METATHESIS CATALYST $WOCl_4/Ph_4Sn$: THE CHEMISTRY OF RIPENING AND TRANSFORMATION TO POLYMERIZATION ACTIVE SPECIES

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Ripening of $WOCl_4/Ph_4Sn$ binary catalyst of composition from 1 : 1 to 1 : 4 in benzene and toluene is a complex reaction in which initially homogeneous solution of the catalyst components continually changes to a colloidal solution, and utterly to a suspension of catalytically active particles consisted of lower-valent tungsten species in the solution of biphenyl, Ph_3SnCl and, eventually, unreacted Ph_4Sn (at composition 1 : 4). The yield of biphenyl is in a simple stoichiometric relation with the initial concentration of $WOCl_4$ and a proof is given that the phenyl groups constituting biphenyl molecules come from Ph_4Sn cocatalyst. The mechanism of the overall process is suggested. Above twenty, mostly phenylated derivatives of phenylacetylene (PhA) and oligomers of two degrees of unsaturation were detected as by-products of PhA reaction with the ripened catalyst formed in addition to main product, poly(phenylacetylene). The excess phenyls built in the oligomers are demonstrated to come from the supplied Ph_4Sn. The mechanism is suggested for formation of the both oligomeric derivatives and growing carbene centers in which oxo ligands of tungsten centers are proposed to play a central role.

Although many stable metal carbene complexes are known to induce metathesis as well as metathesis polymerization (see e.g. refs[1–7]), the other catalysts consisting of two or more non carbene compounds prevail in both laboratory and industrial practice due to their high efficiency and easy accessibility at low price[8–11]. Among the two and more component catalysts, those based on WCl_6 and $WOCl_4$ are perhaps being used most frequently, nevertheless, the mechanism of their transformation to the active metal carbene species is still remaining unknown except for the system WCl_6/Me_4Sn.

The transformation of WCl_6/Me_4Sn catalyst involves the ligand exchanges between Me_4Sn on one side, and WCl_6 and tungsten intermediates on the other side, and the disproportionation of methyl ligands yielding the metal carbene centers and methane as by-product, see Eq. (*A*).

In addition, a not negligible amount of active centers is formed in the sequence starting with side reaction: $WCl_6 + MeWCl_5 \rightarrow 2\ WCl_5 + MeCl$, and continuing with the

$$WCl_6 \xrightarrow[-\ Me_3SnCl]{+\ Me_4Sn} MeWCl_5 \xrightarrow[-\ Me_3SnCl]{+\ Me_4Sn} Me_2WCl_4 \xrightarrow[-\ CH_4]{} CH_2{=}WCl_4 \qquad (A)$$

transformation of WCl_5 into trichloro carbene species $CH_2{=}WCl_3$ along the reaction path analogous to that shown in Eq. (*A*) (refs[11–14]).

The ripening of WCl_6/Ph_4Sn catalyst in hot pentane results in a formation of the solid, which was identified as $PhWCl_3$, and Ph_3SnCl and chlorobenzene as by-products[15]. By itself $PhWCl_3$ was found to induce the olefin metathesis[9,16,17]. However, in benzene[18,19] at room temperature, biphenyl and Ph_3SnCl were found as the main side products formed in the reaction of WCl_6 with Ph_4Sn, and WCl_5 was identified as one of the intermediates. Accordingly, the mechanism shown in Eq. (*B*) was suggested for the ripening of WCl_6/Ph_4Sn catalyst in benzene and species $PhWCl_4$ proposed as the precursors of carbene centers.

$$2\ WCl_6 \xrightarrow[-\ Ph_3SnCl]{+\ 2\ Ph_4Sn} 2\ PhWCl_5 \xrightarrow[-\ Ph{-}Ph]{} 2\ WCl_5 \xrightarrow[-\ Ph_3SnCl]{+\ 2\ Ph_4Sn} 2\ PhWCl_4 \qquad (B)$$

Substantially less is known about the $WOCl_4$-based catalysts though: (i) the carbene mechanism of metathesis propagation was suggested on the basis of experiments carried out with these catalysts[8]; (ii) the contamination with $WOCl_4$ seems to be important factor for the activity of many "WCl_6"-based catalysts[20,21]; and (iii) the published theoretical calculations indicate a central role of oxo ligand in the metathesis propagation via tungstenacyclobutane intermediates[22,23]. Verkuijlen[24] observed formation of Me_3SnCl in the reaction of $WOCl_4$ with Me_4Sn and found that the presence of this by-product in the reaction mixture is essential for the catalyst metathesis activity. As for the $WOCl_4/Ph_4Sn$ catalyst, it was found to reach the highest activity at the molar composition of 1 : 2 (ref.[25]). This indicates that the double ligand exchange, which is known to take place in the WCl_6-based catalysts, might play a central role even in the ripening of $WOCl_4/Ph_4Sn$ catalyst.

In present paper, new experimental observations and analytical data concerning the ripening of $WOCl_4/2\ Ph_4Sn$ catalyst, time stability of the ripe catalyst species as well as their transformation into the polymerization growing centers are reported.

EXPERIMENTAL

Materials

Purification of tungsten oxychloride, tetraphenyltin, benzene and phenylacetylene (PhA) has been described elsewhere[25,26]. Toluene was purified in the same way as benzene. According to GC-MS analysis the purity of the solvents was better than 99.999%. Their quality for catalytic experiments was controlled through the long-time stability (one week) of the UV spectrum of WCl_6 solution ($5 . 10^{-4}$ mol dm^{-3}) prepared from the respective solvent and the standard stock solution of WCl_6. The purity of PhA was measured by the GC-MS method and found to be better than 99.6% – less than 0.4% of styrene and negligible traces of bromoethylbenzene and acetophenone were the only impurities detected. According to Masuda et al.[27], styrene (in substantially higher concentration) does not interfere with the metathesis polymerization of PhA in nonpolar solvents.

