New Approaches to the Synthesis of Pure Conjugated Polymers

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Abstract

This short-review article is based on the lecture presented at the 13th Conference on Materials and Technology held in Portorož, October 10–12, 2005 and summarizes our recent results obtained in the investigation and development of polymerization methods aimed at the synthesis of high-purity conjugated polymers, polyacetylenes and polyanilines in particular. *Part 1. Introduction* provides a survey of main procedures currently used in synthesis of conjugated polymers; *Part 2. Catalytic chain polymerizations in two-phase systems* contains a brief information on the liquid-liquid systems but mainly it deals with a preparation of mesoporous polymerization catalysts and their use and effectivness in the synthesis of high-purity polyacetylenes. The catalyst systems obtained by anchoring of soluble, catalytically active transition-metal complexes on mesoporous supports such as polybenzimidazole beads, all-siliceous molecular sieves MCM 41, MCM 48, and SBA 15, and the sieves with inner pores modified by linkers with $-NH_2$, $-PPh_2$ and $-N(PPh_2)_2$ end groups are discussed as to their activity, stereoselectivity, re-use and transport limitations for guest macromolecules. *Part 3. Transformation of stoichiometric polymerizations to catalytic processes* mainly deals with the polymerization of aniline and its derivatives with the catalytic system Fe^{3+}/H_2O_2. Quality of polyanilines prepared by catalytic and stoichiometric procedures are compared and new results are presented, according to which both active species present in the reaction mixture, Fe^{3+} ions and $HO^•$ radicals, participate in the overall mechanism, creating a synergic system. Concluding *Part 4. Conclusions, limitations and perspectives* provides a summary of results obtained including advances and limitations of these synthesis approaches and perspectives of their use and development.

Keywords: catalytic oxidative polymerization, coordination polymerization, conjugated polymers, functional polymers, hydrogen peroxide, immobilized catalysts, iron trichloride, mesoporous polymerization catalysts, mesoporous molecular sieves, metathesis, polyacetylenes, polyanilines, polybenzimidazole, polyvinylenes.

1. Introduction

For almost three decades, conjugated polymers and oligomers have been under intensive research and development as new functional materials for electronics, photonics, advanced coatings, and related applications.[1,2] Some conjugated polymers such as polypyrrole and polyaniline have already found practical applications in the construction of capacitors, analytical sensors, antistatic films and coatings, materials for electrostatic discharge protection, electrochromic windows, anticorrosion paints, etc. More advanced applications of conjugated polymers in the construction of electronic devices, photovoltaic cells and actuators

are anticipated; the first all-polymeric printed circuits and displays have recently been presented. Neat conjugated polymers are insulators or semiconductors, which, however, become conductive upon partial oxidation or reduction, also referred to as doping; in the case of polyaniline, protonation (proton doping) is also necessary.[3] The doping processes allow the properties of these polymers to tune from insulators to metallic conductors.

The properties of conjugated polymers important for their application in electronics are remarkably sensitive to the presence of impurities, which might act as uncontrolled dopants, traps of charge carriers, quenchers of excited states, etc. Catalyst residues

and side-products from polymer synthesis are typical contaminants of conjugated polymers and are mostly removed by repeated precipitation or by adsorption to silica or alumina or other sorbents. Both of these techniques are time consuming, of limited efficiency and, to a great extent, empirical because the chemical structure of catalyst residues is often unknown. Production of high amounts of waste solvents is another important disadvantage of this approach. Therefore, the development of new preparation procedures giving pure conjugated polymers almost free of catalyst residues and other polymerization side products is highly desirable.

There are about six types of procedures used for the preparation of conjugated polymers:

1. **Homogeneous coordination polymerization (catalytic chain polymerization)** of the insertion or metathesis type, mainly used for syntheses of poly-vinylenes (polyacetylenes), polyphenylenevinylenes and related polymers,[4] for example:

1(1,4),4(1,4)-dibenzena-cyclohexapha-2,5-diene   poly(1,4-phenylenevinylene)


phenylacetylene   poly(phenylacetylene)
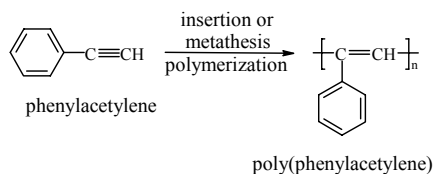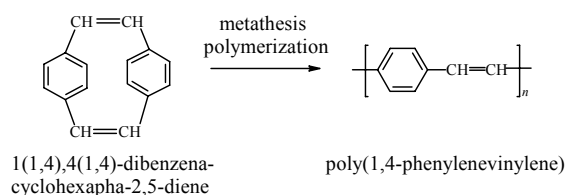
2. **Chemical (stoichiometric) polymerization**, typically an oxidation or dehalogenation polymerization,[3] in which a monomer or mixture of monomers react with the stoichiometric equivalent of a coupling agent giving the corresponding polymer and a high amount of side products. Chemical polymerization has already found applications in industrial production of polyanilines and polythiphenes, for example:


