KINETICS AND MECHANISM OF THE PHENYLACETYLENE METATHESIS POLYMERIZATION CATALYZED WITH $WOCl_4/Ph_4Sn$ IN BENZENE

Jiří VOHLÍDAL, Andreas HOLLÄNDER*, Markéta JANČÁLKOVÁ**,
Jan SEDLÁČEK and Irena SARGÁNKOVÁ

Department of Physical and Macromolecular Chemistry,
Charles University, Albertov 2030, CS-128 40 Prague 2

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Tungsten oxychloride alone and in combination with Ph_4Sn were found to induce a polymerization of phenylacetylene (PhA) to *trans*-rich poly(phenylacetylene) (PPhA). The binary catalyst has a narrow maximum of the activity at the molar ratio $[Ph_4Sn]_0/[WOCl_4]_0 = y = 2$, so that two molecules of Ph_4Sn are necessary for a conversion of one molecule of $WOCl_4$ to the most active precursor specie. An incidental excess of Ph_4Sn acts as a noncompetitive inhibitor (retarder) of the overall polymerization. The order of reaction with respect to catalyst (for $y = 2$) varies with a concentration of the catalyst. It has value 1 for $[WOCl_4]_0$ from 0·1 to ca 4 mmol . . dm^{-3} and gradually increases over this concentration limit. Mutual interactions of partially associated growing species, eliminating inhibitive effects of monomer and organotin compounds, are supposed as a reason of this uncommon behaviour. The self inhibitive effect of polymerizing PhA was deduced from the dependence of the initial rate of polymerization on the concentration of PhA. This inhibition takes part most probably in both, the initiation and the propagation. The attempts to determine molecular wieghts of PPhA by VPO method failed because of a rapid degradation of polymer in diluted solutions exposed to atmospheric oxygen.

Great attention is still being devoted to the synthesis of substituted polyacetylenes, due to their potential use in photoelectronics[1] and membrane separation processes[2]. With respect to these practical aspects, the studies of substituted acetylenes polymerizations are mostly aimed merely to the preparation of new polymeric materials for the next physical research, as it is obvious from the review of Masuda and Higashimura[2]. Considerably less articles is devoted to the main features of polymerization mechanisms and only a few of them deal with kinetic aspects and with elucidation of partial steps of the overall reaction[2,3]. Therefore, being interested in the synthesis of substituted polyacetylenes with the aim mentioned above[4,5], we paid our attention

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* Present address: Institute für Polymerenchemie "Erich Correns", Kantstrasse 5, 1530 Teltow-Seehof, BRD.

** Present address: The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, CS-182 23 Prague 8.

also to the unsolved problems related to kinetics and mechanism of the polymerization. We have used phenylacetylene (PhA) as a monomer for these purposes. This substituted acetylene has probably most often been employed to study these questions.

There are two groups of catalysts for polymerization of PhA: (i) Ziegler type catalysts usually based on titanium or iron compounds[2,6,7] that generally produce insoluble polymers and/or oligomers, (ii) catalysts derived from molybdenum and particularly from tungsten compounds that are usually active also in olefin metathesis reactions and mostly provide soluble and high molecular weight poly(phenylacetylene) (PPhA)[2,3,8-12]. First polymerizations of PhA catalyzed by tungsten compounds were reported[8,13] in 1974. Using W(mes)$(CO)_3$ catalyst, Woon and Farona[13] had observed two-step formation of PPhA. A colorless polymer with main chains composed of condensed cyclobutane rings was formed in the first step and these ladder like chains were then converted into conjugated polyene chains of PPhA by the radical reaction. On the contrary, Masuda et al.[8] had observed direct formation of PPhA using WCl_6 and its combination with cocatalytic amounts of water as catalysts. In the following studies[9-12] they had proposed a metal carbene mechanism for these polymerizations and tested the influences of different cocatalysts and solvents on their course, however, predominately from the qualitative point of view. They had found that WCl_6/Ph_4Sn (1 : 1) was the most active catalyst and made a qualitative kinetic study of this system and semiquantitative kinetic study of the system with water as cocatalyst[8,10]. They had also found the stimulative solvent effect of 1,4-dioxane on the molecular weight of synthesized PPhA (ref.[12]).

Still one interesting effect was registered by Masuda et al., that is the cocatalytic effect of PhA on its own polymerization by WCl_6 (ref.[10]). Later Makowetskij et al.[14] and Katz et al.[15] had observed similar cocatalytic effect of PhA in the ring opening metathesis polymerization of cycloalkenes catalyzed by WCl_6. These interesting phenomena together with the processes of the formation of precursors and active species from WCl_6 and different cocatalysts are studied till now[3,16-22] and seem to be important also for the explanation of a substrate inhibition found in this study.

Reliable evidences for a metal carbene mechanism of substituted acetylenes polymerizations were obtained by Katz et al.[22,23]. They had shown that $XPhC{=}{=}W(CO)_5$ type of metal carbenes (X is phenyl or methoxy substituent) induce PhA and different butylacetylenes to polymerize[22]. Later, by means of the polymerization of the mixture of ^{13}C-labeled and unlabeled phenylacetylenes, they clearly demonstrated that two π-bonds in PhA are cleaved during the polymerization induced by $MoCl_5/Ph_4Sn$ catalyst, while the only one π-bond cleaves in the polymerization induced by Ziegler-type catalyst $Ti(OBu)_4/Et_3Al$:

$$n\mathrm{CH{\equiv}CPh} \rightarrow =(\mathrm{CH{-}CPh}=)_n \quad \text{(metathesis catalyst)}$$

$$n\mathrm{CH{\equiv}CPh} \rightarrow -(\mathrm{CH{=}CPh}-)_n \quad \text{(Ziegler catalyst)}$$

Therefore, the metal carbene mechanism can be regarded as the valid one for the substituted acetylenes polymerizations induced by metahesis catalysts. That is, the propagation of these polymerizations can be depicted by similar schemes as in the case of cycloolefin polymerizations (see e.g. ref.[2]) because the triple bond can be regarded as a special two-membered cycloolefin with none methylene group in the cycle, i.e. with cycle replaced by one carbon–carbon π-bond. Consequently, one can expect that this type of acetylenes polymerizations and olefin metathesis would have many common features.