Procedures

All procedures were carried out using the standard breakseals vacuum technique. The catalyst system was being prepared as follows: Solid Ph_4Sn was dosed into the reactor, dissolved in appropriate amount of benzene (toluene), mixed with the corresponding amount of $WOCl_4$ solution, and allowed to ripen for a given time. The polymerization was initiated by adding PhA to the catalyst and quenched by adding methanol into the reaction mixture. The yield of precipitated poly(phenylacetylene) (PPhA) was determined by gravimetry. For the polymerization activity tests, $WOCl_4/Ph_4Sn$ catalyst system was allowed to ripen for 15 min at concentration (with respect to tungsten) of 3.6 mmol dm^{-3} and then diluted with benzene to 0.83 mmol dm^{-3} for the further aging. The catalyst systems of various age were used for PhA polymerizations in which the catalyst concentration equal to 0.72 mmol dm^{-3} and the monomer/catalyst ratio equal to 1 700 : 1 were applied. All experiments were performed at room temperature.

Measurements

GC-MS analyses were carried out using Varian 3400 gas chromatograph provided with DB-5 column J&W (length 30 m, diameter 0.32 mm, film thickness 0.25 μm) and with Incos 50 (Finnigan-MAT Corp.) mass spectrometer and Data General 10/SP data station. Helium as a carrier gas (over pressure 5 psi) and split less injection at 280 °C were applied. In the typical analysis, temperature was set at 40 °C for 2 min, then increased to 280 °C with the rate 15 °C min^{-1} and finally kept at the reached temperature to the end of analysis. Mass spectrometer was operated in EI mode scanning from 35 to 500 amu in 0.32 s, the ion source was heated to 150 °C, emission current was 800 μA, ionizing electron energy was 70 eV. Finnigan–Incos software (version 10.0) was used for mass spectra evaluation. Biphenyl, Ph_4Sn, and Ph_3SnCl were used as standards for the quantitative analyses of ripened catalyst systems and hexadecane was used as internal standard for the analyses of samples prepared from terminated polymerization mixtures.

Size exclusion chromatography (SEC). HPLC chromatograph (Laboratorni pristroje) fitted with UV-VIS detector LCD 2563 working at wavelength of 254 nm was used for SEC analyses of PPhA samples. Three columns in series packed with the gels: (i) LI 100 (Merck), (ii) SGX 500 (Tessek), (iii) SGX 1000 (Tessek) with integral exclusion limit from 500 to ca $3 . 10^6$ (for polystyrene standards) and distilled tetrahydrofurane (THF) as a mobile phase (0.5 cm^3 min^{-1}) were used. Values of apparent molecular weight averages based on the polystyrene calibration were calculated by a routine procedure. To prevent a random disfiguring of SEC results by rapid autoxidative degradation of dissolved PPhA[28–30], the solution of analyzed samples (2 to 3 mg in 5 cm^3 of THF) has always been prepared within 10 min prior to its injection into SEC columns.

RESULTS AND DISCUSSION

Reaction of $WOCl_4$ with Ph_4Sn

After a mixing with Ph_4Sn in the ratio $y = [Ph_4Sn]_0/[WOCl_4]_0 = 2$, originally red, real solution of $WOCl_4$ turns brown within one minute, the mixture becomes colloidal within ca two hours and, finally, it divides into fine particles of black solid and colorless supernatant. By itself the supernatant was always found to be inactive in polymerization of phenylacetylene (PhA). On the contrary, the black solid is a good catalyst for PhA polymerization and, even more, it keeps its activity for a very long time. For example, the addition of benzene solution of PhA (4.5 mol dm^{-3}) to the precipitate isolated from 13 months old catalyst resulted in slow PhA polymerization (molar ratio monomer/catalyst ca 800 : 1) the yield of 14% of poly(phenylacetylene) (PPhA) of the weight-average molecular weight $\langle M \rangle_w = 450\,000$ and the index of molecular non uniformity $\langle M \rangle_w/\langle M \rangle_n = 2.4$ was obtained within one day. It can be thus concluded that the active species are concentrated in the precipitated solid, whereas the supernatant can comprise the side products of their formation only.

The catalyst mixtures of various composition (y : 1, 2, and 4) aged for various time were terminated by methanol (1 : 1 v/v) and analyzed by the GC-MS method. In addition, the supernatants isolated from the non quenched reaction mixtures aged for 7 days were analyzed. Among the compounds detected, Ph_4Sn, Ph_3SnCl, and biphenyl were found in significant amounts in the samples of both types. Besides, Ph_2SnCl_2 and in some cases also terphenyl and phenol were observed in traces only (in amounts ca two orders of magnitude smaller), see Fig. 1 and Table I. Quantitative analytical reports on

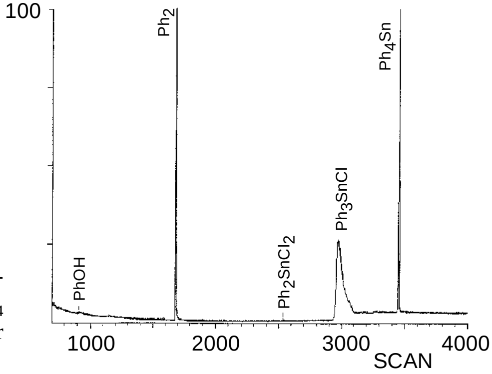


FIG. 1
Reconstructed ion chromatogram of the supernatant of non terminated mixture of $WOCl_4$ (2.2 mmol dm^{-3}) with Ph_4Sn (1 : 4) reacted for 7 days in benzene at room temperature

the both types of samples of the same reaction mixture (aging time 7 days) were always practically identical except for the amounts of Ph_3SnCl. The peaks of Ph_3SnCl were always broad and smudge (see Fig. 1, so it was even in case of the standard solutions of Ph_3SnCl) and the reproducibility of Ph_3SnCl determination was rather poor (error up to 40%), however, no systematic difference between the two types of samples has been observed. The reproducibility of the determination of biphenyl and Ph_4Sn was good (±5%) in the case of one week old catalyst mixtures. The error in a determination of biphenyl in the fresh catalyst systems was ±15%. An uncontrolled formation of biphenyl on quenching the ripening of fresh catalyst mixture by methanol is a probable reason of the low accuracy of biphenyl determination.

