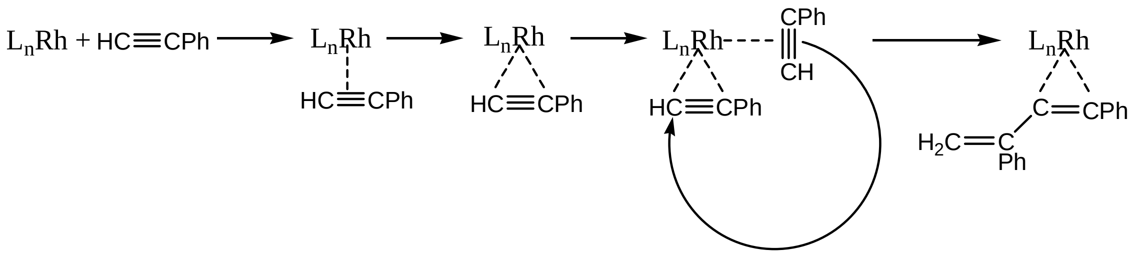
Scheme 3: Metathesis catalyst of the Schrock carbene type.

$$WCl_6 + 2Me_4Sn \longrightarrow Me_2WCl_4 + 2Me_3SnCl \qquad \text{Equation 1}$$

$$Me_2WCl_4 \longrightarrow CH_2{=}WCl_4 + CH_4 \qquad \text{Equation 2}$$

1.1.1.2.Mechanism of insertion polymerization of substituted acetylenes

The preparation of substituted polyacetylenes via insertion coordination polymerization is known from the sixties of the last century. [66-68] However, the interest in this reaction strongly diminished simultaneously with the introduction of the metathesis polymerization into polyacetylene chemistry (late seventies and eighties). Nevertheless, in 1986 Furlani et al. reported the catalytic activity of some Rh(I) complexes in transformation of phenylacetylene (PhA) into highly stereoregular *cis-transoid* poly(phenylacetylene) (PPhA). [69;70] This finding represented an important stimulus for the renaissance of the insertion acetylenes polymerization and today prevailingly Rh catalysts are applied for this reaction. Particularly following type of Rh complexes are used as polymerization catalysts: (i) cationic complexes such as $[Rh^+(nbd)(Ph\text{-}BPh_3)^-]$ and $[Rh^+(cod)_2]BF_4^-$ (nbd = norborna-2,5-diene, cod = cycloocta-1,5-diene), (ii) complexes of the type [RhX(cyclodiene)(phosphine)] (X = alkynyl, vinyl or F) [71-74] and (iii) stable neutral binuclear complexes of the general formula $[Rh(cyclodiene)Y]_2$ where Y stands for the Cl, OCH_3 or OH bridge ligand and cyclodiene is bidentate coordinated nbd or cod. [26;46;47] Although the Rh-catalysed acetylenes polymerization is the frequently applied reaction the reliable and generally accepted propagation mechanism of this polymerization has still not been formulated. An interesting proposal of this mechanism was reported by Ogawa et al. (Scheme 4).



Scheme 4: The propagation mechanism of the insertion PhA polymerization proposed by Ogawa.

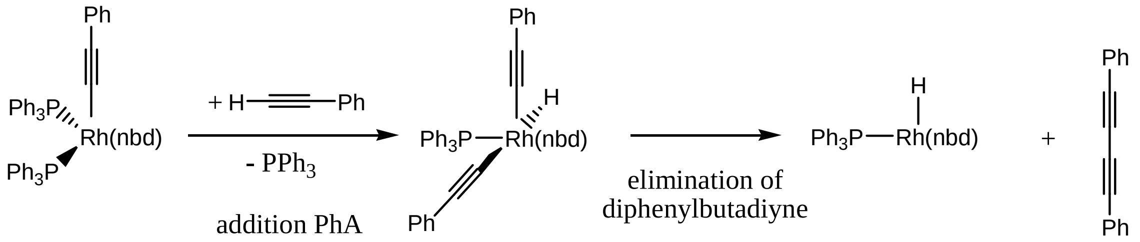
The mechanism assumes that the incorporation of each monomeric unit into the polymer is mediated by the transfer of the acetylenic hydrogen from the coordinated monomer to the preceding monomeric unit of the polymer. This proposal is in a good agreement with the fact (i) that Rh-based catalysts polymerize only monosubstituted acetylenes (i.e. monomers with acetylenic hydrogen) and (ii) that the polymerizability of these monomers is always positively affected by an enhancement of the acetylenic hydrogen acidity. [75;76] However, the unambiguous experimental evidences for this mechanism are still missing.

The initiation stage of the polymerization was partly revealed in the case of reactions catalysed with [Rh(cyclodiene)Cl]$_2$ complexes. Various authors reported that the first step consisted in the dissociation of the binuclear complex into mononuclear particles. This dissociation was mediated either by the proper solvent or cocatalyst the molecules of which coordinated to the mononuclear Rh particles (Scheme 5). [77-79]

$$[\mathrm{Rh(diene)Cl}]_2 \xrightarrow{\text{2 TEA}} 2\ [\mathrm{Rh(diene)(TEA)Cl}]$$

Scheme 5: Dissociation of the bridged Rh complexes mediated by Rh-coordinable solvent. TEA is triethylamine.

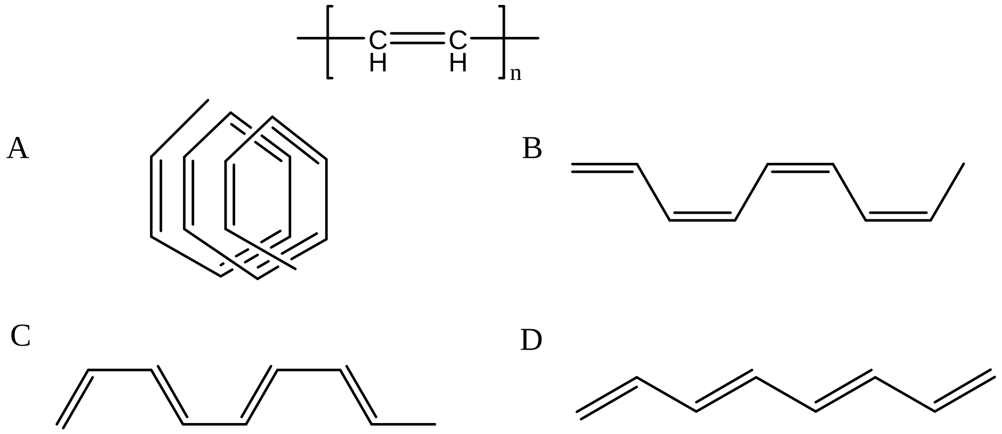
Kishimoto et al. described high efficiency of $[\mathrm{Rh(C{\equiv}CPh)(nbd)(PPh_3)_2}]$ complex with phenylacetylide type ligand in PhA polymerization and proposed mechanism of the initiation consisting in the formation of Rh-hydride complex under evolving of 1,4-diphenylbutadiyne as shown in Scheme 6. [50;77]



Scheme 6: Transformation of [$Rh(C\equiv CPh)(nbd)(PPh_3)_2$] into active centres in reaction with PhA.

1.1.2. Microstructural types of substituted polyacetylenes

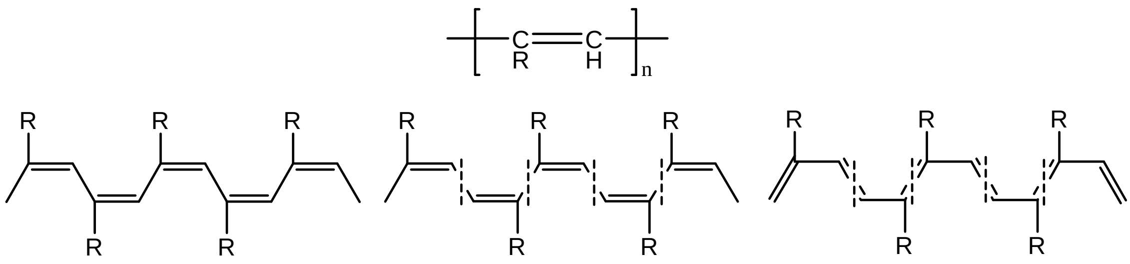
As it has been already mentioned, the partly conjugated main chains of polyacetylenes contain alternating double and single C-C bonds. The double bonds exhibit *cis-trans* isomerism. The formally single bonds of the main chains lose the rotation mobility due to the π electron delocalizations and turn to the rigid centres of configurational isomerism, too. Respective isomers are labelled as *cisoid* and *transoid*. These two isomerisms together give rise to four different stereoisomeric non-substituted polyacetylene main chains: *cis-cisoid*, *cis-transoid*, *trans-cisoid* and *trans-transoid* (Scheme 7A, 7B, 7C and 7D). [47;80]



Scheme 7: Microstructural types of non-substituted polyacetylenes: A) *cis-cisoid*, B) *cis-transoid*, C) *trans-cisoid* and D) *trans-transoid*.

The considerations on the stereoisomerism of substituted polyacetylenes should involve also possible sterical effect of the substituents. The configurational isomerization of monosubstituted polyacetylenes was discussed by Cataldo et. al. who concluded that in the case of PPhA the *trans–transoid* configuration as reported in Scheme 7 can not exist in reality, because of the steric hindrance between the phenyl substituents. [81] The phenyl rings can not lie parallel each other because of steric hindrances derived from the fact that the Van der Waals thickness of each benzene ring is larger than the real space available to accommodate the rings. Furthermore electronic repulsion arises from the π electrons of each benzene ring which is in eclipsed conformation with the others. Thus, the unique possibility for the *trans–transoid* isomer is to assume a helical conformation. [80]

The orientation isomerism of monomeric units must be taken into account for monosubstituted and asymmetrically disubstituted polyacetylenes. The connection between monomeric units can be: (a) Head to Tail (H-T), (b) Head to Head (H-H) and Tail to Tail (T-T). Moreover, the double bonds position in the polymer chains with HH-TT connections is dependent on the polymerization mode applied for the polymer synthesis: (i) double bonds are inside the monomeric unit in the case of polymer formed via insertion polymerization or (ii) double bonds are between two monomeric units in the case of polymer formed via metathesis polymerization. The orientation isomerism is depicted in Scheme 8 for the example of monosubstituted *cis-transoid* polyacetylene.



a)
H-T isomerism

b)
HH-TT isomerism
insertion polymerization

c)
HH-TT isomerism
metathesis polymerization

Scheme 8: Orientation isomerism of monosubstituted *cis-transoid* polyacetylene main chain.

The microstructure of monosubstituted polyacetylenes was found to depend significantly on the catalyst used for the polymer synthesis. Rh catalysts provide mostly highly stereoregular head-to-tail polyacetylenes in which *cis-transoid* configuration strongly prevails. It is even speculated that Rh-based catalysts provide isomerically pure *cis-transoid* polyacetylenes (*cis* double bonds content = 100 %) and that the slightly decreased microstructure uniformity and slightly lowered content of *cis* double bonds determined for these polymers spectroscopically reflect the *cis*-to-*trans* isomerization during isolation and spectral measurements of these polymers. It was proven that Rh catalysts produce the stereoregular *cis-transoid* polymers even when monosubstituted acetylenes with bulky side groups are polymerized. [69;79;82-84] Owing to the high *cis* double bonds content the polyacetylenes prepared with Rh catalysts are often labelled as ‘‘high-*cis*’’ polyacetylenes. [47;85]

Metathesis catalysts based on W and Mo compounds generally provide the non-stereoregular ‘‘*cis*/*trans*’’ monosubstituted polyacetylenes. [29;44;84;86-92] The *cis* double bonds content is mostly higher in polymers prepared with Mo-based catalysts as compared to polymers prepared with W-based catalysts.

The microstructure of monosubstituted polyacetylenes is most frequently studied by ^{1}H NMR spectroscopy. ^{1}H NMR spectra of microstructurally uniform high-*cis* polyacetylenes (prepared with Rh catalysts) consist of sharp well-resolved signals. With decreasing uniformity (polymers prepared with Mo and W catalyst) the resolution and sharpness of the signals is diminished. The ^{1}H NMR spectra of polymers with a high *cis* double bond content contain well-resolved signal of the olefinic hydrogen of the main chain units/segments with *cis* configuration (between 5 and 6 ppm). The particular position of this signal depends on the pendant groups of the polymer. [93] The chemical shift of 5.9 ppm is the reported position of this signal in the case of frequently studied PPhA. In the case of poly(arylacetylene)s the signals of other hydrogens (H from aromatic ring(s) or olefinic H of the main chain units/segments with trans configuration) are located above 6.5 ppm. Due to this character of the ^{1}H NMR spectra the percentage content of double bonds with *cis* configuration in the chains of poly(arylacetylene)s ($C_{\text{high-cis}}$) can be determined according to the Equation 3.

$$C_{high-cis}\,(in\%) = \frac{100(n+1)S_{high-cis}}{S_{total}} \qquad \text{Equation 3}$$

S_{total} denotes the total integrated area of signals of all protons and n stands for the number of aromatic protons in one monomeric unit. Symbol $S_{\text{high-}cis}$ represents the area of resonance of the main-chain protons on monomeric units with *cis* configuration.

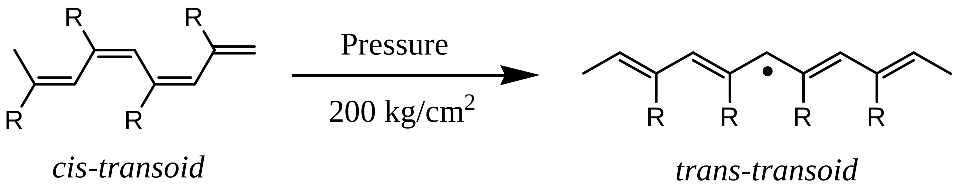
The determination of the *cis* double bonds content in the main chains of selected poly(arylacetylene)s can be done also on the base of IR spectra. In the case of PPhA the ratio of absorbances of bands at 760 cm^{-1} and 740 cm^{-1} serves at the measure of the *cis* double bonds content. [88] The IR approach is advantageous particularly for the insoluble PPhA samples. In some cases also Raman and UV/vis spectroscopies were applied for the qualitative evaluation of configurational structure of polyarylacetylenes. [94-96]

1.2. *Cis*-to-*trans* isomerization of substituted polyacetylenes

The development of methods for the study of polyacetylenes microstructure enabled to investigate the *cis*-to-*trans* isomerization of these polymers. Many studies focused at the pressure and temperature induced *cis*-to-*trans* isomerization of monosubstituted polyacetylenes in the solid state. The mostly studied polymers in this respect were PPhA [79;94] and its ring-substituted derivatives with following groups in the para position of the Ph rings: CH_3O- [79;95], -NO_2 [79;96], -CH_3, C_2H_5O-, Cl-, $(CH_3)_2N$- [79;95;96], CH_3S- [97]. Polymers submitted to the isomerization studies exhibited the *cis-transoid* microstructure and were prepared by insertion polymerization with Rh catalysts.

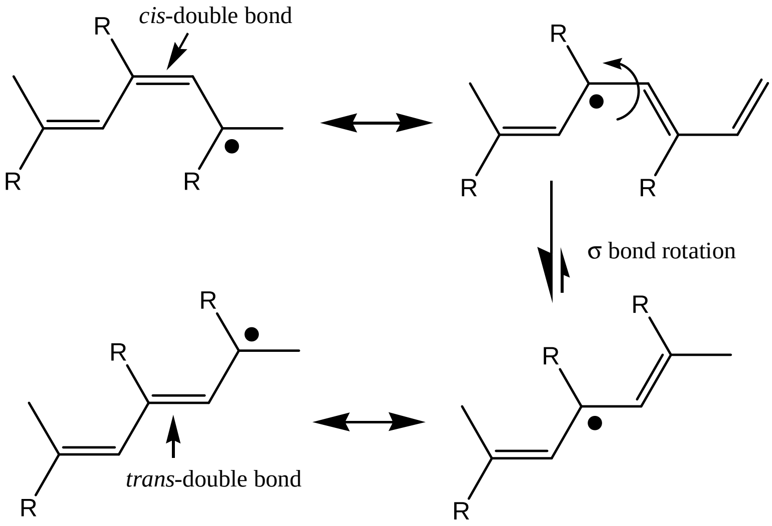
Pressure induced *cis*-to-*trans* isomerization was reported to proceed when PPhA-type polymers were compressed in the solid state mostly at 50-200 kg.cm^{-2} for tens of minutes under dynamic vacuum at room temperature. [79;95-101] The described process caused, unfortunately, the loss of the polymers solubility and thus only the solid-state techniques were applied for the characterization of the isomerized polymers. The *cis*-to-*trans* isomerization was proven by: (i) new bands that appeared in the Raman spectra of isomerized polymers that can be assigned to the polymer sequences with *trans* configuration (1475 cm^{-1} and 1200 cm^{-1}) [95;101;102] and (ii) increase of the vis absorption of the isomerized polymers in the region of higher wavelengths (the absorption red-shift in the visible region) [95;96;102]. The observed red shift in the vis spectra can be considered as a strong evidence for the *cis*-to-*trans* isomerization. The shift of vis absorption edge to the higher wavelengths with increasing *trans* double bond content in PPhAs is well known from the synthetic reports in which the influence of the polymerization catalysts (Rh, Mo, W) on the configurational structure of PPhAs was studied. [26;43]

The schematic depiction of the pressure induced *cis*-to-*trans* isomerization that is often given in the literature is shown in Scheme 9 (taken from reference [79]).



Scheme 9: Pressure induced *cis*-to-*trans* isomerization of monosubstituted polyacetylenes (taken from reference [79]).

Scheme 9 insinuates that the *cis*-to-*trans* isomerization may be accompanied by the formation of unpaired electrons (solitons) along the isomerized PPhAs chains. Several studies used EPR technique to study this phenomenon. [79;95;101;102] Author mostly found (i) the measurable content of solitons even in the non-isomerized high-*cis* PPhAs and (ii) unambiguous increase in the solitons content due to the pressure induced *cis*-to-*trans* isomerization. Although the absolute values of the solitons content are often given in these works the details on the applied quantification method are missing (the used standard in particular). This fact decreases the plausibility of the reported absolute solitons content. Tabata et. al. proposed mechanism of the *cis*-to-*trans* isomerization that assumes the active participation of the solitons on the *cis*-to-*trans* isomerization (Scheme 10). [95] The mechanism considers the rearrangement of the π electrons density and subsequent rotation along σ bond followed by the re-establishment of the double bond with changed configuration. [95]



Scheme 10: Mechanism of pressure induced *cis*-to-*trans* isomerization suggested by Tabata. [95;98]

One of the first studies dealing with the temperature-induced *cis*-to-*trans* isomerization of PPhA in the solid state and in solution were performed by Simionescu et. al. [103] The thermal *cis*-to-*trans* isomerization in solution at temperatures > 120°C was accompanied by intramolecular cyclization, aromatization, and scission of the polymer main chain. [103;104]

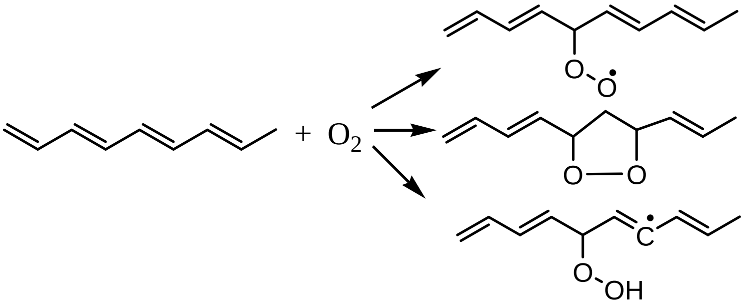
Matsunami et al. published the studies of temperature induced *cis*-to-*trans* isomerization of PPhA at higher temperature (180°C). The author supposed the *cis*-to-*trans* isomerization as a consequence of intramolecular cyclization accompanied by the release of the cyclic trimers (triphenylbenzenes, TPB). Only symmetrical 1,3,5-TPB was detected, the other cyclic trimers, i.e. 1,2,3-TPB and 1,2,4-TPB isomers were not observed. This finding was in agreement with the H-T linkage of monomeric units in the PPhA chains. [94]

Cis-to-*trans* isomerization of polyacetylenes was studied also by Cataldo et. al. [80] Authors showed that besides the enhanced pressure and temperature [105], the *cis*-to-*trans* isomerization of PPhA can be induced also by γ-radiation [81], via reaction with ozone [106] or with halogens (Cl_2 and Br_2) [107]. It has been confirmed by these authors that bulky side groups (4-biphenylyl, 4-phenoxyphenyl, 4-pentylphenyl) improve considerably the thermal stability of polyacetylenes (followed by TGA), however no changes in microstructure were mentioned. [108]

1.3. Oxidative degradation of substituted polyacetylenes

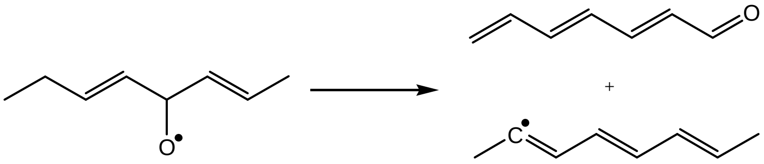
Substituted polyacetylenes exhibit enhanced reactivity due to the partly conjugated system of the double bonds in their main chains. The reaction of the polymer main chains with oxygen that is difficult to be prevented can be expected to lead to the modification of the polymer chains and to the changes in the polymer molecular weight (MW). Changes in MW may reflect (i) degradation of polymer chains and (ii) eventually, polymer chains branching and/or cross-linking. The reaction with oxygen can, of course, change the physical properties of polyacetylenes. Research in this field (performed within last three decades) showed that monosubstituted polyacetylenes were significantly more prone to the reaction with oxygen as compared to their disubstituted counterparts. That is why, in the subsequent paragraphs only the monosubstituted polyacetylenes and non-substituted polyacetylene are discussed.