A theoretical study of olefin metathesis was carried out by Rappé and Goddard[24] in addition to numerous experimental studies of these reactions. By means of *ab initio* calculations they had shown that the oxygen atom bonded directly to the central tungsten atom of the active specie could play an important role in the course of metathesis propagation, due to its ability to equalize a temporary changes of electron density on this central atom through the formation of a partial triple bond $W\equiv O$. Taking into account the conclusions of Rappé and Goddard, higher activity of tungsten catalyst derived from $WOCl_4$ than that of the similar one derived from WCl_6 can be evidently expected. Therefore, the choice of $WOCl_4/Ph_4Sn$ system as a catalyst for the present kinetic study of the polymerization of PhA enables us to compare (at least qualitatively) our results with those published for WCl_6/Ph_4Sn catalyst and, furthermore, to verify the theoretical assumptions concerning the role of oxygen ligand in the propagation.

EXPERIMENTAL

Materials and their Purification

Three different samples of phenylacetylene (PhA) were used: commercial PhA (Fluka) and samples of PhA prepared by dehydrobromination of styrene dibromide using $NaNH_2$ in liquid ammonia[25] or KOH in 2,2′-oxydiethanol[26]. Redistilled PhA was finally dried (using CaH_2 as a drying agent) and degasified in a vacuum glass device and then slowly distilled into vacuum glass vessel provided with a break seal. Next distribution of PhA into calibrated ampoules used in polymerization experiments was carried out by spilling in a common glass vacuum tree-like apparatus.

Tungsten oxychloride, $WOCl_4$, was gained by a fractional distillation* of commercial WCl_6 (Pierce Inorganic B.V.) carried out under the argon atmosphere (initial pressure 73 kPa at 20°C) in a sealed all-glass device consisted of three ampoules with break seals, joined in line. The first ampoule with a crude WCl_6 was heated up to 270°C and evolved $WOCl_4$ was periodically driven over into the second ampoule using a direct flame. WO_2Cl_2, evidently contained in the crude material, reacts with WCl_6 to form $WOCl_4$ during the heating of the first ampoule. That is, WO_2Cl_2 is not present among the products of this fractonal distillation. After the first step of the distillation, the first ampoule with tabular crystals of pure WCl_6, m.p. 285°C, was sealed off.

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* We did not succeed in gaining pure $WOCl_4$ by means of a vacuum sublimation of crude WCl_6.

The ampoule with $WOCl_4$ containing also small amount of WCl_6 was then heated up to ca 230°C and $WOCl_4$ was distilled over into the third ampoule and so stripped of the remaining WCl_6. The red needlelike crystals of $WOCl_4$, m.p. 211°C, were obtained in the third ampoule. This ampoule was than sealed off from the second one containing a mixture of the remaining WCl_6 and $WOCl_4$. A saturated solution of $WOCl_4$ in purified benzene (9·5—10 mmol dm^{-3}) was prepared in vacuum conditions and distributed by spilling into calibrated ampoules provided with break seals. Saturated solution of $WOCl_4$ was used for kinetic experiments directly or after the next dilution with benzene.

Tetraphenyltin (Ph_4Sn) (EGA Chemie) was twice recrystallized from carbon tetrachloride and stored in a dark bottle without further protection. Benzene (Lachema Brno) was purified by standard procedure[27], five days refluxed with NaH and freshly distilled middle fraction was than dried and degasified with a new portion of NaH in a vacuum device and finally distilled into a glass container provided with break seals (the final vacuum distillation must be carried out very slowly to prevent a transfer of dust particles of NaH into the distillate); the following dosage of benzene into calibrated ampoules was carried out by spilling in a proper vacuum device. Methanol (Lachema, analytic grade) and toluene (Lachema, analytic grade) were used for a termination of polymerizations and reprecipitation of PPhA without further purification.

Polymerization Procedures

Determination of the initial rate of polymerization. A reactor with magnetic stirring bar (Fig. 1*a*) was fused-on a vacuum line and cleaned by direct flame during the following evacuation. Afterwards, the device was filled by dried nitrogen and a glass splint with weighed amount of Ph_4Sn was cast into the side tube 3 where it stopped at the narrowing of the tube while Ph_4Sn fell through into the reactor. The glass splint was taken out of the tube which was then closed