thiophene   polythiophene

alkylaniline   polyalkylaniline
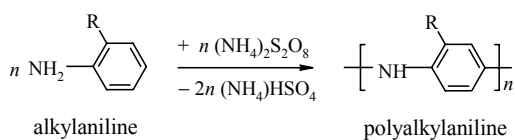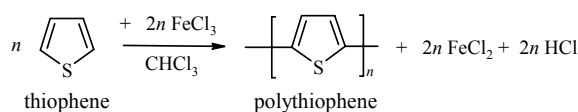
3. **Catalytic versions** of chemical polymerization, such as Suzuki-Miyaura, Heck and Sonogashira couplings, are frequently used to prepare polyaryleneethynylenes and fluorene polymers and copolymers.[5]

polyaryleneethynylene

Sonogashira coupling

Suzuki - Miyaura coupling
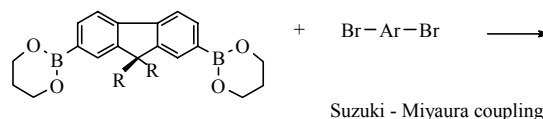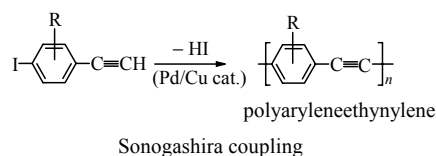
4. **Chemical transformation of a precursor polymer**, such as the transformation of poly{(5,6-bis(trifluoromethyl)bicyclo[2,2,2]octa-5,7-dienevinylene} to poly(vinylene), also known as "Durham polyacetylene" by the retro-Diels-Alder reaction (see, e.g., chapter 13 in ref.[4b]):

"Durham polyacetylene"
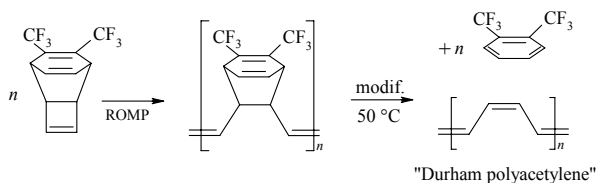
5. **Electrochemical polymerization** of monomers such as aniline, pyrrol or thiophene, yielding a conducting polymer film deposited on the anode material.[3] This method is useful for the preparation of conducting polymer films for electronic devices such as electro-analytical sensors composed of a receptor for a particular compound anchored on a conducting polymer film. On the other hand, electropolymerization is not regarded as a method suitable a the large-scale production of conducting polymers.

6. **Photochemical polymerization**, which is typically used for the polymerization of diacetylenes assembled in Langmuir-Blodget films[6], for example:

diacetylene   polydiacetylene
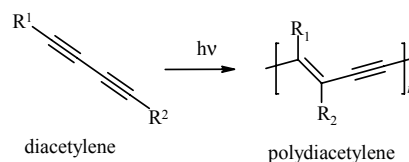
The first two preparative methods have the highest innovation potential:

- homogeneous chain polymerizations can be transformed into reactions in two phase systems, allowing easy and effective separation of the catalyst residues from the polymer formed;

- stoichiometric oxidative polymerizations can be transformed into catalytic processes yielding acceptable side products.

In this contribution, we present the state of the art and our own recent results obtained in these two fields.

2. Catalytic Chain Polymerizations in Two-Phase Systems

A homogeneous catalytic polymerization can be transformed into a two-phase process by: *(i)* dissolving the catalyst in a liquid of poor miscibility with both the polymer formed and the solvent in which the polymer is dissolved, or *(ii)* using heterogeneous polymerization catalysts, mostly originally homogeneous catalyst anchored on a solid support.

The first approach is usually accomplished by using an *ionic liquid* to form the catalytic phase of the system. To achieve an effective catalyst separation from the polymer phase, catalyst species should be ionic or ionizable and the polymer formed should be soluble in a non- or low-polarity solvent. These conditions are well fulfilled, e.g., in the polymerization of phenylacetylene and its derivatives with rhodium complexes.[7] The ionic liquid must be properly chosen since the polymerization activity of Rh catalysts is sensitive to the structure of both the cation and anion of the ionic liquid.

A use of *fluorocarbons* (perfluorinated hydrocarbons), which are immiscible with the majority of other solvents, represents another possibility of implementing two-phase polymerization processes of the liquid-liquid class. However, the use of fluorocarbons as solvents for the catalyst phase is much more complicated because only catalysts comprising highly fluorinated ligands are well soluble in fluorocarbons. This thermodynamic requirement makes this approach difficult since complexes bearing perfluorinated ligands are rather rare and knowledge about their catalytic activity is still quite poor.[8] In addition, fluorinated ligands are expensive, not easily available, and they must be selected carefully in order not to quench the activity of the catalyst.