The non-substituted polyacetylene and poly(methylacetylene) (PMeA) were the first polymers systematically studied from the stability point of view under atmospheric conditions. Various spectral techniques were used for this study. [109-111] It was proven that the reaction of polyacetylene and PMeA with oxygen proceeded without induction period and that it was most probably conditioned by the existence and/or creation of solitons on the polymer main chains. Polymer segments with unpaired electrons (macroradicals) are assumed to react with oxygen that may subsequently lead even to the polymer chain cleavage, i.e. to the polymer degradation. The mechanism was proposed for the propagation stage of the reaction of macroradicals with oxygen. The mechanism involves the formation of hydroperoxides, cyclic peroxides and peroxide radicals on the chains (Scheme 11). [109]



Scheme 11: Formation of the peroxide radicals, cyclic peroxides and hydroperoxide radicals by reaction of the polyacetylene main chain with oxygen.

The main chain cleavage is assumed to be a result of the re-arrangement of the arisen alkoxy radicals (Scheme 12). These alkoxy radicals are generated either during the cleavage of the cyclic peroxides or from the non-cyclic hydroperoxides.



Scheme 12: The scission of the macromolecular main chain with alkoxy group.

The authors of the above degradation mechanism discussed also a possible role of oxygen in the initiation stage of the degradation, i. e. in the process of the solitons formation. It was, however, concluded that solitons are formed spontaneously, without the contribution of oxygen, as the results of the other effects i.e. radiation or diffusion movement of the main chain segments.

In the second half of 1980s many papers focused at the thermal stability of various polyacetylenes (-CF_3, MeO-, *n*Bu-, *t*Bu-, -CO_2Me) exposed to the atmosphere in the solid state. [112-117]

The work of Neoh et al. 1989 was probably the first report that informed on the changes in MW that accompanied ageing of *trans*-PPhA kept in contact to the atmosphere. Authors described the decrease of M_p from $100x10^3$ to $67x10^3$ within 24 hours due to the ageing in THF solution at room temperature. [118] After this work, many papers have appeared describing the MW monitoring of the ageing of polyacetylenes exposed to the air (vide infra). The decrease in polymer MW, i.e. the polymer degradation was reported in all these papers. The opposite process, i. e. the MW increase due to polymer chains branching and or cross-linking, has not been observed. Since the reported degradation is unambiguously conditioned by the presence of oxygen the term of “oxidative degradation” is often used for this process.

The kinetics of degradation of any polymer can be described by the Simha-Montroll equation that follows the changes in distribution of the degree of polymerization during the degradation (Equation 4). [119]

$$\frac{dN_x}{dt} = -\sum_{p=1}^{X-1} k(\mathrm{X},\mathrm{p})N_x + 2\sum_{s=X+1}^{\infty} k(\mathrm{S},\mathrm{X})N_s \qquad \text{Equation 4}$$

k(X, p) and k(S, X) denote the rate constants of the scission of the main chain with the degree of polymerization X resp. S in the position p resp. X from the end of the chain. N_x and N_s is the amount of the macromolecules with given degree of polymerization in time t.

Two limit cases are possible from the kinetic point of view for the chemically induced degradation: random degradation and degradation from the ends of macromolecular chains (depolymerization). The random degradation takes place when all main-chain bonds have the same probability of scission. The solution of Simha-Montroll equation for the random degradation provides equations describing the dependencies of reciprocal values of degrees of polymerization on the degradation time t (Equations 5 and 6). [120]

$$\frac{1}{X_n} = \frac{1}{(X_n)_0} + \nu_n t \qquad \text{Equation 5}$$

$$\frac{1}{X_w} = \frac{1}{(X_w)_0} + \frac{\nu_w}{3}\int_0^t Đ_w dt \qquad \text{Equation 6}$$

X_n and X_w denote the number- and weight-average degrees of polymerization in time t, $(X_\mathrm{n})_0$, and $(X_\mathrm{w})_0$ denote the corresponding degrees of polymerization in $t = 0$, $Đ_\mathrm{w}$ is the dispersity defined: $Đ_\mathrm{w} = X_\mathrm{z}/X_\mathrm{w}$, X_z is the z-average degree of polymerization, ν_n and ν_w are the rate constants of degradation defined from the particular degree of polymerization.

The processing of results of the degradation study according to Equations 5 and 6 enables to evaluate (i) the character of the degradation (random or non-random) and, (ii) eventually, the extent of the deflection of the degradation from the random character. The degradation can be considered as random, if the $1/X_\mathrm{n}$ vs. t and $1/X_\mathrm{w}$ vs. t dependencies are linear and the values ν_n, and ν_w are similar. The dispersities of randomly degrading polymer should approach the constant values of 1.5 (for $Đ_\mathrm{w}$) and 2 (for $Đ = X_\mathrm{w}/X_\mathrm{n}$) in the middle stage of degradation regardless of the width of MW distribution of the parent polymer. [120]

Kinetic data necessary for the evaluation of the character of polymer degradation (X_n, X_w and X_z) are obtained from the SEC monitoring of the polymer ageing. In some cases only the degree of polymerization corresponding to the apex of SEC chromatogram, X_p, can be reliably obtained from SEC measurements. In such a case the obtained data are processed according to Equation 7.

$$\frac{1}{X_p} = \frac{1}{(X_p)_0} + \frac{\nu_p}{2} t$$ Equation 7

The linearity of $1/X_p$ vs. t dependence may indicate the random character of degradation (however it is not an unambiguous confirmation). On the other hand, the nonlinearity of $1/X_p$ vs. t dependence confirms the non-randomness of the degradation.

To summarize the paragraphs dealing with the degradation kinetics a general consideration on the kinetics of the oxidative degradation of polyacetylenes can be done. Providing that the degradation takes part as the entire process in the course of polyacetylenes ageing the random character of degradation is very probable due to the random distribution of solitons on the main chains of the polymer.

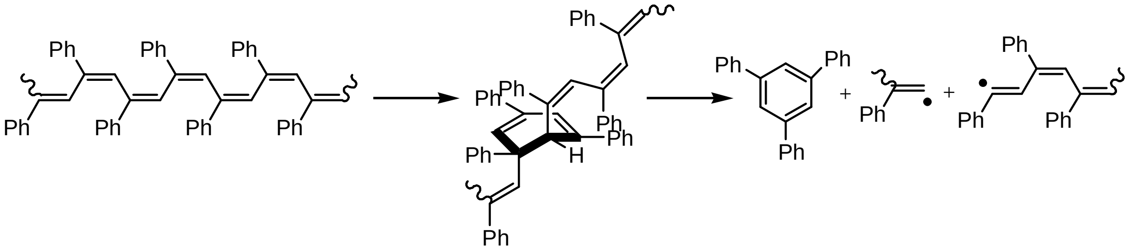
The above kinetic approach was applied by our group for the study of oxidative degradation of high-MW (M_w = 860x10^3) *cis*/*trans* PPhA prepared by W-catalysed metathesis polymerization. This work proved the random character of degradation of *cis*/*trans* PPhA exposed to the atmosphere at room temperature either in solution or in the solid state. The rate of the degradation in the solution (THF, chlorobenzene) was almost hundred times as high as the rate of degradation in the solid state. The diffuse daylight was proven to have no influence on the degradation rate. [121] Further studies focussed at the influence of the ring substitution of *cis*/*trans* PPhAs on the character and rate of oxidative degradation in solution (THF). Random or close to random character of degradation was confirmed for all three positional isomers of poly[(iodophenyl)acetylene] (PIPhA) [45;122;123] and for all three positional isomers of poly[(fluorophenyl)acetylene] (PFPhA). [43] On the contrary, the degradation of statistical copolymer of PhA and (4-nitrophenyl)acetylene exhibited significant deflection from randomness probably as a results of various strength of bonds between individual couples of monomeric units in the copolymer. [91;123] Also the degradation of *cis*/*trans* poly[(4-triisopropylsilylethynylphenyl)acetylene] was of a non-random character (studied polymer represented a monosubstituted polyacetylene with a bulky conjugated rod-like substituent). [123] Degradation of poly[(4-triisopropylsilylethynylphenyl)acetylene] was accompanied by an enhanced formation of low MW fragments. The hypothesis was proposed for this phenomenon that after the (random) scission of the polymer chain the newly formed macromolecule ends are in the excited states (stabilized by the pendant groups conjugation). The deexcitation can proceed either via non-reactive energy dispersion to the solvents molecules or by the reaction accompanied by the cleavage of an oligomeric product from the macromolecule end.

In general, the MW stability of studied *cis*/*trans* PPhAs derivatives in the solution exposed to the atmosphere was found to be positively affected by (i) the bulkiness of the substituent on Ph rings and (ii) vicinity of the substituent on the Ph ring to the polyacetylene main chain. For example, the rate constants of random degradation of PPhA and positional isomers of PIPhA decreased in the following order: PPhA ~ P4IPhA > P3IPhA >> P2IPhA. The positive effect of the substituent bulkiness on the stability of ring-substituted *cis*/*trans* PPhAs in solution (28 – 80°C) was reported also by Kwak et al. for the series of PPhAs with (dialkyl)(phenyl)silyl groups in the para position on Ph rings. [124]

Masuda et al. studied the MW stability of high-*cis* PPhA and its derivatives with substituents in the para position on Ph rings (polymers were prepared by Rh-catalysed insertion polymerization, the stability of polymers in the solution exposed to the atmosphere was monitored in particular). [113] Authors did not report the character of the degradation (random/non-random), however they focussed on the influence of various factors on the rate of decrease of the polymer MW. Similarly as in the case of *cis*/*trans* polymers, they observed the positive effect of the ring-substitution on the stability of high-*cis* PPhAs. The degradation rate was quite slow for any ring-substituted high-*cis* PPhA compared to the unsubstituted counterpart. In dependence on the substituent in the para position of the Ph ring the rate of degradation decreased in the following order: H >> OCH_3 > $COOCH_3$ > *n*-butyl > *t*-butyl. This study also dealt with the comparison of MW stability of high-*cis* PPhA and *cis*/*trans* PPhA in solution. It was shown that high-*cis* PPhA (prepared with Rh-catalyst) degraded more rapidly than its *cis*/*trans* counterpart (prepared with W-catalyst). This conclusion was partly ambiguous due to the different initial molecular weight of both polymers (high-*cis* PPhA, M_n= 347x10^3; *cis*/*trans* PPhA, M_n= 49x10^3). An interesting finding resulted from the study on the influence of the type of the solvent on the MW stability of both *cis*/*trans* and high-*cis* PPhAs. While the degradation rate of *cis*/*trans* PPhA was almost independent on the solvent type, the degradation rate of high-*cis* PPhA strongly increased in the solvent order: THF < toluene << $CHCl_3$. The addition of acid (HCl) into the high-*cis* PPhA solution was reported (i) to accelerate significantly the decrease in polymer MW and (ii) to induce the *cis*-to-*trans* isomerization of high-*cis* PPhA. On the other hand, the high-*cis* PPhA degradation in the acid-free solutions was reported to proceed without changes in the PPhA main chain configuration. In connection to the last statement, it is necessary to notice, that Masuda et al. [113] monitored the high-*cis* PPhA ageing for relatively short period (about 30 hours) and that within this time the configurational changes could hardly be manifested enough to be detected by NMR techniques.

Bondarev et al. compared in ref. [43] the ageing of *cis*/*trans* and high-*cis* PFPhA in THF solution (all three positional isomers from each configurational series were studied). While *cis*/*trans* polymers exhibited random or close to random degradation the strongly non-random character of degradation was observed for high-*cis* polymers. In a given couple of high-*cis* and *cis*/*trans* samples of the same positional isomerism, always the high-*cis* sample exhibited lower MW stability. This confirmed the finding of Masuda et al. on the influence of the configurational structure on the MW-stability of PPhA in solution, see above and ref. [113;125]. The long-time monitoring of high-*cis* PFPhAs ageing in the solution unambiguously confirmed that the oxidative degradation of these polymers was accompanied by significant *cis*-to-*trans* isomerization. Results of Bondarev et al. moreover, indicate a possible interconnection between oxidative degradation and *cis*-to-*trans* isomerization of studied polymers: (i) both the rate of degradation and the rate of *cis*-to-*trans* isomerization decreased in the polymers order: P4FPhA > P3FPhA >> P2FPhA (samples were exposed to the atmosphere in THF during ageing), (ii) when the oxidative degradation was partly suppressed by reduction of the oxygen content in the system the simultaneous suppression of *cis*-to-*trans* isomerization was observed.

The tight connection between degradation and *cis*-to-*trans* isomerization was discussed also by Percec et al. The authors were interested in the ageing of high-*cis* PPhA in solution and in the solid state at room and higher temperature (60°C). [99;126] The observations were reported that the high-*cis* PPhA underwent a decrease in both *cis* double bonds content and MW during its ageing either in solution or in bulk. Percec et al. proposed isomerization mechanism based on the intramolecular cyclization of PPhA chains followed by the chain cleavage with the release of 1,3,5-triphenylbenzene that was spectroscopically detected as the side product of PPhA ageing (Scheme 13). [99;126;127] The chain cleavage due to the isomerization (proceeding without oxygen participation) was assumed to be mainly responsible for the observed decrease in PPhA MW. Nevertheless, authors admitted also the oxidative chain cleavage as a contribution to the high-*cis* PPhA degradation. [99]



Scheme 13: Mechanism of *cis*-to-*trans* isomerization via intramolecular cyclization proposed by Percec et al. (ref. [127])

Percec et al. and Bondarev et al. showed that the MW distribution of high-*cis* PPhAs broadened in the course of ageing. However no explanation was proposed for this observation. Nevertheless, the reported MW distribution broadening stands for an evidence of the non-random character of high-*cis* PPhAs degradation.

As evident from the last paragraphs of this chapter and from the cited works of Masuda et al. [113], Bondarev et al. [43] and Percec et al. [126] there are serious discrepancies and unsolved aspects as the process of ageing of high-*cis* PPhAs is concerned.

The present Ph.D. thesis the aims of which are summarized in the subsequent chapter tries to remove these discrepancies and provide better understanding of the process of substituted polyacetylenes ageing.

2. AIMS OF THE THESIS

Several points of interest have been aimed as the subjects of the present study and some other appeared in the course of research.

1) To obtain a comprehensive survey of the polymerization activity of mononuclear Rh-based complexes as catalysts of homopolymerization and copolymerization of aryl- and alkylacetylenes in various solvents. To optimise reaction systems based on these catalysts for the preparation of high-*cis* poly(arylacetylene)s of desired molecular weight.

2) To evaluate the connection between degradation and isomerization processes during the long-term ageing of high-*cis* poly(phenylacetylene) and high-*cis* poly[(2,4-difluorophenyl)acetylene] in solution exposed to the atmosphere. To explain changes in molecular weight distribution of these polymers in the course of their ageing. To propose a mechanism of simultaneously proceeding isomerization and degradation of these polymers.

3) To perform long-term comparative study of high-*cis* poly(phenylacetylene) and high-*cis* poly[(2,4-difluorophenyl)acetylene] ageing in solution and to compare the molecular weight and configurational stability of these polymers.

4) To evaluate the influence of the parent molecular weight on the molecular weight and configurational stability of high-*cis* poly[(2,4-difluorophenyl)acetylene] samples in solution.

3. EXPERIMENTAL

3.1. Materials

- Monomers:

  Phenylacetylene (PhA) (Sigma-Aldrich) 98%
  (2,4-difluorophenyl)acetylene (dFPhA) (Sigma-Aldrich) 97%
  (4-biphenylyl)acetylene (4-ethynylbiphenyl) (BPhA) (Sigma-Aldrich) 97%
  (2-fluorophenyl)acetylene (2FPhA) (Sigma-Aldrich) 97%
  (2-trifluoromethylphenyl)acetylene ($2CF_3PhA$) (Sigma-Aldrich) 97%
  n-butylacetylene (hex-1-yne) (*n*BuA) (Sigma-Aldrich) 97%
  tert-butylacetylene (3,3-dimethylbut-1-yne) (*t*BuA) (Sigma-Aldrich) 98%
  4-chlorobutylacetylene (6-chlorohex-1-yne) (ClBuA) (Sigma-Aldrich) 98%
  cyclopropylacetylene (cPrA) (Sigma-Aldrich) 97%
  Monomers were distilled or sublimated *in vacuo* prior to use.

- Catalysts:

  Acetylacetonato(norborna-2,5-diene)rhodium(I) [Rh(nbd)(acac)] (Sigma-Aldrich) 97%
  Acetylacetonato(cycloocta-1,5-diene)rhodium(I) [Rh(cod)(acac)] (Sigma-Aldrich) 99%
  Acetylacetonatobis(ethylene)rhodium(I) [Rh(ethylene)$_2$(acac)] (Sigma-Aldrich) 95%
  Catalysts were applied as obtained.

- Solvents and other chemicals:

  Tetrahydrofuran (THF, Sigma-Aldrich) for SEC chromatography was used as obtained, for polymerization it was distilled from $AlLiH_4$.
  Dichloromethane (CH_2Cl_2, Lachema, Czech Republic) was distilled from P_2O_5.
  Cyclooctatetraene (cot, Sigma-Aldrich) was distilled *in vacuo* prior to use.

Methanol (CH_3OH, Sigma-Aldrich for HPLC), 1,3,5-triphenylbenzene (1,3,5-TPB, Sigma-Aldrich), acetylacetone (Hacac, Sigma-Aldrich), $CDCl_3$ (Chemotrade), CD_2Cl_2 (Chemotrade), tetrahydrofuran-d_8 (THF-d_8, Chemotrade) were used as obtained.

3.2. Polymerization

Polymerizations were carried out in glass screw-cap vials equipped with a magnetic stirrer at room temperature. Reactions were started by mixing solution of Rh-based catalyst in respective solvent (THF, CH_2Cl_2, THF-d_8, CD_2Cl_2) with solution of monomer(s) in the same solvent. Polymerizations in bulk were started by addition of monomer to the solid catalyst. Polymerizations were quenched by pouring the reaction mixture into methanol (tenfold volume excess). Precipitated polymers were isolated by the sedimentation in centrifuge or by filtration, several times washed with methanol or mixture methanol/THF (1/1 V/V) and dried to constant weight *in vacuo* at room temperature. The final polymer yields were determined gravimetrically. Time course of selected polymerizations of arylacetylenes was monitored by ^{1}H NMR spectroscopy: at given times 0.7 ml of reaction mixture was transferred into NMR cuvette and submitted for ^{1}H NMR analysis. Data resulting from ^{1}H NMR monitoring of arylacetylenes polymerizations was used for determination of the polymer yield, Y(P), vs. reaction time dependencies. Values of Y(P) were obtained using Equation 8:

$$Y(\mathrm{P})(\mathrm{in\%}) = \frac{100A_\mathrm{P}}{\left(A_\mathrm{M} + A_\mathrm{P}\right)} \qquad \text{Equation 8}$$

A_M and A_P are integral intensities of all ^{1}H NMR signals of monomer and polymer, respectively. The applied method gave values of the final yields (based on the ^{1}H NMR analysis performed just before the termination) that were in good accordance with the final yields obtained gravimetrically (± 5%). Moreover, some polymerizations were monitored by SEC technique: for this purpose the samples of volume from 5 to 20 μl were withdrawn from the reaction mixture at given times. Withdrawn samples were diluted with THF and injected into SEC columns. SEC monitoring provided the reaction time dependencies of molecular-weight characteristics of the formed polymers.

Moreover, the (absolute) area bellow SEC polymer peaks was used for determination of *Y*(P) values at various reaction times for polymerizations which were not monitored by ^{1}H NMR.

3.3. Ageing and fractionation of prepared polymers

3.3.1. Ageing of polymers in THF-d_8 solution: SEC and NMR monitoring

Polymers were dissolved in THF-d_8 (c = 1 mg/ml). Solutions were allowed to age in 20 ml screw-cap vials in contact with the atmosphere and diffuse daylight at room temperature (or 50°C). At given times, samples were taken and analysed by ^{1}H NMR and SEC techniques. For the ^{1}H NMR analysis, 0.7 ml of solution was transferred into an NMR cuvette. For the SEC analysis, 0.02 ml of solution was withdrawn and directly injected into SEC columns.

3.3.2. Ageing of polymer in THF solution: DLS monitoring

Polymer was dissolved in THF (c = 1 mg/ml). Solution was allowed to age in 20 ml screw-cap vial in contact with the atmosphere and diffuse daylight at room temperature. At given times, sample was taken and analysed by DLS technique. The analyses were performed with THF solution of concentrations ranging from 0.125 to 1.0 mg/ml.

3.3.3. SEC and ^{1}H NMR study of ageing of PdFPhA in the solid state

Solid PdFPhA sample was allowed to age in Petri dish in contact with the atmosphere and diffuse daylight at room temperature. At given times, a proper amount of aged sample was dissolved in THF-d_8 and immediately analysed by SEC and ^{1}H NMR.

3.3.4. Molecular-weight fractionation of aged polymers

Polymer was placed into an Erlenmeyer flask (1000 ml) and dissolved in distilled THF (c = 1 mg/ml). Solution was allowed to age in contact with the atmosphere and diffuse daylight at room temperature for a desired time before the fractionation. After the ageing, the thermodynamic quality of solvent for polymer was stepwise decreased by drop-wise adding of methanol (room temperature) under intensive mixing and the stepwise precipitated polymeric fractions were isolated by filtration. Each polymer fraction was repeatedly washed with a THF/methanol mixture of respective composition and then dried to constant weight *in vacuo* at room temperature.

