[Rh(cod)Cl]₂ complex immobilized on mesoporous molecular sieves MCM-41-a new hybrid catalyst for polymerization of phenylacetylene

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Abstract

A new hybrid catalyst affording polymerization of phenylacetylene (PhA) into high-molecular-weight ($M_w = 180\,000$) high-*cis*-polyphenylacetylene (PPhA) was prepared via immobilization of [Rh(cod)Cl]₂ (cod = η^4-cycloocta-1,5-diene) on siliceous mesoporous molecular sieves MCM-41 modified by 3-aminopropyltrimethoxysilane. The polymerization was confirmed to proceed on anchored Rh-species and PPhA formed was continuously released into liquid phase, from which it was easily isolated. In comparison with related homogeneous catalysts, the hybrid catalyst provided comparable or even higher PPhA yields, considerably higher molecular weight of PPhA and reduced amounts of oligomeric by-products. The catalyst was found to be resistant to Rh leaching; however, chemical transformation of anchored Rh-species occurring during polymerization strongly reduced the possibility of catalyst re-using.
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1. Introduction

Substituted polyvinylenes, polymers with conjugated polyene main chains, possess unique properties implicating their applications in electronics and optics [1]. So far, these polymers have been prepared almost exclusively by polymerization of corresponding substituted acetylenes homogeneously catalysed with W-, Mo-, Nb-, Ta-, Rh- and Pd-based catalysts [2–7].

As catalyst residues in polymers may undesirably affect polymer functional properties, new polymerization procedures minimizing the content of catalyst residues in the resulting polymers are of important advantage. Hybrid catalysts prepared by immobilization of catalytically active organometallic complexes on insoluble polymeric or inorganic supports promise to combine high activity and selectivity of homogeneous catalysts and easy separation of reaction products from the catalyst. The first hybrid catalysts that afford the polymerization of phenylacetylene (PhA) and its derivatives into readily isolable high-molecular-weight polyphenylacetylenes have been

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prepared recently (i) by copolymerization of (cod)Rh (AAEMA$^-$) with acrylate-type comonomers and crosslinkers (AAEMA$^-$ is a deprotonated form of 2-(acetoacetoxy)ethylmethacrylate) [8], (ii) by anchoring di-μ-chloro-bis(η^4-cycloocta-1,5-diene)dirhodium(I), [Rh(cod)Cl]$_2$, on porous polybenzimidazole beads (PBI/[Rh(cod)Cl]$_2$ catalyst) [9] and (iii) by anchoring di-μ-methoxo-bis(η^4-cycloocta-1,5-diene) dirhodium(I), [Rh(cod)OCH$_3$]$_2$, on mesoporous molecular sieves MCM-41 (MCM-41/[Rh(cod)OCH$_3$]$_2$ catalyst) [10]. In the case of PBI/[Rh(cod)Cl]$_2$ and MCM-41/[Rh(cod)OCH$_3$]$_2$ we proved that the polymerization activity was bound on the catalyst surface from which the polymer formed was continually released into the liquid phase. Comparing the polymerization activity of PBI/[Rh(cod)Cl]$_2$ and MCM-41/[Rh(cod)OCH$_3$]$_2$ catalysts of the same Rh-loading we found the MCM-41-based catalyst approximately twice as active as the PBI-based one [10]. In addition to this, mesoporous sieves are well known to possess important advantages in comparison with any organic polymer support: higher thermal and mechanical stability, high surface area and regular structure independent on the solvent used. Therefore, molecular sieves seem to be more promising supports for the hybrid catalysts development. In the previous study [10], we have found that surface Si-OH groups of MCM-41 reacted smoothly and quantitatively with bridging methoxy groups of [Rh(cod)OCH$_3$]$_2$ complex under elimination of methanol. On the contrary, we found the affinity of a similar complex, [Rh(cod)Cl]$_2$, to MCM-41 to be so low that it was impossible to anchor [Rh(cod)Cl]$_2$ on MCM-41 by a direct reaction with surface Si-OH groups. This was an unpleasant finding since [Rh(cod)Cl]$_2$ is stable, easy available (even commercially supplied), while [Rh(cod)OCH$_3$]$_2$ must be freshly prepared from [Rh(cod)Cl]$_2$. Therefore, we decided to examine a possibility of anchoring [Rh(cod)Cl]$_2$ on MCM-41 indirectly through an alkylamine linker.

In this paper, we report a new hybrid catalyst active in PhA polymerization prepared by anchoring [Rh(cod)Cl]$_2$ on MCM-41 modified by 3-aminopropyltrimethoxysilane (APTMS). Characterization of this catalyst including comparison of its activity with activity of related homogeneous catalysts is given. The structure, location and stability of catalytic active species are discussed as well.

2. Experimental

2.1. Materials

All-siliceous mesoporous molecular sieves of the MCM-41 type were synthetized by the homogeneous precipitation method using sodium silicate, hexadecyltrimethylammonium bromide and ethyl acetate. The template was removed by calcination at 550 °C for 6 h. Details are given elsewhere [11]. Diphenyldichlorosilane (Ph$_2$SiCl$_2$, Fluka, puriss.), 3-aminopropyltrimethoxysilane (Aldrich, 97%), phenylacetylene (Aldrich), chlorobenzene (PhCl, Fluka puriss.; supplied over molecular sieves) and di-μ-chloro-bis(η^4-cycloocta-1,5-diene)dirhodium(I) ([Rh(cod)Cl]$_2$ Fluka, purum) were used as obtained. Tetrahydrofuran (THF, Riedel de Haen, purity of +99.5) was freshly distilled from Cu$_2$Cl$_2$ and CaH$_2$ under argon atmosphere. CH$_2$Cl$_2$ (Lachema, Czech Republic, p.a. grade) was distilled from P$_2$O$_5$ and stored over molecular sieves (Fluka Type 4A).

