

**METATHESIS POLYMERIZATION OF PHENYLACETYLENE
BY TUNGSTEN ARYLOXO COMPLEXES***Hynek BALCAR^a, Jan SEDLACEK^b, Marta PACOVSKA^b and Vratislav BLECHTA^c^a *J. Heyrovsky Institute of Physical Chemistry,**Academy of Sciences of the Czech Republic, 182 23 Prague 8, The Czech Republic*^b *Department of Physical and Macromolecular Chemistry,**Charles University, 128 40 Prague 2, The Czech Republic*^c *Institute of Chemical Process Fundamentals,**Academy of Sciences of the Czech Republic, 165 02 Prague 6-Suchbát, The Czech Republic*

Received November 11, 1994

Accepted December 12, 1994

Catalytic activity of the tungsten aryloxo complexes $WCl_5(OAr)$ and $WOCl_3(OAr)$, where $Ar = 4-t-C_4H_9C_6H_4$, $2,6-(t-C_4H_9)_2C_6H_3$, $2,6-Cl_2C_6H_3$, $2,4,6-Cl_3C_6H_2$, and $2,4,6-Br_3C_6H_2$ in polymerization of phenylacetylene (20 °C, monomer to catalyst molar ratio = 1 000) was studied. The activity of $WCl_5(OAr)$ as unicomponent catalysts increases with increasing electron withdrawing character of the $-OAr$ ligand. Addition of two equivalents of organotin cocatalysts (Me_4Sn , Bu_4Sn , Ph_4Sn , Bu_3SnH) to $WCl_5(O-C_6H_4Cl_2-2,4,6)$ has only slight positive effect (slightly higher polymer yield and/or molecular weight of poly(phenylacetylene)s was achieved). However, in the case of $WOCl_3(O-C_6H_3Cl_2-2,6)$ catalyst, it enhances the activity considerably by eliminating the induction period. Poly(phenylacetylene)s prepared with the catalysts studied have weight-average molecular weight ranging from 100 000 to 200 000. They are *trans*-prevailing and have relatively low molar fraction of monomer units comprised in cyclohexadiene sequences (about 6%).

As substituted polyacetylenes attract great attention for their potential applications in electronics and optoelectronics, various techniques for their preparation have been developed. Since Masuda¹ synthesized poly(phenylacetylene) (PPhA) by polymerization of phenylacetylene (PhA) with WCl_6 based catalysts, many other transition metal catalysts active in the olefin metathesis have been applied to polymerization of various substituted acetylenes².

Aryloxo complexes of hexavalent tungsten were reported as efficient metathesis catalysts when combined with Al, Sn or Mg containing organometallic cocatalysts³⁻⁵. Recently, Nakayama et al.⁶ applied 2,6-dimethylphenoxotungsten(VI) chlorides in combination with Et_3Al or $EtMgBr$ for polymerization of *tert*-butylacetylene and prepared

* Presented at the XXVth Czech and Slovak Symposium on Catalysis, Prague, November 7 – 8, 1994.

high molecular-weight poly(*tert*-butylacetylene) with a narrow molecular-weight distribution.

In our previous contribution⁷, we have shown that complexes of the type $WCl_5(OAr)$ and $WOCl_3(OAr)$, where Ar is aryl substituted with bulky or electron withdrawing groups, are active in the polymerization of various 1-alkynes without any cocatalysts (i.e. as unicomponent catalyst) at room temperature. Particularly, in the case of polymerization of PhA, the high activity of these catalysts was found, and the high molecular weight PPhAs were prepared in good yields (30 – 60%) even if initial monomer/catalyst molar ratio = 1 000 was used.

The aim of the present contribution is to report on further results concerning the polymerization of PhA by these catalysts (as unicomponent ones) and about changes in their catalytic activity caused by the addition of alkyl- or phenyltin cocatalysts.

EXPERIMENTAL

Chemicals

The complexes $WCl_5(OAr)$ and $WOCl_3(OAr)$ were prepared by direct reaction of WCl_6 and $WOCl_4$, respectively (Fluka, purum – purified by sublimation in vacuo) with equivalent amounts of corresponding phenols in diluted benzene solutions^{5,8}. The complexes so prepared were isolated as solids and characterized by UV-VIS, IR and mass spectroscopy. Their spectroscopic data are given elsewhere⁷. Phenylacetylene (Fluka, purum) was dried by NaH and distilled in vacuo. Purification of benzene is described elsewhere⁹. Me_4Sn (Fluka, purum), Bu_4Sn , Ph_4Sn (Koch Light Lab., purum) and Bu_3SnH (Aldrich, 97%), applied as cocatalysts, were used as received.

