Synthesis of Linear IVth Group Organometallic Polymers by Polyaddition*

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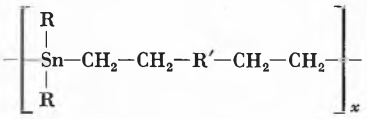
Zusammenfassung

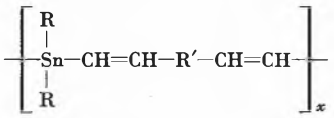
1955 entdeckten van der Kerk, Luijten und Noltes die hohe Reaktionsfähigkeit der organischen Zinnmonohydride und fanden, daß sie sich sehr leicht an ungesättigte Kohlenstoffbindungen anlagern. Diese Reaktion verläuft glatt und ohne Katalysator beim Erhitzen der beiden Komponenten auf mäßige Temperaturen. Die Ausbeuten sind in der Regel sehr gut. Es wird gezeigt, was für ungesättigte Verbindungen als Reaktionspartner in Frage kommen. Der Verlauf der Reaktionen bei der Verwendung eines asymmetrisch substituierten Olefins wird kurz behandelt, und die Vorteile dieser nicht katalysierten Reaktion werden erläutert.

Die Reaktion von Dialkyl- oder Diaryl-Zinndihydriden mit verschiedenen diolefinischen Verbindungen ergeben zahlreiche Vertreter neuer linearer Heteropolymeren der allgemeinen Formel



R′ ist ein aliphatisches oder aromatisches Diradikal und kann auch eine kompliziertere Struktur haben.

Bei Verwendung von Diacetylenverbindungen als Reaktionspartner entstehen Polymere der Formel



Die Reaktion, nach der diese Polymeren entstehen, ist ein Beispiel einer reinen Polyaddition oder – nach der neuen angelsächsischen Nomenklatur – einer Wasserstoffübertragungs-Polymerisation. Die große Ähnlichkeit dieser Reaktion mit der Bildung von Polyurethanen aus Diolen und Diisocyanaten ist auffallend.

Reaktionsbedingungen, Nebenreaktionen und Synthese der Ausgangsstoffe werden im Detail behandelt.

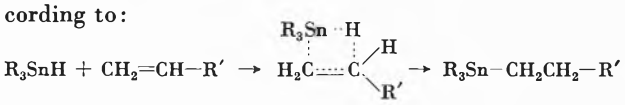
Der Verlauf der Reaktion kann durch Infrarotabsorptionsmessungen bei 1820 bis 1825 cm^{-1} (5,48 μ) verfolgt werden, da die Sn—H-Bindung in diesem Bereich eine charakteristische Streckschwingung zeigt.

Die erhaltenen Endprodukte können je nach der Art von R und R′ und dem Polymerisationsgrad hoch viskose Öle, kautschukähnliche Stoffe oder spröde Festkörper sein. Einzelheiten über Molekulargewicht, Schmelzpunkt, Löslichkeit und besonders über die thermischen Eigenschaften dieser Polymere werden angegeben und diskutiert.

For a little more than two years already, work is going on in the Institute for Organic Chemistry T. N. O. (the dutch organization for applied scientific research) on the synthesis of linear polymers having a carbon-carbon backbone, regularly interrupted by IVth main group metal atoms. Part of this work is a direct and logical consequence of an earlier discovery. In 1955 Van der Kerk, Luijten and Noltes[1-4] at our institute started studying the chemistry of the organotin hydrides. They found these hydrides to be very reactive compounds in a general sense. One of their most interesting and most versatile reaction possibilities in particular, is the addition of an organotin hydride to an unsaturated carbon-carbon bond.

Before discussing the application of this reaction principle to the synthesis of polymers, I would like to deal briefly with its low-molecular aspects. This, at the same time, will lead to a better appreciation of the scope of the reaction.

The general reaction of an organotin monohydride with a monosubstituted olefinic reactant proceeds according to:



We have studied this reaction extensively, varying the nature of either R or R′ or of both of them.