Propylamino-(η^4-cycloocta-1,5-diene)chloro-rhodium (I), [Rh(cod)(PA)Cl], was prepared as a yellow solid by reaction of [Rh(cod)Cl]$_2$ with *n*-propylamine (Aldrich, used as obtained) in CH$_2$Cl$_2$ according to [12]; ^{1}H NMR (CDCl$_3$), ppm: 0.92 t (3H, $J = 7.2$) CH_3CH$_2$CH$_2$NH$_2$; 1.57 m (2H) CH$_3$CH_2CH$_2$NH$_2$; 1.70–1.81 m (4H) CH$_2$–*cod*; 2.11 s (2H) CH$_3$CH$_2$CH$_2$NH_2; 2.32–2.50 m (4H) CH$_2$–*cod*; 2.59 m (2H) CH$_3$CH$_2$CH_2NH$_2$; 3.40–4.70 (4H) =CH–*cod*. ^{13}C NMR (CDCl$_3$), ppm: 11.00 CH$_3$; 25.89 CH$_3$$CH_2CH_2NH_2$; 30.73 s CH$_2$–*cod*; 45.33 CH$_3CH_2$$CH_2NH_2$; (74–77 + 80–83) =CH–*cod*.

2.2. Preparation of hybrid catalysts

The MCM-41 molecular sieves (903 mg) were dried in vacuo at 300 °C for 6 h and, after cooling, suspended in CH$_2$Cl$_2$ (5 ml) under Ar atmosphere in a Schlenk vessel. Then APTMS (1.077 g, 6.0 mmol) was added in CH$_2$Cl$_2$ (15 ml) under vigorous stirring. After 3 h white solid MCM-41/APTMS was separated by decantation, washed four times with 15 ml CH$_2$Cl$_2$ and dried under the stream of Ar at 40–50 °C. Modified molecular sieves MCM-41/APTMS (817 mg) were suspended in CH$_2$Cl$_2$ (5 ml) and a yellow solution of [Rh(cod)Cl]$_2$ (either 20.1 mg, 0.041 mmol for the final Rh-loading of 1 wt.%, or 40.2 mg,

0.082 mmol for the final Rh-loading of 2 wt.%) in CH_2Cl_2 (11 ml) was added under vigorous stirring. The sieves turned yellow while the CH_2Cl_2 phase became colourless within the first 10 min of stirring. The stirring continued for 3 h and then the catalyst, MCM-41/APTMS/[Rh(cod)Cl]$_2$, was separated by decantation, washed three times with 15 ml CH_2Cl_2 and dried under the stream of Ar at 40–50 °C.

Passivation of MCM-41 external surface was performed according to [13]. We let 1 g of MCM-41 react with 1.5 mmol of Ph_2SiCl_2 in THF (30 ml). After washing (THF) and drying, the resulting MCM-41/Ph_2SiCl_2 was modified by the reaction with APTMS and subsequently with [Rh(cod)Cl]$_2$ (as described above) to provide MCM-41/Ph_2SiCl_2/APTMS/[Rh(cod)Cl]$_2$ catalyst with Rh-loading of 1 wt.%.

2.3. Polymerizations

A weighed amount of MCM-41/APTMS/[Rh(cod)Cl]$_2$ was suspended in a solvent (THF, CH_2Cl_2, PhCl, 2.5 ml) in a centrifuge vial provided with a magnetic stirring bar. After 10 min, PhA was added and the reaction mixture was allowed to react under stirring at room temperature. The time course of reaction was monitored by means of size exclusion chromatography (SEC) method. At a given time the reaction mixture was quickly centrifuged, a volume of 5 μl of supernatant was sampled, diluted with 0.5 ml THF and the resulting solution (20 μl) was injected into SEC columns. The content of polymer and oligomers formed was determined from the absolute areas of the corresponding SEC peaks by using final gravimetric yields of polymer and oligomers, respectively, for a calibration (vide infra). Simultaneously, the molecular weight characteristics of the polymer formed were obtained. After a polymerization time of 420 min, the supernatant (containing reaction products) was quantitatively separated from MCM-41/APTMS/[Rh(cod)Cl]$_2$ and added to methanol (50 ml). The precipitated polymer was washed several times with methanol/THF (4/1 by volume) to remove oligomers and then dried in vacuo at room temperature. Oligomers were isolated from supernatant after polymer precipitation by evaporating liquid components at room temperature. The yield of polymer as well as oligomers was determined by gravimetry. Concentrations applied in polymerization experiments were as follows: initial PhA concentration, [PhA]$_0$ = 0.6 mol/l; concentration of MCM-41/APTMS/[Rh(cod)Cl]$_2$ with the Rh-loading of 1 wt.%, c_{cat} = 15 g/l, i.e. [Rh] = 1.5 mmol/l, concentration of MCM-41/APTMS/[Rh(cod)Cl]$_2$ with the Rh-loading of 2 wt.%, c_{cat} = 15 g/l, i.e. [Rh] = 3 mmol/l. Homogeneous polymerizations induced with [Rh(cod)Cl]$_2$ and [Rh(cod)(PA)Cl] complexes were performed similarly ([PhA]$_0$ = 0.6 mol/l, [Rh] = 1.5 mmol/l). Both [Rh(cod)Cl]$_2$ and [Rh(cod)(PA)Cl] were well soluble in all polymerization solvents tested.

2.4. Techniques

^1H and ^{13}C NMR spectra were recorded on a Varian Unity Inova 400 spectrometer, ^1H spectra were referenced to tetramethylsilane, ^{13}C spectra to the solvent line at 77.00 ppm (CDCl$_3$). High resolution ^{29}Si CP MAS NMR spectra of solids were recorded on a Bruker DSX 200 spectrometer equipped with 4 mm rotor. Cross-polarization pulse program with π/2 pulse in proton channel of 5 μs, contact pulse of 10 ms, repetition delay of 6 s, spinning rate of 5 kHz and 12000 scans were applied. UV-Vis spectra in solution were recorded on a Hewlett-Packard 8452 diode-array spectrometer, UV-Vis reflectance spectra (quartz cuvette) on a Perkin-Elmer UV-Vis/NIR spectrometer Lambda. DRIFT spectra were recorded on a Nicolet Avatar 320 FT-IR spectrometer. N_2 adsorption isotherms were measured using an Acusorb 2100E Micrometrics apparatus. Scanning electron microscopy (SEM) Jeol JSM 5500LW was used for MCM-41 particle size determination.