Anchored catalysts. This approach consists in anchoring a homogeneous catalyst on a suitable organic or inorganic support that is easily separable from the polymer solution. Microporous supports widely used in

chemical industry cannot be applied for these purposes because micropores (diameter up to ca 1.5 nm) are too narrow to allow the macromolecules formed to escape into the surrounding solution and make active species free for a formation of further macromolecules. This was clearly demonstrated in attempts to polymerize various acetylenes with H-zeolites and Co^{II} and Ni^{II} exchanged zeolites. Evidence of polymer formation was obtained from Raman spectra, however, the polymers formed remained caged in zeolites and attempts to isolate them by dissolving the supports in hydrofluoric acid were unsuccessful, yielding products of the polymer hydrolysis and hydrofluorination.[9]

The use of mesoporous (pore diameters up to ca 50 nm) or macroporous catalyst supports can eliminate the above-mentioned transport limitations because the nanopores are large enough to enable the formed polymer molecules to escape from the support into a surrounding solution by a reptation and/or diffusion. We used this approach in the synthesis of high-purity, stereoregular polymers of substituted acetylenes. Air-stable dinuclear Rh^I(diene) complexes, which are known to polymerize substituted acetylenes to *cis-transoid* polyacetylenes,[4] were anchored on mesoporous supports of two kinds: *(i)* mesoporous polybenzimidazole (PBI) beads[10a] with high population of pores of the diameter from 10 to 20 nm (ca. 650 m^2/g),[10b,c] and *(ii)* all-siliceous mesoporous molecular sieves with practically uniform pore diameter *d* differing in the pore architecture: MCM-41 (hexagonal pore packing, *d* = 3.4 nm), MCM-48 (cubic pore packing, *d* = 3.2 nm), SBA-15 (hexagonal pore packing, *d* = 6.8 nm).[11] So obtained catalysts were found to polymerize various substituted acetylenes (Scheme 1) and to exhibit the same, i.e., *cis-transoid* stereoselectivity as non anchored catalysts.
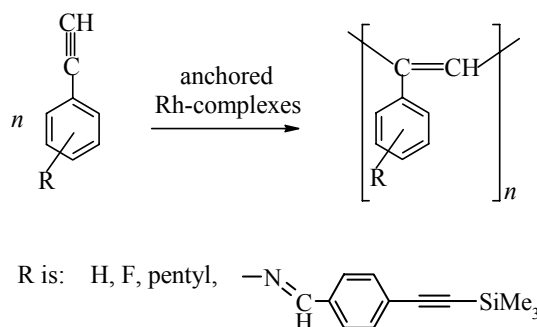
Scheme 1. Polymerizations studied with a use of anchored rhodium-based catalysts.

Preparation of mesoporous polymerization catalysts. Anchoring of Rh complexes was accomplished by the direct adsorption of the complexes from THF or CH$_2$Cl$_2$ solutions. Since Rh complexes are colored, a

course of anchoring can be easily monitored by UV/vis spectroscopy. In addition, the content of Rh in the resulting supported catalysts was determined by ICP mass spectrometry. The ICP MS method was also used to determine contamination of the prepared polymers with Rh residues as well as leaching of Rh species into the surrounding solution during the experiment (via analysis of the supernatant upon isolation of the polymer).
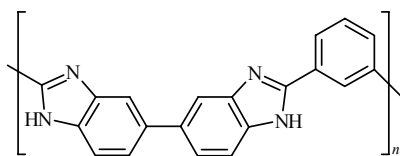

Scheme 2. Chemical structure of PBI beads

Commercially available catalytically active [{Rh(cod)}$_2$(μ-Cl)$_2$] and [{Rh(nbd)}$_2$(μ-Cl)$_2$] complexes (cod and nbd stand for η^2:η^2-coordinated cyclooctadiene and norbornadiene, respectively) are easily anchored onto neat mesoporous PBI beads; practically 100% anchoring is achieved at 3% loading (weight of Rh/weight of PBI).[10a] Analysis of the liquid phase remaining upon anchoring has shown that no compound is released into the liquid phase during the anchoring process. Consistently, the ESCA analysis of the supported catalyst has shown that chlorine atoms remain bound to the anchored Rh species. These observations indicate that, during anchoring, dinuclear Rh species are transformed into the mononuclear ones, which are then bound onto the support via the nitrogen groups of PBI. Rh complexes with μ-methoxo bridge ligands do not anchor onto PBI.

Molecular sieves exhibit anchoring behavior different from that of PBI. Commercially available μ-chloro Rh(diene) complexes do not anchor onto neat molecular sieves at all. On the other hand, rhodium μ-methoxo complex [{Rh(cod)}$_2$(μ-OMe)$_2$] is smoothly, practically totally anchored onto tested neat, all-siliceous mesoporous molecular sieves under the elimination of methanol to the liquid phase. This indicates that this anchoring proceeds via MeO – SiO ligand exchange.[11a]