In case of the catalyst ripening in benzene, the question arises whether the phenyl groups forming biphenyl (and terphenyl) molecules really come from Ph_4Sn or from the solvent. The experiments performed in toluene has answered this question unambiguously – only biphenyl and traces of terphenyl but neither methyl- nor dimethylbiphenyl nor any other derivative of toluene has been observed in the products (see Table I). It is thus certain that the biphenyl (terphenyl) molecules are made up from phenyls coming from Ph_4Sn and that the reactive participation of the solvents in the catalyst ripening need not be taken into account.

The results concerning the catalyst mixtures aged for 7 days have shown that practically all supplied Ph_4Sn is transformed into Ph_3SnCl in the catalyst systems of composition y = 1 and 2, whereas only half of the amount of Ph_4Sn is transformed into

TABLE I

Relative concentrations of Ph_4Sn, Ph_3SnCl and biphenyl (with respect to $[WOCl_4]_0 \equiv c_0 = 2.2$ mmol dm^{-3}) determined in the mixtures of $WOCl_4$ with Ph_4Sn of various composition y aged for time t_a in benzene (B) and toluene (T), at room temperature

y	t_a	$[Ph_4Sn]/c_0$	$[Ph_3SnCl]/c_0$[a]	$[\text{biphenyl}]/c_0$
4 (B)	15 min	2.25	–	0.4
4 (B)	120 min	2.05	–	0.7
4 (B)	7 days	2.05	~ 2	1.0
2 (B)	15 min	0.35	–	0.3
2 (B)	120 min	0.01	–	0.7
2 (B)	7 days	0.02	~ 2	0.95
2 (T)	15 min	0.10	–	0.4
2 (T)	120 min	0.01	–	0.8
2 (T)	7 days	0.01	~ 2	1.0
1 (B)	7 days	0	~ 0.9[b]	0.45[b]

[a] Bad chromatographic behavior; [b] in addition, Ph_2SnCl_2 and terphenyl were found in amounts of 0.1 c_0 and 0.05 c_0, respectively.

Ph_3SnCl and the second half is remaining unreacted in the catalyst system of composition $y = 4$ (Fig. 1). It is further evident that biphenyl is formed in the amount equal to one half of that of the reacted Ph_4Sn in all catalyst mixtures (Table I). This means that in the systems of composition $y = 2$ and 4, one molecule of $WOCl_4$ reacts with two molecules of Ph_4Sn at the most yielding two molecules of Ph_3SnCl and one molecule of biphenyl. In accordance with the above stoichiometry the black, catalytically active solid should have the composition $WOCl_2$. On the contrary, in the system of composition $y = 1$, majority of starting $WOCl_4$ molecules undergoes the single ligand exchange only and the formed solid is green. Both these findings indicate that the solid is $WOCl_3$ (ref.[31]). As both black and green solids are not stable enough in the air, their detail analysis as well as the structure characterization requires a use of special procedures. In addition, in regard of uncertainty in determination of Ph_3SnCl it is not excluded that some amount of this tin compound is bound in the solids. Detailed research of the solids is in progress.

The data concerning to the early stage of catalyst ripening (Table I) provide qualitative information on the dynamics of this process. The decay of Ph_4Sn takes place from 80 to 95% in the first 15 min of ripening, while the yield of biphenyl reach only 30 to 40% of final value in the same time period. This indicates that the decay of Ph_4Sn is considerably faster than the process of biphenyl formation. In view of knowledge on the ripening of similar binary catalysts (see introduction), the first period of the studied interaction should consist in the ligand exchanges between tungsten and tin species.

$$WOCl_4 \xrightarrow[-\ Ph_3SnCl]{+\ Ph_4Sn} \underset{I}{PhWOCl_3} \xrightarrow[-\ Ph_3SnCl]{+\ Ph_4Sn} \underset{II}{Ph_2WOCl_2} \qquad (C)$$

$$WOCl_4 \xrightarrow[-\ Ph_2SnCl_2]{+\ Ph_3SnCl} \underset{I}{PhWOCl_3} \qquad (D)$$

In context with the found ideal composition ($y = 2$) of fresh $WOCl_4/Ph_4Sn$ catalyst[25], reaction (*C*) can be considered as the main path of the catalyst ripening. On the contrary, the ligand exchange (*D*), which explains formation of traces or small amounts of Ph_2SnCl_2 (if $y = 1$) should be regarded as a marginal reaction taking place in the first stage of ripening when $WOCl_4$ is present in higher concentration.

Second stage of the interaction involves a gradual transformation of single tungsten species *II* in to clusters and particles of the solid which is accompanied with the formation of biphenyl. This stage may be denoted as the aging of ripe catalyst. A mechanism of this aging should consist of inter- and/or intramolecular reductive elimination of biphenyl molecules from *II* (if $y = 2$ or 4) followed with an aggregation of dephenylated tungsten species $WOCl_2$, Eq. (*E*).

$$\underset{II}{n\ Ph_2WOCl_2} \longrightarrow (WOCl_2)_n\ (s) + n\ Ph–Ph \qquad (E)$$

Both oxygen-bridging and chlorine-bridging arrangement of $WOCl_2$ species in polymetallic clusters and particles come into consideration because both these arrangements have been identified[31,32] in solid $WOCl_4$ and $WOCl_3$. The formation of solid $WOCl_3$ from species *I* in the system of composition $y = 1$ may be explained analogously.

Interaction of Ripe WOCl4/2 Ph4Sn Catalyst with Phenylacetylene

This process was studied on the catalysts of composition $y = 2$ only but of various aging time (15 min, 120 min, 7 days), using a tenfold excess of PhA with respect to $[WOCl_4]_0$ (quenching by threefold excess (by volume) of methanol one hour after the adding of PhA). Benzene and toluene, respectively, was used as solvent. In all experiments, a small amount of poly(phenylacetylene) (PPhA) has been formed. The polymer was isolated, weighed and characterized by SEC method (see Table II). Rest of the terminated reaction mixture was analyzed by the GC-MS method using hexadecane (20 μg ml^{-1}) as the internal standard (see examples of reconstructed ion chromatograms in Figs 2*a* to 2*d*).