ESCA measurements were carried out on an ESCA 310 electron spectrometer (Grammadata Scientia, Sweden) equipped with a high power rotating anode, wide-angle quartz crystal monochromator, 60 cm diameter hemispherical electron analyser operating in a fixed transition mode with pass energy set to 300 eV and a two-dimensional electron detector. A low energy electron flood gun for compensation of positive charge left on the surface by photoemission was used for measurements. The measurements were performed using Al Kα ($h\nu$ = 1486.6 eV) radiation for electron excitation. The spectrometer was calibrated with respect to Au 4f$_{7/2}$ peak (84.00 eV) with the FWHM (full width at half maximum) of 0.6 eV. The base pressure during spectra acquisition did not

exceed 10^{-7} Pa. The spectra of Si 2p and O 1s electrons of the samples measured were symmetrical, did not show any evidence of differential charging and the corresponding core level binding energies were the same for both fresh and used catalyst (Si 2p: 103.4 eV, O 1s: 532.9 eV).

SEC analyses were carried out on a TSP (Thermo Separation Products, Florida, US) Chromatograph fitted with an UV detector operating at 254 nm. A series of two PL-gel columns (Mixed-B and Mixed-C, Polymer Laboratories Bristol, UK) and THF (flow rate 0.7 ml/min) were used. Weight-average molecular weight, M_w, and number-average molecular weight, M_n, relative to polystyrene standards are reported. Quantitative analyses by inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were performed by Ecochem Co. (Prague, Czech Republic).

3. Results and discussion

3.1. Preparation of MCM-41/APTMS/[Rh(cod)Cl]₂

X-ray powder diffraction and N_2 adsorption isotherm confirmed the high quality of prepared MCM-41 molecular sieves used for subsequent hybrid catalyst preparation [11]. The BET surface area was $1032 \, m^2/g$ and average pore diameter was 3.7 nm. The particle size was about 3 μm according to SEM. After modification of MCM-41 with APTMS linker, the BET surface area of MCM-41/APTMS and average pore diameter decreased to $799 \, m^2/g$ and 3.2 nm, respectively. The elemental analysis of MCM-41/APTMS gave 2.14 wt.% of N (that corresponds to 1.53 mmol of linker per 1 g of MCM-41/APTMS). ^{29}Si CP MAS NMR spectra of MCM-41 and MCM-41/APTMS (Fig. 1) show changes accompanying the modification of MCM-41 surface by APTMS—a strong decrease of Q_3 band at -100.6 ppm ($\equiv$Si–OH) and appearance of a new broad band with the maximum at -59 ppm and shoulder at -63 ppm, which can be ascribed to $(SiO-)_2Si(OMe)[(CH_2)_3NH_2]$ and $(SiO-)_3Si[(CH_2)_3NH_2]$, respectively [14,15].

MCM-41/APTMS reacts with [Rh(cod)Cl]₂ smoothly. The complete disappearance of [Rh(cod)Cl]₂ UV-Vis bands (350, 390 nm, sh, 262 nm) observed in the supernatant indicates the quantitative character of [Rh(cod)Cl]₂ immobilization. Supernatants from immobilization and washing procedures were collected and the amount of Rh in them was determined by ICP-MS. The total amount of Rh found in supernatants corresponded to 0.03% of the original amount used for the immobilization. Therefore, the Rh-loading in the resulting MCM-41/APTMS/[Rh(cod)Cl]₂ catalysts can be calculated from the supplied amount of [Rh(cod)Cl]₂. According to this approach, the
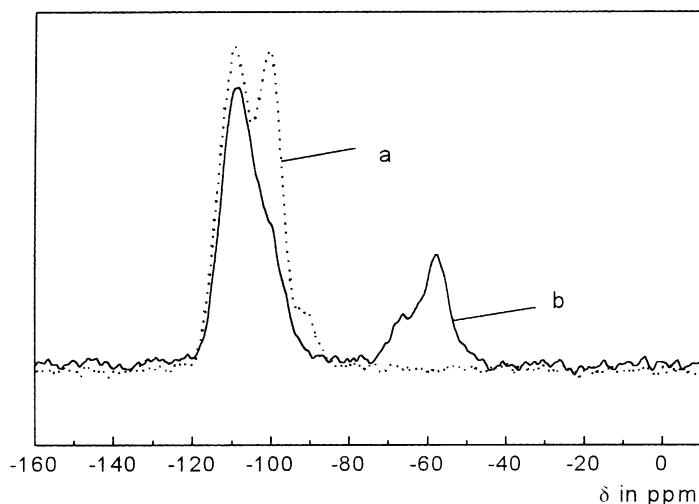

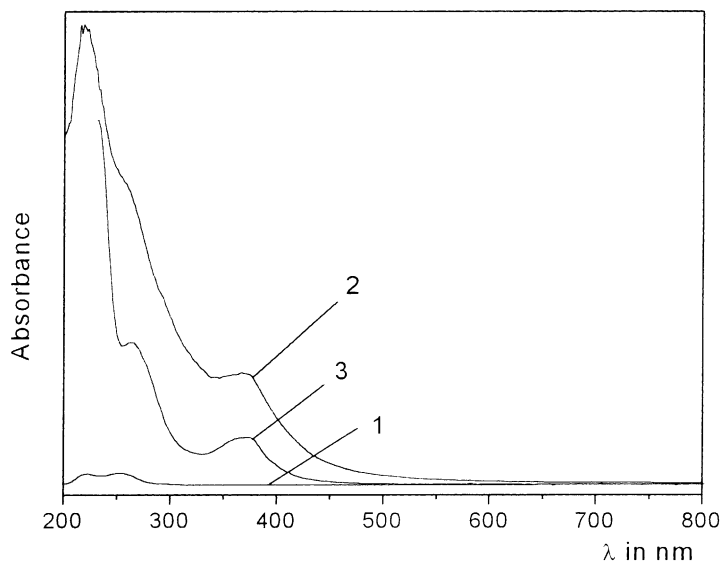Fig. 1. ^{29}Si CP MAS NMR spectra of MCM-41 (a) and MCM-41/APTMS (b).

