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As technological developments have continually placed more and more stringent requirements upon materials, chemists increasingly have had to diversify their interests and talents in order to find new types of chemical structures. Present day considerations revolve around materials with multifunctionality, such as fire retardance, radiation resistance, high or low temperature utility or toxicological properties to only mention a few. Organometallic polymers contain inherently, properties different from the usual carbon compounds and definitely offer the possibility of fulfilling at least some of the requirements needed for polyfunctionally useful materials.

The field of organometallic polymers in general, should arouse the curiosity of a variety of disciplines. To the synthetic chemist, organometallic polymers are a challenge because of the unique reactions involved in organometallic chemistry. To the polymer chemist the introduction of heteroatoms is one more parameter for consideration. To the applied and developmental research chemists, organometallic polymers are potentially useful materials with, as yet, undefined combinations of properties.

The interest, for the purposes of the subject under consideration, will treat polymers containing the Group IVB elements, germanium, tin and lead. Polymers containing silicon obviously must, these days, be treated as a separate subject and indeed, as a result of the unique properties of the silicones consistently receives its share of attention. The three lesser known members of Group IVB, by comparison, are usually only mentioned in passing or are completely ignored.

As a further restriction, the work presented here will limit itself to polymers that have been prepared from well characterized monomers. This means that polymers resulting from hydrolytic reactions or oxidative side reactions will not be considered.

The emphasis here is to consider recent progress in the synthesis of organometallic polymers of germanium, tin and lead and to discuss the properties that have been observed and by so doing to discuss the possibilities for future investigations in this interesting area of chemistry. It is obvious that the chemistry here is basically organic since the polymeric structures being considered are the result of taking advantage of the ability of carbon to build macromolecular structures through carbon chains more or less irrespective of the effect of the metalloid elements.

The initial problem in the preparation of polymers containing germanium, tin and lead was to synthesize compounds containing functional groups capable of participating in polymerization type reactions. As will be shown, many organometallic compounds containing the necessary reactive groups have been prepared in recent years. The second step in the evolution of preparing useful polymers was the study of polymerization systems that would allow satisfactory polymers to be produced. These studies also, most recently, have shown many interesting results. The third step, namely, the systematic characterization of these new organometallic polymers has not been developed to any satisfactory extent. Measurements have normally been limited to molecular weight determinations. Other physical properties have been by and large ignored even though it will be these physical measurements that ultimately determine the usefulness of organometallic polymers of the type being considered.

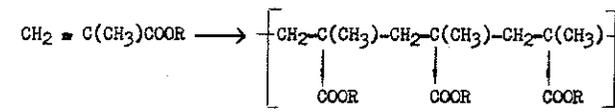
Basically these organometallic polymers can be considered to be of two types, either the heteroelement or metalloid atom can be located in the backbone of the polymer chain or located in a group pendant to a carbon backbone chain. The methods available for synthesizing the required organometallic monomers have traditionally centered around Grignard, acid-base or alkali metal reactions. Polymerizations have usually followed conventional type routes.

GROUP IVB POLYMERS WITH PENDANT HETEROELEMENT GROUP

For the present purposes it is not practical to consider structures containing metalloid-hydrogen bonds nor to consider in any great detail repeating units of metalloid atoms bonded one to the other. These structures are of a lower order of stability than can be considered for the purposes of this paper. This limitation makes it difficult to compare organometallic polymers with seemingly analogous conventional carbon polymers and an awareness of this fundamental difference must be made. Thus methyl acrylate, the methylester of acrylic acid, $\text{CH}_2 = \text{CHCOOCH}_3$ might on first consideration seem to be analogous to trimethylgermyl acrylate, $\text{CH}_2 = \text{CHCOOGe}(\text{CH}_3)_3$. The only safe analogy is to consider these molecules to be of the type RCOOR' where $\text{R} = \text{olefin}$ and R' a group IVB element containing group. These types of molecules have perhaps received the most attention and will be the first type of organometallic Group IVB polymers to be considered.