It appeared that, using triphenyltin hydride, the reaction proceeds very smoothly upon heating the two reactants at a moderate temperature viz. at about 70 to 100 °C. Usually a few hours of heating is required, but also shorter reaction times have been observed. In general, yields are high, viz. 75% to almost quantitative. Trialkyltin hydrides react much slower: only if the olefinic bond is activated sufficiently by the substituent R′ (e.g. when R′ represents an aryl group) a reasonably reaction rate is observed.

As to the structure of the addition products, experimental results show that the organotin group is always added in the terminal position. All evidence points to an ionic mechanism. Predominantly steric factors, however, determine the course of the reaction. Polar effects only influence the rate of the reaction.

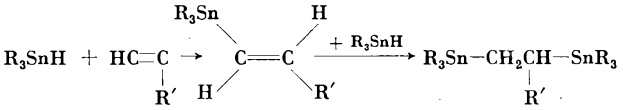
A very important feature of the addition reaction is its proceeding in the absence of any catalyst. This is contrary to the situation with similar reactions of carbon or silicon hydrides[5]. There, peroxides, UV-light or very high tem-

* Paper presented at the «Symposium über Polyadditionsprodukte und ihre praktische Anwendung», Zürich, Oktober 1961 and read by G. M. van der Want.

[1] G. J. M. van der Kerk, J. G. A. Luijten and J. G. Noltes, *Chem. & Ind. 1956*, 352.
[2] G. J. M. van der Kerk, J. G. Noltes and J. G. A. Luijten, *J. Appl. Chem. 7* (1957) 356.
[3] G. J. M. van der Kerk and J. G. Noltes, *ibid. 9* (1959) 106.
[4] J. G. Noltes and G. J. M. van der Kerk, *Functionally Substituted Organotin Compounds*, T. R. I., Greenford 1958.
[5] H. Gilman and J. Eisch, *J. Org. Chem. 20* (1955) 763. R. Fuchs and H. Gilman, *J. Org. Chem. 22* (1957) 1009.

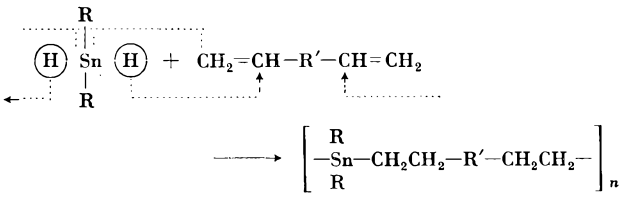
peratures have to be applied, circumstances which also strongly bring about the homopolymerization of the olefine. Thus, in the present case, i.e. when using organotin hydrides, the danger of homopolymerization is almost negligible and can even be eliminated completely by using an inhibitor like hydroquinone. This is clearly of importance for the realization of the reaction on a polymeric level.

Similar addition reactions have been realized using acetylenic derivatives as the unsaturated partner.



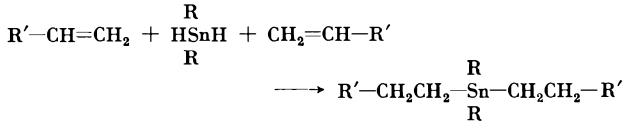
However, the reactivity of organotin hydrides towards a triple bond is much higher than towards a double bond: mostly, these reactions proceed exothermally. Consequently, when applying one mole of a monohydride per mole of a one-triple-bond-containing compound only the olefinic addition product is being formed. Similarly, when applying two moles of a monohydride, two separate reaction steps can be distinguished clearly, the second one requiring more severe reaction conditions. The second organotin group enters, as to be expected, in the ω-position with respect to the first.

Considering the foregoing explanations, the possibility of using the present type of reaction for the synthesis of polymers is evident. Upon reaction of an organotin dihydride with a di-olefine, preferably with both the double bonds in a terminal position, linear polymers are being formed under incorporation of the tin atoms in the main chain[6].