3.4. Techniques

3.4.1. Size exclusion chromatography (SEC)

Size Exclusion Chromatography analyses were performed on Agilent Technologies 1100 Series apparatus fitted with UV/vis Diode Array Detector (DAD) operating in the wavelength region 200-700 nm. Chromatograms recorded at wavelength of 254 nm were used for the molecular weight (MW) characterization. A series of either two PL-gel columns (Mixed B and Mixed C) or three PL-gel columns (Mixed B, Mixed C and Mixed E, Polymer Laboratories, UK) and THF (flow rate 0.7 ml/min) were used. A set of polystyrene (PS) standards (Polymer Laboratories, UK) was used for column calibration. Following apparent (relative to PS) molecular-weight characteristics are reported: number-average molecular weight (M_n), weight-average molecular weight (M_w), molecular weight corresponding to the apex of SEC peak (M_p), number-average degree of polymerization (X_n), weight-average degree of polymerization (X_w), degree of polymerization corresponding to the apex of SEC peak (X_p), dispersity, $Đ = M_w/M_n$ and molecular weight corresponding to the i-th slice of SEC chromatogram (M_i). Application of a DAD detector allowed to monitor UV/vis spectra of the polymer eluted from the columns.

3.4.2. Nuclear magnetic resonance (NMR)

^{1}H NMR, ^{13}C NMR and ^{19}F NMR measurements were performed using Varian $^{\text{Unity}}$ Inova 400 spectrometer. Chemical shifts of signals in ^{1}H NMR spectra were referenced to the solvent peaks (δ = 3.58 ppm for THF-d_8, δ = 5.31 ppm for CD_2Cl_2 and δ = 7.25 ppm for $CDCl_3$). Chemical shifts of signals in ^{13}C NMR spectra were referenced to the solvent peaks (δ = 67.57 ppm for THF-d_8, δ = 54.00 ppm for CD_2Cl_2 and δ = 77.00 ppm for $CDCl_3$). ^{19}F NMR spectra were referenced to F atoms of CF_3COOH (-76.55 ppm). ^{19}F NMR spectra measurements were performed using Wilmad coaxial insert tube in which CF_3COOH (1 μl) dissolved in THF-d_8 (60 μl) was placed.

3.4.3. Dynamic light scattering (DLS)

Dynamic Light Scattering analyses were performed on the light scattering setup (ALV, Langen, Germany) consisted of a 633 nm He-Ne laser, an ALV CGS/8F goniometer, an ALV High QE APD detector, and an ALV 5000/EPP multibit, multitau autocorrelator. DLS data analysis was performed by fitting the measured normalized intensity autocorrelation function $g_2(t) = 1 + \beta|g_1(t)|^2$, where $g_1(t)$ is the electric field correlation function, t is the lag-time and β is a factor accounting for deviation from the ideal correlation. An inverse Laplace transform of $g_1(t)$ with the aid of a constrained regularization algorithm (CONTIN) provides the distribution of relaxation times, $\tau A(\tau)$. Effective angle- and concentration-dependent hydrodynamic radii, $R_H(q,c)$, were obtained from the mean values of relaxation times, $\tau_m(q,c)$, of individual diffusive modes using the Stokes-Einstein equation.

3.4.4. Gas chromatography - Mass spectrometry (GC-MS)

GC–MS analyses were performed using a GCMS-QP2010 Plus instrument (Shimadzu, Japan), equipped with a 20 m × 0.18 mm i.d., 1 μm film thickness Rxi-624SiL MS column (Restek, USA).

Gas Chromatography-High resolution mass spectrometry (GC-HRMS) analyses were performed on an Agilent 7890A gas chromatograph coupled to Waters GCT Premier a benchtop orthogonal acceleration time-of-flight (OA-TOF) mass spectrometer. DB-5 column (Agilent Technologies) was used.

3.4.5. Electron paramagnetic resonance (EPR)

EPR spectra were recorded on an ERS-220 spectrometer (Center for Production of Scientific Instruments, Academy of Sciences of GDR, Berlin, Germany) operated by a CU-1 unit (Magnettech, Berlin, Germany) in the X-band. The samples for the EPR measurements were prepared by homogenization of the solid polymer and filled into quartz capillaries of the same diameter. An equal amount of Mn^{2+} standard was used for the relative comparison of radical quantity in the polymer sample as well as for the determination of the g-value (Mn^{2+} standard at $g = 1.9860$; $M_I = -1/2$ line).

3.4.6. Infrared spectroscopy (IR)

FT IR spectra were recorded on NICOLET MAGNA IR760 using diffuse reflectance technique and KBr diluted samples.

4. RESULTS AND DISCUSSION

4.1. Polymerization of substituted acetylenes with Rh complexes

Various polymerization catalysts and catalyst systems based on Rh(I)-complexes have been developed or studied in our laboratory in the last decade. [47;93;128-133] Among these catalysts, the simple mononuclear Rh(I)(acac) complexes with cycloolefin ligands were found as very efficient for the polymerization of the specialty monomers (e.g. 3-ethynylthiophene, diethynylarenes). [15;134] With the aim to obtain a more comprehensive survey of the polymerization activity of Rh(I)(acac) complexes, the systematic polymerization study was performed in which complexes [Rh(nbd)(acac)], [Rh(cod)(acac)] and [Rh(cot)(acac)] (nbd = norborna-2,5-diene, cod = cycloocta-1,5-diene, cot = cyclooctatetraene) were studied as catalysts of homopolymerization and copolymerization of various aryl- and alkylacetylenes in various solvents.

Studies discussed in this chapter were focussed mainly at:

- Revealing the relations between (i) the reaction conditions and (ii) time course of reactions and parameters of prepared polymers.
- Achievement (partial) control over MW of prepared polymers.
- Contribution to understanding of the mechanism of acetylenes polymerization with Rh-based catalysts.

4.1.1. [Rh(cycloolefin)(acac)] complexes as catalysts of polymerization of aryl- and alkylacetylenes: influence of cycloolefin ligand and reaction conditions

This chapter is based on the results reported in the paper:

Trhlíková O., Zedník J., Balcar H., Brus J., Sedláček J.: [Rh(cycloolefin)(acac)] complexes as catalysts of polymerization of aryl- and alkylacetylenes: influence of cycloolefin ligand and reaction conditions, Journal of Molecular Catalysis A: Chemical, 2013; 378; 57-66.

Three mononuclear Rh-acac complexes [Rh(nbd)(acac)], [Rh(cod)(acac)] and [Rh(cot)(acac)] were applied as catalysts in polymerization of PhA as a model monomer in THF-d_8 and CD_2Cl_2 (Table 1). The last complex was synthesized from [Rh(ethylene)$_2$(acac)] by ligand exchange with cyclooctatetraene. Complexes [Rh(nbd)(acac)] and [Rh(cod)(acac)] were commercially supplied. Polymerizations were monitored by ^{1}H NMR and SEC techniques. Results are summarized in Table 1.

Table 1: Yield of polymers, Y(P), weight-average, (M_w), and number-average, (M_n), molecular weight of PPhA in polymerization with [Rh(cycloolefin)(acac)] complexes at room temperature for various reaction times, t_r. Initial PhA concentration = 0.6 mol/l, initial catalyst concentration = 6 mmol/l. f_{Hacac} = [Hacac]/[[Rh(cycloolefin)(acac)]]$_0$ - fraction of acac ligand released as acetylacetone from catalyst. $(M_n)_{theor}$ - lower estimate of the theoretical number-average molecular weight according to Equation 11.

No.	**Solvent**	**t_r [min]**	**f_{Hacac}**	**Y(P) [%]**	**10^{-3} M_w**	**10^{-3} M_n**	**10^{-3} $(M_n)_{theor}$**	**$(M_n)_{theor}$/ (M_n)**
				[Rh(nbd)(acac)]				
1	THF-d_8	10	nd	80	310	100	nd	nd
2	THF-d_8	180	~0.05	~100	300	89	~200	~2
3	CD_2Cl_2	10	0.10	93	460	87	95	1.1
4	CD_2Cl_2	180	0.13	~100	380	84	79	0.94
				[Rh(cod)(acac)]				
5	THF-d_8	10	nd	40	81	32	nd	nd

6	THF-d_8	180	~0.05	86	86	39	~170	~4
7	CD_2Cl_2	10	0.35	73	30	10	21	2.1
8	CD_2Cl_2	180	0.53	90	29	10	17	1.7
[Rh(cot)(acac)]								
9	THFd_8	10	nd	49	140	50	nd	nd
10	THF-d_8	180	~0.05	90	130	43	~180	~4
11	CD_2Cl_2	10	0.16	71	39	10	45	4.5
12	CD_2Cl_2	180	0.20	94	49	12	48	4.0

^{1}H NMR spectra of all reaction mixtures contained signals of PhA monomer, supplied Rh-acac complex, formed PPhA and new signals of free acetylacetone (Hacac). The highest amount of free Hacac was detected in PhA/[Rh(cod)(acac)]/CD_2Cl_2 system (Figure 1, see signals labelled as CH_3Hacac that correspond to methyls of free acetylacetone).

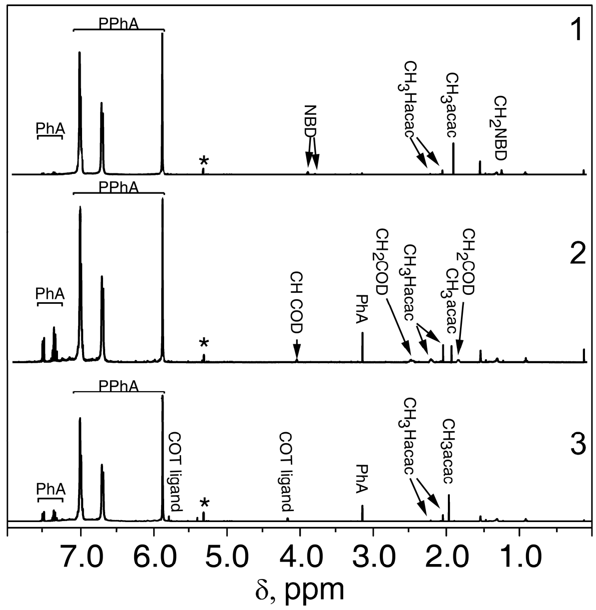
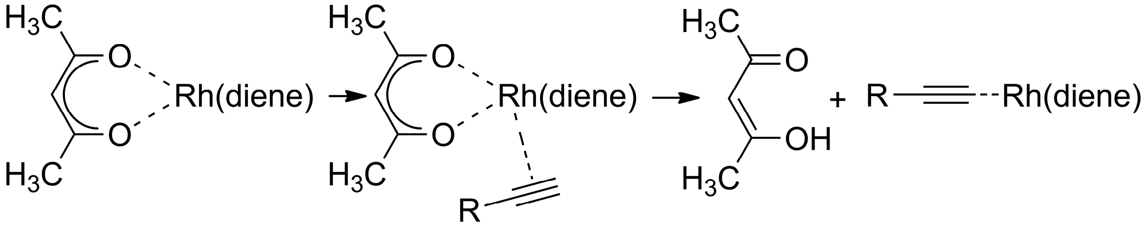


Figure 1: ^{1}H NMR spectra recorded in the course of PhA polymerization with [Rh(nbd)(acac)] (spectrum 1), [Rh(cod)(acac)] (spectrum 2) and [Rh(cot)(acac)] (spectrum 3) in CD_2Cl_2. [Rh] = 6 mmol/l, $[M]_0$ = 0.6 mol/l, reaction time 180 min, room temperature.

Independent GC-MS analyses of systems catalyst/solvent and catalyst/solvent/PhA unambiguously confirmed that the Hacac formation was conditioned by the presence of PhA in the reaction system. The initial step of [Rh(cycloolefin)(acac)] with PhA reaction thus most probably proceeds as a proton transfer from PhA to acac ligand under the release of Hacac. This process probably gives rise to intermediate (cycloolefin)Rh-C≡CPh species (Scheme 14).



Scheme 14: Initial step in [Rh(cycloolefin)(acac)] transformation into polymerization active centres.

The quantification of ^{1}H NMR spectra provided PPhA yield, Y(P), and fractions of acac ligand transformed into free Hacac, f_{Hacac}, for various reaction times, t_{r}. Parameter f_{Hacac} was defined as follows:

$$f_{\mathrm{Hacac}} = \frac{[\mathrm{Hacac}]}{[[\mathrm{Rh(cycloolefin)(acac)}]]_0} \qquad \text{Equation 9}$$

[Hacac] stands for the concentration of free Hacac at a given t_{r}, $[[\mathrm{Rh(cycloolefin)(acac)}]]_0$ stands for the initial catalyst concentration. The values of f_{Hacac} were calculated as follows:

$$f_{\mathrm{Hacac}} = \frac{A^{\mathrm{Hacac}}}{(A^{\mathrm{Hacac}} + A^{\mathrm{acac}})} \qquad \text{Equation 10}$$

A^{Hacac} represents the sum of the CH_3 signal areas of free Hacac while A^{acac} stands for the signal area of CH_3 groups of acac ligand in a [Rh(cycloolefin)(acac)] complex.

Values of f_{Hacac} found for the reaction systems in CD_2Cl_2 increased in the following catalysts order [Rh(nbd)(acac)] < [Rh(cot)(acac)] < [Rh(cod)(acac)] (Figure 2). Low values of f_{Hacac} resulted for all reaction systems in THF-d_8. The higher extent of [Rh(cycloolefin)(acac)] transformation in CD_2Cl_2 (compared to the transformation extent in THF) correlates well with the higher initial rate of polymerization in CD_2Cl_2 than in THF-d_8 (Figures 3 and 4). Evidently, type of solvent influenced significantly the initiation stage of polymerization (formation of active species from the catalyst).

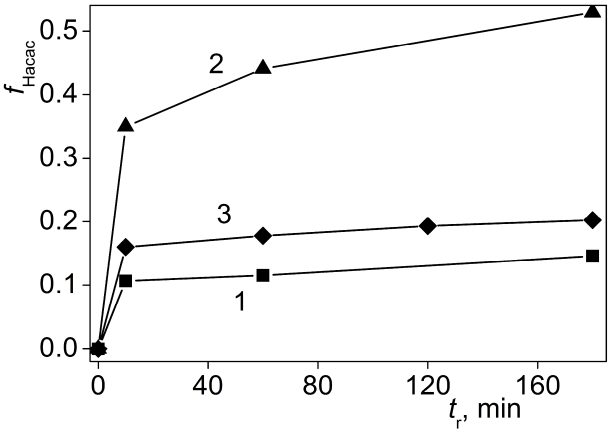


Figure 2: Fractions of free Hacac vs. reaction time for PhA polymerization with [Rh(nbd)(acac)] (curve 1), [Rh(cod)(acac)] (curve 2), [Rh(cot)(acac)] (curve 3). [Rh] = 6 mmol/l, $[M]_0$ = 0.6 mol/l, CD_2Cl_2, room temperature.

Despite the above differences in the initial polymerization rate all three [Rh(cycloolefin)(acac)] complexes provided high PPhA yields (from 86 to 100%, Table 1) in both coordinating (THF-d_8) and non-coordinating (CD_2Cl_2) solvents.

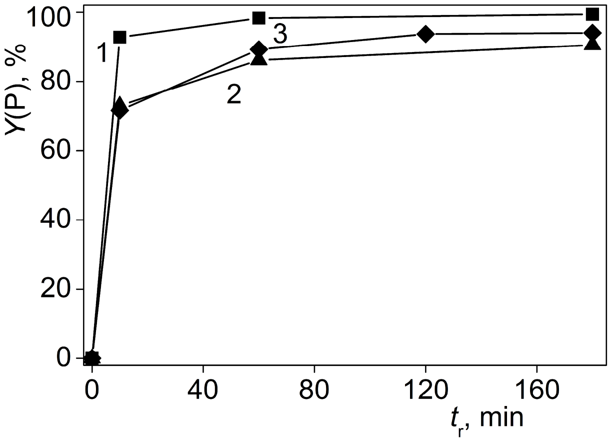


Figure 3: Yield of PPhA vs. reaction time for PhA polymerization with [Rh(nbd)(acac)] (curve 1), [Rh(cod)(acac)] (curve 2), [Rh(cot)(acac)] (curve 3). [Rh] = 6 mmol/l, $[M]_0$ = 0.6 mol/l, CD_2Cl_2, room temperature.

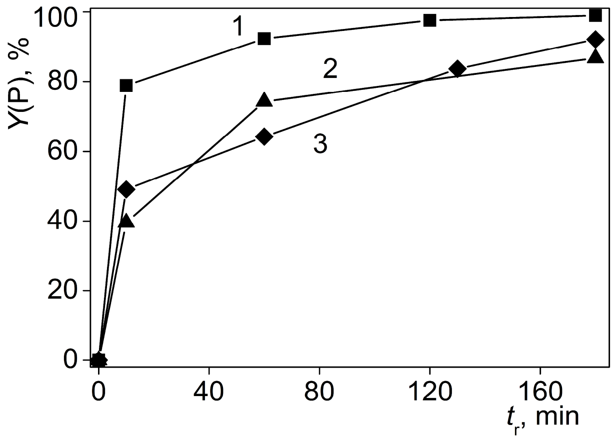


Figure 4: Yield of PPhA vs reaction time for PhA polymerization with [Rh(nbd)(acac)] (curve 1), [Rh(cod)(acac)] (curve 2), [Rh(cot)(acac)] (curve 3). [Rh] = 6 mmol/l, $[M]_0$ = 0.6 mol/l, THF-d_8, room temperature.

Analysis of the molecular weight data summarized for PPhAs revealed that in both solvents the M_w values of PPhA decreased in the catalyst order [Rh(nbd)(acac)] > [Rh(cot)(acac)] > [Rh(cod)(acac)] (Table 1).

Higher M_w and M_n values were achieved in polymerizations induced with [Rh(cot)(acac)] and [Rh(cod)(acac)] complexes in THF-d_8 than in CD_2Cl_2. However, in polymerizations induced with [Rh(nbd)(acac)], slightly higher M_w values resulted in CD_2Cl_2. The proper selection of catalyst ligand and solvent afforded to control PPhA molecular weight over one order of magnitude (M_n from $1x10^4$ to $1x10^5$, M_w from $3x10^4$ to $4x10^5$).

To evaluate influence of transfer reactions on molecular weight data we calculated a lower estimate of the theoretical number-average molecular weight, $(M_n)_{theor}$, with Equation 11 (Table 1).

$$(M_{\mathrm{n}})_{\mathrm{theor}} = \frac{M_{\mathrm{U}} Y(\mathrm{P}) r_{\mathrm{M/C}}}{100\, f_{\mathrm{Hacac}}} \qquad \text{Equation 11}$$

M_U is the relative molecular weight of the monomeric unit (M_U =102.14 in the case of PhA), $r_{M/C}$ is the initial monomer to catalyst molar ratio. Applied f_{Hacac} can be considered as an upper estimate of the overall initiation efficiency.

A comparison of $(M_n)_{theor}$ and M_n values may indicate a higher extent of transfer reactions for polymerization systems with [Rh(cod)(acac)] and [Rh(cot)(acac)] complexes compared to systems based on [Rh(nbd)(acac)] complex (Table 1). This may explain the lower PPhA molecular weights achieved with [Rh(cod)(acac)] and

[Rh(cot)(acac)]. Assuming that the initiation efficiency is proportional to f_{Hacac} one can deduce that the higher values of molecular weight achieved with [Rh(cod)(acac)] and [Rh(cot)(acac)] in THF-d_8 reflect particularly the low initiation efficiency in THF-d_8. It can be concluded that two factors, the initiation efficiency and the extent of transfer reactions, simultaneously affected the MW values achieved in PhA polymerizations with [Rh(cycloolefin)(acac)] complexes.

Comlex [Rh(cot)(acac)] applied in this study was synthesised from [Rh(ethylene)$_2$(acac)] by ligand exchange with cyclooctatetraene. In connection to the polymerizations of PhA with purified [Rh(cot)(acac)] we also studied PhA polymerization catalysed by [Rh(cot)(acac)] complex formed in situ from [Rh(ethylene)$_2$(acac)] via reaction with cot (Table 2). The in situ prepared complex [Rh(cot)(acac)] polymerized PhA even in the systems containing excess of non-reacted free cyclooctatetraene (Table 2). The quantitative course of [Rh(ethylene)$_2$(acac)] into [Rh(cot)(acac)] transformation was confirmed by ^{1}H NMR monitoring. It should be noted that MW of PPhA prepared in system with a high cyclooctatetraene concentration was significantly lower than that achieved with purified [Rh(cot)(acac)] in “standard” polymerization solvents (Tables 1 and 2).

Table 2: Yield of polymers, Y(P) and weight-average, (M_w), and number-average, (M_n), molecular weight of polymers in polymerization of PhA with [Rh(ethylene)$_2$(acac)] activated by cycloctatetraene, cot, at room temperature. Initial monomer concentration = 0.6 mol/l, initial catalyst concentration, = 6 mmol/l, reaction time 3 h, time of activation of [Rh(ethylene)$_2$(acac)] with cot 30 min.

No.	**Solvent**	**[cot]$_0$ [mol/l]**	**Y(P) [%]**	**10^{-3} M_w**	**10^{-3} M_n**
1	[a]	0	0	-	-
2	cot[b]	8.9	65	5.9	3.1
3	THF-d_8/cot	0.06	84	110	40

[a] THF or CH_2Cl_2, without cot addition
[b] reaction performed in neat cot

Two ortho-substituted PhAs, (2-fluorophenyl)acetylene (2FPhA) and (2-trifluoromethylphenyl)acetylene (2CF$_3$PhA) were compared with model monomer (PhA) in polymerizations catalysed with [Rh(nbd)(acac)] with the aim to evaluate the influence of the ortho-substituent bulkiness on the monomers polymerizability (Table

3). The polymer yields achieved in these polymerization decreased with increasing ortho-substituent bulkiness in the monomers order: PhA > 2FPhA >> $2CF_3PhA$. The same trend was observed in both THF-d_8 and CD_2Cl_2 solvents. ^{1}H NMR monitoring of reaction systems showed that the poor $2CF_3PhA$ polymerizability was not due to the suppression of the initial stage of catalyst transformation (Table 3) and that the bulkiness of CF_3 substituent in the vicinity to the monomer triple bond most probably impeded the propagation stage of polymerization.

