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Synthesis and Polymerization of Metal-Containing Monomers

Anatoly D. Pomogailo,
Vladimir S. Savost'yanov

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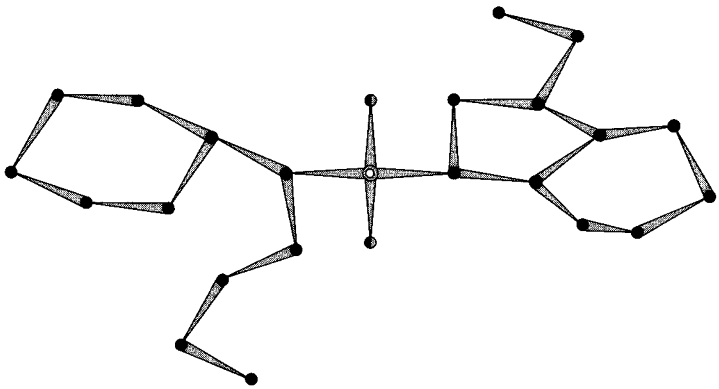

Anatoly D. Pomogailo, D.Sc.
Institute of Chemical Physics
Russian Academy of Sciences
Chernogolovka, Russia

Vladimir S. Savost'yanov, Ph.D.
Institute for Energy Problems of Chemical Physics
Russian Academy of Sciences
Chernogolovka, Russia

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PREFACE

This monograph is devoted to a relatively new branch of chemistry that has emerged in the last two or three decades at the junction where the organometallic, coordination, and high molecular branches of chemistry intersect. Because of the extensive efforts of researchers from different countries, the syntheses and polymerization conversions of organometallic monomers have been developed to the extent that it has become possible to speak about an entirely new interdisciplinary science. It possesses all of the features typical of an independent branch of chemistry (such as unique objects of studies) that have found wide applications and are distinguished by specific structural properties, powerful methods for polymerization conversions, and studies of such monomers and sensitive techniques to investigate the structure of the appearing products, to name a few. Finally, there exists a vast field where metal-containing polymers are used to advantage due to the multifaceted properties of metals enriched with the polymeric nature of the matrix. Upon polymerization, metal-containing monomers give rise to composite materials having new physicochemical and functional properties, catalytically and biologically active macrocomplexes, etc.

Therefore it is only natural that along with general conferences and symposia dealing with the chemistry of high molecular, coordination, and organoelement compounds, as well as catalysis (where much attention is being paid to metal-containing monomers and polymers), there have been a number of special international gatherings on the problems that form the subject of this book. Also, they have been treated in detail by C.U. Pittman, Jr., C.E. Carraher, Jr., J. Sheats, Z. Wojtczak, C.R. Simíonescu, and other researchers. In Russia the same subject has been extensively studied, primarily by V.V. Korshak and V.A. Kabanov.

For these reasons the authors of this volume consider the generalization of numerous experimental and theoretical works as an urgent and a timely issue. First of all, this is associated with a need for coordinating the efforts of specialists whose interests lie in the various fields of chemistry. Moreover, a well-planned approach to the solution of problems of synthesizing metal-containing monomers and also their polymerization and copolymerization is capable of giving a tool for designing a macromolecule at the stage of creating metal-containing polymer systems and programming the desired properties for them.

Further progress in the area under discussion may well be visualized as lying on a path of developing economically advantageous and ecologically clean processes for producing the most important metal-containing monomers and the associated polymers. Moreover, this field is very promising from the theoretical point of view. As a matter of fact, polymerization conversions of metal-containing monomers provide a unique possibility for inserting practically any metal—in all its valent states, ligand environments, and polyhedron configurations—in the polymer chain. At present, the major theoretical considerations concerning structure of metal-containing monomers, their polymerization, and structure of the products are most often based on the logical analysis of experimental data and general scientific statements. However, there is every reason to believe that in the near future a firm research foundation will be established for this branch of chemistry. This conviction is supported by current developments in the field of metal-containing monomers and associated polymers.