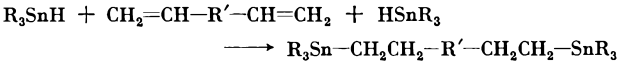
Taking into account the chemical stability of the tin-carbon bond[7], products of this type constitute an interesting novel group of polymers.

Optimal conditions for polymer formation have been determined for each combination of R and R', by studying both the model reactions, viz. between dihydride and monoolefine and between monohydride and diolefine.



[6] J.G. NOLTES and G.J.M. VAN DER KERK, *Rec. Trav. Chim. Pays-Bas 80* (1961) 623. See also: N.A. ADROVA *et al.*, *Vysokomol. Soed. 3* (1961) 1041. H. NIEBERGALL, Germ. Pat. 1,086,896 and 1,087,810, *Chem. Abstr. 55* (1961) 15998 g, 16016 g.

[7] See e.g.: J.G.A. LUIJTEN and G.J.M. VAN DER KERK, *Organotin Chemistry*, T.R.I., Greenford 1955.



It proved necessary:

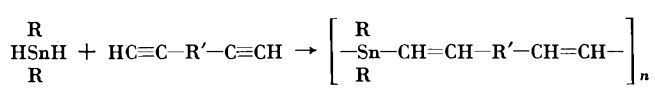
a) to perform the reaction under cover of nitrogen, in order to eliminate oxidative degradation of the organotin hydride;

b) to apply a solvent in the first step of the reaction in order to warrant its smooth course, in particular, to eliminate the occurrence of a disproportionation reaction of the dihydride which would lead to mono- and trifunctional hydrides. Ultimately, after evaporation of the solvent, the reaction mass has to be heated *in vacuo*.

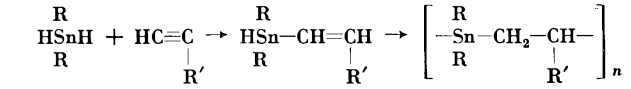
The progress of the reaction can be determined very easily by I.R. absorption measurements. The disappearance of the very characteristic absorption peak in the 1800–1840 cm^{-1} region (5.5 μ)[8], originating from a stretching vibration of the Sn-H bond, together, of course, with the disappearance of vinyl absorption bands, is the most clear-cut indication that the reaction has gone to completion.

Starting from acetylenic compounds as the unsaturated reaction partner, and making use of the earlier mentioned marked difference in reactivity of the organotin hydride toward double or triple bonds, two principally different routes can be followed for polymer formation[9]:

a) Reaction of a diynic compound, having both the triple bonds in a terminal position, with an organotin dihydride in a 1:1 ratio under very mild conditions. In this case the reaction ends after conversion of the triple bonds into double bonds.



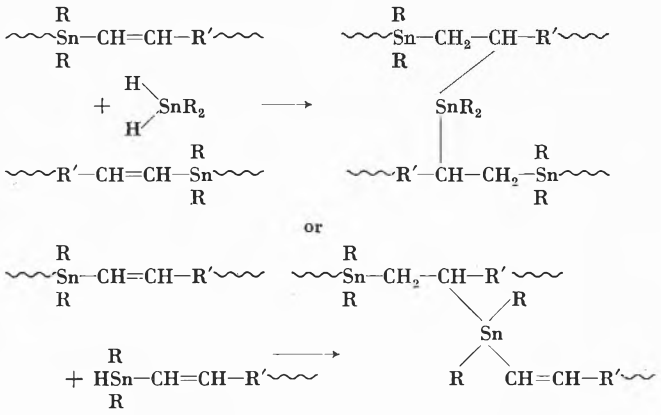
b) Reaction of a monoacetylenic compound again in an exactly 1:1 ratio with an organotin dihydride. Here *two* reaction steps can be distinguished, viz. addition of the dihydride to the triple bond under formation of an olefinic organotin monohydride, the monomer for the second step, and, subsequently, at higher temperature, homoaddition of this monomer.



Of course, in the first case some danger of crosslinking or branching exists, if, by some reason or other, the two reaction stages overlap.