Table 3: Yield of polymers, Y(P), weight-average, (M_w), and number-average, (M_n), molecular weight of polymers achieved in polymerization of PhA, 2FPhA and $2CF_3PhA$ with [Rh(nbd)(acac)] at room temperature for various reaction times t_r. Initial monomer concentration = 0.6 mol/l, initial catalyst concentration = 6 mmol/l. f_{Hacac} = [Hacac]/[[Rh(nbd)(acac)]]$_0$ - fraction of acac ligand released as acetylacetone from catalyst determined by in situ ^{1}H NMR measurement.

No.	Monomer	Solvent	t_r in h	f_{Hacac}	Y(P) in %	10^{-3} M_w	10^{-3} M_n
1	PhA	CD_2Cl_2	3	0.13	~100	380	84
2	PhA	THF-d_8	3	~0.05	~100	300	89
3[a)]	2-FPhA	CD_2Cl_2	3	nd	88	660	260
4	2-FPhA	THF-d_8	3	~0.05	90	650	230
5	2-CF_3PhA	CD_2Cl_2	3	0.66	16	7.7	4.1
6	2-CF_3PhA	CD_2Cl_2	24	0.87	21	8.0	4.1
7	2-CF_3PhA	THF-d_8	3	0.24	8	8.6	4.7
8	2-CF_3PhA	THF-d_8	24	0.45	24	10	4.7

[a)] polymer precipitated from CD_2Cl_2 reaction mixture, however, it was soluble in THF after the isolation

To evaluate the activity of [Rh(cycloolefin)(acac)] complexes in polymerization of alkylacetylenes (AlkAs) we polymerized *n*-butylacetylene (*n*BuA) as a model monomer. The results showed that [Rh(nbd)(acac)] applied in THF and CH_2Cl_2 transformed *n*BuA to poly(*n*-butylacetylene) (P*n*BuA) with yield only up to 20%. No polymer was formed either in THF or in CH_2Cl_2 with complexes containing cod or cot ligands. The enhanced catalytic activity of [Rh(nbd)(acac)] complexes was observed in the bulk polymerization (P*n*BuA yield = 28 %). Some P*n*BuA (yield up to 8%) resulted even from the bulk polymerizations catalysed with [Rh(cod)(acac)] and [Rh(cot)(acac)].

Based on the results obtained in polymerization of *n*BuA we polymerized four different AlkAs: *n*-butylacetylene (*n*BuA), *tert*-butylacetylene (*t*BuA), (4-chlorobutyl)acetylene (ClBuA) and cyclopropylacetylene (cPrA) either in THF or in bulk under the catalysis of [Rh(nbd)(acac)] (Table 4). The replacement of *n*Bu substituent in the monomer by bulky *t*Bu substituent or heteroatom-containing ClBu substituent caused the decrease of the monomer polymerizability. The polymer MW increased in the following monomer order: ClBuA < cPrA < *n*BuA < *t*BuA. [Rh(nbd)(acac)] complex applied as polymerization catalyst always showed higher efficiency in the bulk polymerizations than in the corresponding polymerizations performed in THF. This fact is manifested by values of turn over numbers (labelled as $n_{\mathrm{MU}}/n_{\mathrm{Rh}}$ in Table 4) that were significantly higher in bulk polymerizations compared to polymerizations in THF. Moreover, even the PAlkAs yields of the bulk polymerizations were 1.5 - 4 times as high as the yields of polymerizations in THF.

Comparison of results in Table 4 and Table 1 clearly shows that [Rh(nbd)(acac)] catalyst polymerized AlkAs less readily than it polymerized PhA.

Table 4: Yield of polymers, Y(P) and weight-average, (M_{w}), and number-average, (M_{n}), molecular weight of polymers in polymerization of alkylacetylenes (AlkAs) with [Rh(nbd)(acac)] complex in various solvents at room temperature. $[\mathrm{Rh(nbd)(acac)}]_0$ = 24 mmol/l, reaction time = 24 h. $n_{\mathrm{MU}}/n_{\mathrm{Rh}}$ represents the number of monomeric units incorporated into poly(alkylacetylene) chains per one molecule of submitted catalyst.

No.	**Monomer**	**Solvent**	**$[\mathrm{AlkA}]_0$ [mol/l]**	**Y(P) [%]**	**$n_{\mathrm{MU}}/n_{\mathrm{Rh}}$**	**$10^{-3}\ M_{\mathrm{w}}$**	**$10^{-3}\ M_{\mathrm{n}}$**
1	*n*BuA	THF	2.4	18	18	20	12
2	*n*BuA	bulk	8.7	28	102	27	13
3	*t*BuA	THF	2.4	5	5	47	26
4	*t*BuA	bulk	8.1	19	64	73	44
5	ClBuA	THF	2.4	6	6	3.3	1.8
6	ClBuA	bulk	8.3	15	52	7.4	3.2
7	cPrA	THF	2.4	10	10	6.0	2.0
8	cPrA	bulk	11.8	20	98	11	6.0

The system *t*BuA/[Rh(nbd)(acac)]/THF-d_8 was suitable for the ^{1}H NMR monitoring aimed at the study of the initiation stage of polymerization. This monitoring showed that *t*BuA was quite efficient in liberation of Hacac from the catalyst (f_{Hacac} = 0.71 after 24 hours). Evidently, the low polymerizability of *t*BuA is to be ascribed to the low reactivity of *t*BuA in subsequent stages of the polymerization (subsequent steps of initiation and/or propagation). The same conclusion seems to be probable also for other AlkA-containing polymerization systems from Table 4. The low polymerizability of AlkA monomers (compared to the polymerizability of PhA) may reflect the insufficient acidity of AlkAs acetylenic hydrogen for its efficient transfer in the initiation and/or propagation step of the reaction.

The results of copolymerization of *n*BuA, ClBuA and cPrA with two arylacetylenes (ArA): PhA and (4-biphenylyl)acetylene (BPhA) performed in THF under [Rh(nbd)(acac)] catalysis are summarized in Table 5. The polymerizability of BPhA in [Rh(nbd)(acac)] catalysed homopolymerization was similar to the polymerizability of PhA in the same reaction (Table 5). However, the homopolymer of BPhA, poly[(4-biphenylyl)acetylene] (PBPhA) was completely insoluble (contrary to PPhA).

Table 5: Yield of copolymers (with respect to the mass of both comonomers), *Y*(C), weight-average, (M_w), and number-average, (M_n), molecular weight of copolymers in copolymerization of alkylacetylenes (AlkA) with arylacetylenes ArA catalysed with [Rh(nbd)(acac)] complex in THF at room temperature. $[\mathrm{Rh(nbd)(acac)}]_0$ = 24 mmol/l, $[\mathrm{AlkA}]_0$ = 2.4 mol/l, $[\mathrm{ArA}]_0$ = 0.6 mol/l, reaction time = 24 h.

No.	AlkA	ArA	*Y*(C) [%]	Conversion of AlkA[a] [%]	Conversion of ArA[a] [%]	Copolymer composition -AlkA-/-ArA-	10^{-3} M_w	10^{-3} M_n
1[b]	--	PhA	~100	--	~100	0/100	300	89
2[b]	--	BPhA	91	--	91	0/100	nd[c]	nd[c]
3	*n*BuA	PhA	28	13	77	40/60	48	23
4	*n*BuA	BPhA	29	nd[c]	nd[c]	nd[c]	nd[c]	nd[c]
5	ClBuA	PhA	27	17	73	48/52	61	25
6	ClBuA	BPhA	38	20	86	48/52	93	27
7	cPrA	PhA	24	13	51	50/50	27	11
8	cPrA	BPhA	41	22	69	56/44	30	11

[a] conversion of monomer into monomeric units of copolymer
[b] homopolymerization of ArA
[c] product was insoluble

Molecular weights of soluble AlkA/ArA copolymers were always higher than molecular weights of corresponding AlkA homopolymers (compare Table 4 and Table 5). The conversion of ClBuA and cPrA in copolymerizations with BPhA was even higher than their conversion in copolymerizations with PhA (Table 5). Described copolymerizations of BPhA with either ClBuA or cPrA showed a way for incorporation of the units derived from BPhA into soluble polyacetylene chains. This approach is promissing for incorporation of other bulky-substituted and/or functionalized ArAs (forming insoluble homopolymers) into soluble polyacetylene copolymers.

^{1}H NMR spectroscopy confirmed the high microstructure uniformity with prevailing *cis-transoid* main-chains configuration for all the homopolymers prepared with [Rh(cycloolefin)(acac)] complexes. The broadening of all ^{1}H NMR signals in the spectra of copolymers reflected the random copolymeric character of the analysed samples.

4.2. Molecular weight and configurational stability of high -*cis* polyacetylenes

Ageing of two polyacetylene-type polymers, high-*cis* poly(phenylacetylene) and high-*cis* poly[(2,4-difluorophenyl)acetylene] is discussed in this chapter. Polyacetylenes were prepared by insertion polymerization of respective monomers catalysed with [Rh(cyclodiene)(acac)] complexes (discussed in the Chapter 4.1.1.). Polymer samples were aged mostly in THF solution exposed to the atmosphere and diffuse daylight. Changes in polymer MW and configurational structure were monitored by following techniques: SEC, DLS and UV-vis, FTIR, NMR and EPR spectroscopies.

Studies discussed in this chapter were focussed mainly at:

- Revealing the interconnection between *cis*-to-*trans* isomerization and oxidative degradation that proceed in the course of ageing of high-*cis* polyacetylenes in various conditions.
- Revealing the origin of significant changes in MW distribution accompanying the oxidative degradation of high-*cis* polyacetylenes.
- Evaluation of the mechanism proposed for high-*cis* poly(phenylacetylene) ageing by Percec et al.
- Evaluation of the influence of the parent polyacetylene MW on its MW and configurational stability.
- Evaluation of the power of individual techniques used for the study of polyacetylenes ageing.

4.2.1. Molecular weight and configurational stability of high-*cis* poly(phenylacetylene)

This chapter is based on the results reported in the paper:

Trhlíková O., Zedník J., Vohlídal J., Sedláček J.: Molecular weight and configurational stability of poly(phenylacetylene) prepared with Rh catalyst, Polymer Degradation and Stability, 2011; 96; 1310-1320.

Studied polymer, poly(phenylacetylene) (PPhA) (M_n = 37 000, M_w = 89 000, *cis* double bonds content = 92%), has been prepared by polymerization of PhA catalysed with [Rh(cod)(acac)]. This polymer was allowed to age in THF-d_8 in contact with the atmosphere and diffuse daylight at room temperature.

The representative SEC chromatograms recorded in the early stage of PPhA sample ageing showed the decrease in the PPhA molecular weight and formation of 1,3,5-triphenylbenzene (1,3,5-TPB) (Figure 5). The MW distribution of the sample passed through a significant maximum (the highest *Đ* value = 6.5).

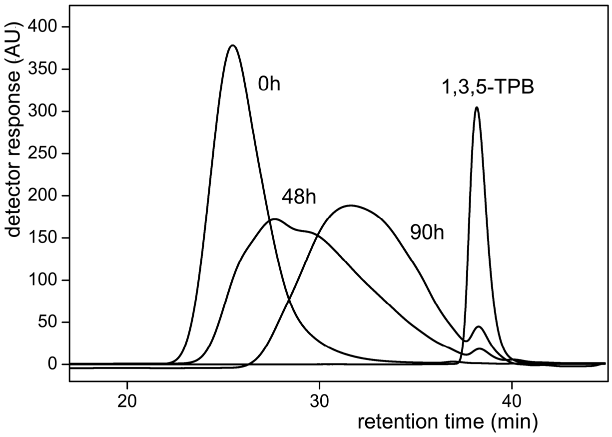


Figure 5: SEC chromatograms of PPhA aged in THF-d_8 solution for various times and SEC chromatogram of 1,3,5-triphenylbenzene (1,3,5-TPB) standard. (UV detection at 254 nm)

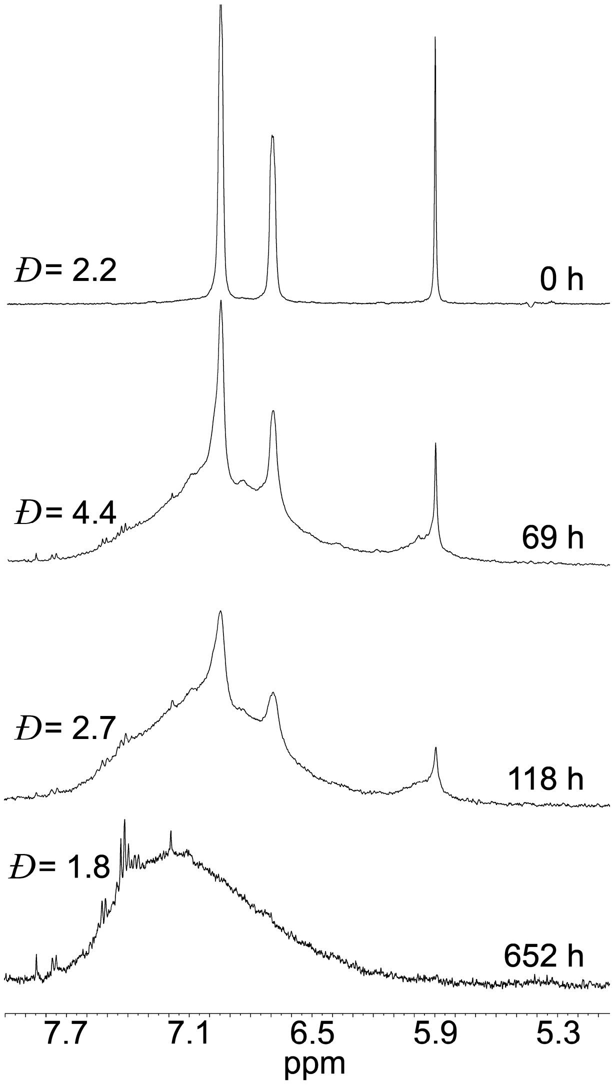


Figure 6: ^{1}H NMR spectra of PPhA (non-fractionated polymer) aged for various times in THF-d_8 solution. *Đ* is dispersity determined by SEC.

The primary results of ^{1}H NMR monitoring of PPhA ageing in THF-d_8 are shown in Figure 6. Spectrum of freshly dissolved PPhA consisted of sharp signals in region 6.7 – 7.0 ppm (aromatic protons) and a sharp singlet at 5.9 ppm (main-chain protons on the monomeric units with *cis* configuration) (Figure 6), the sharpness and good resolution of signals testify to the high degree of microstructure uniformity and predominant *cis* configuration of the main-chain double bonds. The broadening of all signals and decrease in the intensity of the signal corresponding to the main-chain proton on *cis* monomeric units caused by the *cis*-to-*trans* isomerization is obvious with the increasing ageing time (Figure 6). The SEC and ^{1}H NMR monitoring confirmed that PPhA had undergone the simultaneously proceeding oxidative degradation and *cis*-to-*trans* isomerization during the ageing in THF-d_8. Figure 6 confirms also the pass of the width of MW distribution of PPhA through a maximum in the course of polymer ageing. Detailed inspection of ^{1}H NMR spectra revealed that despite the progressive stage of isomerization (and degradation as well) the original sharp signals were still evident (spectrum t = 118 h in Figure 6). These signals disappeared completely only in the very late stage of ageing (Figure 6). This fact indicated that even in the progressive stage of ageing some sufficiently long microstructurally unperturbed *cis* sequences and/or chains were present in the system. With the aim to investigate the distribution of unperturbed sequences/chains along the MW distribution of the aged PPhA sample, a preparative MW-based fractionation of partly aged PPhA sample was performed. For this purpose, THF solution of PPhA aged for 48 hours under atmospheric conditions at room temperature was used. Characteristics of partly aged PPhA just before fractionation were: M_w= 24 000, M_n = 3 800, *cis* content ~ 50 %.

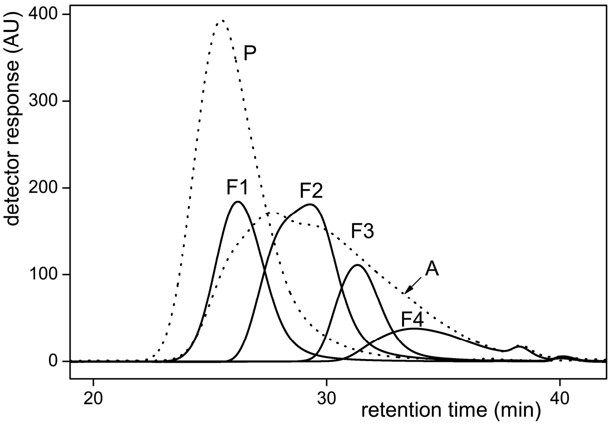


Figure 7: SEC chromatograms of: freshly dissolved parent PPhA (curve P), non-fractionated aged PPhA (curve A) and individual fractions obtained by preparative fractionation of the aged PPhA (curves F1, F2, F3 and F4). Ageing conditions: THF, t = 48 h, solution of PPhA was kept in contact with the atmosphere and diffuse daylight at room temperature.

The MW fractionation from the solvent system methanol/THF provided three polymeric fractions (F1, F2 and F3, Table 6) and one oligomeric fraction (F4, Table 6). SEC chromatograms of individual fractions are shown in Figure 7, together with chromatograms of non-fractionated PPhA recorded for t = 0 h and for t = 48 h.

Table 6: Molecular-weight and configurational characteristics of non-fractionated PPhA aged in THF-d_8 and in THF. Ageing conditions: exposure to the atmosphere and diffuse daylight, concentration in aged solution 1 mg/ml, t = 48 h. Molecular-weight and configurational characteristics of PPhA fractions obtained by fractionation of PPhA aged in THF.

Sample	MeOH/THF (V/V)	Content in wt. %[a)]	10^{-3} M_w	$Đ$	% *cis*
PPhA aged in THF-d_8 non-fractionated	-	-	18	5.8	~50
PPhA aged in THF non-fractionated	-	-	24	6.4	nd
Fraction F1	51/100	17	53	1.5	91
Fraction F2	137/100	33	15	1.8	56
Fraction F3	400/100	17	4.3	1.4	<50
Fraction F4	[b)]	nd	1.5	2.2	<50

[a)] Weight fractions of isolated F1, F2 and F3 calculated with respect to the total mass of PPhA submitted for the fractionation.
[b)] Isolated by solvents evaporation.

It is clearly seen from ^{1}H NMR spectra of individual fractions and non-fractionated PPhA aged in THF (Figure 8) that the ^{1}H NMR signals were being broadened and the signal of *cis* main-chain protons was diminishing in the intensity with decreasing MW of the fraction. The ^{1}H NMR spectrum of the highest MW fraction (F1) was identical with that of the freshly dissolved non-fractioned PPhA sample (Figure 6). Thus, despite the ageing for 48 h, the highest MW fraction consists exclusively of microstructurally unperturbed PPhA macromolecules. On the other hand, in the ^{1}H NMR spectrum of the lowest MW polymeric fraction (F3) the sharp signals of microstructurally unperturbed sequences/chains were almost absent i.e. predominantly deeply isomerized PPhA macromolecules formed the fraction F3. The fraction F2 represents “an intermediate state” between F1 and F3. The sharp signals in ^{1}H NMR spectrum of the oligomeric fraction F4 (region from 7.2 to 7.8 ppm) well corresponded to signals of 1,3,5-TPB standard (Figure 8). Thus, ^{1}H NMR spectroscopy confirmed the formation of 1,3,5-TPB in the course of PPhA ageing.

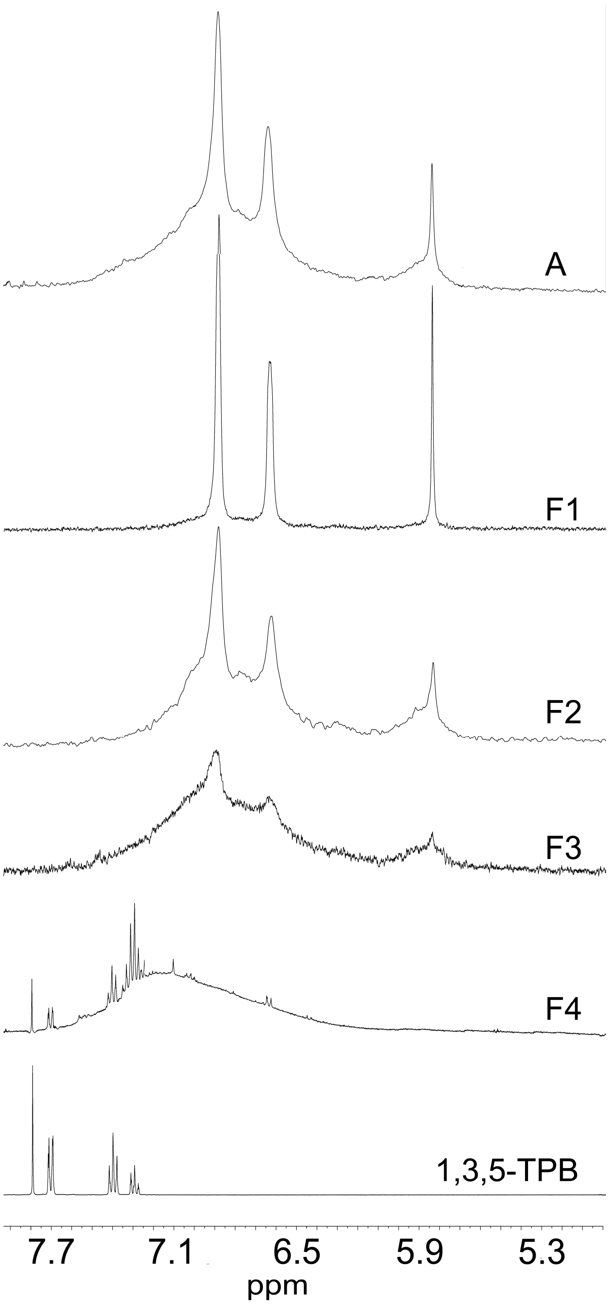


Figure 8: ^{1}H NMR spectra (in THF-d_8) of: (i) non-fractionated PPhA isolated after the ageing in THF (A), (ii) individual fractions obtained by preparative fractionation of the aged PPhA (F1, F2, F3 and F4) and (iii) 1,3,5-TPB standard. Ageing conditions: THF, t = 48 h, solution of PPhA was kept in contact with the atmosphere and diffuse daylight at room temperature.