In order to exploit easily available μ-chloro Rh complexes in designing new mesoporous catalysts, we modified inner pores of molecular sieves by reaction with compounds such as (CH$_3$O)$_3$Si-(CH$_2$)$_3$-NH$_2$, (C$_2$H$_5$O)$_3$Si-(CH$_2$)$_2$-PPh$_2$ and (CH$_3$O)$_3$Si-(CH$_2$)$_3$-N(PPh$_2$)$_2$. In this way we introduced ligands coordinating to Rh species onto pore walls. The pore modification proceeds under the liberation of the corresponding alcohol (methanol or ethanol) into the liquid phase, while the following catalyst anchoring proceeds without a release of any byproduct.[11b,c] Typical loading of the molecular-sieve-supported catalysts that we used in our experiments was 1%. It should be mentioned

here that the alcohol liberation is not quantitative, most probably owing to the sorption of a part of formed alcohol on the support pores. Solid-state NMR analyses of the resulting hybrid catalysts show that, on average, 0.7 to 0.8 of OCH$_3$ groups per one linker molecule remain unreacted.[11c] This indicates the following structures of catalyst species formed by anchoring an Rh μ-chloro complex onto a modified molecular sieve:
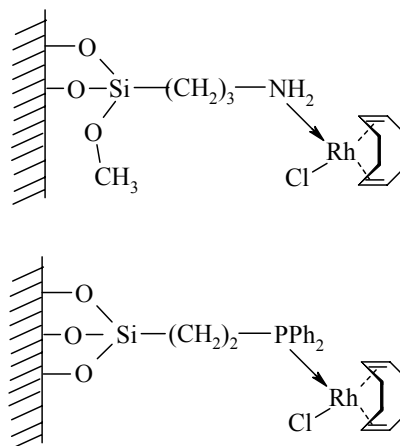
Scheme 3. Assumed structures of Rh catalysts with modified molecular-sieves supports.

Summary of results of polymerization experiments. The polymerizations of substituted acetylenes (phenylacetylene and its 4-pentyl-, 2-fluoro-, 4-fluoro- and 4-(Me$_3$Si-C≡C-C$_6$H$_4$CH=N-) derivatives) to readily isolable *cis-transoid* polyvinylenes were performed in batch reactors. The course of the reaction was monitored by size exclusion chromatography (SEC) of the liquid phase sampled from the reaction mixture upon short centrifugation. Catalyst leaching was monitored by the mass-spectrometry (ICP-MS) analysis of both the used supported catalyst and the isolated polymer (obtained by pouring a centrifuged reaction mixture into a twenty-fold excess of methanol). The supernatant from the polymer isolation was also analyzed for rhodium content. In addition, experiments were done to examine whether the polymerization really proceeds in the catalyst pores and does not proceed in the liquid phase: an already reacting polymerization mixture was, upon short centrifugation, split into two parts of equal volume – that containing all the supported catalyst and that free of the supported catalyst. The further course of polymerization in both mixtures was then monitored. Typically, polymerization continued in the system with the supported catalyst only, which proves that the reaction takes only part in the supported-catalyst species. Exceptionally, the polymerization also took place in the system without supported catalyst, which points to leaching of active species from the heterogeneous catalyst.

Rh(cod) complexes immobilized on mesoporous PBI, non-modified molecular sieves, and molecular sieves modified with $(CH_3O)_3Si\text{-}(CH_2)_3\text{-}NH_2$ spacers exhibit good polymerization activity and provide high-*cis-transoid* polyacetylenes, same as the corresponding complexes used as homogeneous catalysts.[11] This proves that anchoring does not alter the product stereoselectivity of rhodium catalysts. The polymers formed, including that with $4\text{-}(Me_3Si\text{-}C{\equiv}C\text{-}C_6H_4CH{=}N\text{-})$ ring substituents, are continuously released from the hybrid catalyst to the surrounding solvent, which allows easy polymer separation from the catalyst. Molecular weight of so prepared polymer ($<M>_w$ typically ranges from $1{\cdot}10^5$ to $3{\cdot}10^5$) is equal to or higher than that of the corresponding polymer prepared homogeneously. According to molecular dimensions recently determined[12a] for poly(phenylacetylene) and calculated[12b] for polyvinylene chains of various configurations, diameters of macromolecules formed exceed diameter of the host mesoporous channels mainly in the case of catalysts supported on the MCM-41 and MCM-48 molecular sieves (free-pore diameter 3.4 and 3.2 nm, respectively). This shows that the reptation mode (snake-like movement) plays important role in releasing macromolecules from pores.

The immobilized catalysts give high-purity neat polymers containing from 0.00002 to 0.0001 wt.% of Rh, which represents 0.002 – 0.015% of the catalyst used. Reference polymers prepared by corresponding homogeneous processes under comparable conditions contain from 0.01 – 0.1 wt.% of Rh (1 – 15% of the catalyst used). This means that the transformation of homogeneous processes to heterogeneous ones brings about thousand-fold reduction in the neat polymer contamination with catalyst residues. In addition, a formation of oligomers, typical side products of the polymerization of substituted acetylenes with rhodium catalysts, is also significantly reduced although not completely eliminated on anchored catalysts (vide infra).

Unlike the preceding systems, Rh(cod) complexes anchored on molecular sieves modified with $(C_2H_5O)_3Si\text{-}(CH_2)_2\text{-}PPh_2$ do not provide effective polymerization catalysts, most probably owing to too high concentration of $\text{-}PPh_2$ groups in the vicinity of the active sites. Namely, it is known that triaryl phosphines help to control homogeneous polymerization processes induced with Rh catalysts if they are applied in the equimolar amount with respect to the catalyst, and that they disturb the polymerization when used in higher amounts.[4e, 13] The phosphine-linker-anchored Rh catalysts can be activated towards polymerization by organic amines, which, however, also promote significant leaching of anchored rhodium species to the solvent phase, so counteracting the target intended by the catalyst anchoring.