Procedures

All operations were carried out using standard vacuum break-seals technique⁸. Polymerizations were initiated at room temperature by adding PhA to the benzene solution of a catalyst (tungsten aryloxo complex, concentration 5 mmol/l); when a cocatalyst was applied, it was charged (in benzene solution, concentration 10 mmol/l) simultaneously with PhA. Polymerizations were performed at 20 °C and were quenched by pouring the reaction mixture into methanol (purged with argon). Methanol-insoluble polymers were dried in vacuo (40 °C), and the polymer yields were determined gravimetrically. The samples for further analyses were stored in vacuo.

Techniques

UV-VIS spectra of catalyst/cocatalyst mixtures were measured in sealed evacuated cuvettes on a Hewlett-Packard HP 89500 spectrometer.

Size exclusion chromatography (SEC) analyses of PPhAs were performed using TSP liquid chromatograph equipped with CM 3200 pump and SM 3200 UV detector working at 254 nm. A column packed with PL-gel (Mixed-C) and tetrahydrofuran as the mobile phase (0.7 ml/min, 20 °C) were applied. For molecular-weight characterizations the standard polystyrene calibration method was used. Special attention was paid to the preparation of the samples for SEC, to minimize the influence of polymer degradation¹⁰.

^1H NMR spectra of PPhAs were measured in CCl_4 at room temperature on a Varian Unity 500 spectrometer (500 MHz). Simple one-pulse sequence was employed with flip angle 45° , the acquisition time 4 s and the relaxation delay 5 s. TMS in CCl_4 was used as an external standard. Exponential weighting function (line-broadening constant 4 Hz) and polynomial baseline correction of the order 8 were applied to the spectra.

RESULTS AND DISCUSSION

Catalyst Activity

The catalytic activity of $\text{WCl}_5(\text{OAr})$ complexes as unicomponent catalysts in the PhA polymerization depends significantly on the kind of the aryloxo ligand. An example of the course of polymerization is shown in Fig. 1 (curve 5) where the polymer yield vs reaction time is plotted for the polymerization catalyzed by $\text{WCl}_5(\text{O}-\text{C}_6\text{H}_2\text{Cl}_3-2,4,6)$. The curves having similar shape were obtained when other $\text{WCl}_5(\text{OAr})$ complexes were used as unicomponent catalysts⁷. There was no induction period, the reactions proceeded most rapidly at the initial stage, but were slowed down significantly on prolonged reaction times and ceased before all the PhA was consumed. Therefore, the initial rate of polymerization and the polymer yield achieved after 24 h (the final yield) represent data suitable for evaluation of the activity of the catalysts. These data are summarized in Table I where two quantities characterizing the aryloxo ligands (the ionization constant of the corresponding phenols^{11,12} and the wavenumber of the W–O bond stretching vibration in the complexes) are also given. As it is seen from Table I, the catalytic activity of the complexes increases in the following series: $\text{WCl}_5(\text{O}-\text{C}_6\text{H}_4t-\text{C}_4\text{H}_9-4) < \text{WCl}_5[\text{O}-\text{C}_6\text{H}_3(t-\text{C}_4\text{H}_9)_2-2,6] < \text{WCl}_5(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2-2,6) < \text{WCl}_5(\text{O}-\text{C}_6\text{H}_2\text{Cl}_3-2,4,6) < \text{WCl}_5(\text{O}-\text{C}_6\text{H}_2\text{Br}_3-2,4,6)$. This is in accord with the increas-

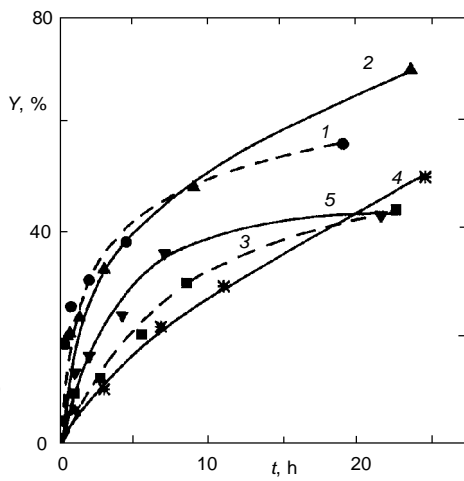


FIG. 1

Effect of cocatalysts on the polymer yields in PhA polymerization (Y , %) with $\text{WCl}_5(\text{O}-\text{C}_6\text{H}_2\text{Cl}_3-2,4,6)$ (monomer/W molar ratio = 1 000, Sn/W molar ratio = 2, initial catalyst concentration $c_w^0 = 1.9$ mmol/l, benzene, 20°C). Cocatalysts: 1 Me_4Sn , 2 Ph_4Sn , 3 Bu_4Sn , 4 Bu_3SnH , 5 no cocatalyst; t polymerization time