The authors wish to express their gratitude to Mr. A.Z. Aravsky whose creative approach to the translation of this book has made it accessible to the audience. Our thanks are also due to our colleagues from various research establishments, who have made many valuable suggestions and comments to improve the content of the book.

It is our hope that this volume will not be lost among the publications devoted to the development of this interesting and promising domain of science but will attract more attention to its problems.

A.D. Pomogailo
V.S. Savost'yanov

Chernogolovka
August 1993

AUTHORS

Anatolii D. Pomogailo, D.Sc. (Chem.), is Professor of Polymer Chemistry at the Institute of Chemical Physics, Russian Academy of Sciences, in Chernogolovka. Born in 1939 in Kiev Region (Ukraine), he graduated from Odessa State University (Ukraine), Department of Physics and Chemistry of Polymers. He received his Ph.D. in 1970 from the Institute of Chemical Sciences (Kazakh Academy of Sciences). The title of his Ph.D. thesis was "Kinetics and mechanism of catalytic (co)polymerization of ethylene by modified systems on the base of complexes of high valency titanium and vanadium halids". Since 1972, Dr. Pomogailo is working at the Institute of Chemical Physics, Russian Academy of Sciences. He received his Doctorate in Chemistry in 1981 from the Institute of Chemical Physics. The title of his thesis was "Immobilization of Metal Complexes by Macromolecular Supports and Catalytic Properties of Such Systems in Polymerization Reactions". He received the title of Professor in 1991. Since 1982 he has been the head of a group involved with metal-containing polymers that was transformed in the laboratory in 1993.

The scope of his scientific interest includes: immobilized metal complexes, catalysis by macromolecular complexes, (co)polymerization of alfa-olefines, and metal-containing monomers and polymers. Dr. Pomogailo is the author of over 250 articles and about 100 patents. He has also authored four monographs: "Polymer-Immobilized Metal Complex Catalysts", Moscow, Nauka, 1988, 303 pp, in Russian; "Catalysis by Immobilized Complexes", Moscow, Nauka, 1991, 448 pp, in Russian; "Metal-Containing Monomers and their Polymers", Moscow, Khimiya, 1988, 384 pp, in Russian, with V.S. Savost'yanov; and "Macromolecular Metal Chelates", Moscow, Khimiya, 1991, 304 pp, in Russian, with I.E. Uflyand.

Vladimir S. Savost'yanov, Ph.D. (Chem.), is a researcher at the Institute for Energy Problems of Chemical Physics, Russian Academy of Sciences. Born in 1954 in the Moscow Region (Russia) he received his M.D. in 1977 from the Moscow Chemical Technological Institute and a Ph.D. in 1987 from the Institute of Chemical Physics, Russian Academy of Sciences.

Dr. Savost'yanov has been working in the field of metal-containing monomer polymerization. Originally he was interested in the radiation-induced graft polymerization of metal-containing monomers (metal acrylates and metal salts acrylamide complexes) onto polyethylene.

Dr. Savost'yanov's main interest at present is the investigation of frontal and spontaneous polymerization of metal nitrates acrylamide complexes.