The above-described successful results obtained with anchored Rh(cod) complexes have not been achieved with anchored Rh(nbd) complexes. Surprisingly, the last gave considerably lower polymer yields although the parent Rh(nbd) complexes, when applied as homogeneous catalysts, show higher activity than the corresponding Rh(cod) ones. This might be explained in two ways. First, Rh(nbd) complexes are known to induce, under proper conditions, living stereoregular polymerization of substituted acetylenes,[13] in which kinetic-chain transfer is practically absent. Therefore, it can happen that the polymer chains formed on the anchored Rh(nbd) catalysts remain bound to active polymerization centers and thus cannot be released from the catalyst pores into the surrounding solution. However, in our experiments, we did not use reaction conditions needed for living polymerization. Another explanation consists in a formation of insoluble, so called columnar forms of polyphenylacetylenes inside pores.[14a,b] Molecules of substituted polyacetylenes behave as random coils in solutions,[12] however, if practically stereoregular, *cis-transoid* macromolecules are rapidly formed in a restricted volume element inside pores and they do not have time to undergo a partial isomerization,[14c] a formation of insoluble forms can be promoted.

Another key point of the development of heterogeneous polymerization catalysts is obtaining robust, recyclable catalysts for environmentally friendly and economical processes. Unfortunately, the new catalysts developed so far show a slow but continuous decrease in polymerization activity when used repeatedly.[10,11] The ESCA method has revealed a change in the chemical structure of anchored Rh species upon polymerization,[11] interpretation of which, however, is still uncertain.

Mesoporous molecular sieves MCM-41 have also been used as a support for anchoring Mo Schrock carbene complexes $Mo(=CHCMe_2Ph)(=N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(OR)_2$, where $OR = OCMe_3$ or $OCMe(CF_3)_2$, via a ligand exchange reaction with OH groups of MCM-41 by the elimination of the corresponding alcohol.[15a] The Mo/MCM-41 heterogeneous metathesis catalysts were found active in ROMP of cyclooctene and norbornene, as well as in metatheses of alkenes and cross-metatheses of alkenes and cycloalkenes. In the case of ROMP of cycloalkenes, chain transfer agents such as hept-1-ene or hexen-5-yl acetate can efficiently regulate the polymer molecular weight. The catalyst was found to be Mo-leaching resistant and to keep its activity unchanged upon addition of a new dose of substrate. However, a decrease in the catalytic activity was observed upon catalyst recycling, which should be ascribed to contaminants entering pores during this operation. Nevertheless, the results obtained show that such a catalyst can be effectively used for the preparation of pure soluble polymers by metathesis polymerization as well as for other metathesis reactions. Ruthenium-based mesoporous catalysts prepared by other authors showed better stability.[15b]
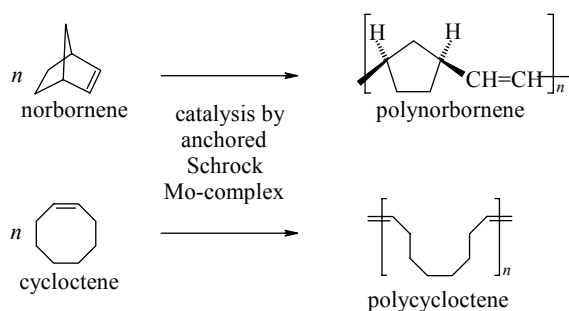
Scheme 4. Metathesis polymerizations studied with a use of anchored Schrock complexes.

3. Transformation of Chemical Polymerizations to Catalytic Processes

The replacement of chemical polymerization by a catalytic process is of potential importance mainly in the case of oxidative polymerization of anilines, pyrroles, and thiophenes, since this approach can considerably reduce contamination of neat polymers. Polyaniline (PANI) and its derivatives are routinely prepared by the stoichiometric oxidative polymerization of aniline (ANI), which gives a high amount of side products.[3] The most frequently used oxidant for polymerization of ANIs is ammonium peroxodisulphate, which is transformed into ammonium hydrogensulphate. Although this side product does not deteriorate properties of formed PANIs, its removal from neat PANI represents about half of cost of this product.[3a] We currently use this oxidant in our research of homo- and co-polymerization of various anilines carried out in the last years, in particular 2- and 3-aminobenzenesulfonic acids,[16a-f] 2-methoxyaniline,[16c-g] and 2- and 3-aminobenzoic acids.[16e,f] Nevertheless, it is clear that a replacement of the stoichiometric process by the catalytic one should bring about substantial improvement in the production of polyanilines and related polymers. Such process can be based on catalytic oxidation, in which the main inorganic oxidant is present in a catalytic amount and is continuously re-oxidized by a supporting oxidant such as molecular oxygen or ozone or hydrogen peroxide which itself is ultimately transformed into water during the polymerization, as depicted below for a system with H_2O_2 as supporting oxidant (Scheme 5).
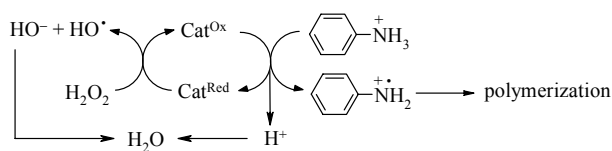

Scheme 5. Assumed catalytic cycle for a catalytic oxidative polymerization of ANI with a use of H_2O_2.