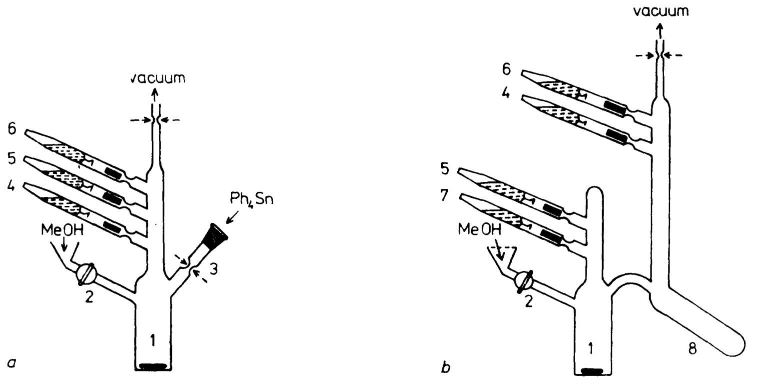


FIG. 1

Vacuum devices for the determination of the initial rate of polymerization in systems with concentrations of PhA; *a* higher then ca 0·75 mol dm^{-3}, *b* lower then ca 1·2 mol dm^{-3}. 1 Reaction vessel, 2 tube closed by high vacuum PTFE stop cock for an introduction of terminating methanol, 3 side tube for a dosing of Ph_4Sn, 4, 5, 6, and 7 ampoules with PhA or its solution, solution of $WOCl_4$, benzene, and solution of Ph_4Sn, respectively, 8 side tube for a collecting of benzene distilled off the solution of Ph_4Sn and for mixing of PhA with benzene and fused-off the reactor. During the following evacuation the whole polymerization apparatus except of its bottom with Ph_4Sn (m.p. 228°C) was periodically heated by a direct flame to remove the rest of impurities from the inner walls. Evacuated reactor was then fused-off the vacuum line and prepared dose of the $WOCl_4$ solution added into the reaction vessel through a break seal. Stirred reaction mixture was retained to ripen for ca 15 min (a proper time was chosen on the base of preliminary experiments) and a measured volume of benzene was than added to the solution of the catalytic species precursors. Immediately afterwards, the dose of PhA was added into the reaction mixture as fast as possible (short heating by a direct flame is necessary for a quick expulsion of PhA from ampoule through the broken seal). After ca 20 s terminating methanol (ca 2 cm^3) was injected into the reactor through the PTFE high vacuum ventil from a side tube **4**. Precipitated PPhA was redissolved in reactor by toluene, glass splints (from broken seals) were removed from solution by filtration through a sinter. PPhA was reprecipitated by methanol, separated and finally dried in a vacuum oven to a constant weight at 40°C. The value of the initial rate of polymerization was estimated from the yield of PPhA as an average rate in the applied reaction time.

To determine values of the initial rate of polymerisation, v_0, for low concentrations of PhA low concentrations of catalyst were necessary as well, to keep the conversions in the region acceptable for the v_0 measurements. A modified polymerization procedure was used in such cases, at which also Ph_4Sn and PhA were dosaged into the reactor (Fig. 1*b*) from ampoules as solutions prepared in advance under vacuum conditions. The solution of Ph_4Sn in benzene was added into the sealed evacuated reaction device (residual pressure ca 1 mPa) and benzene was distilled off the reaction vessel into the side tube **8** in order to have higher concentration of reactants during the ripening of a catalyst. The solution of $WOCl_4$ was then mixed with dried Ph_4Sn and the resulting mixture retained to ripen. Then PhA or its solution was mixed with the benzene in the side tube and, immediately afterwards, this solution was quickly mixed with the ripe catalyst. After a termination by methanol the whole reaction mixture was redissolved in proper amount of toluene and the concentration of PPhA was determined from solution absorption at 400 nm, using calibration curve.

Determination of conversion curves. Glass apparatus provided with a second reaction vessel joined to the first one through a tube with glass sinter was used for these purposes (see Fig. 2). The polymerization was started essentially by the same manner as stated at determination of v_0 and, immediately afterwards, the polymerizing mixture was filtered into the second vessel provided with a sampling device. Filled vessel was then fused off the rest of apparatus, connected to the vacuum line through glass joint and its outer parts were evacuated. After, the valve **9** was closed and ca 1 cm^{-3} of the reaction mixture was quickly sampled through the valve **8**

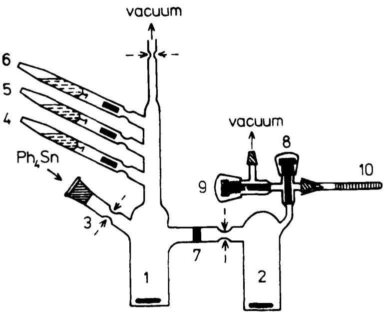


Fig. 2

Vacuum device for the determination of conversion curves: **1** and **2** reaction vessels, **3**, **4**, **5**, and **6** see legend to Fig. 1, **7** glass sinter, **8** and **9** high vacuum PTFE stop cocks of the sampling device, **10** calibrated test tube into the calibrated test tube which was slightly undercooled. As the valve 8 was closed, the test tube with a sample was taken out and PPhA precipitated by methanol, separated and dried to a constant weight in a vacuum oven. The opened parts of the sampling device were cleaned by toluene, the reactor reconnected to the vacuum line, evacuated and so prepared for a next sampling.

Measurements

IR spectra were recorded in a KBr disk using Perkin–Elmer instrument with data-station 3600. UV-VIS spectrometer Specord and a colorimeter Specol (both fy Karl Zeiss Jena) were used for spectrometric determination of the concentration of PPhA in solutions. Molecular weights of PPhA samples were estimated using vapour pressure osmometer Knauer. The measurements were carried out with solutions of PPhA in benzene at 37°C.

RESULTS AND DISCUSSION

Polymerizations of PhA induced by $WOCl_4$ and $WOCl_4/Ph_4Sn$ catalysts lead to dark-red, usually powdered PPhA. According to IR spectra the content of *trans* structure in these polymers is comparable to, or even higher than, its content in PPhA synthesized by catalysts derived from WCl_6 (the band at 740 cm^{-1} characteristic for *cis* structure is almost undeveloped). Values of $\langle M \rangle_n$ from 3 to 15 thousands were obtained using VPO method. However, these values are very questionable because the osmotic behaviour of PhA solutions testifies to a continual degradation of the dissolved PPhA and, consequently, estimated values of $\langle M \rangle_n$ cannot correspond to the actual ones; due to this they can be considered only as a lower limits of $\langle M \rangle_n$ and no reliable conclusions can be therefore done from them. Further investigations are necessary to elucidate this problem.