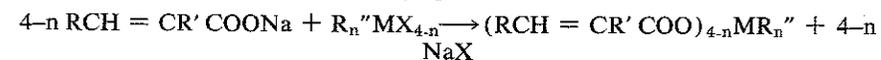
Polyester-Group IVB Macromolecules

The commercially available polyacrylates and polymethacrylates are polymers derived from α - β unsaturated esters. The resulting polymers are linear polymers with pendant ester groups as illustrated below:



A number of organometallic polyesters of this basic type have been prepared where the R group contains the heteroelements under consideration.

Monomer synthesis. Two satisfactory general methods may be employed for the synthesis of organometallic monomers of the type $-\text{C} = \text{C} - \text{COOMR}_3$. The first method^{1,2} is the reaction of an α - β unsaturated acid salt with the IVth Group halides in general, but germanium and tin in particular. The nature of this reaction is illustrated by the following equation:



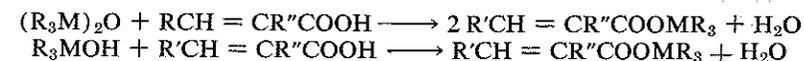
where: $n = 0-3$

$\text{M} = \text{germanium, tin}$

$\text{R}, \text{R}' = \text{hydrogen, alkyl, aryl, alicyclic, aralkyl}$

$\text{R}'' = \text{alkyl, aryl, alicyclic, aralkyl}$

The second method is based upon the reaction of IVth Group organometallic oxides or hydroxides with olefin containing organic acids. This reaction has been utilized only for tin and lead and has been particularly successful because of both the ready availability and higher reactivity of the oxides or corresponding hydroxides of these two elements.³⁻¹²



where: M = tin, lead

R'R'' = hydrogen, alkyl, aryl, alicyclic, aralkyl

R = alkyl, aryl, alicyclic, aralkyl

Disubstituted metal oxides, in comparison, react with olefin containing acids to form the corresponding diesters⁶ as follows:

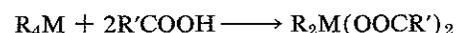


where: M = tin, lead

R = alkyl, aryl, alkaryl

R' = olefinic radical (CH₂ = CH-) etc.

Organic compounds of the IVth Group, tetrasubstituted with aryl groups, alkoxy or aryloxy groups,¹³ also react with olefinic acids, usually to form the corresponding diester by acid cleavage of the substituent groups as follows:

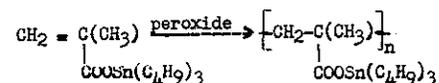


where: M = tin, lead

R = phenyl, aryloxy or alkoxy

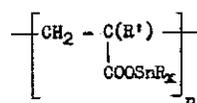
R' = olefinic radical (CH₂ = CH-) etc.

Polymerizations. Polymerizations of organometallic esters containing olefinic linkages may be carried out using heat, free radical catalysts or with persulfate-mercaptan initiators, in bulk or by water emulsion techniques. This general polymerization may be illustrated for the case of tributyltin methacrylate.



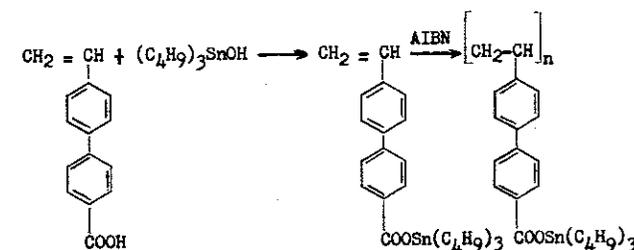
Polytrimethyltin methacrylate and polytriethyltin methacrylate are solid glasses whereas polybutyltin methacrylate is a clear elastic gel. It is interesting to note that, in a comparison study, triphenyltin methacrylate polymerizes faster than triphenyllead methacrylate which in turn polymerizes more rapidly than methylmethacrylate.¹⁴

Polyorganotin acrylates and methacrylates having the structure,

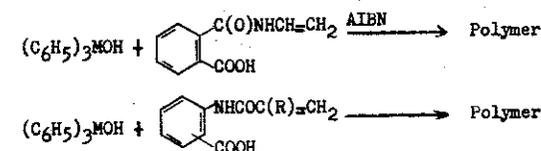


where R = a monovalent hydrocarbon radical, and R' = hydrogen or a monovalent carbon radical have been prepared from their respective monomers and polymerized using peroxide bulk polymerizations and emulsification polymerizations using potassium persulfate and laurylmercaptan as initiators.^{11,15,16} When x = 3, chain type elastomers are obtained, where x = 2, nonelastomeric cross-linked plastics result. Molecular weights are in the neighborhood of 162,000. These polymers may be useful as films, foils, coatings and impregnating agents. Russian¹⁷ and Australian workers¹⁸ have prepared similar types of polymers. In addition to organotin polyesters, organogermanium and organolead polymethacrylates and polyacrylates have been prepared.^{1,19,22} The lead polymers have been suggested as being useful as shielding elements.