The ^{1}H NMR analysis of PPhA fractions proved that the aged non-fractionated PPhA was not microstructurally uniform along the MW distribution and that it exhibited decrease in *cis* main-chain double bond content with decreasing MW. The same way as

^{1}H NMR spectra, also the FTIR spectra of individual fractions confirmed the decrease in content of main-chain *cis* double bonds in the order F1 > F2 > F3. Moreover, in the FTIR spectra of F2 and F3 a new weak band was distinguishable at about 1730 cm^{-1}. This band can be ascribed to carbonyl groups that are considered as products of oxidative degradation of polyacetylenes. [43;121;135]

The MW of all macromolecules of the microstructurally unperturbed fraction F1 falls well within the interval of MW values of parent PPhA. The fraction F1 can be thus interpreted as containing the parent macromolecules that survived the ageing without changes in MW and configurational structure and/or macromolecules that might be formed by degradation from the higher MW ones, however, without isomerization. The fraction F3 can be interpreted as consisting predominantly of macromolecules that were not present in the parent sample and that were formed by degradation and progressive isomerization from the higher MW ones.

The described microstructure analysis of partly aged PPhA revealed this sample to contain both deeply isomerized and microstructurally unperturbed macromolecules. We propose the following explanation for this finding: the course of *cis*-to-*trans* isomerization may be influenced by a “domino effect”, i. e. once a particular double bond of a PPhA chain is isomerized the probability of isomerization of the other double bonds of this chain is increased. This mechanism may lead to the presence of both microstructurally unperturbed and deeply isomerized macromolecules in the partly aged sample. It is evident that the content of the former ones should decrease in favour of the latter ones with the ageing time. Assuming the *cis*-to-*trans* isomerization to proceed (at least partly) via the rotational scission of the main-chain double bonds, this process should be accompanied by an increase in the content of unpaired electrons on the isomerized PPhA chains. [95;96;101;102;136;137] The isomerized PPhA macromolecules should be thus more prone to the oxidative degradation in comparison to the high-*cis* microstructurally unperturbed macromolecules with a lower unpaired electron content. The difference in rates of degradation of microstructurally unperturbed and isomerized PPhA macromolecules can be considered as responsible for (i) the non-uniform distributions of these two kinds of macromolecules along the MW distribution of the partly aged sample and (ii) broadening of the MW distribution in the initial stage of ageing. Because of the low MW-stability, the deeply isomerized macromolecules rapidly degrade and thus predominate in the lower MW fractions of the partly aged sample while the highest MW fraction of this sample consists of microstructurally unperturbed high-*cis* macromolecules that are more degradation-resistant.

As already discussed, the ageing of (non-fractionated) high-*cis* PPhA was accompanied by formation of symmetrical cyclotrimer, 1,3,5-TPB. The formation of 1,3,5-TPB was observed also if the PPhA fractions F1 and F3 were separately submitted to the ageing experiments in which they were allowed to age in THF-d_8 solution exposed to the atmosphere and diffuse daylight at room temperature. The amount of 1,3,5-TPB formed during the ageing of PPhAs (parent non-fractioned sample and fractions F1 and F3) was quantified on the base of the precise SEC detector calibration. For the evaluation of changes in PPhA/1,3,5-TPB composition of the sample during its ageing the parameters $(w_{\mathrm{TPB}})_{\mathrm{t}}$, $(x_{\mathrm{TPB}})_{\mathrm{t}}$ and $(x_{\mathrm{M}})_{\mathrm{t}}$ were defined by Equations 12 - 14.

$$(w_{\mathrm{TPB}})_{\mathrm{t}} = \frac{(m_{\mathrm{TPB}})_{\mathrm{t}}}{(m_{\mathrm{M}})_{0}} \qquad \text{Equation 12}$$

$$(x_{\mathrm{TPB}})_{\mathrm{t}} = \frac{(n_{\mathrm{TPB}})_{\mathrm{t}}}{(n_{\mathrm{M}})_{0}} = \frac{(w_{\mathrm{TPB}})_{\mathrm{t}}(M_{\mathrm{n}})_{0}}{(M_{\mathrm{TPB}})} \qquad \text{Equation 13}$$

$$(x_{\mathrm{M}})_{\mathrm{t}} = \frac{[(n_{\mathrm{M}})_{\mathrm{t}} - (n_{\mathrm{M}})_{0}]}{(n_{\mathrm{M}})_{0}} = \left[\frac{(M_{\mathrm{n}})_{0}}{(M_{\mathrm{n}})_{\mathrm{t}}}\right][1 - (w_{\mathrm{TPB}})_{\mathrm{t}}] - 1 \qquad \text{Equation 14}$$

$(m_{\mathrm{M}})_0$ is the original mass of PPhA at $t = 0$, $(m_{\mathrm{TPB}})_{\mathrm{t}}$ is the mass of 1,3,5-TPB found at time t, $(M_{\mathrm{n}})_0$ and $(M_{\mathrm{n}})_{\mathrm{t}}$ are the number-average molecular weight of PPhA for $t = 0$ and for a given time t, respectively, M_{TPB} is the relative molecular weight of 1,3,5-TPB (M_{TPB} = 306,41), $(n_{\mathrm{TPB}})_{\mathrm{t}}$ is the amount of 1,3,5-TPB molecules in the sample aged for time t, $(n_{\mathrm{M}})_0$ and $(n_{\mathrm{M}})_{\mathrm{t}}$ are the amounts of PPhA macromolecules of various lengths in the sample at $t = 0$ and at a given ageing time t, respectively. Parameter $(w_{\mathrm{TPB}})_{\mathrm{t}}$ represents the weight fraction of 1,3,5-TPB in the aged sample. Parameters $(x_{\mathrm{TPB}})_{\mathrm{t}}$ and $(x_{\mathrm{M}})_{\mathrm{t}}$ have the meaning of increase [relative to $(n_{\mathrm{M}})_0$] in amount of substance of 1,3,5-TPB molecules and PPhA macromolecules, respectively.

The SEC monitoring revealed that in the case of all studied samples (parent non-fractioned PPhA and fractions F1 and F3) about 2 wt. % of PPhA submitted to the ageing was transformed into 1,3,5-TPB at the terminal stage of ageing experiment (t =

1000 h). The ageing time dependence of $(x_{TPB})_t$ and $(x_M)_t$ parameters are shown in Figure 9 (the non-fractioned high-*cis* PPhA) and in Figure 10 (*cis*/*trans* fraction F3). Figures 9 and 10 show that the values of $(x_{TPB})_t$ were about twenty times lower than corresponding values of $(x_M)_t$ in the whole period of experiment and that the $(x_M)_t/(x_{TPB})_t$ ratio did not depend on the *cis* double bonds content in the sample submitted for the ageing.

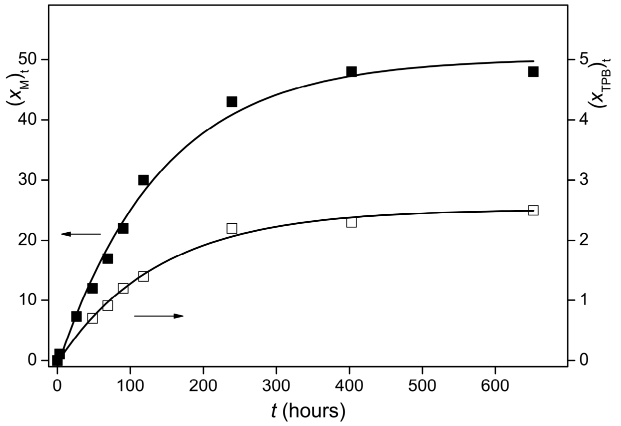


Figure 9: Ageing time dependencies of composition parameters $(x_{TPB})_t$ and $(x_M)_t$. Sample submitted for the ageing: parent non-fractioned PPhA, $(M_n)_0$ = 37 000 $(M_w)_0$ = 89 000. For $(x_{TPB})_t$ and $(x_M)_t$ definition see Equations 13 and 14.

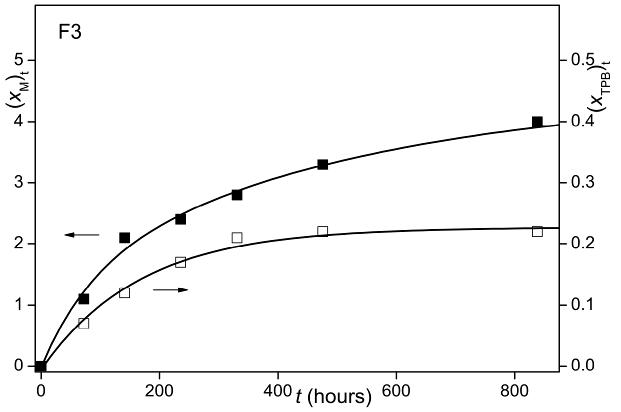


Figure 10: Ageing time dependencies of composition parameters $(x_{TPB})_t$ and $(x_M)_t$. Sample submitted for the ageing: PPhA fraction F3, $(M_n)_0$ = 3 100 $(M_w)_0$ = 4 300, see Table 6. For $(x_{TPB})_t$ and $(x_M)_t$ definition see Equations 13 and 14.

We discussed the observed relation $(x_{TPB})_t << (x_M)_t$ from the point of view of the mechanism proposed by Percec et al. for the degradation of high-*cis* PPhAs. The mechanism of Percec [99;126] assumes the intramolecular cyclization of a PPhA chain followed by the chain cleavage with the release of a 1,3,5-TPB molecule. If the chain cleavage proceeded exclusively via this mechanism the formation of each new PPhA macromolecule should be accompanied by a formation of one 1,3,5-TPB molecule (in other words, the values of parameters $(x_{\mathrm{M}})_{\mathrm{t}}$ and $(x_{\mathrm{TPB}})_{\mathrm{t}}$ should be equal). The non-equality $(x_{\mathrm{TPB}})_{\mathrm{t}} << (x_{\mathrm{M}})_{\mathrm{t}}$ found in our study indicates that the PPhA degradation (under the conditions of our study) may obey this mechanism only partly. Either only a small part (up to 8 %) of particular PPhA chains cleavages simultaneously gave rise to 1,3,5-TPB molecules or 1,3,5-TPB was formed independently.

4.2.2. SEC/DAD and ^{1}H NMR study of molecular weight and configurational stability of poly[(2,4-difluorophenyl)acetylene] and poly(phenylacetylene) prepared with Rh catalyst

This chapter is based on the results reported in the paper:

Trhlíková O., Zedník J., Vohlídal J., Sedláček J.: SEC/DAD and ^{1}H NMR study of molecular weight and configurational stability of poly[(2,4-difluorophenyl)acetylene] and poly(phenylacetylene) prepared with Rh catalyst, Macromolecular Chemistry and Physics, 2011; 212; 1987-1998.

When the detailed ageing study of high-*cis* PPhA dissolved in THF and THF-d_8 kept in contact with the atmosphere and diffuse daylight was done (see Chapter 4.2.1.), the idea had arisen to study the time course of ageing also for a more stable derivative of PPhA. Based on the results published recently by our group [43] we have proposed and prepared a new high-*cis* poly[(2,4-difluorophenyl)acetylene] (PdFPhA). Preliminary experiments showed that this polymer exhibited (i) an increased stability (owing to the F substituent in the ortho position on the Ph ring) and (ii) good solubility (supported by the F substituent in the para position on the Ph ring). By a proper selection of Rh catalyst and solvent, similar MW characteristics of newly prepared parent high-*cis* PdFPhA were obtained as those reported for high-*cis* PPhA in the previous Chapter 4. 2.1. This allowed us to reliably compare the behaviour of high-*cis* PdFPhA and high-*cis* PPhA in the course of their ageing. This comparison is the main subject of this chapter. For the clarity of this comparison some data on the PPhA ageing (given already in the previous Chapter 4.2.1.) had to be repeated also in this Chapter.

Samples of high-*cis* PdFPhA ($(M_w)_0$= 120 000, $(M_n)_0$ = 60 000, $C_{\text{high-cis}}$ = 92 %) prepared with [Rh(cod)(acac)] in CH_2Cl_2 and high-*cis* PPhA ($(M_w)_0$= 89 000, $(M_n)_0$ = 37 000, $C_{\text{high-cis}}$ = 92 %) prepared with [Rh(cod)(acac)] in THF were allowed to age separately in THF-d_8 in contact with the atmosphere and diffuse daylight at room temperature under monitoring by SEC/DAD and ^{1}H NMR techniques. Two facts are obvious from the representative SEC chromatograms recorded in the course of ageing for both polymers: (i) the decrease in the polymers MW due to the degradation and (ii) passage of the width of MW distribution through the significant maximum (for PdFPhA see Figure 11 and for PPhA see Figure 12).

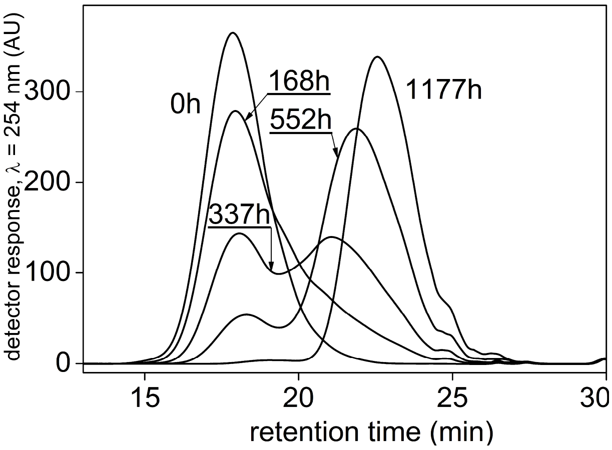


Figure 11: SEC chromatograms of PdFPhA aged in THF-d_8 solution for various times (in hours). Solution of PdFPhA was kept in contact with the atmosphere and diffuse daylight at room temperature during the ageing.

In the case of PdFPhA ageing (contrary to PPhA ageing) the original unimodal MW distribution was gradually transformed into the bimodal one (middle period of ageing) and the bimodal distribution was reconverted back to the unimodal one positioned at a higher retention time, t_{ret}, (late stage of ageing).

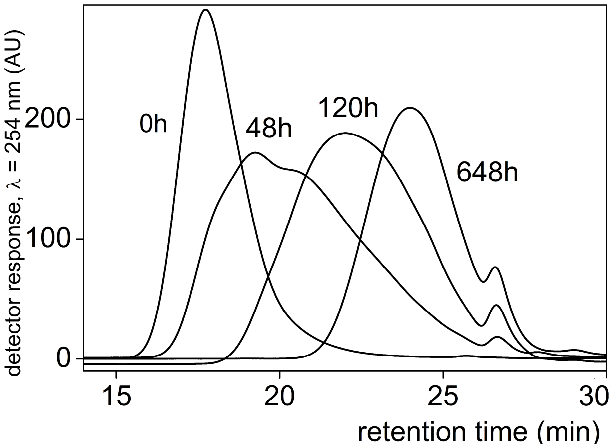


Figure 12: SEC chromatograms of PPhA aged in THF-d_8 solution for various times (in hours). Solution of PPhA was kept in contact with the atmosphere and diffuse daylight at room temperature during the ageing.

The rate of degradation was considerably slowed down (compare Figures 11 and 12) and the position of maximum of *Đ* vs. *t* dependence was shifted to the higher ageing time in the case of PdFPhA compared to PPhA (Figure 13). The maximal values of *Đ* determined in the course of ageing were similar for both samples (*Đ* = 7.5 for PdFPhA and *Đ* = 6.3 for PPhA, Figure 13).

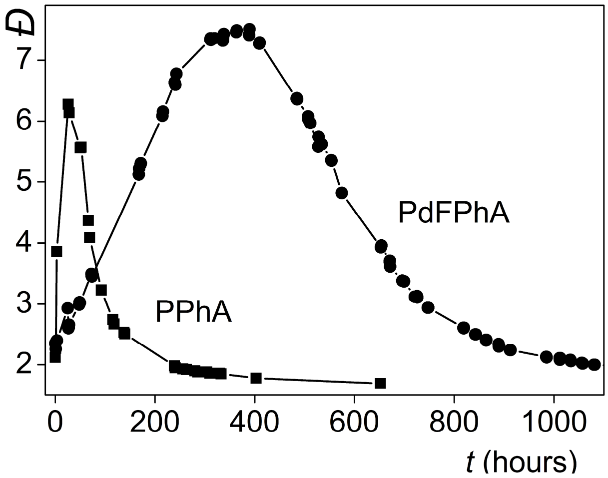


Figure 13: Ageing time dependencies of dispersity *Đ* resulting from the experiments in which PdFPhA and PPhA (dissolved in THF-d_8) were allowed to age (separately) in contact with the atmosphere and diffuse daylight at room temperature.

^{1}H NMR spectrum of freshly dissolved PdFPhA (Figure 14) consisted of well resolved multiplet in the region 6.70 – 6.60 ppm (aromatic protons of pendant 2,4-difluorophenyls) and a singlet at 5.75 ppm (main-chain protons with *cis* configuration). As already discussed in Chapter 4.2.1., the ^{1}H NMR spectrum of freshly dissolved PPhA (Figure 15) consisted of well resolved multiplet in the region 7.00 – 6.70 ppm (aromatic protons) and a singlet at 5.90 ppm (main-chain protons with *cis* configuration). Sharpness and good resolution of signals testify to the high degree of microstructure uniformity of both polymers.

In the course of ageing the following continuous changes in ^{1}H NMR spectra of PdFPhA and PPhA were observed: broadening of all signals, decrease in the intensity of the signal corresponding to the main-chain protons on *cis* monomeric units (*cis*-to-*trans* isomerization) and appearance of small sharp signals in the region of 7.9 – 7.0 ppm (oligomeric products).

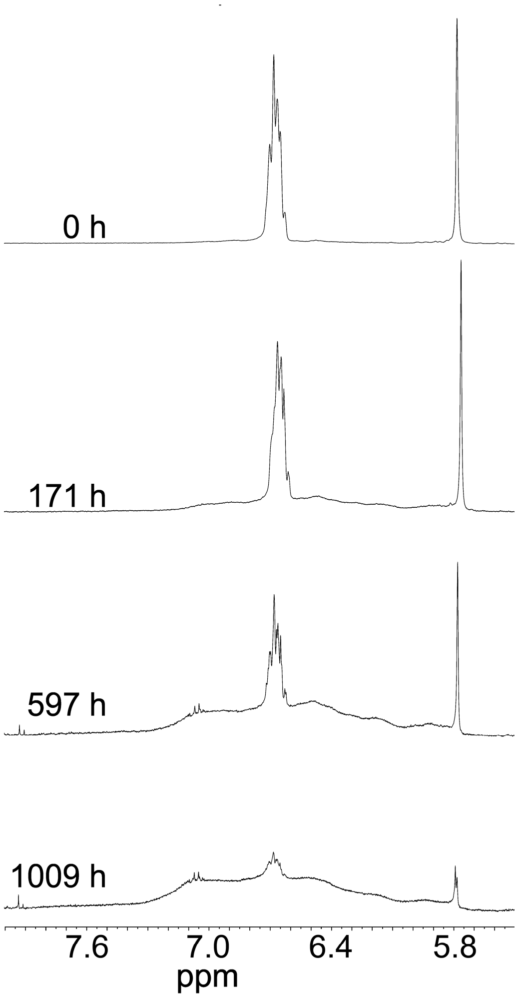


Figure 14: ^{1}H NMR spectra of PdFPhA aged for various times (in hours) in THF-d_8 solution. Solution of PdFPhA was kept in contact with the atmosphere and diffuse daylight at room temperature.

Detail inspection of ^{1}H NMR spectra revealed that despite of the progressive stage of ageing the parent sharp signals including those of *cis* main-chain protons had been still persisted in ^{1}H NMR spectra of both samples (diminished in the intensity). The sharp signals disappeared completely only in the case of long-time aged PPhA (t > 300 h) (Figure 15), in the case of PdFPhA, the sharp signals were apparent in the spectrum even after 1000 h of ageing (Figure 14). This fact indicated that even in the progressive stage of ageing some sufficiently long microstructurally unperturbed *cis* chains (denoted as “high-*cis*”) had been present in both samples. The continuous broadening of parent signals of main-chain protons in the spectra of both samples indicated the gradual formation of chains containing randomly distributed *cis* and *trans* main-chain double bonds (denoted as “*cis*/*trans*”).

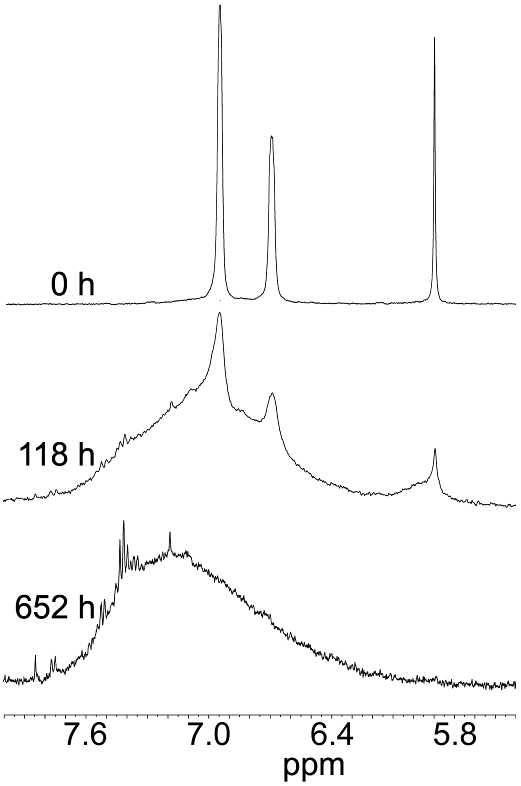


Figure 15: ^{1}H NMR spectra of PPhA aged for various times (in hours) in THF-d_8 solution. Solution of PPhA was kept in contact with the atmosphere and diffuse daylight at room temperature.