The Influence of the Composition of the Catalyst

It was found that pure $WOCl_4$ induces a polymerization of PhA and that its catalytic activity can be considerably increased by the addition of cocatalytic amount of Ph_4Sn. The dependence of the initial rate of polymerization, v_o, on the catalyst composition, $y = [Ph_4Sn]_o/[WOCl_4]_o$, and conversion curves for different values of y clearly demonstrate a double role of Ph_4Sn in the polymerization of PhA: (i) for values of y from 0 to 2 it acts as a typical cocatalyst that monotonously increases the catalytic activity of $WOCl_4$, (ii) for values of $y > 2$ it also acts as an inhibitor of the overall polymerization. Found optimum ratio of $WOCl_4$ to Ph_4Sn (1 : 2) corresponds to the idea that a transformation of $WOCl_4$ to precursors of the active species probably requires two consecutive arylations of $WOCl_4$ (assuming an analogy with the WCl_6/Ph_4Sn catalyst[10,20,21]). Insinuated wave at $y = 0{\cdot}5$ can be explained by some participation of Ph_3SnCl (assumed as a side product of the ripening of the catalyst) in the formation of precursors. However, this question has not yet been studied in detail.

A special attention requires the rapid decrease of v_0 in a very narrow interval of values y (from 2·0 to 2·5) to the almost constant value for $y > 2·5$. It is clear that the superfluous Ph_4Sn does not act as a terminating agent but rather as a noncompetitive inhibitor (see Figs 3 and 4). The inhibitive effect of Ph_4Sn can be explained assuming that: (i) low stationary concentration of active centres is achieved almost immediately after the start of the reaction, (ii) the superfluous Ph_4Sn binds selectively to the growing active centres and not to their precursors. The first assumption is a fundamental one because, if all precursor species were changed to active centres at the beginning of reaction, such a small excess of Ph_4Sn could not have so strong influence on initial rate of polymerization. The second assumption is rather special, nevertheless, the selective binding of Ph_4Sn to carbene centres and to their non-carbene precursors seem reliable. It is known that e.g. cycloolefins polymerize easy on carbene tungsten complexes but not on their non-carbene precursors[14,15,22,28]. Similar phenomenon can be supposed also in our system. Steric and/or electronic effects of coordinated Ph_4Sn can bring on the decrease of the activity of growing species. Thanks to a low stationary concentration of growing species, even a small excess of the inhibiting Ph_4Sn can considerably influence the rate of polymerization. Assuming a noncompetitive type of inhibition, further increase of the excess of Ph_4Sn will have no effect on the activity of polymerization centres because they have already been saturated by this inhibitor.

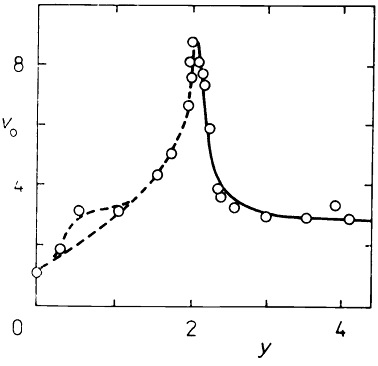


FIG. 3

Dependence of the initial rate of polymerization, v_0 (mmol dm^{-3} s^{-1}), on the composition of catalyst, $y = [Ph_4Sn]_0/[WOCl_4]_0$; conditions: $[M]_0 = 1·52$ mol dm^{-3}, $[WOCl_4]_0 = 3·17$ mmol dm^{-3}. Full line is drawn out according to Eq. (*1*) for parameters k'_p/k^0_p 0·3 and K_r 3 150 mol dm^{-3}

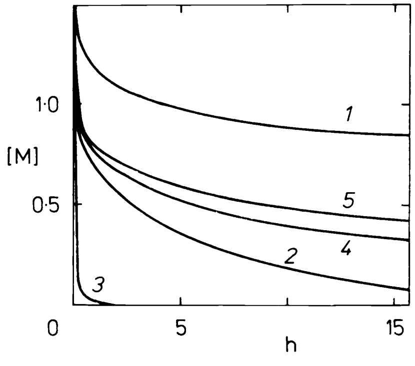
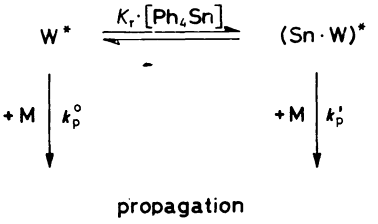


FIG. 4

Conversion curves for different values of catalyst composition ratio, y: *1* 0, *2* 0·97, *3* 1·98, *4* 2·77, *5* 4·0. For all reactions $[WOCl_4]_0 = 3·2$ mmol dm^{-3} and $[M]_0 = 1·52$ mol dm^{-3}

The idea given above is in the simplest way depicted in Scheme 1, where W* is non-inhibited active centre, {Sn . W}* inhibited active centre, M monomer (i.e. PhA), K_r an equilibrium constant of the formation of inhibited active centres, k_p^0



SCHEME 1

and k_p' propagation constants for non-inhibited and inhibited centres, respectively. Taking into account that an overall stationary concentration of active centres is given by an equation, $[W^*]_{st} = [W^*] + [Sn \,.\, W^*]$, and assuming the same dependencies of the reaction rates on [M] for both types of active centres, the following relation for the initial rate of polymerization is obtained:

$$v_o = v_o^{max}\{1 + (k_p'/k_p^0)\, K_r[Ph_4Sn]_{exc}\}/\{1 + K_r[Ph_4Sn]_{exc}\}\,, \qquad (1)$$

where $[Ph_4Sn]_{exc}$ is the concentration of the excess of Ph_4Sn and $v_o^{max} = k_p^0[W^*]_{st}\,.\, f([M])$, where $f([M])$ is a function of monomer concentration, yet unknown. The fit of Eq. (*1*) to experimental points provided following values of parameters: $k_p'/k_p^0 = 0{\cdot}3$ and $K_r = 3\,150$. A good agreement of experimental points with Eq. (*1*) shown in the Fig. 3 testifies to a convenience of the hypothesis given above, that Ph_4Sn coordinates fast and selectively to the active species but not to their precursors. The manner of this coordination is discussed in the closing subsection.