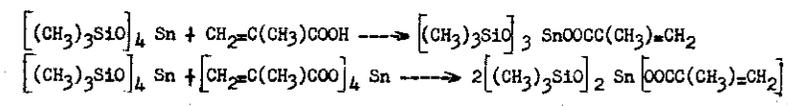
Adrova³ has prepared polytributyltin-4'-vinyl-4 biphenylcarboxylate and reported it to be a colorless polymer, soluble in toluene and stable to 165°C.



A final example of the polyester type polymer is illustrated by the synthesis of polymerizable organolead and tin derivatives of the N-vinylamide of phthalic acid and N-(p,o-carboxyphenyl) acrylyl-(methacrylyl) amides to give slightly colored infusible powders insoluble in organic solvents.⁴



Tris-(trialkylsiloxy) tin methacrylate and bis-(trialkylsiloxy) tin dimethacrylate monomers have been prepared by reacting tetrakis-trimethylsilyoxytin with methacrylic acid or tin tetramethacrylate as follows:²³

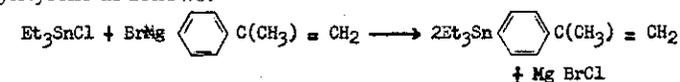


A curious induction period was noted in the peroxide polymerization of these monomers. In petroleum ether, at 65°C., a 2-12 hour induction period was reported. The polymerization, at the end of the induction period, set in rapidly and the products dropped out of solution in a matter of a few minutes. Strain-temperature studies in the range of 50-500°C. did not show any flow properties and the polymers were probably highly crosslinked.

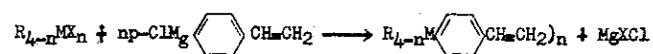
Organometallic Styrene Derivatives

A second type of organometallic polymers, in which the metal atoms are pendant to the main chain, are the substituted styrene type. These polymers have a linear structure analogous to polystyrene.

Monomer synthesis. The first organometallic derivative of styrene was prepared in 1951 by Bachman²⁴ who prepared p-triethyltin α-methyl styrene, Et₃SnC₆H₄C(CH₃) = CH₂. This monomer was prepared by Korshak^{25,26} by the reaction of triethyllead chloride and the Grignard reagent derived from p-bromo-α-methylstyrene as follows:



A variety of workers^{27,30} have prepared p-styrenyl and α -methyl-p-styrenyl-substituted derivatives of germanium, tin and lead using the appropriate organometallic halide and Grignard reagent as follows:



where: $n = 1, 2$ or 4
 $R =$ alkyl, aryl

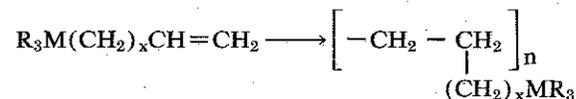
Polymer synthesis. Polymerizations of metallostyrenes may be accomplished using ultraviolet light or 2,2'-azo-bis-isobutyronitrile. In the case of p-trimethyl- and p-triethyl tin styrenes, polymerizations have been carried out at a temperature of 80° at pressures of 1-6000 atmosphere and for a period of 6-10 hours.^{31,32} Other monomer systems that have been polymerized include p-tricyclohexyltin-styrene and 4-triphenyltin-4' vinyl biphenyl.³³

Organometallic styrene derivatives of the homologous series $p-(CH_3)_3M^{IV}C_6H_4CH=CH_2$ display surprising differences in rate of polymerizations, in the order $Pb > Si > C > Ge > Sn$. It would appear that in the case of lead some homolytic cleavage of the lead-carbon bond occurred and a crosslinked polymer resulted. The polymers containing silicon, germanium and tin have softening points in the range of $170-180^\circ$. Films could be prepared from these polymers, the brittleness of which decreased in the order $Sn > Ge > Si$.