ANI has already been polymerized catalytically with (i) Cu^{2+}/O_2[3a] and Fe^{3+}/ozone[3a, 17] systems, which both show rather low polymerization activity, (ii) enzyme-based systems H_2O_2/peroxidase[18], which is too expensive, and (iii) Fe^{3+}/H_2O_2 and Ru^{3+}/H_2O_2 systems[19]. So far, the best results have been obtained using the Fe^{3+}/H_2O_2 system, which has been used in polymerizations of aniline and its 2-ethyl and 2-propyl derivatives[19] to yield the corresponding polyanilines even at an Fe/aniline molar ratio of 1:500 (this ratio should be 2.5 when the half-oxidized form of polyaniline, so-called emeraldine form, is synthesized by stoichiometric chemical polymerization). Sun et al.[19c,d] have observed that the polymerization of aniline could also be induced by hydrogen peroxide alone at temperatures above 60 °C. Hence they proposed that, in the Fe^{3+}/H_2O_2 system, iron ions induce decomposition of H_2O_2 into $HO^{\bullet}$ radicals, which indeed polymerize ANI. However, there are still other possible mechanisms of this reaction: (i) ANI might be polymerized with Fe^{3+} ions and the formed Fe^{2+} ions reoxidized by H_2O_2 (Scheme 3), or (ii) both reaction modes can take part in the overall reaction (vide infra).

To obtain a better insight into this reaction system, we have examined activity of the $FeCl_3/H_2O_2$ and $CuCl_2/H_2O_2$ systems in the polymerization of ANI, 2-methoxyaniline (OMA), and 2-chloroaniline (CANI). We found that the $FeCl_3/H_2O_2$ system applied in aqueous HCl (1 M) smoothly polymerizes all studied monomers at room temperature as well as at 5 °C giving high isolated polymer yields (70 - 90%) comparable to those obtained by the stoichiometric process even at an $FeCl_3$/aniline molar ratio of 1 : 1 000. On the other hand, the $CuCl_2/H_2O_2$ system, which also decomposes H_2O_2 to $HO^{\bullet}$ radicals, as well as H_2O_2 by itself, is practically inactive at room temperature. This clearly indicates that the presence of Fe^{3+} species in the reaction mixture is essential for the oxidative polymerization of aniline and aniline derivatives, i.e., that Fe^{3+} ions are key oxidants in this process.

Although results of catalytic polymerization experiments are very promising, quality of so prepared polymers is lower than that of polyanilines prepared by stoichiometric processes. Typical UV/vis spectra of PANIs prepared using various oxidation systems (Fig. 1) show that the $FeCl_3/H_2O_2$ system polymerizes ANI and CANI to the emeraldine forms, which, however, show lower intensity of the Q-band (band at ca 600 nm assigned to quinoid units)[16b,20] compared to that observed for PANIs prepared stoichiometrically. Consistently, also conductivity of the polymers prepared with the Fe^{3+}/H_2O_2 system reaches only 10% to 50% ($\sigma \approx 0.5$ S/cm) of that observed for stoichiometrically prepared polymers.[3d]
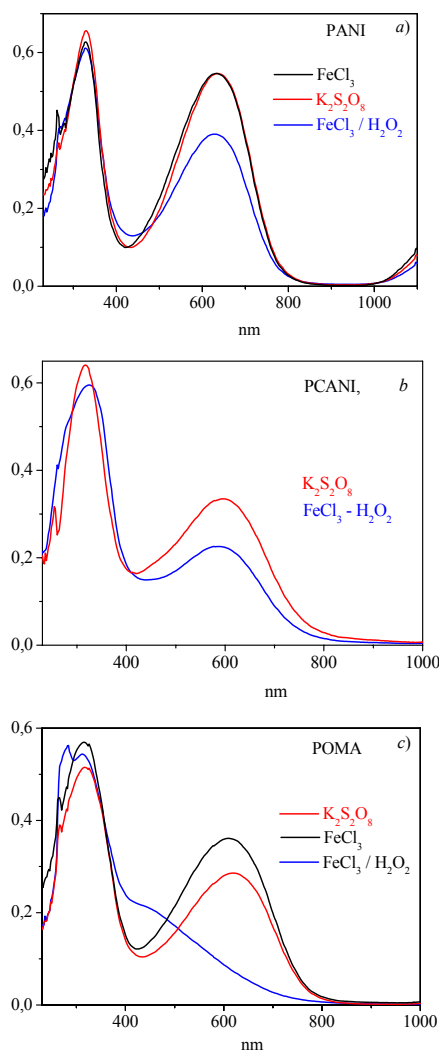
Figure 1. UV/vis spectra of: a) PANI, b) PCANI and c) POMA samples prepared by various procedures