ing acidity of the corresponding phenols, except for 2,6-di-*tert*-butylphenol. In this case, the steric hindrance of two bulky *tert*-butyl substituents in the *ortho* positions prevents the manifestation of the electronic effect of these groups. The IR data from Table I, indicating differences in the W–O bond length of the complexes with 4-*tert*-butylphenoxo and 2,6-di-*tert*-butylphenoxo ligands, respectively, confirm this assumption.

Mechanism of the transformation of the high valent tungsten chlorides by the reaction with substituted acetylenes into metallocarbene species (which are considered as the active centres of the polymerization²) has not been clarified in detail. Recently, Vohlídal et al.¹³ have studied polymerization of PhA with WOCl₄ and suggested that tungsten is reduced to the lower oxidation state by PhA. Consecutively, a tungsten carbene complex is formed from PhA probably with participation of the aromatic solvent. Similar conclusions were reported by Makovetsky et al.¹⁴ for WCl₆ catalyst. Assuming the principal similarity with our systems, the influence of the kind of the aryloxo ligand on the catalytic activity of the complexes studied may be discussed. Increasing electronegativity of the aryloxo ligand reduces the electron density at the tungsten atom and decreases thus the redox potential of the complex. Due to this, the easier reduction of the tungsten complex may be expected, which might positively affect formation of the carbene species. The increase in catalytic activity of WCl₅(OAr) complexes with increasing electron withdrawing character of the OAr ligand (Table I) is in accord with this assumption. Moreover, the electronegativity of the aryloxo ligand bound in tungsten carbene complex might influence its activity in the propagation step, since for this activity, the proper polarization of the tungsten–carbene bond is believed to be important.

TABLE I

Initial rates, v_0 (mol/l h), and final yields of PPhA, Y_{total} (%) for the PhA polymerization catalyzed by WCl₅(OAr) unicomponent catalysts with various OAr ligands (PhA/catalyst molar ratio = 1 000, initial catalyst concentration $c_w^0 = 3$ mmol/l, benzene, 20 °C, 24 h)

ArO	v_0	Y_{total}	pK_a^a	ν , cm ^{-1,b}
2,4,6-Br ₃ C ₆ H ₂ O	3.0	61	6.0	900
2,4,6-Cl ₃ C ₆ H ₂ O	0.79	64	6.2	900
2,6-Cl ₂ C ₆ H ₃ O	0.40	60	6.8	900
2,6-(<i>t</i> -C ₄ H ₉) ₂ C ₆ H ₃ O	0.19	38	11.7	907
4-(<i>t</i> -C ₄ H ₉)C ₆ H ₄ O	0.11	29	10.4	915

^a pK_a Ionization constant of phenols corresponding to OAr ligands (25 °C, H₂O) taken from refs ^{11,12}.

^b ν Wave number of W–O bond vibration taken from IR spectra of WCl₅(OAr) complexes in benzene solution.

The addition of organotin cocatalysts to the $WCl_5(OAr)$ complex should facilitate the reduction of tungsten and enhance thus the catalytic activity. However, only little effect was observed when the influence of cocatalysts on the polymerization activity of $WCl_5(O-C_6H_2Cl_3-2,4,6)$ catalyst was tested (Fig. 1). From four organotin compounds investigated (Me_4Sn , Ph_4Sn , Bu_4Sn and Bu_3SnH) only two exhibited positive effect on the initial rate of PhA polymerization (Me_4Sn and Ph_4Sn) when they were added together with PhA to the catalyst solution. On the contrary, the addition of Bu_4Sn or Bu_3SnH has led to a slight decrease of the initial rate of polymerization. The shape of the conversion curves (Fig. 1) indicates, however, that all two-component catalysts investigated are active for a longer time, compared with the unicomponent one.