TABLE II
Degree of conversion of monomer, *p*, and the yield, *Y*, and weight-average molecular weight, $\langle M \rangle_w$, of the polymer as a function of the time of catalyst aging, t_a. Catalyst system $WOCl_4$/2 Ph_4Sn, ($[WOCl_4]_0$ = 2.2 mmol dm^{-3}), monomer [PhA] = 22 mmol dm^{-3}, reaction time 1 h, room temperature

	t_a in benzene				t_a in toluene		
	15 min	120 min	7 days	90 days[a]	15 min	120 min	7 days
p, %	98	85	25	50	99.5	97	25
Y, %	40	30	5	35	60	50	10
$\langle M \rangle_w \cdot 10^{-3}$	4.2	7.7	18	30	9.8	11	22

[a] Reaction time 10 h.

The following low-molecular-weight compounds were detected in the products formed in both solvents, in addition to nonreacted PhA, styrene (introduced with PhA), and the tin cocatalyst residues:

– chlorostyrene, (the only chloro derivative observed);

– two isomers of triphenylbenzene (PhA cyclotrimer), *m*/*z* 306 (M^+), the most abundant products;

– two isomers of tetraphenylbenzene (phenylated PhA cyclotrimer), *m*/*z* 382 (M^+), next to the most abundant products;

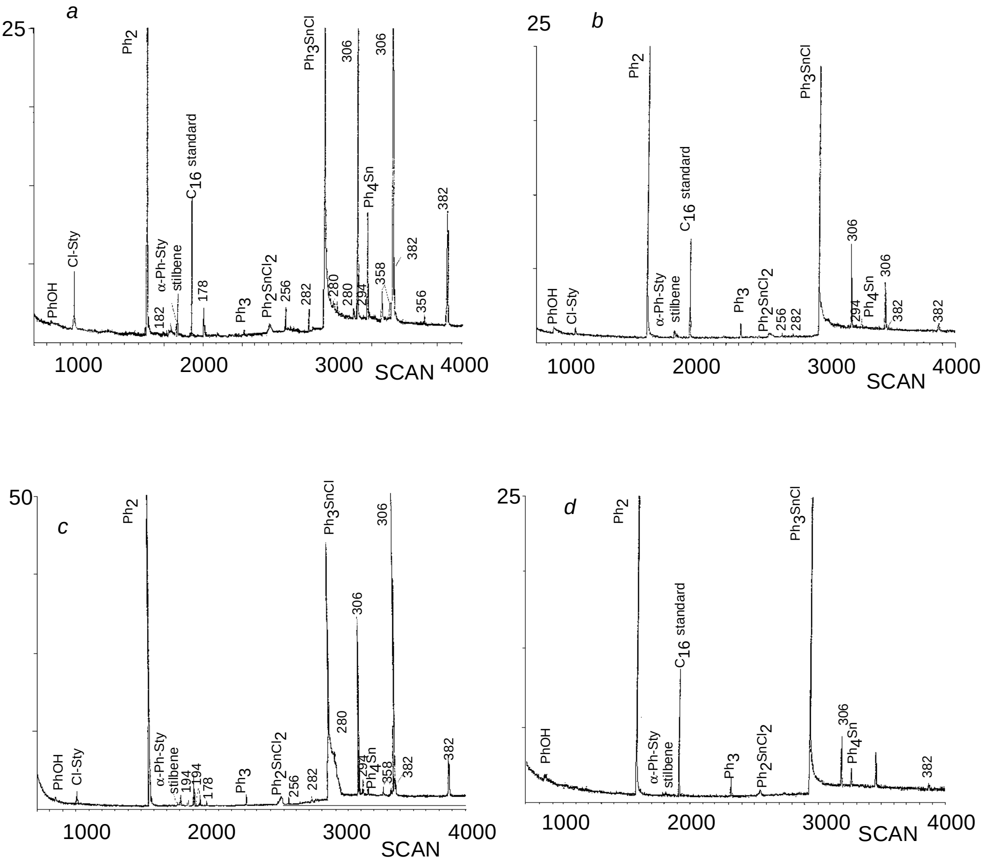


FIG. 2

Reconstructed ion chromatograms of terminated reaction mixtures freed from polymer. $WOCl_4$ (2.2 mmol dm^{-3})/2 Ph_4Sn catalyst ripened for time t_a, then reacted with only tenfold excess of PhA for 1 h at room temperature; termination by threefold excess (v/v) of methanol. Solvent, t_a: *a* benzene, 15 min; *b* benzene, 7 days; *c* toluene, 2 h; *d* toluene, 7 days

– traces of pentaphenylbenzene (double phenylated PhA cyclotrimer), *m*/*z* 458 (M^+) (scan 4 490, not involved in the chromatograms in Figs 2);

– small amounts of diphenylacetylene, *m*/*z* 178 (M^+), 1,1-diphenylethene (α-phenylstyrene), *m*/*z* 180 (M^+), 1,2-diphenylethene (stilbene), *m*/*z* 180 (M^+), 1,1-diphenylethane, *m*/*z* 182 (M^+), triphenylethene, *m*/*z* 256 (M^+), and a few monophenylated and diphenylated PhA dimers ((M^+) equal to 280, 282, and 356, 358, respectively);

– one isomer of a derivative with *m*/*z* 294 (M^+). Despite the apparently correct value of molecular weight, this derivative cannot be a tolylated dimer of PhA because it is formed in benzene as well. According to its simple mass spectrum, in which molecular peak predominates, it might be an isomer of triphenylcyclopentadiene.

In reaction mixtures prepared in toluene also three isomers of tolylstyrene, *m*/*z* 194 (M^+) (most probably α isomers), as the only tolylated derivatives, were detected. These derivatives were evidently formed with a reactive assistance of toluene and, accordingly, a part of α phenylstyrene formed in benzene system might be regarded as the product of PhA unit phenylation by the solvent. It is also noteworthy that neither ditolylated nor phenylated–tolylated oligomers were observed in the mixtures prepared in toluene solvent.