Characteristics of catalytically prepared poly(OMA) (POMA) are still worse: (i) the Q-band is not developed in its UV/vis spectrum (Fig. 1c), and (ii) POMA does not become conductive upon doping with HCl ($\sigma \approx 10^{-11}$ S/cm). Surprisingly, no principal difference can be observed between both FTIR and FT Raman spectra of POMA samples prepared by the catalytic and stoichiometric procedures, respectively. However, broadening of the signal of aromatic protons in the ^{1}H NMR spectrum of POMA prepared using the $FeCl_3/H_2O_2$ system indicates the presence of more than three types of benzene rings and a broad signal at 3.7 ppm indicates the presence of free amino groups and oxymethylene units in this polymer. These observations can be explained by the partial oxidation of CH_3 groups of the monomer molecules and transformation of the oxidized monomer molecules into $-O-CH_2-O-C_6H_4-$ units incorporated in POMA chains. Such units interrupt the main chain conjugation, which is consistent

with the deteriorated conductivity of this polymer. It is quite probable that such units are formed through oxidation of the methyl groups induced by hydroxyl radicals formed as a side product in the reoxidation of the main oxidant (see Scheme 5).

The above observations indicate that PANIs prepared catalytically contain relatively high number of structure defects deteriorating their functional properties, and that the amount of these defects is a function of the ring substituents of PANI chains. Unsubstituted PANI and PCANI with electron-withdrawing chlorine substituent contain substantially lower number of structure defects compared to POMA carrying electron-donating $-OCH_3$ substituents. Also it is notable that POMA prepared by stoichiometric polymerization with $FeCl_3$ exhibits the Q-band intensity higher than POMA prepared with peroxodisulphate, which is also well known initiator of radical reactions. This fact supports the hypothesis that side reactions of free HO$^\bullet$ radicals are responsible for creation of defects deteriorating functional properties of catalytically prepared PANIs.

Valuable information can be drawn from the found stoichiometry of the catalytic polymerization. For ANI to be polymerized to the emeraldine form, 2.5 equivalents of the oxidant per one ANI equivalent are needed.[3c] The $[H_2O_2]/[ANI]$ mole ratio equal to 1.25 was found to be sufficient to accomplish total polymerization of ANIs with $FeCl_3/H_2O_2$ system. It means that HO$^\bullet$ radicals formed as side product of the reoxidation of Fe^{2+} ions (see Scheme 1) really participate as oxidant species in the overall polymerization process. The above-stated observation that neither H_2O_2 by itself nor $CuCl_2/H_2O_2$ polymerize ANI at temperatures up to 20 °C indicates that the presence $FeCl_3$ is essential for starting the polymerization, i.e., it is essential for the oxidation of anilinium ions (Scheme 3). Hence it can be suggested that HO$^\bullet$ radicals act as oxidant in further steps of ANI polymerization, most probably in the dehydrogenation of the intermediate formed in the combination of two anilinium or anilinium and polyanilinium cation-radicals (Scheme 6).
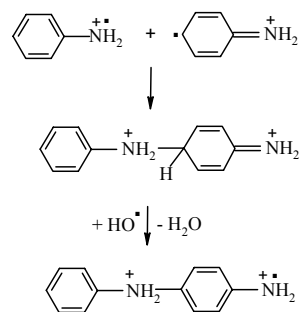
Scheme 6. Possible role of H_2O_2 in the catalytic polymerization of ANI with the system Fe^{3+}/H_2O_2.

Another notable observation is that at temperatures about 5 °C a stoichiometric polymerization with $FeCl_3$ gives only about 3% yield of PANI (MW = 6 000) and about 20% yield of POMA (MW = 8 000) within two days, whereas the catalytic polymerization with $FeCl_3/H_2O_2$ gives the yield about 80% for both polymers (MW is 31 000 for PANI and 3 200 for POMA). This suggests that, at lowered temperatures, the ability of Fe^{3+} ions to eliminate ring-hydrogen from the last-inbuilt monomeric unit is insufficient (Scheme 4). This is most probably the reason of the low to negligible polymerization activity of $FeCl_3$ observed at lowered temperatures.[3a] It can be concluded that Fe^{3+} ions and $HO^\bullet$ radicals actually form a synergic system, in which iron ions are key component in the first stage and $HO^\bullet$ radicals in the second stage of the incorporation of an ANI unit into a PANI chain.

4. Conclusions, Limitations and Perspectives

There is no doubt that purity is one of the most important factors for obtaining conjugated polymers with desired functional properties. It is also clear that a decrease in a contamination of crude, as synthesized polymers is perhaps the most effective way toward high-purity final materials. Results of recent investigations summarized in this paper points to possibilities as well as limitations of two advanced preparative approaches to the synthesis of pure conjugated polymers, which are based on transformations of (i) homogeneous catalytic processes into heterogeneous ones, and (ii) stoichiometric (chemical) processes into catalytic ones.