To study the role of Me_4Sn cocatalyst in the catalyst system, the reaction between $WCl_5(O-C_6H_2Cl_3-2,4,6)$ and Me_4Sn in the absence of PhA (room temperature, benzene) was followed by UV-VIS spectroscopy (Fig. 2). Unfortunately, the reaction product responsible for the appearance of the band at 475 nm is not stable enough and therefore only a decrease in the charge transfer band of the starting complex at 540 nm gives information (only qualitative due to the slight overlapping of bands at 475 nm and 540 nm) about the rate of this reaction. As evident from Fig. 2, this decrease (540 nm) is rather slow and very probably cannot explain the increase in the catalytic activity upon the addition of Me_4Sn to $WCl_5(O-C_6H_2Cl_3-2,4,6)$ (Fig. 1). This seems to be confirmed also by the polymer yield vs reaction time curves obtained for polymerization experiments (Fig. 3), in which $WCl_5(O-C_6H_2Cl_3-2,4,6)$ was allowed to react with Me_4Sn for varying times τ , prior to PhA was introduced. Formation of carbene active centres or their precursors by reaction of $WCl_5(O-C_6H_2Cl_3-2,4,6)$ with Me_4Sn may be expected. Results in Fig. 3 show that the catalytic activity is significantly higher for $\tau = 2.5$ h compared to $\tau = 25$ min, indicating that the amount and/or activity of the active centres

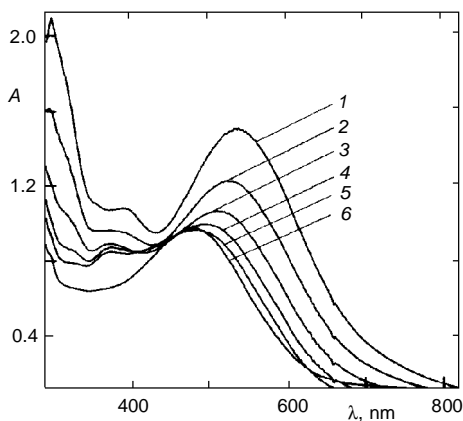


FIG. 2

Changes in UV-VIS spectra (A) in the course of the reaction of $WCl_5(O-C_6H_2Cl_3-2,4,6)$ with Me_4Sn (room temperature, benzene, initial catalyst concentration $c_w^0 = 1.9$ mmol/l, Sn/W molar ratio = 2, cuvette length l 0.1 cm). Reaction times: 1 1 min, 2 22 min, 3 55 min, 4 2 h, 5 3.5 h, 6 29 h

or their precursors resulting from this reaction is higher for $\tau = 2.5$ h. However, Fig. 3 also shows that the catalyst system studied was most efficient for $\tau = 0$. In this case, majority of active centres is probably formed from precursors resulted from rapid reaction of $\text{WCl}_5(\text{O}-\text{C}_6\text{H}_2\text{Cl}_3-2,4,6)$ with PhA. Thus, the cocatalytic effect of Me_4Sn (introduced simultaneously with PhA) may consist predominantly in its participation on the transformation of these precursors to carbene active centres.

The complexes $\text{WOCl}_3(\text{OAr})$, where $\text{Ar} = 2,6-(t\text{-C}_4\text{H}_9)_2\text{C}_6\text{H}_3$ and $2,6\text{-Cl}_2\text{C}_6\text{H}_3$, are also active in polymerization of PhA as unicomponent catalysts⁷. The reaction, however, exhibits relatively long induction period⁷, as evident from Fig. 4 (curve 1) where the polymer yield is plotted vs reaction time for the polymerization induced by $\text{WOCl}_3(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2-2,6)$ catalyst. Addition of organotin cocatalysts (Me_4Sn , Bu_4Sn) to $\text{WOCl}_3(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2-2,6)$ eliminates the induction period completely (Fig. 4). Almost no difference in the activity between the system with Me_4Sn and that with Bu_4Sn was observed. UV-VIS spectra recorded in the course of the reaction of $\text{WOCl}_3(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2-2,6)$ with Me_4Sn in the absence of PhA (room temperature, benzene) are shown in Fig. 5. The decrease of the band at 510 nm, characteristic for the starting tungsten complex, is evident. However, changes in the spectrum suggest that the reac-