The Influence of Catalyst Concentration

The catalyst having the optimum composition, $y = 2$, and thus the highest activity was used in these experiment. The influence of catalyst concentration on the reaction rate v_o is shown in the Figs 5 and 6. As it can be clearly seen, for values of $[WOCl_4]_o$ smaller than ca 4 mmol dm^{-3} the first order of reaction with respect to catalyst can be assumed, however, for higher concentrations the reaction order increases so that in the interval of $[WOCl_4]_o$ from 4 to 8 mmol dm^{-3} it has an average value ca 1·5 (concentration of the saturated solution of $WOCl_4$ is ca 10 mmol dm^{-3}). Such a behaviour is not common for the coordination polymerization catalysts. Their catalytic activity usually decreases with the increase of their concentration, due to the aggregation and mutual saturation of active centres resulting eventually in their bimolecular termination. The actual behaviour of $WOCl_4 + 2\,Ph_4Sn$ catalyst is just opposite. The increase of catalyst concentration results in an excessive acceleration of the propagation and the fact that a power of the dependence v_0 vs . . $[WOCl_4]_0$ is even higher than 1 testifies to the absence of a bimolecular termination of the respective active centres. Therefore, the first order termination of active centres should be taken into account. For the sake of lack of reliable values of $\langle M \rangle_n$ (see Experimental) we could not discuss this question more in detail.

The observed dependence of v_0 on $[WOCl_4]_0$ is evidently caused by mutual interactions of active centres. Such interactions can potentially lead to the formation of some bimetallic or multimetallic active centres similar to that described by Levisalles et. al.[20] for low-valent tungstene carbonyl complex, however, they must in catalytic activity substantially exceed the monometallic ones (so that the increase of the reaction order may be explained). There is still another idea explaining the observed facts. The interacting active centres can mutually act each to others from their outer coordination spheres as e.g. Lewis acid accelerators[24] while the propagation proceeds independently on each centre. The association of growing species that coheres with the supposed reason of inhibitive effects of Ph_4Sn and PhA is supposed in both cases (see the closing subsection).

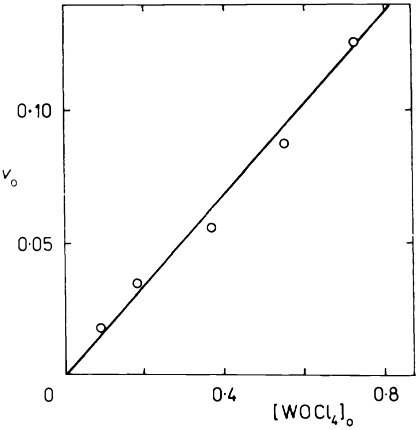


FIG. 5

Dependence of the initial rate, v_0 (mmol . . $dm^{-3}\,s^{-1}$), on the catalyst concentration, $[WOCl_4]_0$ (mmol dm^{-3}), for diluted reaction mixtures, $[M]_0 = 0{\cdot}04$ mol dm^{-3}, $y = 2$

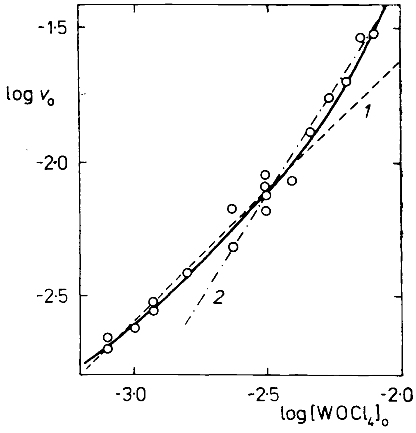


FIG. 6

Bilogarithmic dependence of v_0 (mmol dm^{-3}. . s^{-1}) vs $[WOCl_4]_0$ (mmol dm^{-3}), for $[M]_0 = 1{\cdot}52$ mol dm^{-3}, $y = 2$. Dashed lines indicate dependences for the values of the reaction order with respect to the catalyst equal to: *1* 1·0, *2* 1·5

The Influence of Phenylacetylene Concentration

Again, the catalysts with optimum composition, $y = 2$, had been used in these experiments. The influence of the concentration of PhA on its own polymerization seems to be the most interesting peculiarity of this reaction. The dependence of the initial rate of polymerization on [M] corresponds to significant inhibition of the reaction by polymerizing monomer, as it is seen from Fig. 7.

To verify a possible role of impurities we had tested three different samples of PhA, as mentioned above (see Experimental), and any substantial differences exceeding experimental errors had not been found. The contradictory role of PhA is undoubtedly connected with the results of Katz et al.[15,29]. They had found that PhA used as the cocatalyst for WCl_6 in a cyclopentene polymerization simultaneously decreases the final yields and the values of $\langle M \rangle_n$ of the resulting copolymers. Katz et al. assume a rapid bimolecular termination of active centres with PhA ends as a reson of both decreases mentioned above, contrary to our present findings. It is clear that their results can be also explained by an inhibitive effect of PhA similar to that one found in this study. However, these considerations must be done carefully because it is also clear that the systems with catalysts derived from WCl_6 and $WOCl_4$ respectively do not behave identically. The presence of additional coordination vacancy in a centre derived from $WOCl_4$ (replacement of two chlorine in WCl_6 by one oxygen) can explain the differences in the behaviour of these two systems (see also closing subsection).