Fig. 2. UV-Vis spectrum of MCM-41(1) and MCM-41/APTMS/[Rh(cod)Cl]$_2$ (2) and UV-VIS spectrum of [Rh(cod)(PA)Cl] in CH$_2$Cl$_2$ ($c = 0.3$ mg/ml, $l = 0.1$ cm) (3).

Rh-loading in two independently prepared MCM-41/APTMS/[Rh(cod)Cl]$_2$ samples (see Section 2) was 1 and 2 wt.%, respectively. Moreover, for the former sample, repeated ICP-AES determinations gave (0.99 ± 0.05) wt.% of Rh, and for the latter one, ESCA analysis provided surface stoichiometry of Si$_{1.00}$O$_{1.84}$C$_{0.72}$N$_{0.11}$Cl$_{0.02}$Rh$_{0.014}$ that is, within the limit of experimental errors, in a good agreement with the 2 wt.% of Rh.

The UV-Vis reflectance spectrum of MCM-41/APTMS/[Rh(cod)Cl]$_2$ coincides well with the UV-Vis spectrum of [Rh(cod)(PA)Cl] in solution (Fig. 2). This finding indicates that in the course of immobilization, [Rh(cod)Cl]$_2$ undergoes dissociation and transformation to the mononuclear –NH$_2$RhCl(cod) species linked via the aminoligand to the support as proposed in Scheme 1.

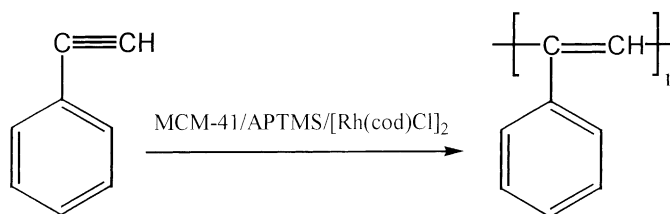### 3.2. Polymerization activity of MCM-41/APTMS/[Rh(cod)Cl]$_2$

The activity of MCM-41/APTMS/[Rh(cod)Cl]$_2$ (Rh-loading of 1 wt.%) in polymerization of PhA (Scheme 2) was examined in THF, PhCl and CH$_2$Cl$_2$ solvents. In all solvents tested, high-molecular-weight PPhA (M_w in the range from 130 000 to 190 000) was found to be continuously released from MCM-41/APTMS/[Rh(cod)Cl]$_2$ into the liquid phase, which enabled monitoring the reaction course by SEC technique (see Section 2). The catalytic activity, however, was steadily bound to the solid catalyst. This is clearly demonstrated by experiment depicted in Fig. 3. After 30 min of reaction, the polymerization mixture was divided into two volume-equal parts. The first part consisted of the liquid phase only, whereas the second one contained the rest of the liquid and all the solid catalyst. As it is seen from Fig. 3, the polymerization continued only in the system with the solid catalyst.

The dependences of PPhA yield and M_w and M_n values on polymerization time are given in Fig. 4. In all solvents tested, the polymerization proceeded similarly reaching the PPhA final yields from 43 to 64%. The effect of the solvent on the molecular weight characteristics of PPhA prepared was negligible. The small decrease in PPhA molecular weight observed during polymerization in all solvents is probably due to the formation of shorter polymer chains in the later stages of polymerization and/or slight polymer degradation that is known to proceed in various solvents [16–19]. In THF, the influence of PhA to Rh mole ratio on the polymerization was tested using MCM-41/APTMS/[Rh(cod)Cl]$_2$ catalysts differing
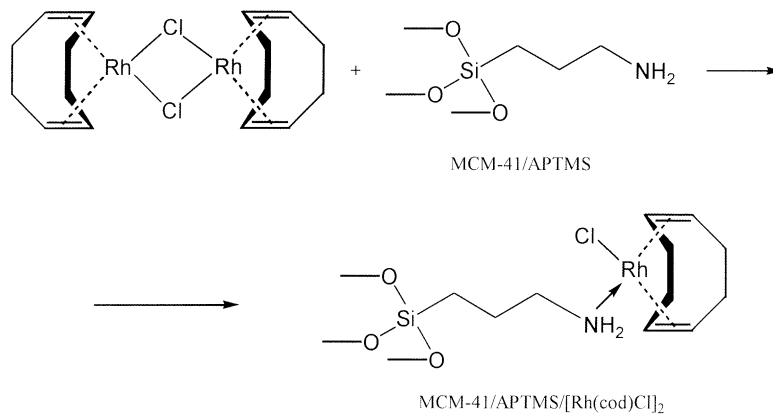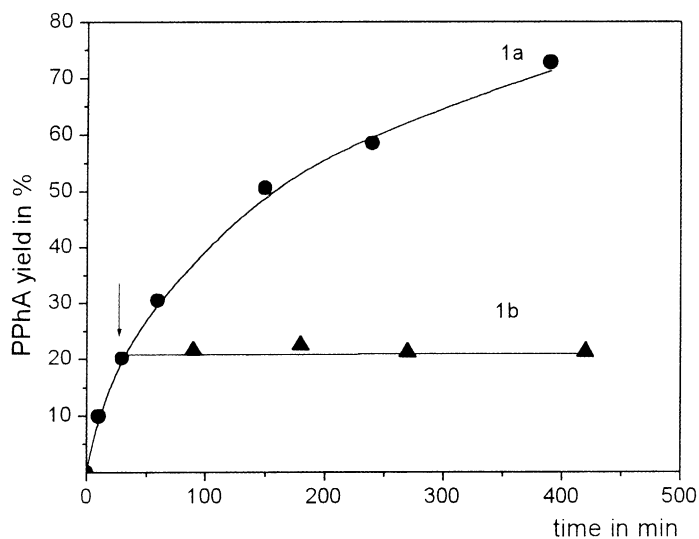
Scheme 1.