Organometallic Vinyl Monomers and Polymers

Allyl derivatives of tin and lead and vinyl derivatives of tin do not polymerize under conditions of radical polymerization and indeed actually inhibit the polymerization of styrene, methylmethacrylate and other vinyl monomers. This inhibitory effect increases with the number of vinyl and allyl groups in the organometallic compound. The relative inhibitory effects are as follows: tetraallyltin > tetraallylgermanium > diallyldiphenyltin > allyltriphenyltin > vinyltriphenyltin > vinyltrimethyltin.^{34,38}

Ziegler type catalysts of the vinyl type, i.e., obtained from compounds of the transition elements of groups IV-VI with organometallic compounds of group I-III, are able to catalyze the polymerization of IVB organometallic vinyl derivatives and, in general, monomers of the type $R_3M(CH_2)_xCH=CH_2$ as follows:



where $M = Si, Ge, Sn$ and Pb
 $x = 0-4$
 $R =$ hydrogen, alkyl, cyclohexyl

These polymers are highly crystalline, stereospecific and have isotactic structures.³⁹

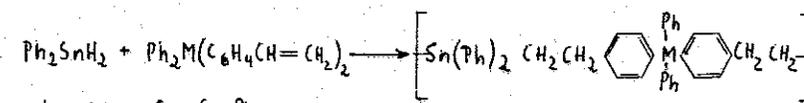
POLYMERS WITH IVTH GROUP ELEMENTS IN THE CHAIN

From the purists point of view this class of polymers contains perhaps the best examples of true organometallic polymers. This type of linear polymer contains a carbon-carbon backbone regularly interspersed with IVth main group metal atoms. This type of polymer has been prepared most successfully by the organometallic hydride addition reaction to olefinic double or triple bonds.

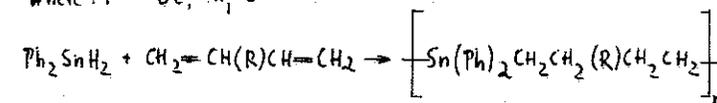
Organometallic Hydride Reactions

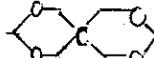
Although the IVth Group organometallic hydride addition reaction with olefinic bonds has been shown to occur under suitable conditions for silicon, germanium, tin and lead, the only element (other than silicon) to have been used for these types of polyadditions has been the organotin dihydrides. Organolead dihydrides are thermally too unstable for extensive use of this reaction. Organogermanium dihydrides, which are surprisingly stable, have not been reported to undergo poly-addition reactions. Organotin dihydrides are more reactive and lend themselves to a study of poly-additions much more readily than do the organogermanes.

Noltes and Van der Kerk^{40,42} have synthesized heteropolymers containing germanium, tin, and lead in the main polymer chain as follows:



where $M = Ge, Sn, Pb$



where $R =$ , $-(CH_2)_2$, $-(CH_2)_5$, 

The products obtained in these cases were glasses, soluble in organic solvents. The polymers had poor mechanical properties, i.e., the films and fibers formed were brittle. A variety of types of polymers were obtained using these polyaddition reactions. The final products range from viscous liquids to elastomeric materials to hard glasses.

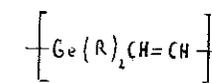
Similar type poly-additions have been carried out by the same workers⁴² using diacetylenic compounds as follows:



where $R =$ $-(CH_2)_2$, $-(CH_2)_5$, 

The products obtained ranged from viscous liquids to elastomers with reported molecular weights of up to 100,000.

In attempting to form germiranes, Volpin⁴³ noted considerable polymer formation during the reaction of germanium iodide with acetylene. Molecular weight determinations of these polymers gave values of 33,000. This unique polymer may have the structure represented below:



where: $R = CH_3, -C_6H_5$

Leavitt⁴⁴ and Adrova⁴⁵ have also reported studies involving organotin di-

hydrides with acetylenic compounds, however, only low molecular weight polymers were obtained which in the presence of air decomposed to organotin oxides.

Dibutyltin dihydride and diphenyltin dihydride have also been reported to form polymers by a polyaddition reaction to ethyleneglycol and hydroquinone dimethacrylates which have repeating acryl organic residue units.⁴⁶ Reported molecular weights range from 1300–5800 (3–13 repeating units).