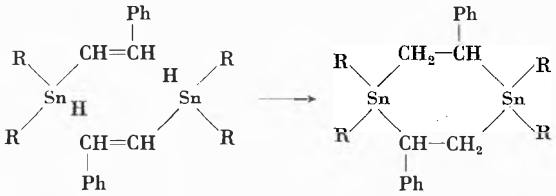
[8] D.R. LIDE, *J. Chem. Physics 19* (1951) 1605. R. MATHIS-NOËL *et. al.*, *C. R. Acad. Sci. 243* (1956) 215. See also: M.C. HENRY and J.G. NOLTES, *J. Amer. Chem. Soc. 82* (1960) 555.

[9] J.G. NOLTES and G.J.M. VAN DER KERK, *Rec. Trav. Chim. Pays-Bas*, in press.



In the second case just mentioned, a side reaction manifests itself, viz. formation of cyclic oligomers.

This is a not uncommon feature in polymer-forming reactions, and, therefore, receives more and more attention nowadays. Two molecules of the 1:1 addition-intermediate might form a six-membered cyclic dimer with the two tin atoms in 1,4-position. This course was observed upon reaction of e.g. diphenyltin dihydride with phenylacetylene[9]. As appears from an absorption peak at 988 cm^{-1} originating from the C–H bonding vibration of *trans*-disubstituted ethylene groups, the intermediate has the *trans* structure, its formation presumably being promoted by steric factors. The *trans* structure, in its turn, favours the formation of the distannacyclohexane system.

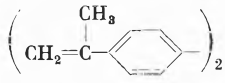


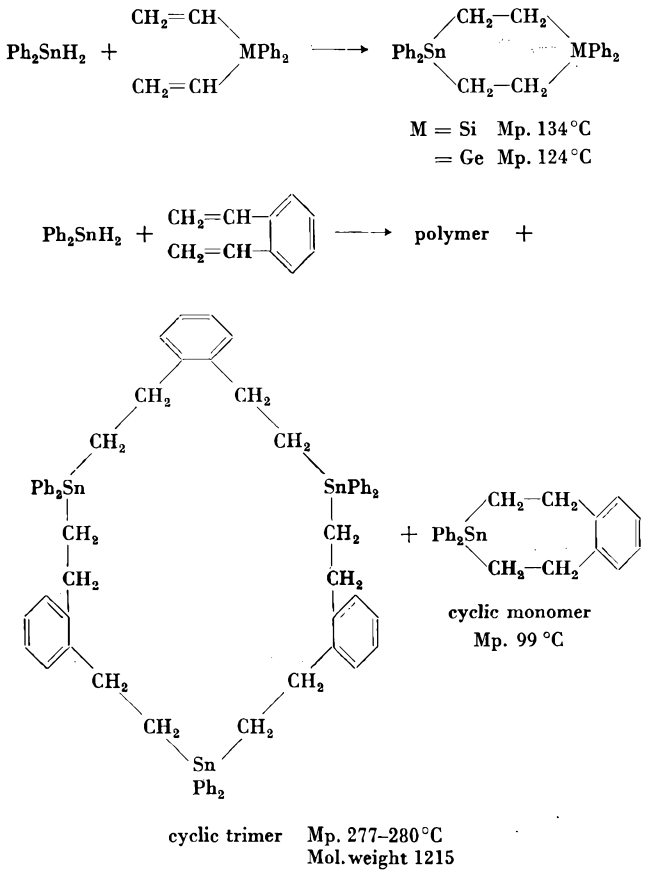
R = Pr (not isolated)
= Ph Mp. 72 and 144 °C (*cis* and *trans* isomers)

Ring formation has not only been observed in this case. Reaction of an organotin dihydride with dienic or diynic compounds having the two unsaturated groups in a sterically favourable position also leads, partly or mainly, to cyclic compounds rather than to linear polymers only. This occurs when using divinylorganometallic derivatives[10] or upon reaction with *o*-divinylbenzene[11]. The reaction of the last mentioned compound even lead to the cyclic trimer.