Scheme 2.

Fig. 3. PPhA yield vs. reaction time for PhA polymerization with MCM-41/APTMS/[Rh(cod)Cl]$_2$ for experiment in which the reaction mixture was divided into two parts: (1a) containing all the catalyst particles, and (1b) free of catalyst particles (separation indicated by an arrow). CH$_2$Cl$_2$, room temperature, [Rh] = 1.5 mmol/l, [PhA]$_0$ = 0.6 mol/l.
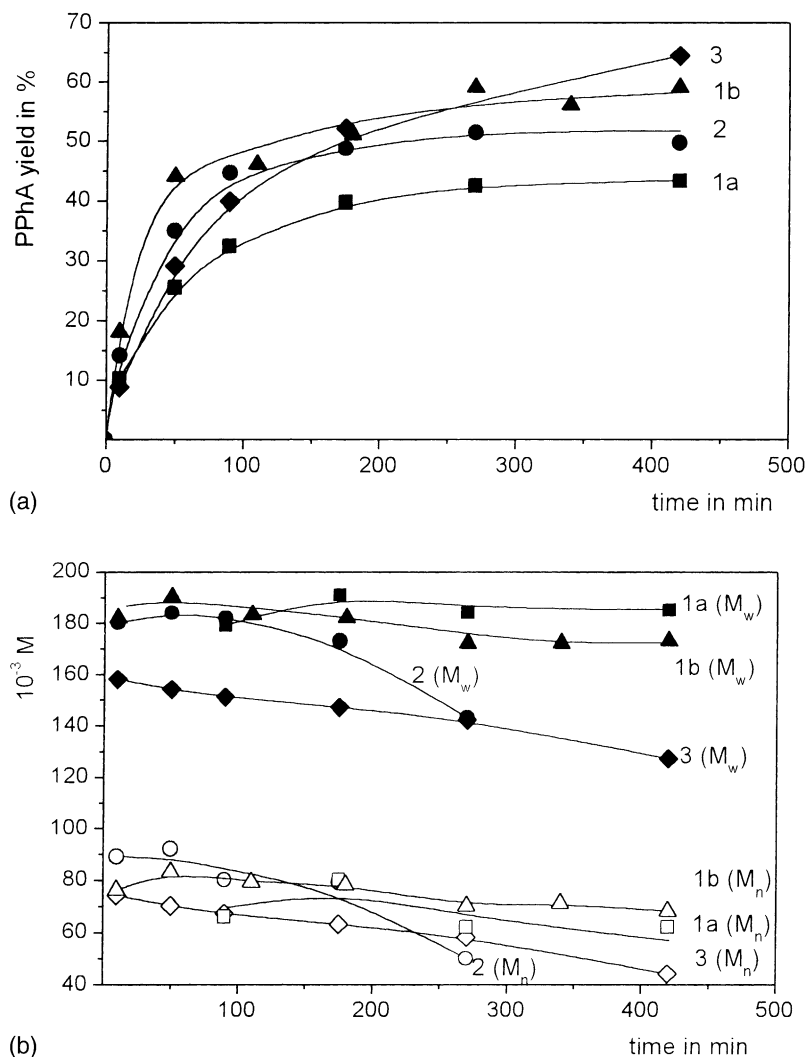
Fig. 4. PhA polymerization with MCM-41/APTMS/[Rh(cod)Cl]$_2$. Reaction time dependences of PPhA yield (a) and weight-average and number-average molecular weight of PPhA, M_w and M_n, respectively (b). Solvents: THF (curves 1a, 1b), PhCl (curve 2) and CH$_2$Cl$_2$ (curve 3). Concentrations: [Rh] = 1.5 mmol/l (curves 1a, 2, 3), 3 mmol/l (curve 1b), [PhA]$_0$ = 0.6 mol/l. Room temperature.

in the Rh-loading (1 and 2 wt.%, respectively; see Section 2). As evident from Fig. 4, an increase in Rh concentration (i.e. a reduction of [PhA]$_0$/[Rh] ratio) led to the appropriate increase in the initial polymerization rate and to a slight increase in the final PPhA yield, however, it had no influence on PPhA molecular weight. The similarly low sensitivity of polyacetylenes molecular weight to the [monomer]$_0$/[Rh] ratio has been observed earlier [10].

Using MCM-41/APTMS/[Rh(cod)Cl]$_2$ as a catalyst in polymerization reaction, the question may arise whether the growth of macromolecules is really located inside the mesoporous channels of the catalyst. We tried to answer this question by means of a special experiment performed with MCM-41 the external surface of which (approximately 10% of the total surface) was passivated by the reaction with Ph$_2$SiCl$_2$. Rohlfing et al. [13] showed that, due to the rapid
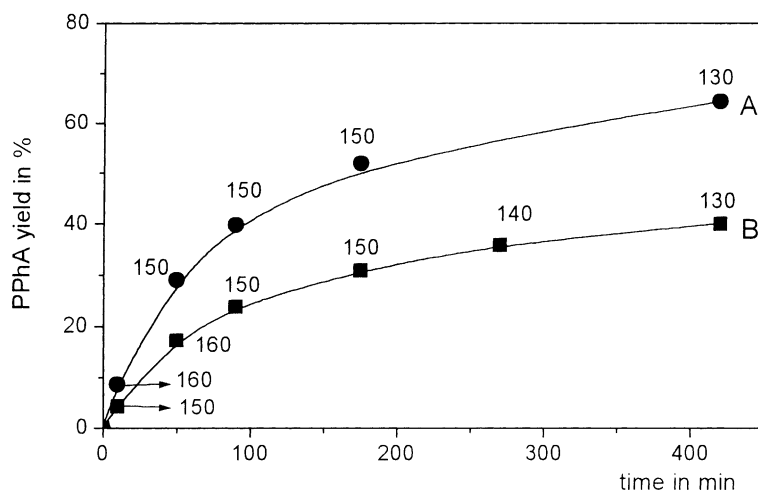
Fig. 5. PPhA yield vs. reaction time for PhA polymerization with MCM-41/APTMS/[Rh(cod)Cl]$_2$ (A) and MCM-41/Ph$_2$SiCl$_2$/ APTMS/[Rh(cod)Cl]$_2$ (B). CH$_2$Cl$_2$, room temperature, [Rh] = 1.5 mmol/l, [PhA]$_0$ = 0.6 mol/l. Numbers at experimental points denote weight-average molecular weight of PPhA (in kDa).