The integration of ^{1}H NMR spectra recorded in the course of PdFPhA and PPhA ageing allowed determining the ageing time dependencies of content of *cis* double bonds in high-*cis* chains, i.e. the parameter $C_{\text{high-cis}}$ defined by Equation 3 (see Introduction). Comparison of the ageing time dependencies of $C_{\text{high-cis}}$ for PdFPhA and PPhA ageing in THF-d_8 reveals that the process of *cis*-to-*trans* isomerization was significantly slower for PdFPhA compared to PPhA (Figure 16). Evidently, the higher MW stability of PdFPhA was accompanied by an enhanced stability of the configurational structure of this polymer.

The distribution of high-*cis* and *cis*/*trans* chains (along the MW distribution) in partly aged PdFPhA and PPhA samples was revealed by means of the preparative fractionation. For the more precise description of this approach see Chapter 4.2.1. Samples partly aged in THF were submitted for this fractionation (PdFPhA ageing time 240 h and PPhA ageing time 48 h). Both samples had similarly broad MW distributions before the fractionation as it is evident from Table 7.

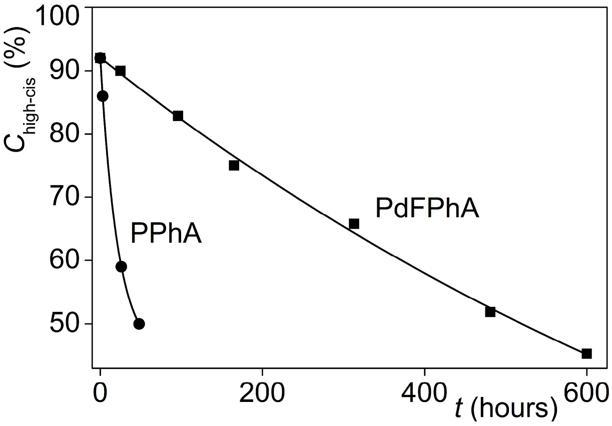


Figure 16: Ageing time dependencies of parameter $C_{\text{high-cis}}$ resulting from the experiments in which PdFPhA and PPhA (dissolved in THF-d_8) were allowed to age in contact with the atmosphere and diffuse daylight at room temperature. $C_{\text{high-cis}}$ – the content of monomeric units in high-*cis* chains determined by ^{1}H NMR. For $C_{\text{high-cis}}$ definition see Equation 3, in Introduction.

Two fractions resulting from the fractionation of each PdFPhA and PPhA samples are reported in Table 7: the low-MW fractions (labelled $F_{L(PdFPhA)}$ and $F_{L(PPhA)}$, respectively) and the high-MW fractions (labelled $F_{H(PdFPhA)}$ and $F_{H(PPhA)}$, respectively). SEC chromatograms of PdFPhA fractions, aged non-fractionated PdFPhA and parent freshly dissolved PdFPhA are shown in Figure 17, part I. SEC chromatograms of PPhA fractions, aged non-fractionated PPhA and parent freshly dissolved PPhA are shown in Figure 18, part I. The MW characteristics and $C_{\text{high-cis}}$ values of PdFPhA and PPhA fractions are summarized in Table 7.

Table 7: MW characteristics and content of monomeric units in high-*cis* chains (according to Equation 3, in Introduction) for PdFPhA (aged for 240 h) and PPhA (aged for 48 h) and for fractions isolated from partly aged polymers.

Sample	10^{-3} M_w	*Đ*	$C_{\text{high-cis}}$ (in %)
PdFPhA - aged	71	6.5	79
$F_{H(PdFPhA)}$	75	2.3	96
$F_{L(PdFPhA)}$	5.0	1.7	<50
PPhA - aged	18	5.8	~50
$F_{H(PPhA)}$	53	1.5	91
$F_{L(PPhA)}$	4.3	1.4	<50

The ^{1}H NMR spectra of individual polymer fractions and non-fractionated aged polymers are given in Figure 17 part II (PdFPhA) and in Figure 18, part II (PPhA).

Figures 17 and 18 revealed that the distribution of high-*cis* and *cis*/*trans* chains along the MW distribution of partly aged PdFPhA and PPhA had not been uniform. The ^{1}H NMR spectra obtained for $F_{H(PdFPhA)}$ and $F_{H(PPhA)}$ were nearly identical with those of the freshly dissolved non-fractioned PdFPhA and PPhA, respectively (Figures 14 and 15). Thus, despite of the ageing in THF, $F_{H(PdFPhA)}$ and $F_{H(PPhA)}$ consisted predominantly of microstructurally unperturbed high-*cis* macromolecules.

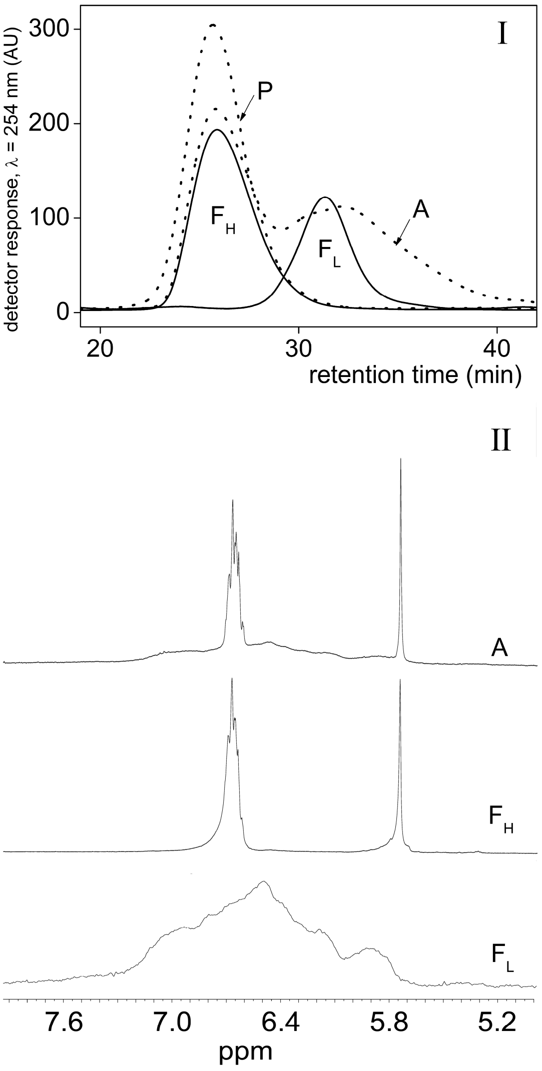


Figure 17: **(Part I)** SEC chromatograms of: freshly dissolved parent PdFPhA (curve P), non-fractionated aged PdFPhA (curve A) and two fractions obtained by preparative fractionation of the aged PdFPhA (curves F_H – high-MW fraction and F_L – low-MW fraction). **(Part II)** ^{1}H NMR spectra (in THF-d_8) of non-fractionated PdFPhA isolated after the ageing in THF, A, and fractions F_H and F_L. Ageing conditions: THF, t = 240 h, solution of PdFPhA was kept in contact with the atmosphere and diffuse daylight at room temperature.

On the other hand, in the ^{1}H NMR spectra of $F_{L(PdFPhA)}$ and $F_{L(PPhA)}$ the sharp signals of microstructurally unperturbed sequences/chains were absent, i.e. the $F_{L(PdFPhA)}$ and $F_{L(PPhA)}$ fractions consisted predominantly of deeply isomerized *cis*/*trans* macromolecules of PdFPhA and PPhA, respectively. The mechanism has been proposed in Chapter 4.2.1. explaining the non-uniform distribution of high-*cis* and *cis*/*trans* chains along the MW distribution of the partly aged PPhA. The same non-uniform distribution of high-*cis* and *cis*/*trans* chains along the MW distribution was revealed in the partly aged PdFPhA despite the enhanced MW and configurationl stability of this polymer (compared to PPhA). Evidently, the acceleration of the oxidative degradation by the preceding *cis*-to-*trans* isomerization (see Chapter 4.2.1.) plays an important role in the course of ageing of both polymers under study.

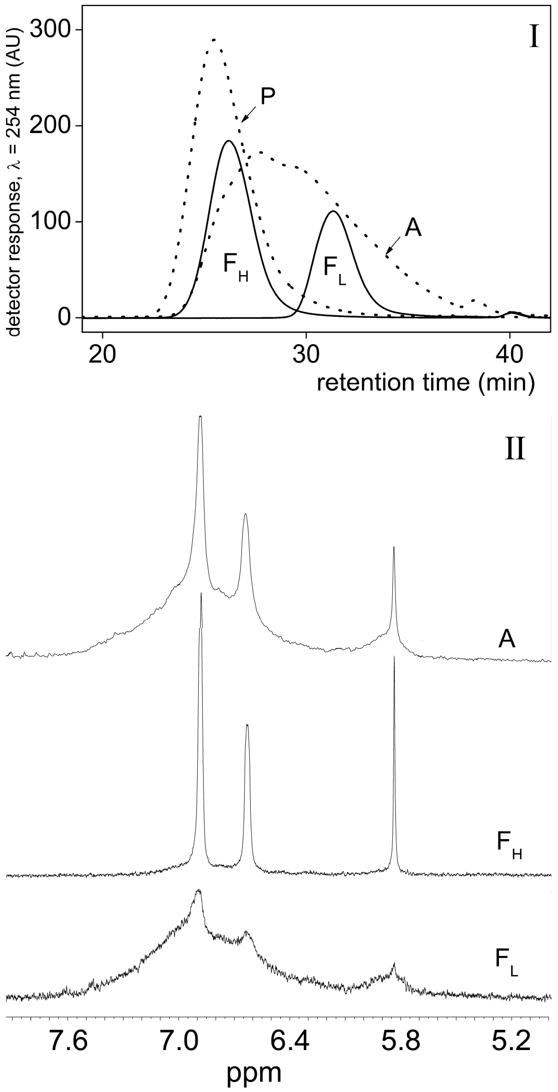


Figure 18: **(Part I)** SEC chromatograms of: freshly dissolved parent PPhA (curve P), non-fractionated aged PPhA (curve A) and two fractions obtained by preparative

fractionation of the aged PPhA (curves F_H – high-MW fraction and F_L – low-MW fraction). **(Part II)** ^{1}H NMR spectra (in THF-d_8) of non-fractionated PPhA isolated after the ageing in THF, A, and fractions F_H and F_L. Ageing conditions: THF, t = 48 h, solution of PPhA was kept in contact with the atmosphere and diffuse daylight at room temperature.

SEC/DAD technique used for this study provided not only the standard SEC chromatograms (reported here as UV detector response at 254 nm vs. retention time, t_{ret}) but allowed also the monitoring of UV/vis spectra along the MW distribution of a SEC-fractionated polymer sample. A possible depiction of SEC/DAD results is given in Figures 19 and 20. The insert part of each figure shows the standard SEC chromatogram and the main part of each figure provides UV/vis spectra of several SEC fractions of analysed polymer. The curve labelled M expresses the dependence of the wavelength of absorption maximum in the vis region, λ_{max}, on t_{ret} and was accessible only for fractions with distinguishable absorption maximum in the vis region. Curve labelled E expresses the dependence of the wavelength of absorption edge, λ_{edge}, on t_{ret}.

UV/vis spectra of PdFPhA and PPhA always consisted of a UV band with maximum at about 250 nm (absorption of pendant Ph groups) and a broad UV/vis band in the wavelength region from 300 to 600 nm (π-π* transition in the conjugated main chains). The former band was almost independent on the ageing time of a sample and on the MW of the analysed SEC fractions. Thus, only the changes in the vis part of spectra are discussed in the subsequent paragraphs.

There are two simultaneous processes proceeding in the course of ageing of PdFPhA and PPhA in THF-d_8: degradation and *cis*-to-*trans* isomerization. The degradation proceeding by itself leads to a shortening of the main chains resulting in the reduction of the main-chain conjugation. This should be manifested by a blue shift in the vis spectrum providing that the degree of polymerization of macromolecules formed by degradation is comparable to the effective conjugation length of studied polymer. Isomerization proceeding by itself should lead to formation of more conjugated *cis/trans* main-chain sequences that should be manifested by a red shift in the vis spectrum. [95;96;101;102;136]

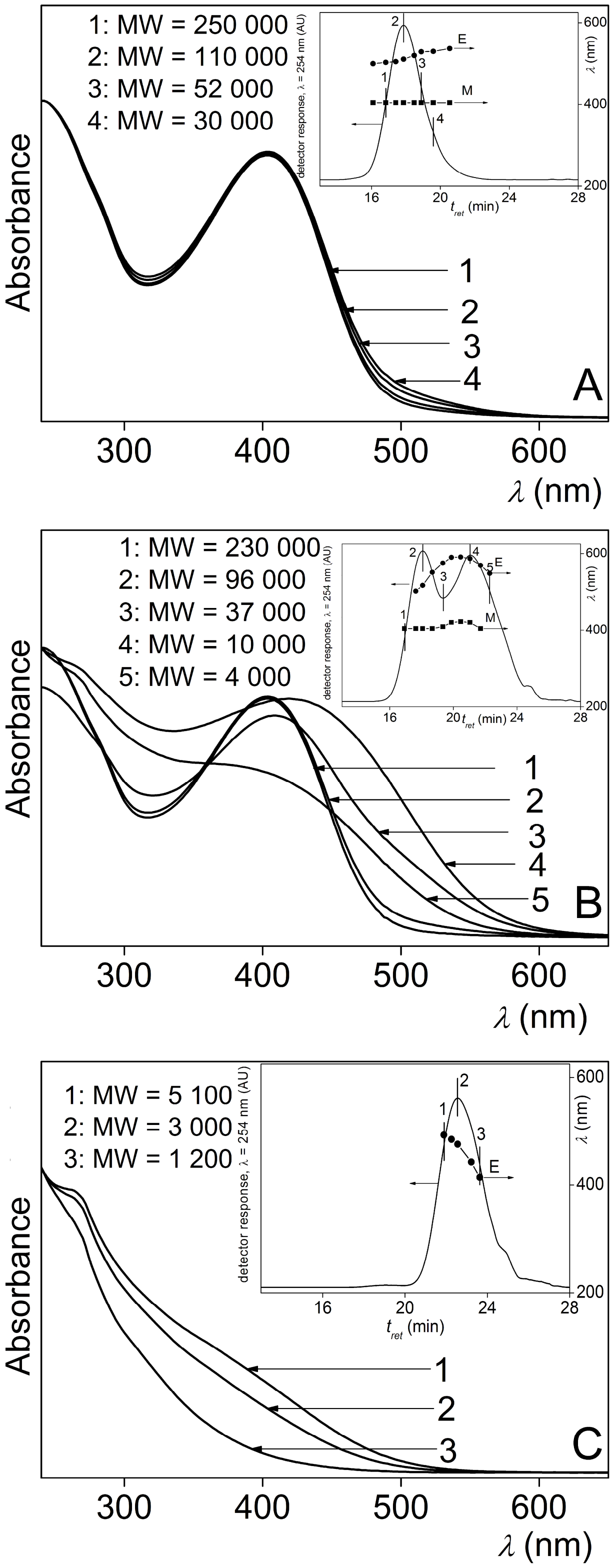


Figure 19: SEC/DAD results obtained for PdFPhA aged in THF-d_8 for: 0 h (A), 337 h (B) and 1177 h (C). The solution of PdFPhA was kept in contact with the atmosphere and diffuse daylight at room temperature in the course of ageing. UV/vis spectra are labelled with PdFPhA MW. Each series of UV/vis spectra is completed with SEC chromatogram recorded at 254 nm; curve M - dependence of the wavelength of

absorption maximum in the vis region on t_{ret} and curve E - dependence of the wavelength of absorption edge on t_{ret}.

Results for almost microstructurally uniform high-*cis* (freshly dissolved) PdFPhA are shown in Figure 19A. The values of λ_{max} were not influenced by MW of analysed fractions (λ_{max} = 404 nm resulted for MW ranging from 15 000 to 450 000). The values of λ_{edge} exhibited a slight red shift with decreasing MW that indicated the presence of a small amount of *cis*/*trans* chains in low-MW fractions of the analysed sample. Figure 19B shows the results of partly aged PdFPhA for which a bimodal SEC chromatogram was obtained. As evident, both λ_{max} vs. t_{ret} and λ_{edge} vs. t_{ret} dependencies passed through maxima. While for the fraction corresponding to the apex of high-MW SEC peak (MW = 230 000) values of λ_{max} = 404 nm and λ_{edge} = 502 nm were determined, for the fraction corresponding to the apex of low-MW SEC peak (MW = 10 000) values of λ_{max} = 422 nm and λ_{edge} = 587 nm resulted. The described finding evidently reflected the microstructural non-uniformity of the partly aged PdFPhA that has already been shown by ^{1}H NMR spectroscopy. The higher-MW part of sample in Figure 19B consisted of high-*cis* macromolecules, the lower MW part of sample contained predominantly isomerized *cis/trans* macromolecules. The increase in conjugation of the isomerized *cis/trans* macromolecules (compare to high-*cis* ones) evidently overwhelmed the decrease in conjugation due to the shortening of the length of these macromolecules. Figure 19C shows the SEC/DAD results for deeply isomerized low-MW PdFPhA sample (aged for 1177 h). Results reflected just the decrease in conjugation due to the decrease in MW.

The results for almost microstructurally uniform high-*cis* PPhA (Figure 20A) showed a marginal blue shift of the vis band with decreasing MW of fractions. The blue shift of vis band with decreasing MW of fractions was pronounced for PPhA aged for 26 h in THF-d_8 (Figure 20B). Nevertheless, an imperceptible maximum appeared on the E curve. For the higher ageing times only pronounced monotonous blue shift of the vis band with decreasing MW of SEC fraction was observed accompanied by disappearance of vis band maximum. The character of vis spectra of PPhA was thus predominantly governed by the polymer MW while the configurational structure played a marginal role in this case.

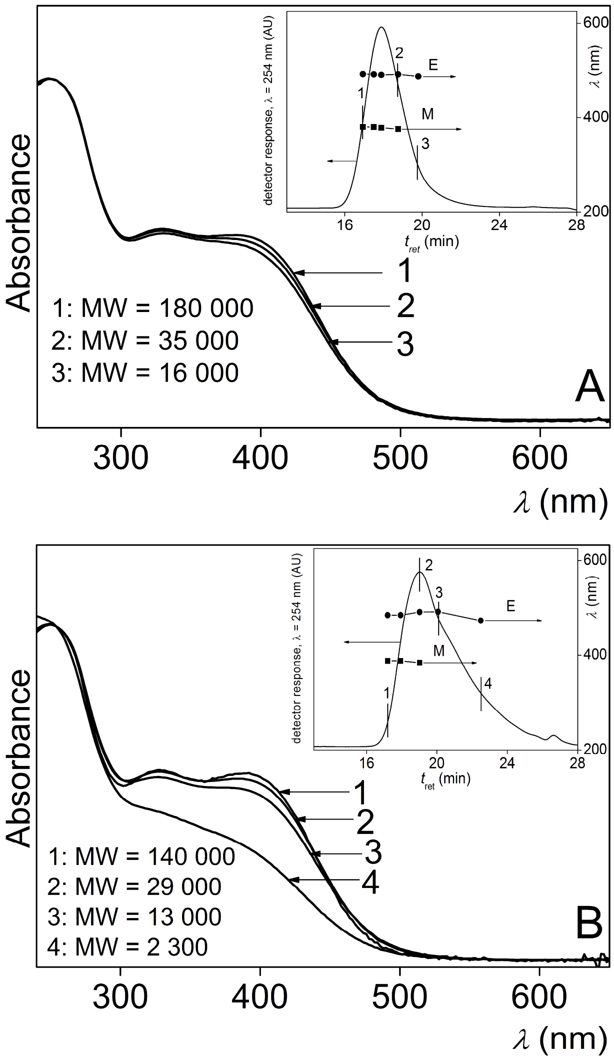


Figure 20: SEC/DAD results obtained for PPhA aged in THF-d_8 for: 0 h (A) and 26 h (B). The solution of PPhA was kept in contact with the atmosphere and diffuse daylight at room temperature in the course of ageing. UV/vis spectra are labelled with PPhA MW. Each series of UV/vis spectra is completed with SEC chromatogram recorded at 254 nm; curve M - dependence of the wavelength of absorption maximum in the vis region on t_{ret} and curve E - dependence of the wavelength of absorption edge on t_{ret}.

The described successful application of SEC/DAD technique for the study of PdFPhA microstructure shows this technique as a potential powerful tool for the monitoring of structural differences along the MW distribution also in the case of other conjugated (coloured) polymers.

4.2.3. Degradation and *cis*-to-*trans* isomerization of poly[(2,4-difluorophenyl)acetylene]s of various initial molecular weight: SEC, NMR, DLS and EPR study

This chapter is based on the results reported in the paper:

Trhlíková O., Zedník J., Matějíček P., Horáček M., Sedláček J.: Degradation and *cis*-to-*trans* isomerization of poly[(2,4-difluorophenyl)acetylene]s of various initial molecular weight: SEC, NMR, DLS and EPR study, Polymer Degradation and Stability; DOI: 10.1016/j.polymdegradstab.2013.05.020.