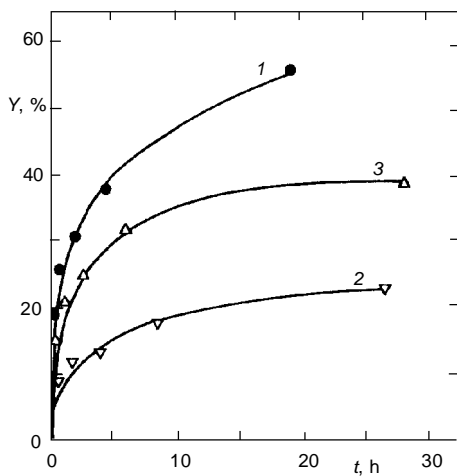


FIG. 3

Effect of the time (τ) of the reaction between $\text{WCl}_5(\text{O}-\text{C}_6\text{H}_2\text{Cl}_3-2,4,6)$ and Me_4Sn (prior to addition of monomer) on the polymer yields in PhA polymerization (Y , %) (initial catalyst concentration $c_w^0 = 1.9$ mmol/l, monomer/W molar ratio = 1 000, Sn/W molar ratio = 2, benzene, 20 °C). τ : 1 0 min, 2 25 min, 3 2.5 h; t polymerization time

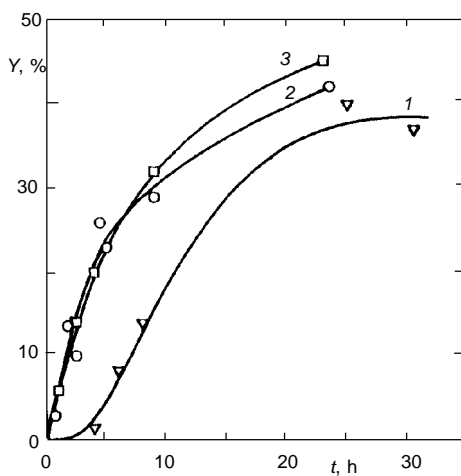


FIG. 4

Effect of cocatalysts on the polymer yields in PhA polymerization (Y , %) with $\text{WOCl}_3(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2-2,6)$ (initial catalyst concentration c_w^0). (Monomer/W molar ratio = 1 000, Sn/W molar ratio = 2, benzene, 20 °C). 1 no cocatalyst ($c_w^0 = 3$ mmol/l), 2 Me_4Sn ($c_w^0 = 1.9$ mmol/l), 3 Bu_4Sn ($c_w^0 = 1.9$ mmol/l); t polymerization time

tion of $\text{WOCl}_3(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2-2,6)$ with Me_4Sn proceeds too slowly to be considered as an explanation of the disappearance of the induction period shown in Fig. 4. More probably, the cocatalyst accelerates transformation of the precursors (formed by the reaction of $\text{WOCl}_3(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2-2,6)$ with PhA) to the carbene active centres as already proposed for $\text{WCl}_5(\text{O}-\text{C}_6\text{H}_2\text{Cl}_3-2,4,6)$.

Polymer Properties

PPhAs prepared with the studied catalyst systems were orange-red solids (VIS maximum about 440 nm). Figure 6 shows weight-average molecular weights (\overline{M}_w) of polymers plotted against the polymer yield for some experiments from Figs 1 and 4. Slight increase in \overline{M}_w as a result of the cocatalyst addition is evident. The decrease in \overline{M}_w observed at prolonged polymerization times in some cases may indicate the polymer degradation induced by the polymerization catalyst. The polydispersity index ($\overline{M}_w/\overline{M}_n$) was in the range from 1.9 to 2.3 for all the PPhA samples. No systematic dependence on the type of catalyst used and/or on the polymerization time was observed.

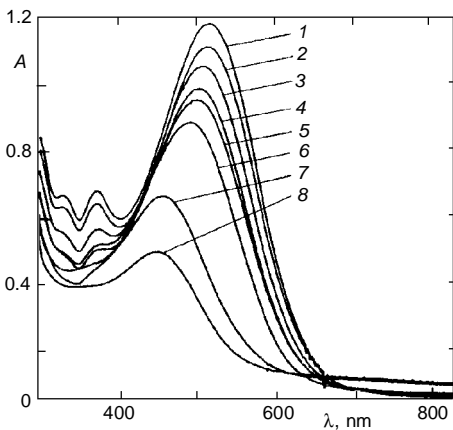


FIG. 5

Changes in UV-VIS spectra (A) in the course of the reaction of $\text{WOCl}_3(\text{O}-\text{C}_6\text{H}_3\text{Cl}_2-2,6)$ with Me_4Sn (room temperature, benzene, initial catalyst concentration $c_w^0 = 1.9$ mmol/l, Sn/W molar ratio = 2, cuvette length l 0.1 cm). Reaction times: 1 2 min, 2 12 min, 3 1 h, 4 2 h 20 min, 5 3 h 20 min, 6 5 h 20 min, 7 30 h, 8 3 days