Heterogeneous processes based on the transformations ad (i) provide polymers that are almost free of catalyst residues and enable easy separation of the catalyst from the polymer formed. On the other hand, this method has limitations summarized below:

a) It is applicable for the synthesis of soluble polymers only.

b) It requires a use of mesoporous supports for anchoring the active catalyst to eliminate transport limitations of bulky macromolecules inside pores. Nevertheless, a diameter of the support pores needs not be as high as the static diameters of formed macromolecules because the reptation of macromolecules participates in their release from the pores.

c) In some cases also a chemical modification of inner pore walls is needed to make anchoring of catalyst species possible. On the other hand, such modification can be exploited as a method of tuning the chemical surroundings of active species towards their more effective function as well as increased long-time stability.

d) The method cannot be used for a design of living polymerization systems in which growing polymer chains are solidly linked to active species.

e) Besides, this method is not favorable for the preparation of highly stereoregular polymers, which can undergo a rapid crystallization in restricted volume elements inside pores.

Polymerizations with anchored catalysts can be potentially applied not only for the synthesis of high-purity polyacetylenes but also for syntheses of other high-purity polymers, maybe for polymers with applications in medicine and pharmacology, too. However, such an application requires further detailed study in which a fulfillment of pharmacological limits for contaminants of various kinds needs to be examined.

Relatively low attention has been paid to the catalytic oxidative polymerization of ANI despite that this process is known for ca. fourteen years[19]. As a result, the contemporary knowledge on this process is rather poor. Although it is not mentioned in published papers, PANIs prepared by catalytic processes exhibit worse quality compared to polymers prepared by stoichiometric reactions, mainly evidenced by the lowered conductivity, lowered intensity of Q-band in UV/vis spectra and increased content of structure defects, at least according to our observations. It seems clear that roots of these defects lie in side reactions of the catalytic oxidation, the mechanism of which is yet not well understood.

Our observations collected till now point to high complexity of the catalytic reaction. It is obvious that both kinds of oxidant species present in the reaction mixture, Fe^{3+} ions and $HO^\bullet$ radicals, participate in the overall mechanism, creating a synergic reaction system. As to the roles of individual oxidants, Fe^{3+} ions are crucial for starting the polymerization (oxidation of anilinium ions) while $HO^\bullet$ radicals seems to be highly active mainly at the dehydrogenation of intermediates formed in the combination of ion-radicals. Unfortunately, $HO^\bullet$ radicals most probably enter yet not well-recognized side reactions leading to structure defects deteriorating functional properties of PANIs. Better knowledge on the fate of $HO^\bullet$ and other radicals occurring in the reaction system should open a way to a desired improvement of properties of catalytically prepared PANIs.

As we have found, the content of structure defects in catalytically prepared PANIs is a function of the ring substituent; this content is low in unsubstituted PANI and CPANI carrying electron-withdrawing Cl substituent, whereas it is high in POMA with electron-donating $-OCH_3$ substituents. Taking into account

requirements for diverse applications of PANI, it can be concluded that the quality of catalytically prepared PANI is acceptable for its applications in the fields of anticorrosion and perhaps also antistatic coatings, whereas it is insufficient for more advanced applications in the field of electronics. Nevertheless, there is a space for improvement of the already known catalytic polymerization procedures toward lowering the undesirable reactions of radicals to an acceptable level and/or introduction of new, low-cost catalytic systems for oxidative polymerization of ANIs. Advances in these fields might bring about a breakthrough in this area of science of steadily increasing practical importance.

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6. References

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Povzetek

Vsebina kratkega preglednega članka je bila tematika predavanja na 13. konferenci o materialih in tehnologijah v Portorožu, 10.-12. oktobra 2005, in povzema dosežke naših laboratorijev na področju raziskav in razvoja sinteze konjugiranih polimerov visoke čistote, predvsem poliacetilenov in polianilinov. V uvodu je podan pregled pomembnejših postopkov, ki se trenutno uporabljajo za sintezo konjugiranih polimerov. Poglavje o katalitski verižni polimerizaciji v dvofaznih sistemih podaja jedrnato informacijo o sistemih tekoče-tekoče s poudarkom na pripravi mezoporoznih katalizatorjev ter njihovi uporabi in učinkovitosti za sintezo poliacetilenov visoke čistote. Za katalitske sisteme, ki so bili pripravljeni z imobilizacijo topnih, katalitsko aktivnih kompleksov kovin prehoda na mezoporoznih nosilcih, je bila raziskana katalitska učinkovitost, stereoselektivnost, ponovna uporaba in omejitve pri transportu makromolekul. Za nosilce so bili uporabljeni polibenzimidazol, molekularna sita iz silicijevega dioksida MCM 41, MCM 48 in SBA 15 in molekularna sita, pri katerih je bila notranjost por modificirana s spojinami s končnimi skupinami $-NH_2$, $-PPh_2$ in $-N(PPh_2)$. Poglavje pretvorbe stehiometričnih polimerizacij v katalitske procese obravnava predvsem polimerizacijo anilina in njegovih derivatov s katalitskim sistemom Fe^{3+}/H_2O_2. Podana je primerjava lastnosti polianilinov, pripravljenih po katalitski in stehiometrični polimerizaciji. Glede na rezultate je razvidno, da so aktivne zvrsti v reakcijski mešanici ioni Fe^{3+} in radikali $HO^{\bullet}$, ki v sinergiji sodelujejo pri polimerizaciji. V zaključnem delu je podan povzetek rezultatov naših raziskav z nakazanimi prednostmi in omejitvami sinteznih pristopov ter perspektive za njihovo uporabo in nadaljnji razvoj.