Ageing of poly[(2,4-difluorophenyl)acetylene]s of various initial molecular weight in THF-d_8 solution

Proper selection of (i) catalysts of the general formula [Rh(cycloolefin)(acac)] and (ii) polymerization solvents [138] enabled us to synthesize poly[(2,4-difluorophenyl)acetylene]s (PdFPhA(H), PdFPhA(M) and PdFPhA(L)) with initial weight-average molecular weight, $(M_w)_0$, ranging from 2.2x10^4 to 9.7x10^5 (Table 8). Sharpness and good resolution of ^{1}H NMR signals testified to the high degree of microstructure uniformity and prevailingly *cis* configuration of the main-chain double bonds of all prepared polymers.

Table 8: Yields of PdFPhA, Y(P), initial weight-averages molecular weight, $(M_w)_0$ and initial number-averages molecular weight, $(M_n)_0$, achieved in polymerization of dFPhA with Rh-based catalysts. Initial concentration of monomer, $[dFPhA]_0$ = 0.6 mol/l, initial concentration of Rh-based catalyst, $[Rh]_0$ = 6.0 mmol/l, room temperature, reaction time 3 hours, $C_{high\text{-}cis}$ – content of monomeric units in high-*cis* chains of PdFPhA.

Catalyst	Solvent	Y(P) %	10^{-3} $(M_w)_0$	10^{-3} $(M_n)_0$	$C_{high\text{-}cis}$ %	Polymer code
[Rh(nbd)(acac)]	THF	60	970	100	90	PdFPhA(H)
[Rh(cod)(acac)]	CH_2Cl_2	87	120	60	92	PdFPhA(M)
[Rh(cot)(acac)]	CH_2Cl_2	50	22	11	90	PdFPhA(L)

PdFPhAs were allowed to age separately in THF-d_8 (or THF) in contact with the atmosphere and diffuse daylight at room temperature (or 50°C). ^{1}H NMR spectra confirmed the *cis*-to-*trans* isomerization during the samples ageing in THF-d_8 solution (Figure 21) (discussed in previous chapters). Figure 21 allows a qualitative conclusion that the extent of ^{1}H NMR spectra changes (for a given ageing time) increased with increasing MW of the parent sample in the order: PdFPhA(H) > PdFPhA(M) > PdFPhA(L).

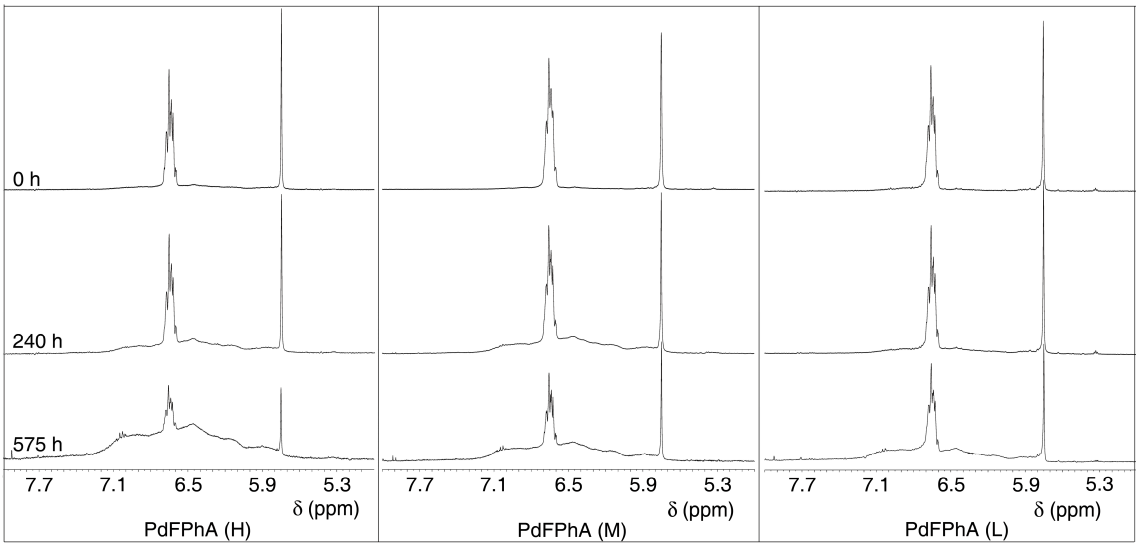


Figure 21: Representative ^{1}H NMR spectra of PdFPhA(H), PdFPhA(M) and PdFPhA(L) aged for 0, 240 and 575 hours in THF-d_8 solution. Solutions of polymers were kept in contact with the atmosphere and diffuse daylight at room temperature.

The representative SEC chromatograms recorded in the course of ageing confirmed the decrease in polymer MW due to the degradation (Figure 22A, 22B and 22C). In the case of PdFPhA(H) and PdFPhA(M), the original unimodal MW distribution was gradually transformed into the bimodal one (74 h for PdFPhA(H) and 240 h for PdFPhA(M), Figures 22A and 22B). On the other hand, only a slight indication of bimodality of MW distribution was observed during the ageing of PdFPhA(L) (Figure 22C).

SEC chromatograms of all progressively aged PdFPhAs contained two peaks in the low-MW region. The first one corresponded to the solvent peak (Figure 22, labelled S). The retention time of the second one (a shoulder to the main peak) corresponded to that of 1,3,5-tris(2,4-difluorophenyl)benzene standard (verified by SEC analysis). We estimated the content of 1,3,5-tris(2,4-difluorophenyl)benzene in the aged PdFPhA samples to be around 1 wt. % in the terminal stage of ageing.

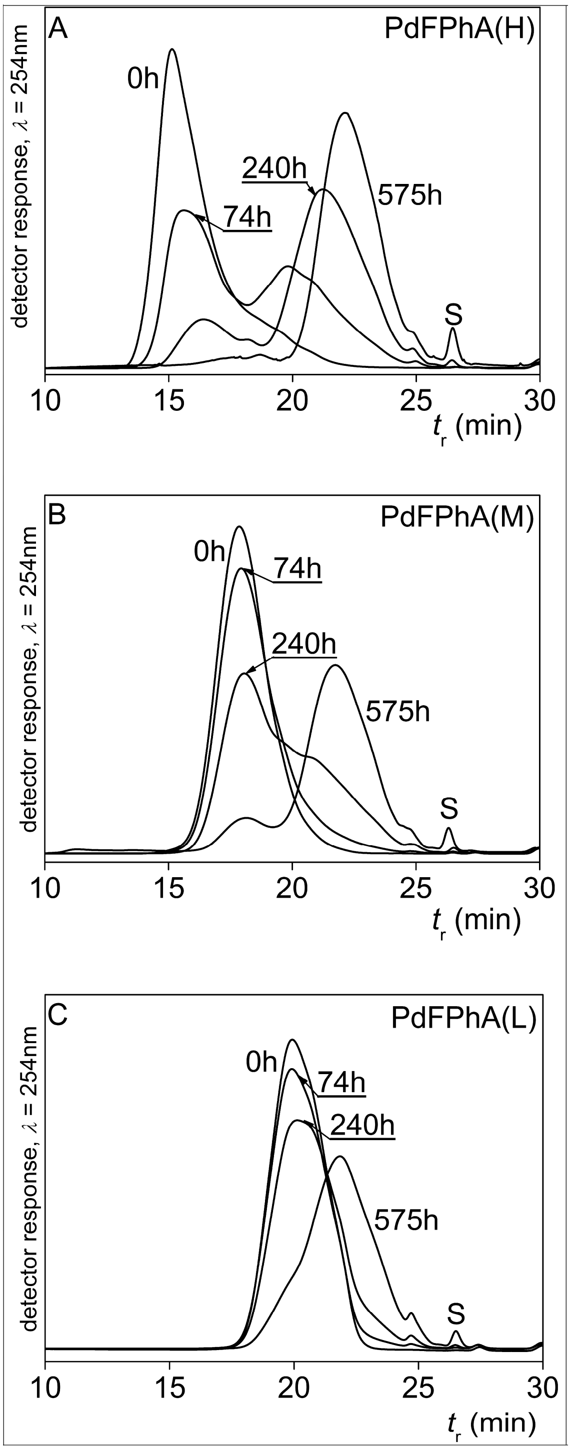


Figure 22: The representative SEC chromatograms of PdFPhA(H) (part A), PdFPhA(M) (part B) and PdFPhA(L) (part C) aged in THF-d_8 solutions for 0, 74, 240 and 575 hours. Solutions of polymers were kept in contact with the atmosphere and diffuse daylight at room temperature during the ageing. S denotes the solvent peak.

The integration of ^{1}H NMR spectra recorded in the course of PdFPhAs ageing in THF-d_8 solution allowed us to determine the ageing time dependence of the content of *cis* double bonds in high-*cis* chains, $C_{\text{high-cis}}$, (see Equation 3, in Introduction and also Chapter 4.2.2.). Values of $C_{\text{high-cis}}$ obtained for the freshly dissolved PdFPhA(H), PdFPhA(M) and PdFPhA(L) did not depend on either the samples MW or the conditions applied for the sample synthesis (Table 8). As the time of PdFPhAs ageing increased, the $C_{\text{high-cis}}$ values decreased. The rate of $C_{\text{high-cis}}$ decrease strongly depended on the initial MW of the PdFPhA submitted for the ageing experiment. The isomerization rate decreased with the decreasing initial MW of PdFPhA in the order: PdFPhA(H) > PdFPhA(M) > PdFPhA(L) (Figure 23).

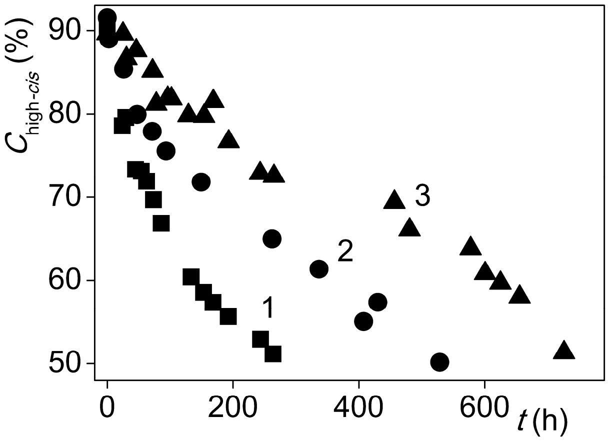


Figure 23: Dependencies of parameter $C_{\text{high-cis}}$ vs. t for ageing of PdFPhA(H) (1), PdFPhA(M) (2) and PdFPhA(L) (3) in THF-d_8 solution. Solutions of polymers were kept in contact with the atmosphere and diffuse daylight at room temperature.

Figure 24 shows the $M_w/(M_w)_0$ vs. t dependencies for PdFPhAs samples under study (M_w stands for the weight-average MW obtained for the ageing time t, $(M_w)_0$ is the weight-average MW of the parent polymer). The comparison of the $M_w/(M_w)_0$ drop of particular samples clearly shows that the rate of degradation decreased in the samples order: PdFPhA(H) > PdFPhA(M) > PdFPhA(L) (Figure 24). Summarizing the results from Figures 23 and 24 we can conclude that both the rate of *cis*-to-*trans* isomerization and the rate of degradation decreased with decreasing $(M_w)_0$ of the parent samples.

Dependencies in Figure 24 allowed to determine (i) times ($t_{(M_w)_0/2}$) necessary for $(M_w)_0$ of individual samples to fall to half its value [i.e. to $(M_w)_0/2$] and (ii) valus of $c_{high-cis,(M_w)_0/2}$ i.e. the content of monomeric units in high-*cis* chains in samples aged for the time $t_{(M_w)_0/2}$ (Table 9 No. 1-3). As evident, the values of $c_{high-cis,(M_w)_0/2}$ did not exhibit any systematic dependence on the initial MW of the parent samples (Table 9 No. 1-3). It means that the fall of $(M_w)_0$ to half its value was accompanied by a similar change in the configurational structure in the case of all studied PdFPhA samples.

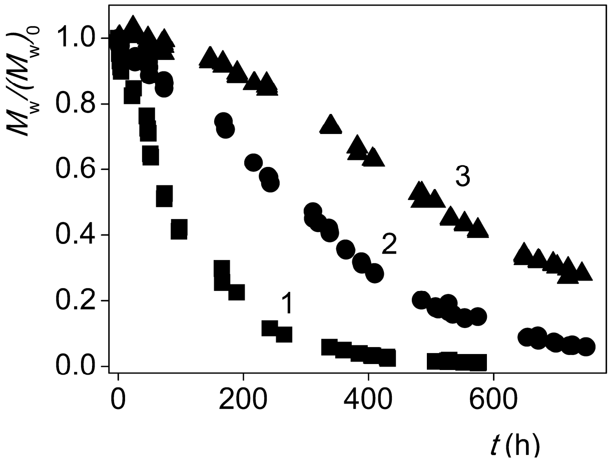


Figure 24: Dependencies of parameter $M_w/(M_w)_0$ vs. t for ageing of PdFPhA(H) (1), PdFPhA(M) (2) and PdFPhA(L) (3) in THF-d_8 solution. Symbol M_w stands for the weight-average molecular weight determined at ageing time t, symbol $(M_w)_0$ represents the weight-average molecular weight of the freshly dissolved sample. Solutions of polymers were kept in contact with the atmosphere and diffuse daylight at room temperature.

Table 9: Degradation of PdFPhA samples exposed to the atmosphere and diffuse daylight under various conditions. $(M_w)_0$ is the weight-average molecular weight of the parent sample, $t_{(M_w)_0/2}$ is the time necessary for $(M_w)_0$ to fall to half its value. $c_{high-cis,(M_w)_0/2}$ stands for the content of monomeric units in high-*cis* chains in the degraded samples of weight-average molecular weight equal to $(M_w)_0/2$. $k_{cis/trans}$ is the slope of $1/X_p$ vs. t dependencies for *cis*/*trans* polymer fractions, r.t. = room temperature.

No.	Polymer code	10^{-3} $(M_w)_0$	Conditions of ageing	$t_{(M_w)_0/2}$ (h)	$c_{high-cis,(M_w)_0/2}$ (%)	$k_{cis/trans}$ (min^{-1})
1	PdFPhA(H)	970	THF-d_8, r.t.	74	69	$9.4\ 10^{-7}$
2	PdFPhA(M)	120	THF-d_8, r.t.	310	63	$7.0\ 10^{-7}$
3	PdFPhA(L)	22	THF-d_8, r.t.	510	65	$8.3\ 10^{-7}$
4	PdFPhA(M)	120	THF-d_8, 50ºC	58	63	nd
5	PdFPhA(H)	970	solid state, r.t.	4300	88	nd

With the aim to investigate a possible influence of the ageing temperature we monitored also PdFPhA(M) ageing in THF-d_8 at 50°C. The rate of both degradation and *cis*-to-*trans* isomerization increased due to the temperature increase. As evident, the value of $t_{(M_w)_0/2}$ of PdFPhA(M) decreased, however, no change in the value of $c_{high-cis,(M_w)_0/2}$ was observed due to the change of temperature (Table 9 No. 2 and 4). Evidently, regardless of the ageing temperature the fall of $(M_w)_0$ to half its value was accompanied by the same extent of the configurational structure change.

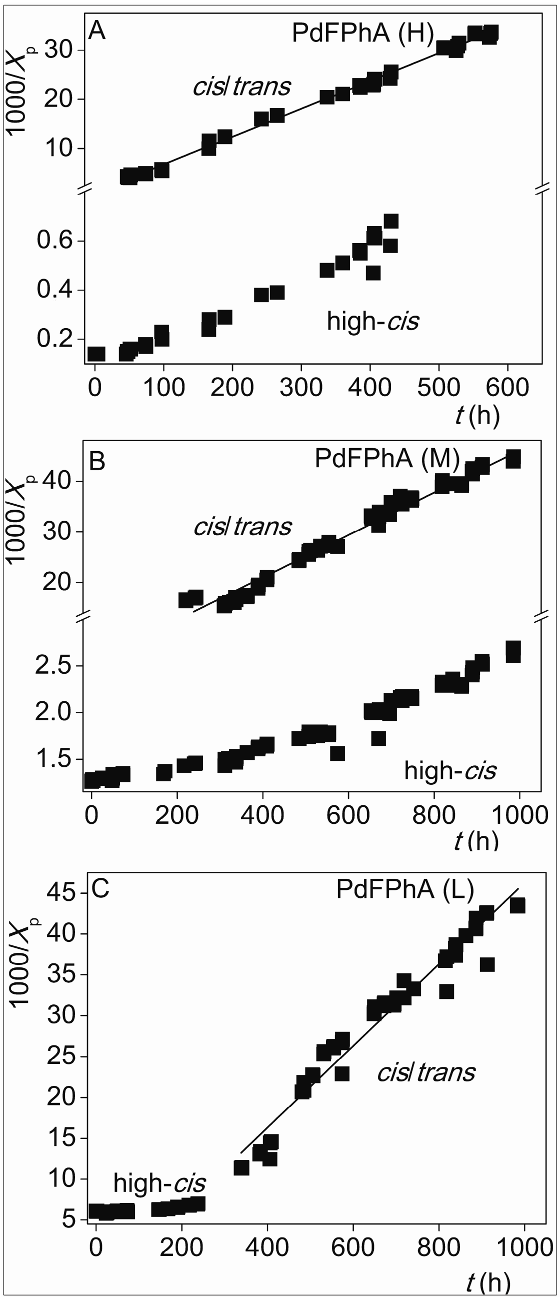


Figure 25: Dependencies of parameter $1/X_p$ vs. t of *cis*/*trans* and high-*cis* fractions of PdFPhA(H) (part A), PdFPhA(M) (part B) and PdFPhA(L) (part C). Solutions (in THF-

d$_8$) of polymers were kept in contact with the atmosphere and diffuse daylight at room temperature.

Partial SEC separation of the original high-*cis* and the newly formed *cis*/*trans* fractions was achieved in the case of partly aged PdFPhA(H) and PdFPhA(M) samples (Figure 22). This enabled to evaluate the MW vs. *t* changes for these partly SEC-separated fractions. The apparent value of the degree of polymerization corresponding to the apex(es) of SEC chromatogram (X_p) was chosen as the appropriate parameter for this evaluation. Only X_p values corresponding to high-*cis* fractions were obtained at the early stage of ageing of PdFPhA(H) and PdFPhA(M) (unimodal MW distribution) while X_p values of both fractions resulted from the chromatograms at the later ageing stage (bimodal MW distribution). Only one distinct maximum was evident in the chromatograms recorded in the whole course of PdFPhA(L) ageing. We assume that the position of maximum was influenced mainly by the presence of high-*cis* fraction at the onset of PdFPhA(L) ageing. On the contrary, mainly the *cis*/*trans* fraction affected the maximum position at the late stage of PdFPhA(L) ageing.

Figure 25 shows $1/X_\mathrm{p}$ vs. *t* dependencies obtained on the base of the SEC monitoring of PdFPhAs ageing in THF-*d*$_8$. As evident, the X_p values of remaining part of high-*cis* fraction decreased only slowly for all PdFPhA samples (Figure 25). On the contrary, the X_p values of *cis*/*trans* fraction decreased more rapidly (Figure 25). This decrease was not slowed down even in the late stage of ageing when the content of *cis*/*trans* fraction only marginally increased due to the *cis*-to-*trans* isomerization of the high-*cis* fraction. Thus, the rapid continuous degradation seems to be prevailingly responsible for the observed rapid decrease in X_p values of the *cis*/*trans* fractions. The $1/X_p$ vs. *t* dependencies obtained for the *cis*/*trans* fractions of individual samples were represented by straight lines with the slopes, labelled as $k_\mathrm{cis/trans}$. The values of $k_\mathrm{cis/trans}$ were similar for all the analysed samples (Table 9). The linearity of $1/X_p$ vs. *t* found for *cis*/*trans* fractions of partly aged samples is consistent with the random mechanism of polymer degradation [62]. However, the unambiguous confirmation of randomness of the degradation of *cis*/*trans* PdFPhAs fractions would required further proofs to be collected.

Ageing of poly[(2,4-difluorophenyl)acetylene] in the solid state

The highest MW sample, PdFPhA(H), was allowed to age also in the solid state under atmosphere and diffuse daylight exposure at room temperature. The ageing was accompanied by decrease in MW and by a slight broadening of the MW distribution (Figure 26). However, the MW distribution was remaining unimodal in the whole course of ageing. The molecular weight of PdFPhA(H) was continuously decreasing in the whole period of ageing in the solid state, obtained $t_{(M_w)_0/2}$ value was two orders of magnitude lower than $t_{(M_w)_0/2}$ obtained for PdFPhA(H) ageing in THF-d_8 (Table 9).

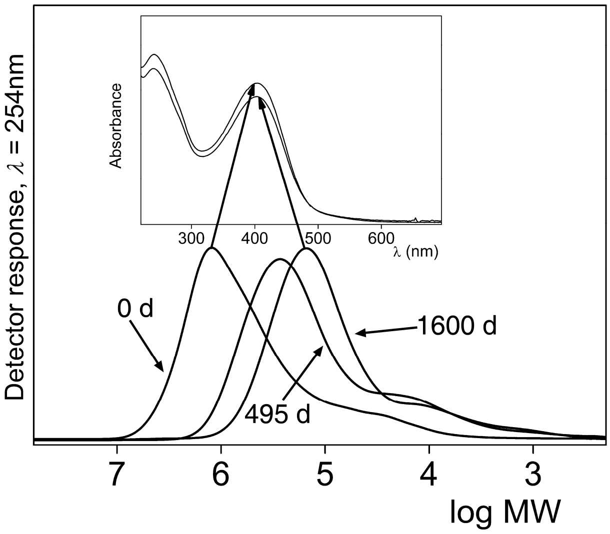


Figure 26: Representative SEC chromatograms of PdFPhA(H) aged exposed to the atmosphere in the solid state (room temperature) for 0, 495 and 1600 days and UV/vis spectra corresponding to the maximum of SEC chromatograms recorded by SEC/DAD technique for the parent PdFPhA(H) and PdFPhA(H) aged for 1600 days.