[10] M. C. Henry and J. G. Noltes *J. Amer. Chem. Soc. 82* (1960) 561.
[11] J. G. Noltes, unpublished results.

Table 1: Reactions of organotin dihydrides and dienic compounds

R $HSnH$ R R=	Dienic compound	Initial product	Appearance of polymer	Soluble in	Polymer-melt temperatures °C	$\bar{M}_w$
Pr		only 1 : 1 adduct				
Ph	*id.*	*id.*				
Pr	$(CH_2{=}CHCOOCH_2{-})_2$	polymer	tough			
Ph	$(CH_2{=}C(CH_3)COOCH_2{-})_2$	*id.*	very tough			
Ph	$(CH_2{=}C(CH_3)CO)_2O$	*id.*	hard, brittle			
Ph	$(CH_2{=}CH{-}CH_2OOCCH_2)_2O$	*id.*	viscous oil			
Ph	$CH_2{=}C(CH_3)COOCH_2CH{=}CH_2$	*id.*	soft			
Pr		*id.*	soft, tacky viscous flow			
Ph	*id.*	*id.*	glasslike	C_6H_6	70	110,000
Bu		*id.*	very viscous			
Ph		*id.*	glasslike	C_6H_6; $CHCl_3$	90	19,000



The basic reaction underlying the polymer-forming interactions just discussed, is an example of a true polyaddition reaction. Modern anglosaxon nomenclature here prefers the term hydrogen transfer polymerization. The close resemblance to the formation of polyurethane from diols and diisocyanates is evident. In our case an active hydrogen atom bound to tin reacts with a carbon-carbon double or triple bond; in the other process an active hydrogen of a hydroxyl group reacts with a carbon-nitrogen double bond of an isocyanate.

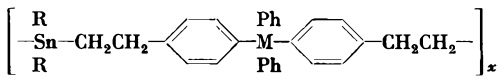
A survey of the various combinations of reaction partners investigated and the results obtained is given in table 1 to 4. It is indicated, whether polymer formation has been observed or mainly formation of oligomers. Details about the polymers are given as well; viz. appearance, solubility, softening point, and average molecular weight determined according to the Archibald method[12].

In general polymer-melt temperatures are quite low. This ist not surprising after all: interchain forces will be rather weak, because of lack of hydrogen-bonding. Moreover, the relatively large metal atoms and their sometimes bulky substituents (e.g. phenyl groups) will hamper both Van der Waals interaction between the chains and crystallization.

As to the formation of obviously crosslinked material, as has been observed in a few cases when using dienic compounds, one has to keep in mind that terminal Sn–H groups might undergo a reductive coupling reaction with chain Sn–R groups under the reaction conditions during the last stage of polymer formation. This would give rise to Sn–Sn branchings. Also exchange reactions of the Sn–H group might occur, leading in a secondary reaction to branchings or crosslinks.

[12] W. J. Archibald, *J. Physic. Chem. 51* (1947) 1204.

Table 2: Polymers from reactions of organotin dihydrides and organometallic dienic compounds



R =	M =	Appearance of polymer	Polymer-melt temperatures °C	Soluble in	$\bar{M}_w$
Pr	Sn	tough $\xrightarrow{130°}$ rubbery		slightly crosslinked	
Bu	Sn	hard, slightly tough	~ 200	*id.*	
Pr	Ge	tough $\xrightarrow{100°}$ rubbery	240	C_6H_6	
Pr	Pb	tough $\xrightarrow{90°}$ rubbery		slightly crosslinked	
Pr; Ph(1:1)*	Ge	hard $\xrightarrow{120°}$ rubbery	250	C_6H_6	
Pr; Ph(1:1)*	Sn	hard $\xrightarrow{90°}$ rubbery	130	*id.*	
Ph	Ge	hard and brittle	110	C_6H_6; $CHCl_3$	27,000
Ph	Sn	*id.*	100	*id.*	48,000
Ph	Pb	*id.*	70	*id.*	14,000

* An equimolecular mixture of Pr_2SnH_2 and Ph_2SnH_2 was used.