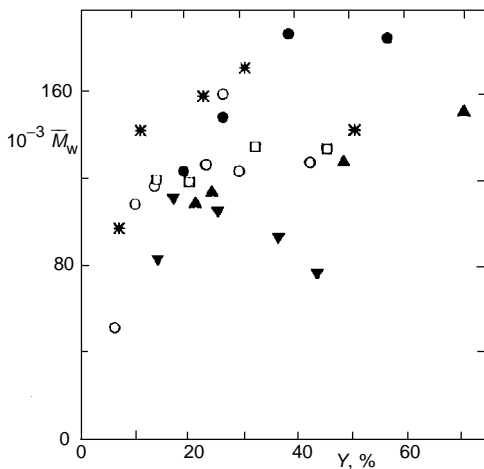


FIG. 6

Weight-average molecular weight \overline{M}_w , of PPhA synthesized with various catalyst systems as a function of the polymer yield (Y , %). For the reaction conditions and data designation see Figs 1 and 4.

Microstructure of the PPhA samples prepared in the experiments from Figs 1 and 4 was studied by ^1H NMR spectroscopy. A typical spectrum is shown in Fig. 7. It represents a *trans*-prevailing polymer. The signal at 5.82 ppm indicates some amount of *cis* monomeric units. However, its relative intensity is below the limit for the determination of the content of these units from ^1H NMR spectra¹⁵. No variations of the shape of ^1H NMR spectra were observed in dependence on the type of the catalyst system and/or polymerization time. From the area of the low intensity band in the region from 2.8 to 4.6 ppm, the molar fraction of the units comprised in cyclohexadiene sequences [$f(cx)$] was determined according to Percec¹⁶. The results are shown in Fig. 8. It is seen that $f(cx)$ is relatively small and does not depend on the catalyst system. With increasing PPhA yield, this fraction is either constant or slightly decreases. It might indicate that under the conditions applied, the formation of cyclohexadiene sequences proceeds during the growth of polymer chains and does not result from isomerization of the already formed PPhA chains. The slight decrease in $f(cx)$ at the higher conversions may be explained by the release of benzene and/or triphenylbenzene from the polymer chains, as already proposed by Simionescu and Percec¹⁵.

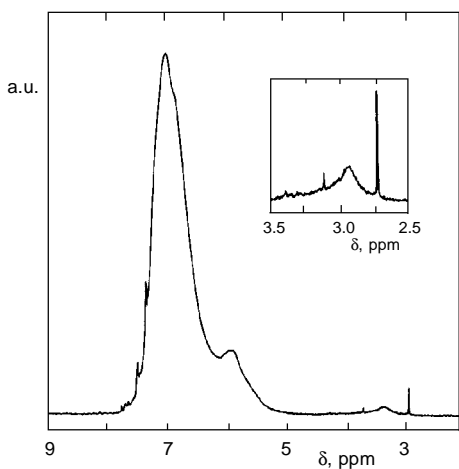


FIG. 7

^1H NMR spectrum of PPhA sample prepared with $\text{WCl}_5(\text{O}-\text{C}_6\text{H}_2\text{Cl}_3-2,4,6)$ as unicomponent catalyst. Polymerization time 5 h, for the other reaction conditions see Fig. 1

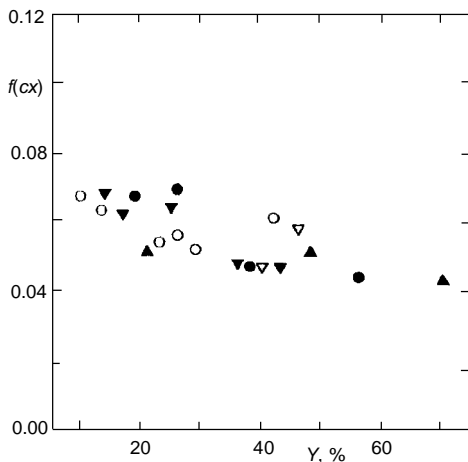


FIG. 8

Molar fraction of the units comprised in cyclohexadiene sequences, $f(cx)$, in PPhA samples as a function of the polymer yield (Y , %). For polymerization conditions and data designation see Figs 1 and 4.

Financial support from the Grant Agency of the Czech Republic (Grant No. 203/93/2453) is gratefully acknowledged.

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