The reaction of dicarboxylic acids with IVth group organometallic dihalides oxides or diacid salts as illustrated for the case of tin presents a method for preparing linear polyester type polymers as follows:⁴⁷

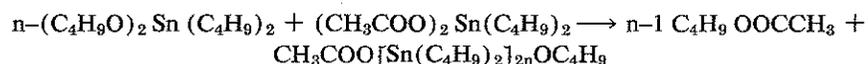


where X = O, Cl, CH₃COO— and R = alkyl, aryl

Lower alkyl substituted tin compounds yield polymers that are readily soluble with decreasing solubility as higher alkyl substituents are used. Aromatic substituents yield polymers that are practically insoluble. The incorporation of methoxy or hydroxy groups in the alpha position to the carboxy groups considerably lowers the solubility of the polymers in organic solvents.

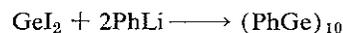
Herterofunctional Polycondensation

The co-condensation of dibutyltin dibutoxide and dibutyltin diacetate has been reported by Zhubukhin⁴⁸ to yield low molecular weight polymers containing a linear chain of tin atoms.



The melt reaction was carried under vacuum conditions for a period of 16–18 hours and the product, mol. wt. 4200, had a melting point of 96–100°C. and was soluble in benzene. The melt could be drawn into fibers and showed good glass adhesive properties.

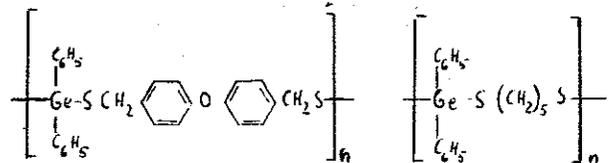
Organogermanium polymers containing ten germanium atoms in a row have been reported recently⁴⁹ from the reaction of germanium di-iodide and phenyllithium as follows:



The product was a red brown amorphous polymer which inflamed in the presence of nitric acid.

Polymers of this general type do not appear to be sufficiently stable to be considered as potentially useful.

The reaction of oxidibenzylmercaptan and 1,5 pentanedithiol with diphenylgermanium halides form the following type polymers.⁵⁰

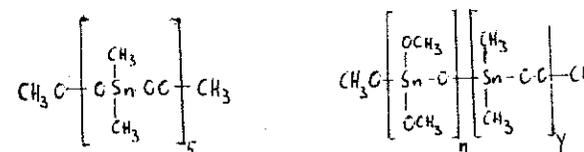


Colorless plastic soluble in benzene, toluene and chloroform

Colorless viscous liquid slightly soluble in benzene, toluene and chloroform

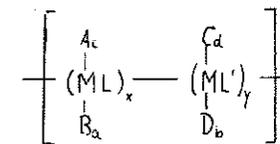
Lower molecular weight dithiols result in ring formation.

Polymeric dimethyltin peroxide may be prepared from the reaction of dimethyltin dichloride with hydrogen peroxide.⁵¹ Two polymeric species have been identified thus far as follows:



Organometallic Polymers Containing Mixed Group IVB Elements in the Polymer Chain

Organometallic polymers of the general type, have been prepared and described in an Ethyl Corporation patent⁵² and by Russian workers.⁵³



M and M' are dissimilar metals of Groups III, IV, V, VI, and VII. One of which can form a polyhydroxide which releases a proton in the presence of strong base. L and L' represent oxygen, sulfur, carbon or = NR. Products range from oils to intractable solids and have, reportedly, good thermal stability, good dielectric properties, inert and may have uses in hydraulic fluids having low volatility and wide liquid temperature range.

ORGANOMETALLIC COPOLYMERS

Thus far only polymers types have been considered which have been derived from a single monomer or homopolymer. A second type of polymer, the copolymer, has also been receiving increasing attention in recent years.

Copolymers are polymers derived from two different monomers, polymerized to form repeating units in the polymer chain consistent with the two reacting monomers. Terpolymers, although not studied in the organometallic series, are polymers made up of three different monomers copolymerized together. As polymer chemistry becomes more advanced, organometallic terpolymer systems will undoubtedly be forthcoming.