Another important fact is the absence of unsubstituted linear PhA oligomers in all prepared reaction mixtures (mass spectra of these oligomers as well as their GC retention times were known from analyses of PhA dimers, trimers and tetramers obtained by thermal oligomerization of PhA). It most probably means that preformed, short linear chains ligands of tungsten centers (their presence in the reaction mixture should be taken for granted in view of the formation of PPhA) are rather fast transformed into longer polymer chains.

The above survey provides further important information on the mechanism of studied interaction. (i) The fact that identical phenylated PhA oligomers are formed in both solvents (benzene and toluene) together with the absence of tolylated compounds in the products formed in toluene (except for the case mentioned above) demonstrates that the excess phenyls built in the molecules of these derivatives come from the supplied Ph_4Sn. (ii) As a rule, the variety and yield of formed oligomers decrease with the time of catalyst aging (see Figs 2). In the reaction induced by 100 days old catalyst system, only PhA cyclotrimers but no phenylated PhA derivatives were detected as by-products to PPhA. This observation corresponds with the spontaneous dephenylation of ripe tungsten precursors during their aggregation (reaction (*E*)). It can be thus concluded that phenylated oligomers of PhA are formed on phenyl tungsten species only. As far as PhA cyclotrimers are concerned, they are certainly formed on dephenylated tungsten species, i.e. on $WOCl_2$, however, their formation also on phenyl tungsten species cannot be excluded. (iii) The observation of PhA oligomers of different degree of unsaturation indicates that the overall reaction mechanism should involve the transfers of hydrogen between different PhA units. (iv) Absence of ditolylated and tolylated–phenylated derivatives indicates that the arylation by solvent does not take place on already arylated PhA units. (v) Absence of tolylated cyclotrimers demonstrates that PhA units arylated by solvent do not participate in the formation of cyclotrimers.

It is worth mentioning that the heterogenization of fresh $WOCl_4$/2 Ph_4Sn catalyst is considerably (ca ten times) accelerated by the addition of tenfold excess of PhA. This visual observation is in a good agreement with the formation of phenylated derivatives of PhA. The added PhA fast deprives the tungsten species of phenyls. Because the added amount of PhA is low, it little influence the solubility power of solvent. As a result, the aggregation and precipitation of dephenylated tungsten species ($WOCl_2$) is accelerated.

Influence of Aging of WOCl4/2 Ph4Sn Catalyst on Its Catalytic Activity

The effect of aging on the catalyst polymerization activity was tested in two series of experiments. In the first series, the polymerizations were induced by the catalyst system aged in a normal manner for various time t_a. In the second series, the pure catalyst system was mixed with tenfold excess of PhA after 30 min of normal ripening and the polymerizations were induced by the resulting mixture which was allowed to age for

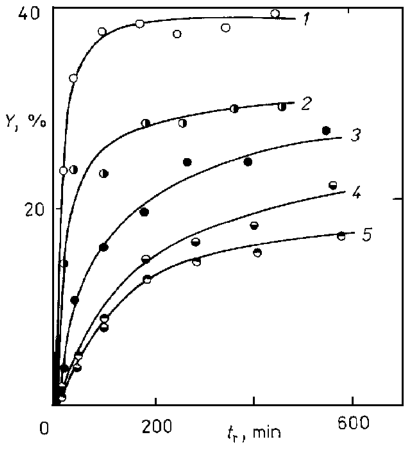


FIG. 3
Conversion curves for PhA polymerizations induced by the $WOCl_4$/2 Ph_4Sn catalyst ripened for various time t_a: *1* 30 min; *2* 10 h; *3* 94 h; *4* 695 h; *5* 2 156 h. Reaction conditions: $[PhA]_0$ = 1.2 mol dm^{-3}, $[WOCl_4]_0$ = 0.72 mmol dm^{-3} (during the polymerization), benzene, room temperature

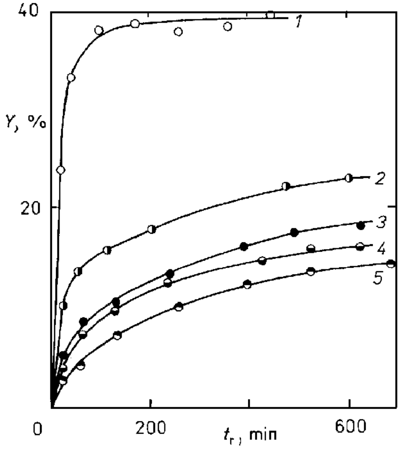


FIG. 4
Conversion curves for PhA polymerizations induced by the three-component catalyst $WOCl_4$/2 Ph_4Sn/10 PhA. Pure catalyst was allowed to ripen for 30 min prior to the addition of cocatalytic amount of PhA; the overall time of the catalyst aging (since mixing $WOCl_4$ with Ph_4Sn): *1* 30 min; *2* 60 min; *3* 11.5 h; *4* 80 h; *5* 1 080 h. Reaction conditions: $[PhA]_0$ = 1.2 mol dm^{-3}, $[WOCl_4]_0$ = 0.72 mmol dm^{-3} (during the polymerization), benzene, room temperature

further time period (t_a – 30 min). Benzene as the solvent and the monomer/catalyst mole ratio of ca 1 700 were used in both series. The conversion curves of the respective series of PhA polymerizations are shown in Figs 3 and 4. Dependences of the weight-average molecular weight, $\langle M \rangle_w$, of formed PPhA on the reaction time t_r are shown in Fig. 5 for both series.

In both series of polymerization experiments the rate of polymerization and as well yield of PPhA go down as the catalyst aging time increase. This can be considered as the consequence of progressive heterogenization of catalyst system. The fresh catalyst system which contains well accessible tungsten centers (molecular species and their small clusters) can give rise to the high number of simple growing species and thus also to a good yield of PPhA in short reaction time. On the contrary, the aged catalyst system in which majority of tungsten atoms is closed (buried) inside the particles, so being inaccessible for PhA molecules, could give rise to a considerably lower number of polynuclear growing species which might result in the reduced yield of PPhA.