Table 3: Polymers from reactions of organotin dihydrides with phenylacetylene

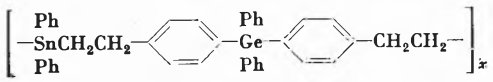
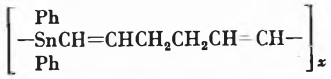
R =	Initial product	Appearance of polymer	Soluble in	Polymer-melt temperatures °C	$\overline{M}_w$
Pr	pol. + cycl. dimer	very viscous oil	benzene		3400
Bu	*id.*	*id.*	*id.*		
Ph	*id.*	hard, brittle	*id.*	80	

Table 4: Polymers from reactions of organotin dihydrides with diynic compounds

R =	R′ =	Initial product	Appearance of polymer	Soluble in	$\overline{M}_w$
Me	$-(CH_2)_2-$	pol. + cycl. monomer	soft, slightly rubbery	slightly crosslinked	
Et	*id.*	*id.*	rubberlike	*id.*	
Pr	*id.*	*id.*	soft, slightly elastic, showing some flow		50,000
Bu	*id.*	*id.*	soft, slightly viscous		50,000
Ph	*id.*	*id.*	rubberlike, slowly but completely resilient		75,000
Bu	$-(CH_2)_5-$	pol.	very viscous oil	C_6H_6; $CHCl_3$	45,000
Ph	*id.*	*id.*	soft, showing some flow	*id.*	100,000
Ph		*id.*	solid $\xrightarrow{160\,°}$ rubbery	C_6H_6	65,000

Table 5: Thermogravimetric analysis of some IVth Group metal polymers

Rate of heating: 2.5 °C per minute
For explanation of symbols see text

Polymer	$T_{5\%}$ °C	$T_{50\%}$ °C	RW_∞ %	% of inorganic elements
	300	385	28	29.3
	325	460	30	27.1
	280	355	27	33.6

The more interesting representatives, e.g. the polymer from diphenyltin dihydride and hexadiyne-1,5 (table 4), will be investigated further, in particular as to their mechanical properties.

An interesting feature of new polymers, receiving much attention nowadays, is their thermal behaviour. This holds particularly for mixed inorganic-organic polymers. A few of the samples obtained in these investigations, therefore, have been subjected to a thermogravimetric analysis. In such an experiment a sample is heated in a Chevenard thermobalance under nitrogen at a heating rate of 2.5 °C per min. Usually, temperatures are indicated, at which 5 and 50% weight-loss respectively have occured ($T_{5\,\%}$ and $T_{50\,\%}$). Also a comparison of the asymptotic value of the residual weight (RW_∞) and the percentage of "inorganic" elements of the original polymer is of interest, because it indicates, whether nearly complete degradation to the inorganic elements has occurred. These data are given in table 5.

A few remarks have to be made about the synthesis of the organotin dihydrides. The dihydrides can best be prepared from the corresponding organotin dihalides, which are easily accessible, by reduction with lithium-aluminium hydride in ether[13]. Recently, also the preparation by means of dialkylaluminium hydrides at temperatures below 0° has been recommended[14].

The aliphatic dihydrides can be purified easily by distillation; diphenyltin dihydride is a somewhat more labile compound, but, if not too impure, can be distilled also. The dihydrides have to be stored under nitrogen in the dark at low temperature. Disproportionation, followed by degradation, is the main cause for deterioration.

$$2\ R_2SnH_2 \longrightarrow R_4Sn + [SnH_4] \longrightarrow Sn + 2\,H_2$$

$$R_2SnH_2 \xrightarrow[H_2O]{O_2\ or} R_2SnO$$

In addition, the hydrides are very liable to oxidation and hydrolysis.

Acknowledgment

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[13] A.E. Finholt *et al.*, *J. Amer. Chem. Soc. 69* (1947) 2692.

[14] W.P. Neumann, *Angew. Chem. 73* (1961) 542. Brevet Franç. 1,246,364 (1961 to Kali Chemie).