The UV/vis spectra from the maxima of SEC chromatograms for the parent PdFPhA(H) and PdFPhA(H) aged for 1.6×10^3 days in the solid state were almost identical that indicated the preservation of the high-*cis* configuration of PdFPhA(H) during the ageing (Figure 26). This fact was confirmed also by ^{1}H NMR technique. Within more than 6 years of PdFPhA(H) ageing in the solid state the $C_{\text{high-cis}}$ value decreased only marginally from 90% to 87%. It can be thus concluded that the PdFPhA(H) degradation in the solid state was associated with either no or only minor change in the PdFPhA(H) configuration structure.

Study of poly[(2,4-difluorophenyl)acetylene] ageing in THF-d_8 (or in THF) by ^{13}C NMR, ^{19}F NMR, DLS and EPR techniques

The title techniques represent either less common or hitherto not-applied techniques for the investigation of polyacetylenes ageing.

^{19}F NMR and ^{13}C NMR spectroscopies were used to monitor the ageing of PdFPhA(M) sample in THF-d_8. Figure 27 shows ^{19}F NMR spectra of PdFPhA(M) freshly dissolved in THF-d_8 and PdFPhA(M) aged for 575 h in THF-d_8.

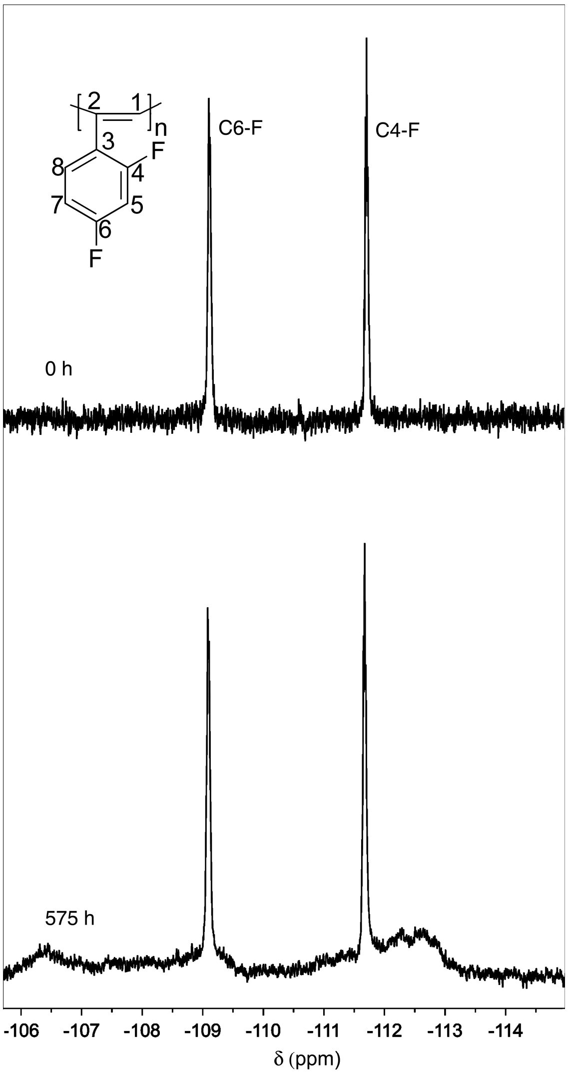


Figure 27: ^{19}F NMR spectra of PdFPhA(M) aged for 0 and 575 hours in THF-d_8 solution. Solution of PdFPhA(M) was kept in contact with the atmosphere and diffuse daylight at room temperature.

Both spectra consisted of two signals belonging to two fluorine substituents on the pendant phenyl groups of the polymer. A remarkable broadening was observed at the basement of these signals in the spectrum of the aged sample that can be ascribed to the presence of (newly formed) structurally non-uniformed *cis*/*trans* fraction due to the sample ageing. The *cis*-to-*trans* isomerization of PdFPhA(M) during its ageing in THF-d_8 resulted in the broadening of all signals in ^{13}C NMR spectrum similarly as it was observed for the signals of ^{1}H NMR and ^{19}F NMR spectra.

The presence of two different polymer fractions in PdFPhA(H) partly aged in THF was confirmed also by DLS technique. The polymer solutions were allowed to age in contact with the atmosphere and diffuse daylight at room temperature. Typical distributions of hydrodynamic radii, R_H, obtained for various ageing times are in Figure 28. It is clearly seen that only one mode was detected for the freshly dissolved PdFPhA(H). However, the second mode, faster than the first one, developed in the course of sample ageing. The slow mode evidently corresponds to the high-MW microstructurally unperturbed high-*cis* fraction detected also by SEC/DAD technique. The fast mode revealed by DLS is evidently identical with the low-MW *cis*/*trans* fraction which was also detected by SEC/DAD.

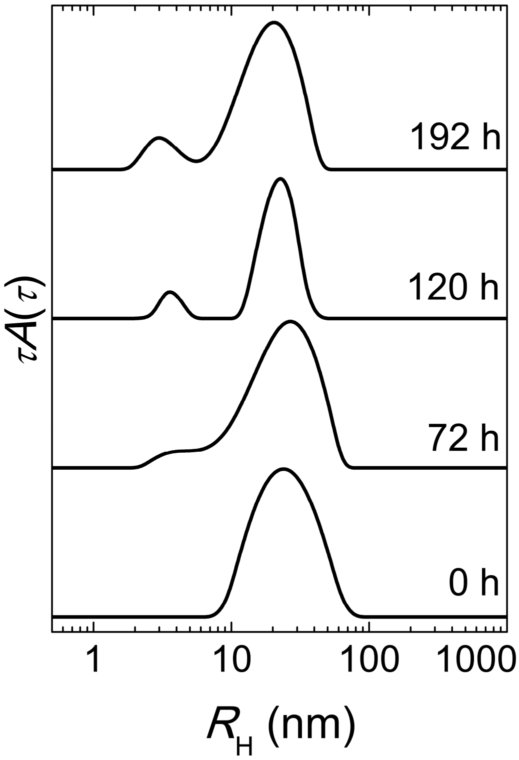


Figure 28: Distributions of hydrodynamic radii, R_H, (scattering angle = 90°), obtained for PdFPhA(H) aged in THF solution (c = 1 mg/ml) for 0, 72, 120 and 192 hours. The

polymer solutions were allowed to age in contact with the atmosphere and diffuse daylight at room temperature.

The EPR method was applied for the analysis of PdFPhA(H). PdFPhA(H) aged for 210 h in THF at room temperature and atmosphere exposure was fractionated from the solvent system methanol/THF. The fractionation provided two PdFPhA(H) fractions: (i) high-MW high-*cis* PdFPhA(H) fraction (M_w = 1.4x10^5, M_n = 3.7x10^4) and (ii) low-MW *cis*/*trans* PdFPhA(H) fraction (M_w = 4.3x10^3, M_n = 2.8x10^3). These fractions were analysed by EPR method and the same analysis was performed for the parent PdFPhA(H). Resulting EPR spectra are shown in Figure 29.

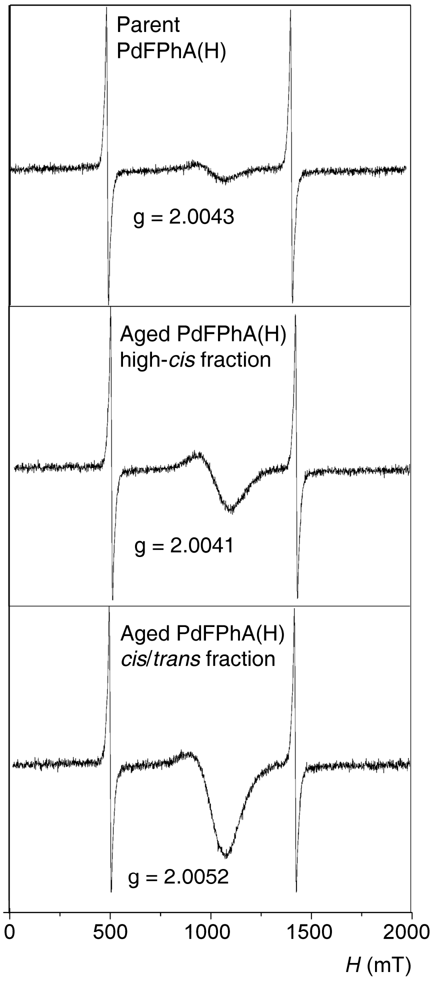


Figure 29: EPR spectra of parent PdFPhA(H), high-*cis* and *cis*/*trans* fractions of PdFPhA(H). Fractionation was performed after ageing for 210 h in THF.

The unpaired electrons were detected in all the analysed samples. Values of *g* (from 2.0041 to 2.0052) corresponded well to those reported for the unpaired electrons present on the main chains of ring substituted PPhAs. [136] As it can be seen from Figure 29, the samples differed significantly in the content of unpaired electrons. This content increased in the polymers order: parent PdFPhA(H) < high-*cis* PdFPhA(H) fraction < *cis*/*trans* PdFPhA(H) fraction. Evidently, the ageing in THF resulted in the increase of the unpaired electron content. The comparison of EPR spectra of *cis*/*trans* PdFPhA(H) fraction and high-*cis* PdFPhA(H) fraction revealed that the former fraction contained 2.4 times more unpaired electrons than the latter fraction. This represents a confirmation that the *cis*-to-*trans* isomerization of PdFPhA(H) caused an increase in the unpaired electrons content.

In Chapter 4.2.2., we firstly expressed the idea on the tight interconnection of *cis*-to-*trans* isomerization and oxidative degradation processes in the course of polyacetylenes ageing under atmosphere. This idea can be very briefly summarized as follows: *cis*-to-*trans* isomerization (influenced by a “domino effect”) should lead to an increase in the content of unpaired electrons on the isomerized chains. As a consequence, the isomerized macromolecules degrade more rapidly in comparison to the high-*cis* microstructurally unperturbed macromolecules with a lower unpaired electron content. Different degradation rates of high-*cis* and *cis*/*trans* macromolecules lead to significant broadening of MW distribution. For a more comprehensive description of this idea see Chapter 4.2.2. Results of this Chapter 4.2.3. support this idea in the following points: (i) The EPR spectroscopy applied for the analysis of PdFPhA(H) clearly confirmed that the *cis*-to-*trans* isomerization resulted in the increase of the unpaired electron content on the isomerized PdFPhA chains. (ii) The evaluation of the MW vs. *t* changes for the partly SEC-separated high-*cis* and *cis*/*trans* fractions of PdFPhAs (Figure 25) clearly showed that the isomerized *cis*/*trans* fractions degraded more rapidly than the microstructurally unperturbed high-*cis* fractions. (iii) The ageing experiments performed with high-*cis* PdFPhAs of various parent MW showed simultaneous increase of both the configuration and MW stability in THF-d_8 with decreasing MW of the parent samples. It can be assumed that with the decreasing chains length of the parent high-*cis* polymer the rotation scission of the main chain double bonds (leading to *cis*-to-*trans* isomerization) is suppressed owing to the decreasing straining of the polymer chain segments. The decreased rate of *cis*-to-*trans* isomerization impacts the overall rate of degradation that is decreased as well. (iv) The degradation of PdFPhA(H) in the solid state was found to proceed without changes in the main-chains configuration. The unpaired electrons that are in a small amount present even on the microstructurally unperturbed PdFPhA chains are most probably responsible for the observed degradation. The suppression of the *cis*-to-*trans* isomerization in the solid state reflects the minimization of the motion of the polymer chain segments that could result in the rotation scission of the double bonds. The suppression of the *cis*-to-*trans* isomerization is manifested by the preservation of the unimodal character of MW distribution of PdFPhA(H) in the whole period of ageing in the solid state.

5. CONCLUSION

- Rhodium mononuclear complexes [Rh(cycloolefin)(acac)] with nbd, cod and cot ligands exhibited high activity in arylacetylenes polymerization and moderate activity in polymerization of alkylacetylenes and copolymerization of alkylacetylenes with arylacetylenes. In the arylacetylenes polymerization, similar yields of polymers were achieved in both coordinating (THF) and non-coordinating (CH_2Cl_2) solvents. Complex [Rh(cot)(acac)] prepared in situ by ligand exchange of [Rh(ethylene)$_2$(acac)] with cot exhibited high polymerization activity even in neat cot. Contrary to the frequently applied [Rh(nbd)Cl]$_2$ catalyst, [Rh(cycloolefin)(acac)] catalysts did not need either a cocatalyst or a coordination solvent for their activation.
- The onset of initiation in the [Rh(cycloolefin)(acac)]/monomer systems proceeded as the acetylenic proton transfer from the coordinated monomer molecule to the acac ligand under the release of acetylacetone and coordination of -C≡CR ligand to Rh(cycloolefin) moiety.
- The control over polymer molecular weight (M_n from 1×10^4 to 1×10^5, M_w from 3×10^4 to 4×10^5) was attained in PhA polymerization with [Rh(cycloolefin)(acac)] by affecting (i) the extent of initiation and (ii) extent of transfer reactions. The extent of these processes was controlled by selection of polymerization solvent and cycloolefin ligand of the catalyst.
- The MW and configurational stability of high-*cis* PPhA and newly prepared high-*cis* PdFPhAs dissolved in THF or THF-d_8 was investigated in long-term ageing experiments in which polymer solutions were kept in contact with the atmosphere and diffuse daylight.
- The tightly connected processes of (i) *cis*-to-*trans* isomerization of the main-chain double bonds and (ii) oxidative degradation proceeded during the ageing of both PPhA and PdFPhA in the solution. Moreover, the ageing was accompanied by formation of a small amount (~1-2 wt.%) of corresponding cyclotrimers. However, the extent of cyclotrimers formation was too low for explaining the degradation and isomerization of polymers in terms of cyclization mechanism of Percec et al.
- PdFPhA and PPhA partly aged in solution were found to contain two polymer fractions: (i) higher-MW fraction of microstructurally unperturbed high-*cis*

macromolecules with a low amount of unpaired electrons and (ii) lower-MW fraction of deeply isomerized *cis*/*trans* macromolecules with a higher amount of unpaired electrons.

- For the explanation of the coexistence of high-*cis* and *cis*/*trans* macromolecules in the partly aged samples the mechanism was proposed assuming that the *cis*-to-*trans* isomerization of particular high-*cis* polymer chains was influenced by a kind of rapid “domino effect”. This process gave rise to deeply isomerized *cis*/*trans* polymer chains that were enriched with unpaired electrons (resulting from the rotation scission of the double bonds). The isomerized *cis*/*trans* chains are assumed to be more prone to oxidative degradation than the microstructurally unperturbed high-*cis* chains with a low unpaired electrons content. The different rates of oxidative degradation of isomerized and non-isomerized chains were responsible for the observed broadening of polymers MW distribution and for the non-uniform distribution of high-*cis* and *cis*/*trans* chains along the MW distribution of partly aged PdFPhA and PPhA samples.
- The comparative study in which PPhA and PdFPhA samples of a similar MW were aged in THF showed significantly higher configurational and MW stability of PdFPhA compared to PPhA. The observed high PdFPhA resistance to the *cis*-to-*trans* isomerization is most probably given by the steric effect of the ortho substitution of the pendant phenyl groups of this polymer. Due to this effect the rotation scission of the main chain double bonds (leading to *cis*-to-*trans* isomerization) is suppressed that also leads to the consecutive suppression of the oxidative degradation of PdFPhA.
- The comparative study in which PdFPhA samples differing in MW were aged in THF showed increase of both configurational and MW stability with decreasing MW of the parent samples. It can be assumed that with the decreasing length of the parent polymer chains the rotation scission of the main chain double bonds is suppressed owing to the decreasing straining of the polymer chain segments. The decreased rate of *cis*-to-*trans* isomerization impacts the rate of degradation that is decreased as well.
- Various techniques were reported for the study of the microstructure of PPhA and PdFPhA in the course of their ageing. Among the methods applied, the SEC/DAD technique was demonstrated as a powerful tool for the rapid monitoring of

structural differences along the MW distribution of the studied polymers. This method seems to be promising also for the characterization of other conjugated polymers.

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7. LIST OF ABBREVIATIONS

acac	acetylacetonato
AlkA	alkylacetylene
ArA	arylacetylene
$C_{\text{high-cis}}$	content of double bonds with *cis* configuration
cod	cycloocta-1,5-diene
cot	cyclooctatetraene
dFPhA	(2,4-difluorophenyl)acetylene
DLS	dynamic light scattering
$Đ$	dispersity defined: $Đ = X_\mathrm{w}/X_\mathrm{n}$
$Đ_\mathrm{w}$	dispersity defined: $Đ_\mathrm{w} = X_\mathrm{z}/X_\mathrm{w}$
EPR	electron paramagnetic resonance
f_{Hacac}	fractions of acac ligand transformed into free Hacac
Hacac	free acetylacetone
IR	infrared spectroscopy
n	number of aromatic protons in one monomeric unit
nbd	norborna-2,5-diene
NMR	nuclear magnetic resonance
M_n	number -average molecular weight
M_p	molecular weight corresponding to the apex of SEC peak
M_w	weight-average molecular weight
MW	molecular weight
PdFPhA	poly[(2,4-difluorophenyl)acetylene]
PFPhA	poly[(fluorophenyl)acetylene]
PhA	phenylacetylene
PIPhA	poly[(iodophenyl)acetylene]
PMeA	poly(methylacetylene)
PPhA	poly(phenylacetylene)
$S_{\text{high-}\mathit{cis}}$	area of resonance of the main-chain protons on monomeric units with *cis* configuration

S_{total}	total integrated area of ^{1}H NMR signals of all protons
SEC	size exclusion chromatography
TEA	triethylamine
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TPB	triphenylbenzene
X_{n}	number-average degrees of polymerization in time t
X_{p}	degree of polymerization corresponding to the apex of SEC chromatogram
X_{w}	weight-average degrees of polymerization in time t
X_{z}	z-average degree of polymerization
$(X_{\text{n}})_0$	number-average degrees of polymerization in time $t = 0$
$(X_{\text{w}})_0$	weight-average degrees of polymerization in time $t = 0$
$Y(\text{P})$	polymer yield

8. LIST OF PUBLICATIONS

List of publications constituting the Thesis:

1. Trhlíková O., Zedník J., Vohlídal J., Sedláček J.: Molecular weight and configurational stability of poly(phenylacetylene) prepared with Rh catalyst. Polymer Degradation and Stability 2011; 96: 1310-1320.

2. Trhlíková O., Zedník J., Vohlídal J., Sedláček J.: SEC/DAD and ^{1}HNMR study of molecular weight and configurational stability of poly[(2,4-difluorophenyl)acetylene] and poly(phenylacetylene) prepared with Rh catalyst. Macromolecular Chemistry and Physics 2011; 212: 1987-1998.

3. Trhlíková O., Zedník J., Balcar H., Brus J., Sedláček J.: [Rh(cycloolefin)(acac)] complexes as catalysts of polymerization of aryl- and alkylacetylenes: Influence of cycloolefin ligand and reaction conditions. Journal of Molecular Catalysis A: Chemical 2013; 378: 57-66.

4. Trhlíková O., Zedník J., Matějíček P., Horáček M., Sedláček J.: Degradation and *cis*-to-*trans* isomerization of poly[(2,4difluorophenyl)acetylene]s of various initial molecular weight: SEC, NMR, DLS and EPR study. Polymer Degradation and Stability DOI: 10.1016/j.polymdegradstab.2013.05.020.

List of other publications not included in the Thesis:

1. Svoboda J., Sedláček J., Zedník J., Dvořáková G., Trhlíková O., Rédrová D., Vohlídal J., Balcar H.: Polymerization of 3-Ethynylthiophene with homogeneous and heterogeneous Rh catalysts. Journal of Polymer Science Part A: Polymer Chemistry 2008; 46: 2776-2787.

2. Trhlíková O., Vystrčilová L., Bondarev D., Zedník J., Svoboda J., Sedláček J., Vohlídal J.: Polymerization, cyclotrimerization and polycyclotrimerization of substituted acetylenes induced with [Rh(diene)(acac)] complexes, 9-th Pannonian International Symposium On Catalysis, Štrbské pleso, Slovakia, pp. 475 – 480, publisher: Slovak University of Technology, 2008, ISBN978-80-227-2923-9.

3. Trhlíková O., Zedník J., Vohlídal J., Sedláček J.: Ring-substituted polyphenylacetylenes prepared with insertion catalysts: preparation, characterization, study of molecular weight and configurational stability, 10th Pannonian International Symposium on Catalysis, Kraków, Poland, pp. 284-291, publisher: Polish Zeolite Association and Institute of Catalysis and Surface Chemistry, PAS Krakow, 2010, ISBN 978-83-929430-4-4.

9. APPENDIX

I. Trhlíková O., Zedník J., Vohlídal J., Sedláček J.: Molecular weight and configurational stability of poly(phenylacetylene) prepared with Rh catalyst. Polymer Degradation and Stability 2011; 96: 1310-1320.

II. Trhlíková O., Zedník J., Vohlídal J., Sedláček J.: SEC/DAD and ^{1}HNMR study of molecular weight and configurational stability of poly[(2,4-difluorophenyl)acetylene] and poly(phenylacetylene) prepared with Rh catalyst. Macromolecular Chemistry and Physics 2011; 212: 1987-1998.

III. Trhlíková O., Zedník J., Balcar H., Brus J., Sedláček J.: [Rh(cycloolefin)(acac)] complexes as catalysts of polymerization of aryl- and alkylacetylenes: Influence of cycloolefin ligand and reaction conditions. Journal of Molecular Catalysis A: Chemical 2013; 378: 57-66.

IV. Trhlíková O., Zedník J., Matějíček P., Horáček M., Sedláček J.: Degradation and *cis*-to-*trans* isomerization of poly[(2,4difluorophenyl)acetylene]s of various initial molecular weight: SEC, NMR, DLS and EPR study. Polymer Degradation and Stability DOI: 10.1016/j.polymdegradstab.2013.05.020.