reaction of Ph$_2$SiCl$_2$ with Si-OH groups, the external surface Si-OH groups in MCM-41 are saturated preferentially being transformed into ∼SiO-SiPh$_2$Cl or (∼SiO)$_2$-SiPh$_2$. Thus, the pre-treatment of MCM-41 with appropriate amount of Ph$_2$SiCl$_2$ ensures that molecules of subsequently submitted linker are bound exclusively on the walls of channels. The hybrid catalyst prepared in this way, MCM-41/Ph$_2$SiCl$_2$/APTMS/ [Rh(cod)Cl]$_2$ (Rh-loading of 1 wt.%) (see Section 2) was tested in PhA polymerization (in CH$_2$Cl$_2$) under the same conditions as applied for previous experiments. The results (Fig. 5) show that passivation of external surface led to a partial decrease in polymerization rate and final polymer yield most probably due to the narrowing of the MCM-41 channel openings; on the other hand, the passivation had no influence on the molecular weight of PPhA formed. It indicates that the high-molecular-weight PPhA is formed on the inner catalyst surface, i.e. inside the channels of MCM-41/Ph$_2$SiCl$_2$/APTMS/[Rh(cod)Cl]$_2$. The finding that limited space of channels does not represent a serious obstacle for the formation of high-molecular-weight PPhA suggests that also in the case of MCM-41/APTMS/[Rh(cod)Cl]$_2$ the inner surface of catalyst is active in formation of PPhA. However, we cannot specify the distribution of Rh-species active in polymerization along the channels of the

catalyst. We assume the beginning of the channels as the most probable place where the formation of high-molecular-weight PPhA prevailingly proceeds.

IR and ^{1}H NMR spectroscopy of polymers prepared with MCM-41/APTMS/[Rh(cod)Cl]$_2$ confirmed (i) their polyphenylacetylene structure (as given in Scheme 2), and (ii) regardless of the polymerization solvent applied, always a high-*cis*-double bond content (90–95%), which is typical for polyacetylenes prepared with Rh-based homogeneous catalysts. The same microstructure of PPhA formed with hybrid MCM-41/APTMS/[Rh(cod)Cl]$_2$ and homogeneous Rh-based catalysts indicates high similarity as concerns the kind and action of respective catalytic species.

The polymerization activity of MCM-41/APTMS/ [Rh(cod)Cl]$_2$ was compared with that of two homogeneous catalysts: (i) parent [Rh(cod)Cl]$_2$ and (ii) mononuclear [Rh(cod)(PA)Cl], the structure of which we suppose to be close to the structure of anchored Rh-species (Scheme 1). Results of this comparison are given in Fig. 6. To our knowledge, [Rh(cod)(PA)Cl] has not been tested in acetylenes polymerization till now. We found [Rh(cod)(PA)Cl] to polymerize PhA in a non-living manner similarly to [Rh(cod)Cl]$_2$ (M_w/M_n = 2.0–3.0 for both complexes). As evident from Fig. 6, the activity of both homogeneous catalysts
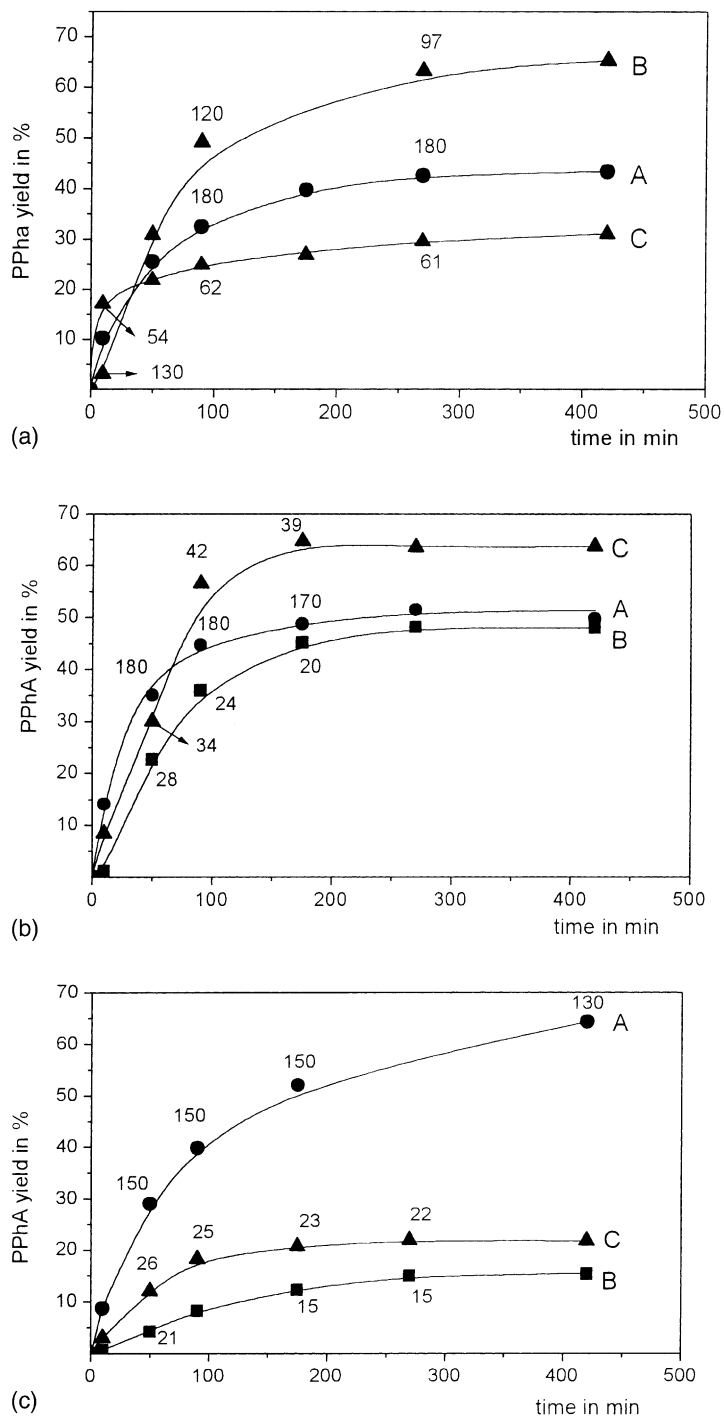
Fig. 6. PPhA yield vs. reaction time for PhA polymerization in THF (a), in PhCl (b) and in CH$_2$Cl$_2$ (c) Catalysts: MCM-41/APTMS/[Rh(cod)Cl]$_2$ (curves A), [Rh(cod)Cl]$_2$ (curves B) and [Rh(cod)(PA)Cl] (curves C). Room temperature, [Rh] = 1.5 mmol/l, [PhA]$_0$ = 0.6 mol/l. Numbers at experimental points denote weight-average molecular weight of PPhA (in kDa).