The yields of PPhA attained after ca 10 h of polymerization (last points of conversion curves in Figs 3 and 4) are plotted against logarithm of t_a in Fig. 6 for the both

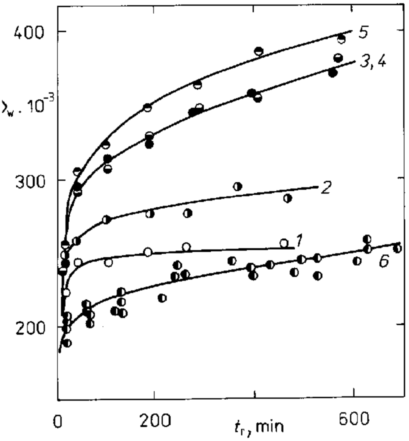


FIG. 5

Weight-average molecular weight of PPhA, $\langle M \rangle_w$, as a function of reaction time, t_r. Polymerization induced by $WOCl_4/2\ Ph_4Sn$ catalysts of various age t_a: *1* 30 min, *2* 10 h, *3* 94 h, *4* 695 h, *5* 2 156 h (all complementary to samples shown in Fig. 3); *6* common curve for polymers prepared by $WOCl_4/2\ Ph_4Sn/10$ PhA three-component catalyst under the same reaction conditions (samples corresponding to curves *2* to *5* in Fig. 4)

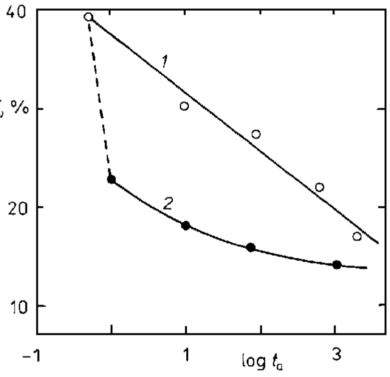


FIG. 6

Yield of PPhA achieved after ca 10 h of the polymerization of PhA (the last points of conversion curves in Figs 3 and 4) induced by: *1* $WOCl_4/2\ Ph_4Sn$; *2* $WOCl_4/2\ Ph_4Sn/10$ PhA, as a function of the logarithm of aging time of catalyst, t_a (in h, measured since the mixing of $WOCl_4$ with Ph_4Sn)

series of polymerization experiments. Continuous decrease in the yield of PPhA observed for the first series strongly contrasts with almost right-angle shape of this dependence for the second series. The initial steep drop is evidently caused by the interaction of the ripe $WOCl_4/2\ Ph_4Sn$ catalyst with tenfold excess of PhA. It can be ascribed to the accelerated aging of the catalyst by means of its dephenylation by PhA “cocatalyst”. Following slow decrease in the yield of PPhA testifies to a small progress in further aging of the catalyst. These observations and conclusions are in coherence with those discussed in the preceding section.

As far as molecular weight of PPhA samples is concerned, the two tested types of polymerization system behave in a different way. For samples prepared with pure $WOCl_4/2\ Ph_4Sn$ catalyst values of $\langle M \rangle_w$ rise as the aging time increases, whereas for those prepared with catalyst treated with cocatalytic amount of PhA prior to polymerization no influence of aging time has been observed (see Fig. 5). The fact that $\langle M \rangle_w$ values of samples of the second series are lower than those of the first series might be surprising. It namely obvious that in the first series of polymerization tests the $\langle M \rangle_w$ values of PPhA increase parallelly with the catalyst age to a limiting value of ca $4 . 10^5$. According to the both polymerization curves and visual look, the catalysts pretreated with PhA (used in the second series) are more aged than those untreated which were used in the first series. Consequently, higher values of $\langle M \rangle_w$, or at least comparable with those of the first series, should be expected for PPhA samples of the second series. The very opposite experimental result is explainable by the effect of chain transfer to PhA derivatives formed in the course of the pretreatment of catalyst with PhA. This idea as well explains the course of $\langle M \rangle_w$ values in the first experimental series. The fresh catalyst system rich in phenyl tungsten species give rise (during the initiation) to a higher amount of oligomeric PhA derivatives (transfer agents) than the more aged system in which dephenylated tungsten species predominate.

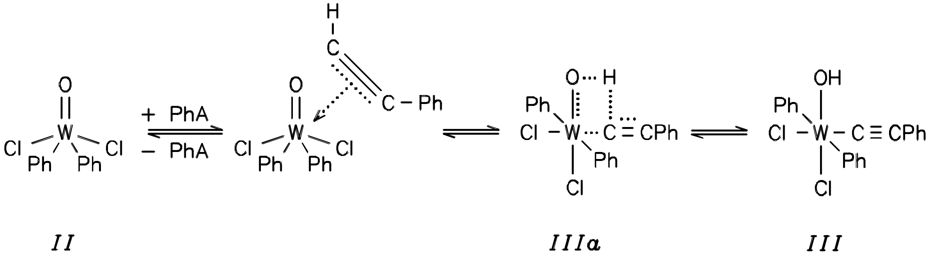
There are some aspects concerning to the catalyst activity to be worth mentioning here. At first, it is the long-time stability of the catalyst systems under the applied experimental conditions. In our experience, the used vacuum technique warrants that the catalyst mixture is not contaminated by terminating impurities. For example, the UV spectra as well as the catalytic activity of benzene solutions of $WOCl_4$ (which is highly sensitive to the atmosphere) sealed in vacuum ampoule has not been changed for two years, at least. Also preliminary results of experiments made with the $WOCl_4/Ph_4Sn$ catalyst aged in the benzene/1,4-dioxane mixed solvent have shown almost absolute stability of this homogeneous system for at least one year. It thus seems sure that the decrease in polymerization activity observed in the present study (Fig. 2) is the internal property of the catalyst system and not a result of a slow termination induced by unknown impurities. At second, the catalyst activity tests were carried out successfully at the mole ratio monomer/catalyst equal to 1 700 which fairly exceeds the ratios usually being used in experiments of this type[10]. This testifies to the high activity of the catalyst and as well to a good purity of the reaction mixtures.

MECHANISTIC CONSIDERATIONS

High variety of the tungsten species as well as derivatives formed in their interaction with PhA testifies to a high complexity of the studied processes. Nevertheless, some suggestions concerning the mechanism of the initiation, formation of various PhA derivatives, and arylation of PhA units by aromatic solvent can be drawn from the above results.