Organometallic Esters

A variety of types of copolymers have been prepared, however the majority of the work has been concentrated on the copolymerization of α , β -unsaturated organometallic acid esters, $RCH=CHR'COO_nMR_{4-n}$, with activated vinyl or vinylidene group containing monomers. Thus, vinyl ethers, vinyl ketones, vinyl esters, styrenes, acrylates, methacrylates, acrylonitrile and even cyclopentadiene have been copolymerized using standard techniques and catalysts.^{1,5,12,15,16,23,54,58}

The potential uses of these copolymers have only been suggested for one or two cases. The copolymer of vinyl chloride and tributyltin methacrylate has been reported to have good heat and light resistance and thus can be used in tubing applications.⁵⁷ The basic properties of the copolymers are widely different from the analogous homopolymer, however, only little work has been done as regards

physical measurements of these copolymers. In recent years more interest has been shown in the physical properties other than melting points and molecular weights. Triethyltin methacrylate-methylmethacrylate copolymer has been studied by Shostakovskii¹² and the properties of this copolymer are listed in TABLE 1.

TABLE 1
Triethyltin Methacrylate-Methyl Methacrylate Copolymer

Impact Strength (Dinstat Method)	8.33 kg/cm ²
Hardness Test (Brinell)—25 kg load	26.5 kg/mm ²
Specific Surface Resistance	1.4×10^{-15} ohms
Specific Volume Resistance	3.0×10^{-15} ohm-cm
Av. Disruptive Voltage	13.5 kv/mm
Dielectric loss—tan δ at 10 ⁶ hertz	0.027 ^a
at 50 hertz	0.037 ^a
Dielectric penetrability at 10 ⁶ hertz	4.3
at 50 hertz	5.0
Hydrolytically stable	13 mo.

Diphenyllead dimethacrylate and methacrylic acid were copolymerized by Kochkin^{5,16} using peroxide catalysts or AIBN catalyst to yield a copolymer described as being a mechanical strong, slightly turbid solid decomposing at 180°C. This copolymer had a specific impact strength of 18–19 kg/cm.² and was deformed appreciably at 180–190° and was reported to be effective at stopping X-rays.

Copolymerization of α - β olefinically unsaturated carboxylic monomers or anhydrides with 0.0005–6.0 per cent of an organometallic monomer, R_nMY_{4-n} where M = Si, Ge, Sn, Pb; R = hydrocarbon and Y = terminally substituted olefin, yields copolymers with excellent thixotropic properties able to thicken water in conc. of 0.25 per cent in the presence of large amounts of dissolved ionic salts and maintain constant viscosity over long periods of time. These products were described by Jones⁵⁴ to be greatly superior to naturally occurring water swellable gums such as gum tragacanth which are normally used as thickening or suspending agents. These properties make these copolymers potentially useful for pastes, polishes, cleaning agents, dentifrices, jellies, creams or ointments.

Other copolymerizations have been carried out in the hydrocarbon series between p-triethyltin α -methylstyrene and butadiene^{24,49,59} to yield a crumbly rubber and between triethyl vinyllead and styrene to yield a product useful for radiation shielding.

CONCLUSION

The variety of types of organometallic polymers of germanium, tin and lead, without even considering silicon, has indicated that considerable synthetic effort has now opened up the field of organometallic polymers as a potentially useful field of endeavor. The question that now arises is to what next must be investigated.

It is apparent that more emphasis should be placed upon the characterization of the polymers themselves. Too often, once the polymer has been formed, physical characterization has been neglected.

Secondly, the reactivity of the metal-carbon bond has not been fully utilized in these polymeric systems. As an example of this cleavage of metal-carbon bonds could be utilized as crosslinking sites in a manner not possible with carbon type

polymers. Another possibility that arises is in utilizing the coordinating ability of especially tin and lead either for mixed covalent-coordination polymers or as crosslinking sites.

These are only a few of the possibilities which have yet to be investigated, others will become apparent as time goes on.

In conclusion then, it should be obvious that the possibilities for developing useful organometallic polymers are as yet virtually unexplored, however, the future looks bright based upon the limited work done in this field. It should be mentioned that several excellent current reviews are available for initial perusal which cover the major portion of Group IVB chemistry in general.⁶⁰⁻⁷⁰

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