strongly depends on the polymerization solvent: (i) final PPhA yield decreases in dependence on solvent in the order THF (65%) > PhCl (48%) > CH_2Cl_2 (15%) for $[Rh(cod)Cl]_2$ and in the order PhCl (64%) > THF (31%) > CH_2Cl_2 (22%) for $[Rh(cod)(PA)Cl]$, (ii) PPhA molecular weight decreases in the order THF > PhCl > CH_2Cl_2 for both $[Rh(cod)Cl]_2$ and $[Rh(cod)(PA)Cl]$ (for values see Fig. 6). The effect of a solvent on the polymerization activity of Rh-based homogeneous catalysts is usually explained in terms of solvent ability to dissociate dinuclear Rh complexes and/or to stabilize catalytic species or their precursors [3]. Thus, better results of homogeneous polymerizations achieved in THF as compared with PhCl and CH_2Cl_2 may be explained by THF higher polarity and ability to coordinate Rh atoms in comparison with less polar PhCl and CH_2Cl_2. Contrary to the above homogeneous catalysts, the polymerization activity of MCM-41/APTMS/$[Rh(cod)Cl]_2$ was found to be significantly less sensitive to the polymerization solvent applied, particularly as the molecular weight of resulting PPhA is concerned. The PPhA yield

achieved with MCM-41/APTMS/$[Rh(cod)Cl]_2$ was either comparable (in THF and PhCl) or even higher (in CH_2Cl_2) than that obtained in homogeneous polymerizations. A very strong effect of $[Rh(cod)Cl]_2$ anchoring is, however, apparent from the comparison of M_w values of PPhA: regardless of the solvent applied, MCM-41/APTMS/$[Rh(cod)Cl]_2$ provided PPhA of considerably higher molecular weight than that achieved with homogeneous catalysts; especially high differences were found in PhCl and CH_2Cl_2. It may indicate that specific surroundings of catalytic centres in channels of MCM-41/APTMS/$[Rh(cod)Cl]_2$ suppress termination of polymer chains growth (probably by reducing chain transfer).

With homogeneous Rh catalysts, the polymerization of PhA is known to be accompanied by formation of oligomers (molecular weight from 1000 to 2000). Using MCM-41/APTMS/$[Rh(cod)Cl]_2$ this oligomerization was significantly reduced in all solvents tested (Fig. 7). The reduction of oligomerization activity of Rh catalysts as a consequence of their immobilization was also observed earlier for $[Rh(cod)OMe]_2$
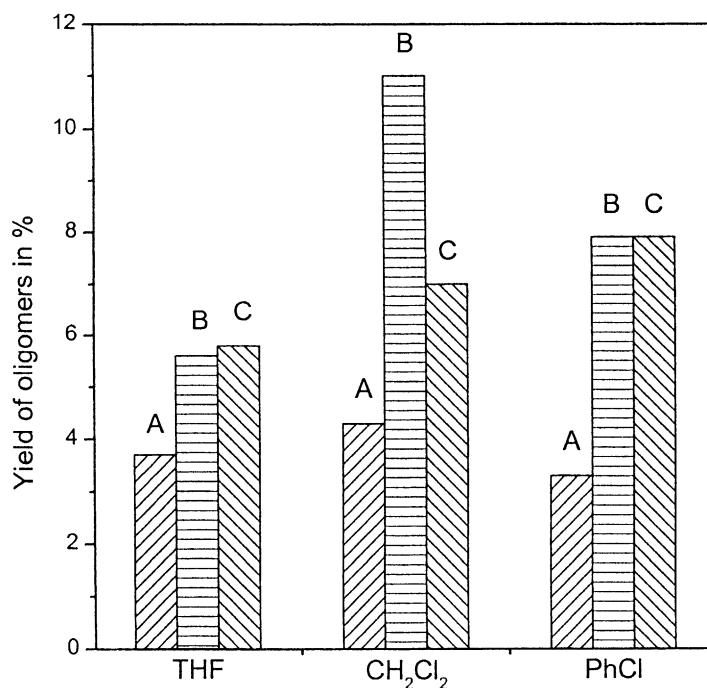

Fig. 7. Yield of oligomers resulting in PhA polymerization with MCM-41/APTMS/$[Rh(cod)Cl]_2$ (A), $[Rh(cod)Cl]_2$ (B) and $[Rh(cod)(PA)Cl]$ (C) in various solvents. Room temperature, [Rh] = 1.5 mmol/l, $[PhA]_0$ = 0.6 mol/l, reaction time = 7 h.

anchored on MCM-41 and [Rh(cod)Cl]$_2$ anchored on polybenzimidazole [9,10]. As oligomerization and polymerization probably proceed on distinct catalytic centres [20], it may suggest that immobilization of Rh complexes reduces the extent of conversion of Rh-moieties into species inducing PhA oligomerization.