The observed self inhibition of polymerization of PhA cannot be in any case explained by an acceleration of termination because even at high initial concentrations of PhA the polymerizations proceed a few hours what testifies to long life time of active centres. Therefore, a substrate inhibition taking part in the initiation and/or

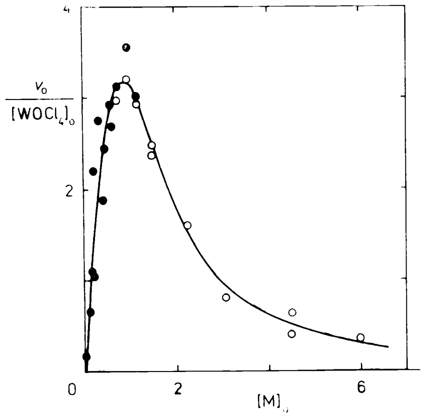
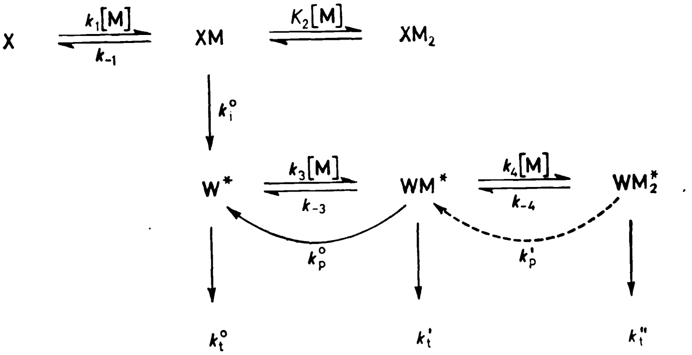


FIG. 7

Dependence of the reduced initial rate, $v_0/[WOCl_4]_0$ (s^{-1}), on the monomer concentration, $[M]_0$ (mol dm^{-3}). The line is drawn out according to Eq. (*2*) with parameters given in Table I. Data were gained using the devices depicted in Fig. 1*a* (open circles) and in Fig. 1*b* (full circles) and corresponding procedures (see Experimental) in the propagation can be assumed as a base for kinetic analysis of the dependence v_0 vs $[M]$. This idea is depicted in Scheme 2 where X and W* are precursors and



SCHEME 2

active centres, respectively, XM, XM_2, WM^*, and WM_2^* corresponding complexes of X or W* with monomer M (i.e. with PhA) and k_i, k_p, and k_t rate constants of initiation, propagation, and termination, respectively. Neglecting the second mode of propagation, characterized by the rate constant k_p', and using an approximation of stationary state for initiation and propagation as well, the following rate equation can be derived from the Scheme 2,

$$v_0/[X]_0 = [M]^2/\{A + B[M] + C[M]^2 + D[M]^3 + E[M]^4\}\,, \tag{2}$$

where $[X]_0$ is the initial overall concentration of precursors (it can be replaced by $[WOCl_4]_0$ in an analysis of the experimental results), $[M]$ is the initial concentration of PhA, and the meanings of the other coefficients are the following,

$$A = k_t^0 K_3^{pt} K_1^i / k_i^0 k_p^0 \tag{3a}$$

$$B = (k_t' K_1^i + k_t^0 k_t'' K_1^i / k_3 K_4^t + k_t^0 K_3^{pt}) / k_i^0 k_p^0 \tag{3b}$$

$$C = (k_t' + k_t^0 k_t'' / k_3 K_4^t + k_t^0 K_2 K_3^{pt} + k_t'' K_1^i / K_4^t) / k_i^0 k_p^0 \tag{3c}$$

$$D = (k_t'' / K_4^t + k_t' K_2 + k_t^0 k_t'' K_2 / k_3 K_4^t) / k_i^0 k_p^0 \tag{3d}$$

$$E = k_t'' K_2 / K_4^t k_i^0 k_p^0\,, \tag{3e}$$

where

$$K_1^i = (k_{-1} + k_i^0) / k_1 \tag{4a}$$

$$K_2 = k_2/k_{-2} \tag{4b}$$

$$K_3^{pt} = (k_{-3} + k'_p + k'_t)/k_3 \tag{4c}$$

$$K_4^t = (k_{-4} + k''_t)/k_4 \,. \tag{4d}$$

Taking into account both modes of propagation, i.e. considering the full reaction Scheme 2, the following rate equation is obtained,

$$v_0/[X]_0 = (1 + F'[M])\,[M]^2/\{A' + B'[M] + C'[M]^2 + D'[M]^3 + E'[M]^4\}\,, \tag{5}$$

where the coefficients $A' \dots E'$ differ from $A \dots E$ defined by Eqs (*3a*–*3e*) only in that the constant K_4^t is replaced by K_4^{pt} defined by the Eq. (*6a*). Coefficient F' is given by Eq. (*6b*).

$$K_4^{pt} = (k_{-4} + k'_p + k''_t)/k_4 \tag{6a}$$

$$F' = k'_p/k_p^0 K_4^{pt} \,. \tag{6b}$$

If only either initiation or propagation is inhibited by PhA, just the first mode of propagation can be taken into account and the following type of rate equation is obtained,