Initiation and Formation of Phenylated Derivatives

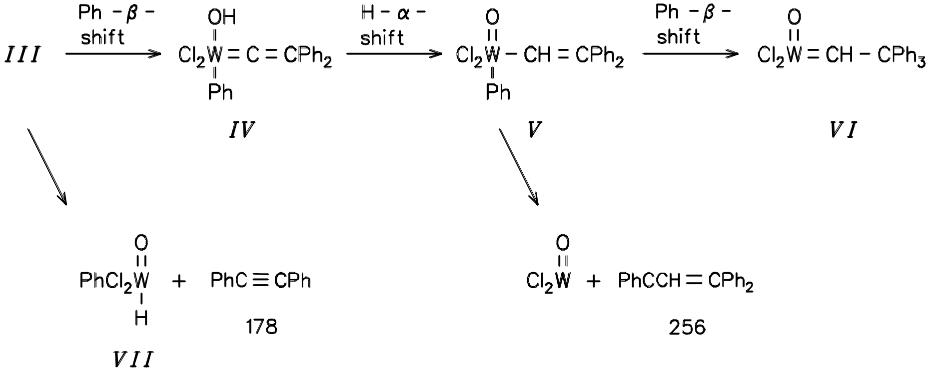
The following discussion is limited to the mononuclear tungsten species *II* which are assumed to prevail in the fresh catalyst systems (y = 2). Electronic structure of *II*, Ph_2WOCl_2, can be estimated on the basis of theoretical calculations done by Rappé and Goddard[22,23] for WCl_6, $WOCl_4$, $CH=WOCl_2$, metallacycles and other related structures. In Ph_2WOCl_2 molecule, four of the six valence electrons of tungsten atom should be involved in two, partially ionic σ-bonds to the two Cl ligands and two covalent σ-bonds to the phenyls, and two remaining electrons should be involved in $d\pi$ orbitals making two covalent π bonds with oxygen. One of the two lone electron pairs of oxygen should be partially aligned with the W to O bond axis pointing at the empty $d\sigma$ orbital of tungsten, thus giving to the W to O bond partial triple character. It can be thus expected that on the π-coordination of PhA molecule to the tungsten central atom, the electrons involved in the W=O bond should be shifted towards the oxygen, thus making the last capable of accepting the acetylenic hydrogen from the weakened H–C≡ bond. As a result the species *III* involving hydroxo and phenylethynyl ligands could be formed (Scheme 1). In other words, we assume that the activation of PhA molecule with *II* (and similar oxo tungsten species) can proceed as the reversible addition of PhA to the covalent W=O double bond.



SCHEME 1

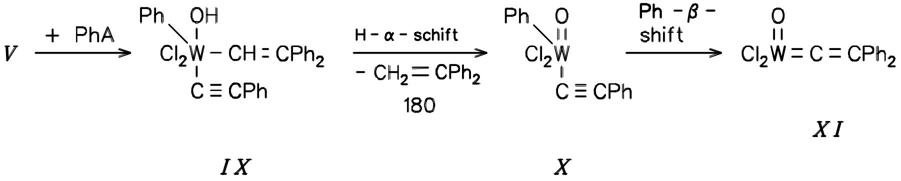
The addition described in Scheme 1 can be also regarded as the first step of the hydrogen transfer between two PhA units. The hydrogen undergoing the transfer can be "temporarily stored" on the oxygen (changed into hydroxo ligand) and later on shifted onto α-carbon of another PhA unit. The reverse shift of hydrogen (H-α-shift) should be directed towards the α-carbon of acceptor which should be activated through the equilibrium of the type *IIIa* ↔ *III* (Scheme 1). In addition, the H-α-shift on the same but in the meantime changed PhA unit can take place in a formation of some observed PhA derivatives.

Starting with *III*, the mechanism can be drawn which explains formation of both tungsten carbene centers and majority of the observed oligomeric side products. The possible pathway for straightforward transformation of *III* into carbene growing species *VI* accompanied with competitive formation of two observed side products is shown in Scheme 2. Species *VI* have the structure of the ideal metathesis center, so they can be supposed to grow fast to PPhA chains.



SCHEME 2

In Scheme 2, the formation of species *VII* instead of $PhCl_2W(OH)$ is proposed because in regard of the stabilization effect of W=O bond. The addition of PhA to *VII* (according to Scheme 1) followed with reaction sequence analogous to that shown in Scheme 2 (hydride-β-shift, H-α-shift, Ph-β-shift) yields carbene growing species $Cl_2W(=O)=CH–CHPh_2$ (*VIII*) or the couple $WOCl_2$ and stilbene. The addition of a PhA molecule to *V* (yielding *IX*) followed with H-α-shift to the alkenyl ligand explains formation of α-phenylstyrene (Scheme 3). Species *X* can be either transformed into

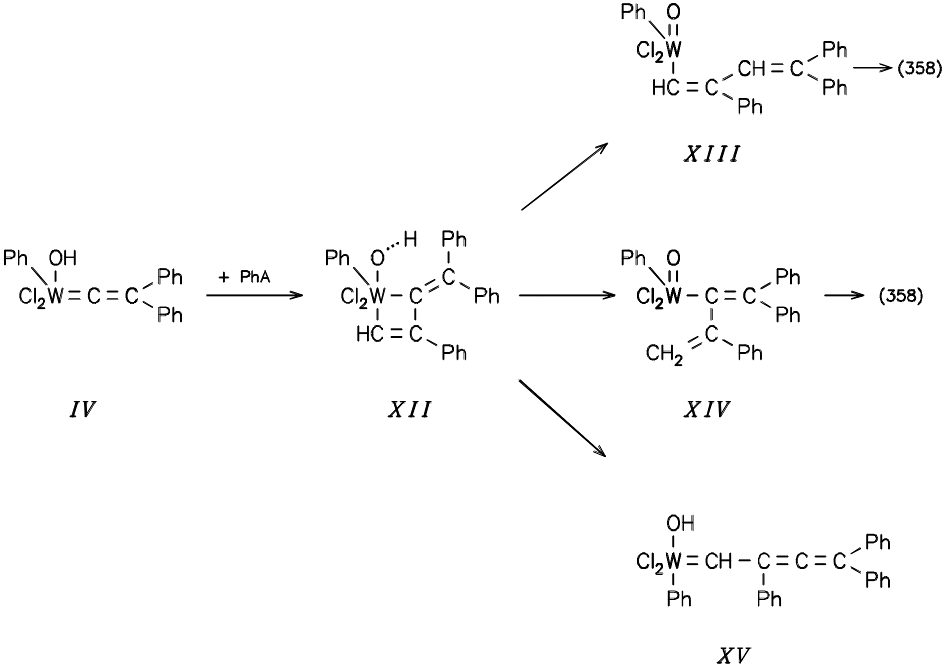


SCHEME 3

growing centers *XI* (Scheme 3) or decomposed to diphenylacetylene and $WOCl_2$. In addition, enyne dimer *m*/*z* 280 (M^+) can be eliminated from species *IX*.