3.3. Characterization of MCM-41/APTMS/[Rh(cod)Cl]$_2$ used in polymerization

After PhA polymerization in THF had finished (reaction time 7 h, PPhA yield 59%) the catalyst MCM-41/APTMS/[Rh(cod)Cl]$_2$ (Rh-loading of 2 wt.%) was separated, washed with THF and examined for re-using under the same reaction conditions (for conditions see Fig. 4). The catalyst activity in the second polymerization cycle was found to be strongly depressed. After 7 h of reaction, the PPhA yield of 2% ($M_w = 145\,000$, $M_n = 60\,000$) was achieved; at the prolonged reaction time of 24 h, the PPhA yield increased up to 10%, however, the molecular weight of polymer decreased considerably ($M_w = 60\,000$, $M_n = 11\,000$). To find the reason for the catalyst deactivation, we studied the sample of used MCM-41/APTMS/[Rh(cod)Cl]$_2$ (Rh-loading of 2 wt.%), i.e. catalyst isolated after the first polymerization cycle (in THF), carefully washed with THF and dried under Ar. In comparison with fresh MCM-41/APTMS/[Rh(cod)Cl]$_2$, the surface stoichiometry determined by ESCA (see above) did not reveal any decrease in Rh concentration in the used catalyst. However, the value of 3d electron binding energy of Rh atoms in the fresh (308.8 eV) and used (309.4 eV) MCM-41/APTMS/[Rh(cod)Cl]$_2$ differed significantly (Fig. 8). This increase in the binding energy can be attributed to the rise in the positive charge of Rh atom probably due to the replacement of its substituent(s) by more electron withdrawing one(s). The same shift in binding energy from 308.5 to 309.0 eV was observed for previously studied MCM-41/[Rh(cod)OCH$_3$]$_2$, the activity of which in the second polymerization cycle was also very low [21]. Thus, similar chemical transformations of anchored Rh-species very probably occurred during the PhA polymerization, in both cases. These transformations seem to be the main reason for the observed catalyst deactivation, since a blocking of
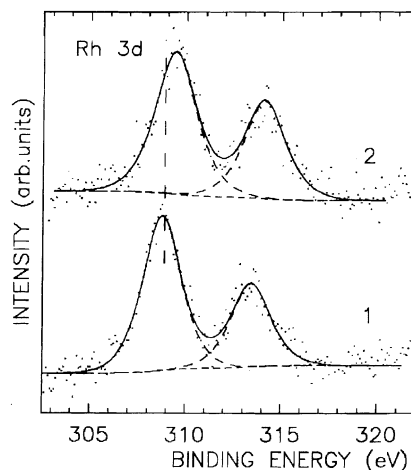

Fig. 8. High resolution spectra of Rh (3d) electrons for MCM-41/APTMS/[Rh(cod)Cl]$_2$ before using (1) and after using (2) in PhA polymerization.

catalyst pores by insoluble polymer deposition is not probable (no signals of PPhA were found in DRIFT spectra of the used catalysts). The character of these transformations is not yet completely clear. For MCM-41/[Rh(cod)OCH$_3$]$_2$, we observed a liberation of *cod* ligand from the anchored complex into the liquid phase during PhA polymerization in THF [21]. Similarly, evolution of free 1,5-cyclooctadiene during PhA polymerization with [Ir(cod)Cl]$_2$ homogeneous catalyst was observed recently [22]. Although we have not succeeded in detection of free cyclooctadiene in the course of PhA polymerization with MCM-41/APTMS/[Rh(cod)Cl]$_2$, we suggest oxidative addition of two PhA molecules (and/or two segments of an oligomer molecule) to the anchored Rh atom (with a possibility of *cod* liberation) under formation of species of rhodacyclopent-ene/-adiene-type [23] as a possible way of Rh centres deactivation for both MCM-41/[Rh(cod)OCH$_3$]$_2$ and MCM-41/APTMS/[Rh(cod)Cl]$_2$ hybrid catalysts.

4. Conclusions

A new hybrid catalyst for polymerization of PhA into high-molecular-weight PPhA was prepared by anchoring stable and commercially available [Rh(cod)Cl]$_2$ on siliceous mesoporous molecular sieves

MCM-41 modified with APTMS. The polymerization proceeded on the catalyst surface and PPhA formed was continuously released into the liquid phase, from which it was easily isolated. In comparison with homogeneous catalysts, parent [Rh(cod)Cl]$_2$ and mononuclear [Rh(cod)(PA)Cl] complexes, the hybrid MCM-41/APTMS/[Rh(cod)Cl]$_2$ catalyst exhibited comparable or even higher polymerization activity. Especially, the Rh complex anchoring brought about the considerable increase in the molecular weight of polymer formed and parallel reduction in formation of undesirable oligomeric by-products. The stereoselectivity of Rh homogeneous catalysts leading to the formation of high-*cis*-polyacetylenes was preserved in polymerization with MCM-41/APTMS/[Rh(cod)Cl]$_2$. The hybrid catalyst described was resistant to Rh leaching. However, the observed chemical transformation of anchored Rh-species during polymerization caused the catalyst deactivation and strongly reduced a possibility of catalyst re-using.

Acknowledgements

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