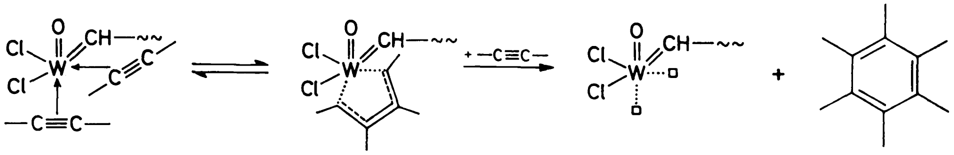
$$v_0/[X]_0 = [M]^2/\{A'' + B''[M] + C''[M]^2 + D''[M]^3\}\,, \tag{7}$$

where again $A'' = A$ and coefficients $B'' \dots D''$ can be simply derived from Eqs (*3b*–*3d*) considering: (i) $K_4^t \to \infty$ if only initiation is inhibited, (ii) $K_2 = 0$ if only propagation is inhibited.

It is evident, from the definition Eqs (*3*), (*4*), and (*6*) and relations among the coefficients stated above, that all parameters $A \dots D''$ must be positive because they consist of products and sums of positive constants. This condition can serve as a crucial (or at least a very significant) criterion of validity of the results obtained by a nonlinear regression analysis of the measured dependence of v_0 vs $[M]$ using Eqs (*2*), (*5*), and (*7*). Executed regression analysis had shown that just Eq. (*2*) can be fitted to experimental points with positive values of all coefficients $A \dots E$. In the cases of Eqs (*5*) and (*7*) always one or two regression coefficients are negative. Hence, following conclusions can be done: (i) the substrate inhibition of both, the initiation and the propagation, takes part in polymerizations of PhA induced by $WOCl_4/Ph_4Sn$ catalyst, (ii) the only first mode of propagation takes part in these polymerizations, i.e. species WM_2^* are most probably inactive in the propagation.

Values of some constants contained in Scheme 3 can be potentially calculated from regression coefficients $A \dots E$ (see Table I), however, the accuracy and reliability of the coefficients determined are too low for this purposes (standard error ca 50%).

Furthermore, it is also clear that the significance of the agreement between experimental dependence v_0 vs $[M]$ and Eq. (2) should not be overestimated because acceptable values of the coefficients do not exclude the existence of more plausible reaction scheme. Therefore, qualitative conclusions only and not quantitative ones can be drawn out from the present results.



SCHEME 3

Comparison with Catalysts Derived from WCl_6 *and Notes to the Mechanism of Inhibition in Systems with* $WOCl_4/Ph_4Sn$

Although polymerizations of PhA induced by catalysts derived from WCl_6 have been the most in detail studied reactions of this type, unfortunately, there are not almost any initial rate data available in the literature for direct quantitative comparison with our results. Consequently, only qualitative comparison of the systems with catalysts derived from WCl_6 and $WOCl_4$ respectively can be done.

It is clear that $WOCl_4$ without any cocatalyst induces a polymerization of PhA to *trans* rich PPhA. Just the same catalytic reactivity was found for pure WCl_6 by Masuda et al.[8] who had used the syringe technique and polymerized PhA under a dry nitrogene atmospheres. The final yields of PPhA gained with $WOCl_4$ and WCl_6 are comparable, so it can be concluded that a positive role of oxygen ligand[24] is

TABLE I

Parameters obtained by the fits of Eqs (2), (5), and (7) to the dependence shown in Fig. 7 using a nonliner regressions

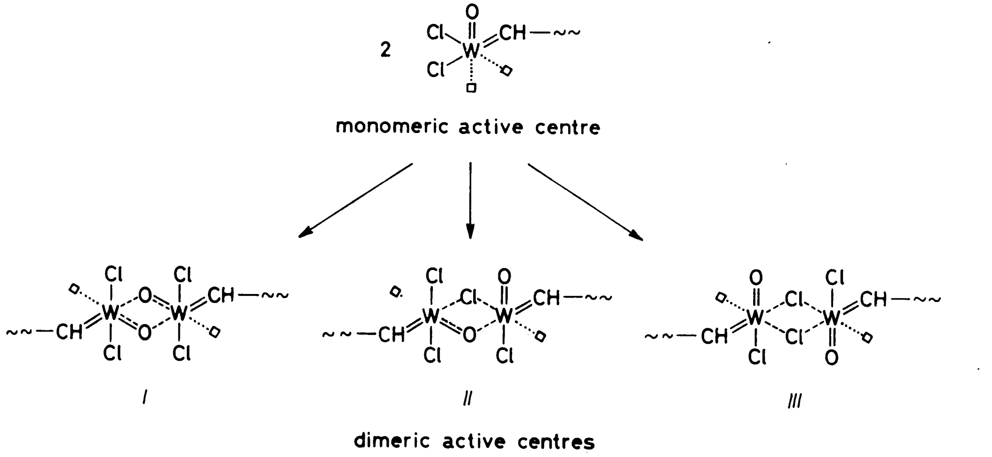
Parameters	Eq. (2)	Eq. (5)	Eq. (7)
A, A', A''	$2\cdot55 \,.\, 10^{-3}$	$4\cdot03 \,.\, 10^{-3}$	$-3\cdot33 \,.\, 10^{-3}$
B, B', B''	$1\cdot42 \,.\, 10^{-1}$	$1\cdot10 \,.\, 10^{-1}$	$2\cdot74 \,.\, 10^{-1}$
C, C', C''	$5\cdot17 \,.\, 10^{-2}$	$2\cdot24 \,.\, 10^{-1}$	$-3\cdot89 \,.\, 10^{-1}$
D, D', D''	$3\cdot42 \,.\, 10^{-2}$	$-1\cdot69 \,.\, 10^{-1}$	$4\cdot46 \,.\, 10^{-1}$
E, E'	$8\cdot95 \,.\, 10^{-2}$	$2\cdot00 \,.\, 10^{-1}$	—
F'	—	$1\cdot65 \,.\, 10^{-1}$	—