Metathesis Insertion of PhA to Hydroxo Tungsten Species

In addition to suggested dichloro oxo tungsten carbene species *VI*, *VIII*, and *XI*, on which easy metathesis insertion is supposed, various dichloro hydroxo tungsten carbene structures (e.g. species *IV*) can be derived. The possibility of metathesis insertion on these species is doubtful. It was namely proposed by Rappe and Goddard[22,23] that for the metallacycle formation to occur it is essential for the metal to make at least partial, triple W-to-O bond which stabilizes the cycle. If the hydroxo tungsten species forms the metallacycle, the shift of electrons from oxygen towards the tungsten atom must weaken the O–H bond, thus making easy the H-α-shift to the one of two possible α-carbons of metallacycle. As a result, the oxo–tungsten species *XIII* or *XIV* should be formed instead of normally expected carbene species *XV* (Scheme 4).



SCHEME 4

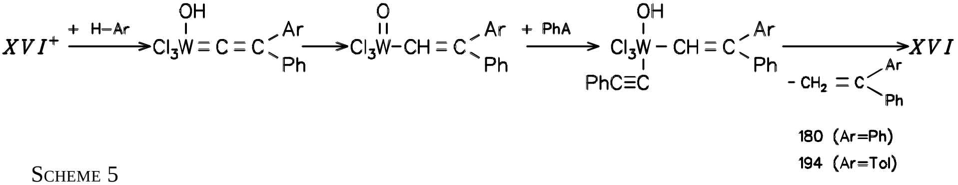
The formed species *XIII* and *XIV* can decompose to $WOCl_2$ and diphenylated PhA dimers, *m*/*z* 358 (M^+) (tetraphenylbutadienes). Besides, they can add a PhA molecule, so being transformed into hydroxo tungsten species of the type *IX* (see Scheme 3) from which a molecule of triphenylbutadiene, *m*/*z* 282 (M^+) can be eliminated by means of H-α-shift.

Arylation of PhA Units with the Solvent

The presence of aryls coming from the solvent in α-arylstyrenes has been demonstrated experimentally using toluene as the solvent (formation of the derivatives of *m*/*z* 194 (M^+)). For this observation to be explained the Friedel–Crafts (F–C) type arylation of a PhA unit with the solvent molecule comes into consideration.

The F–C reactions involving acetylenes are known to be rather rare and to yield unusual products[33–34]. However, Makowetsky et al. have recently observed formation of α-tolylstyrene, *m*/*z* 194 (M^+), tolylchlorostyrene, *m*/*z* 228 (M^+), phenylditolylethane, *m*/*z* 286 (M^+), and diphenyltolylbutadiene, *m*/*z* 296 (M^+) in the reaction of WCl_6 with PhA in toluene[21]. They have proposed that the tolyl derivatives are formed by means of the F–C reactions of toluene with corresponding chloro derivatives. However, they did not observe chloro precursors to each of those tolyl derivatives and vice versa. It thus seems probable that the F–C side products might be formed also in another way. The direct arylation of coordinated PhA unit with solvent molecule comes into consideration as a possible reaction path.

According to the known mechanism of F–C reactions[33], for the F–C arylation of PhA unit to occur it is essential for the PhA ligand to possess a positively charged carbon. The partial positive charge on may appear for example on β-carbon of 2-phenylethynyl ligand bonded in trichloro oxo tungsten species $(O{=})Cl_3W{-}C{\equiv}CPh$ (*XVI*) ↔ $(^-O{-})Cl_3W{=}C{=}C^+{-}Ph$ (*XVI*$^+$) thanks to simultaneous effect of one oxygen and three chlorine atoms. The species *XVI* may be formed from *I* in a similar way as the species *X* was derived from *II* (Scheme 3). The type 1,4-addition of arene molecule to *XVI*$^+$ followed with the H-α-shift should yield *XVII*, the precursor of α-arylstyrene (Scheme 5). On the elimination of α-arylstyrene from *XVIII*, the species *XVI* can be restored. Thus, the F–C arylation might in principal proceed in the catalytic cycle.



SCHEME 5

The absence of phenylated-tolylated PhA derivatives (see the respective section) indicates that F–C arylation most probably does not take place on phenyl tungsten species, for example Ph(O)Cl_2W≡C=CPh (*X*). Absence of one chlorine and a partial donation of electrons from phenyl to tungsten atom does not allow a formation of sufficient charge on β-carbon of organic ligand.

Formation of Cyclotrimers

Formation of cyclotrimers is often reported as the side reaction to polymerization of acetylenes with metathesis catalysts[9,10]. In the literature, two substantially different reaction pathways are proposed: (i) the straightforward catalytic cyclotrimerization of acetylenes; and (ii) the back-biting reaction of the growing chain ends. On the basis of present experimental data, the both mechanisms can be neither confirmed nor excluded. Apparently, the mechanism (ii) should be preferred because the formation of mono- and diphenylated PhA cyclotrimers, m/z 382 (M^+) and 458 (M^+), respectively, cannot be explained by the back-biting reaction of a PPhA homopolymer chain. However, it can be explained by the backbiting reaction of a PPhA copolymer chain comprising diphenylacetylene monomeric units. Thus the mechanism of formation of PhA cyclotrimers is still remaining open for further investigation.

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