not confirmed in this case. However, the results[30] of our preliminary experiments with WCl_6, carried out by the vacuum polymerization technique, did not prove the results of Masuda[8] et al. about the polymerization acivity of pure WCl_6, what makes also the conclusions about the role of oxygen ligand questionable. Nevertheless, it is clear the activities of both these tungsten compounds can be considerably increased (and/or achieved in the case of WCl_6) by cocatalyst Ph_4Sn. Dependences of the activities of both binary catalysts $WOCl_4/Ph_4Sn$ and WCl_6/Ph_4Sn on the ratio [Sn]/[W] are different. While the activity maximum of the former is very sharp (at $y = 2$) as mentioned above, the activity of the latter passes through considerably broader and flat maximum (almost constant catalytic activity for values of y from 1 to 2 can be deduced from the data published in ref.[10]). The inhibition of the overall reaction by superfluous Ph_4Sn is undoubted in both systems, however, in the case of WCl_6/Ph_4Sn catalyst not so explicit as in the case of $WOCl_4/Ph_4Sn$ catalyst.

Evident difference between the systems in question is in the reaction orders with respect to the catalyst. The order of reaction is probably smaller than 1, in the case of WCl_6/Ph_4Sn catalyst, while values equal or even higher than 1 were found for $WOCl_4/$ $/Ph_4Sn$ in this study. There are still initial rate data published for $WCl_6/\frac{1}{2}H_2O$ catalyst[8], according to which the first orders with respect to both, the catalyst and PhA, were found for concentrations of $[WCl_6]_0$ from 2·5 to 10 mmol dm^{-3}. The different dependencies of the reaction rate on the PhA concentration can be regarded as the second considerable difference between the systems in discussion. While polymerizations induced by $WOCl_4/Ph_4Sn$ catalyst are evidently self inhibited by polymerizing PhA (clarify foregoing subsection), the changes of conversion curves with increasing PhA concentration for reactions induced by WCl_6/Ph_4Sn catalyst can be simply explained by a gradual saturation of polymerization centres by PhA.

The character of differences mentioned above lead us to conclusions that they are caused by a presence of additional coordination sites in the centres derived from $WOCl_4$, due to the substitution of two chlorine ligands by one oxygen atom. The considerable inhibitions of the polymerizations induced by $WOCl_4/Ph_4Sn$ catalysts caused by superfluous Ph_4Sn and by monomer can be then simply explained by influences of coordinated molecule of tin compound or PhA occupying the excess coordination vacancy of the active specie. The fact that superfluous Ph_4Sn acts only as a noncompetitive inhibitor can be imputed to a bulkiness of this ligand due to which the only one molecule of Ph_4Sn can be coordinated to one active centre. Consequently, the second coordination site remains free for an addition of a molecule of polymerizing PhA and thus polymerization can proceed. The retardation of the overall reaction can be explained by the change of the electron density on the central tungsten atom with Ph_4Sn ligand and by the steric hindrances. In the case of the inhibition by substrate, another mechanism comes into account in addition to the previous one, that is an equilibrium formation of a metallacyclopentadiene cycle from the active specie (Scheme 3). This complex is assumed to be an intermediate in catalytic cyclotrimerization of alkynes[2], which is competitive reaction to alkyne polymerization by common type of catalyst. It is known, that in the case of PhA polymerization by catalysts derived from WCl_6 the cyclotrimerization does not proceed, and we did not observe a formation of measurable amounts of triphenylbenzenes in the case of $WOCl_4/Ph_4Sn$ catalyst, as well. Nevertheless, we cannot exclude the formation of metallacyclopentadiene species that do not react with another molecules of PhA and can be therefore considered as temporary dormant active species, (reversibly inhibited centre). The inhibition reactions described above are to be supposed as a reason of the failure of the theoretical prediction of Rappé and Goddard[24] supposing that a replacement of two chlorine by one oxygen will bring about the increase of polymerization activity.

In terms of the idea of two free coordination sites in active centres derived from $WOCl_4$ also the observed dependence of ln v_0 on ln $[WOCl_4]_0$ (Fig. 6) in the region of higher catalyst concentrations can be reasonably explained. A formation of some associated active centres connected e.g. through the oxygen and/or chloride bridges (*I*–*III*, Scheme 4) can positively influence a propagation thanks to mutual blockade of the additional coordination sites that are responsible for the inhibition reactions. The existence of similar linear and/or cyclic associates composed of three, four and more active centres can be assumed as well. This hypothesis is supported by relatively small solubilities of $WOCl_4$ (see Experimental), ripen catalytic precursors and particularly of a products of their reaction with a catalytic amount of



SCHEME 4

PhA in benzene[31], that demonstrates a tendency of active centres and their precursors to aggregate even to macroscopic particles.

Growing species arisen from the catalysts derived from WCl_6 with the only one coordination vacancy cannot be inhibited by similar manner as species derived from $WOCl_4$. The observed inhibition[10] by superfluous Ph_4Sn can be considered as competitive, in this case, in full agreement with the conception of structure differences described above. This conception coheres also with the influence of the concentration of PhA on the course of polymerization that testifies to the gradual saturation of active centres rather than to an inhibition by substrate. Furthermore, the substrate inhibition can shade the positive influence of the oxygen ligand on the course of polymerization what can explain the observed comparable polymerization efficiencies of $WOCl_4/Ph_4Sn$ and WCl_6/Ph_4Sn catalysts.

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