LIST OF ABBREVIATIONS

AA	Allylamine
AAAm	*N-tert*-amyl acrylamide
AAc	Acrylic acid
AAl	Allyl alcohol
AAm	Acrylamide
AIBN	Azobisisobutyronitrile
AN	Acrylonitrile
BAAm	*N-tert*-butyl acrylamide
BP	Benzoyl peroxide
BVSO	Butylvinyl sulfoxide
CN	Coordination number
D	Exposure dose
Dipy	Dipyridyl
DMFA	Dimethyl formamide
DMPA	Dimethylolpropionic acid
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
DTA	Differential thermal analysis
DTGA	Differential thermogravimetric analysis
e	Polar factor
E_a	Activation energy
EMP	Ethylene glycol methacrylate-phthalate
ESCA	Electron spectroscopy for chemical analysis
ESR	Electron spin resonance
G_{-M}	Radiation yield
HAAm	N-tert-hexyl acrylamide
HMPA	Hexamethyl phosphoramide
HP	Hydroperoxide
I	Initiator, exposure dose rate
IR	Infrared
K_D	Diffusion coefficient
K_{diss}	Constant of dissociation
k_i	Constant of initiation rate
k_p	Constant of chain propagation rate
k_t	Constant of chain termination rate
L	Ligand
M	Monomer
MA	Methylacrylate
MAA	Methacrylic acid
MAn	Maleic anhydride
MAN	Methacrylonitrile
MCM	Metal-containing monomer
MM	Molecular mass
MMA	Methyl methacrylate
M_n	Number-average molecular mass
M_w	Weight-average molecular mass
MVP	2-Methyl-5-vinylpyridine
4-M-2VP	4-Methyl-2-vinylpyridine
MX_n	Metal compound
NMR	Nuclear magnetic resonance

P_n	Degree of polymerization
PAA	Polyacrylic acid
PAAm	Polyacrylamide
PE	Polyethylene
PETP	Poly(ethylene terephthalate)
Phen	1,10-Phenanthroline
PMAA	Polymethacrylic acid
PMMA	Polymethyl methacrylate
PMR	Proton magnetic resonance
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
Q	Resonance stabilization parameter
r	Relative reactivity parameter
TBTA	Tributyltin acrylate
TBTM	Tributyltin methacrylate
T_d	Destruction temperature
T_f	Flow temperature
T_g	Vitrification temperature
T_m	Melting point
T_v	Vitrification temperature
THF	Tetrahydrofuran
Tpy	2,2, 2´´-Tripyridyl
UV	Ultraviolet
VA	Vinyl acetate
VBI	1-Vinylbenzimidazole
VBT	1-Vinylbenzotriazole
VIA	1-Vinylimidazole
VMIA	1-Vinyl-2-methylimidazole
VP	Vinylpyridine
2-VP	2-Vinylpyridine
4-VP	4-Vinylpyridine
VPr	*N*-Vinylpyrrolidone
w	Polymerization rate
w_{fr}	Front propagation rate
w_i	Initiation rate
w_0	Initial polymerization rate
w_p	Chain propagation rate
ν	Bending mode frequency
η	Inherent viscosity
λ	Wavelength
μ_B	Bohr magneton
μ_{ef}	Effective magnetic moment
δ	Stretching mode frequency

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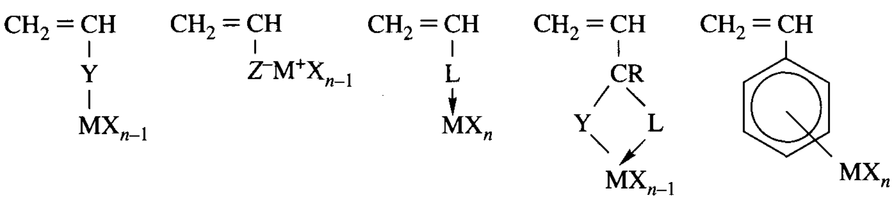
INTRODUCTION

Production of materials that combine the properties of metals and polymers has long been a matter of interest to researchers. There are a large variety of techniques to obtain such combinations, from preparing mixed polymer compositions with fine-powdered metals to the introduction of metal ions into preformed macromolecules using polymer-analogous methods.[1] Polycondensation of organometallic compounds is also used to advantage to obtain such products. As this takes place, the metal ions can be found in both the main and the side chains. Interestingly, all these materials are covered by the same broad term, namely, "metallopolymers".

However, this problem can be treated differently. According to the high molecular compound chemistry, metallopolymers are expected to be preceded by metal-containing monomers (MCMs). They can be regarded as compounds composed of a multiple bond (bonds) with its (their) ability to open and a chemically bonded metal-containing group. It should be noted that in the overwhelming majority of cases multiple MCM bonds are of the vinyl type, although there are rare examples of monomers containing allyl, ethynyl, and vinylethynyl groups.

Until very recently the literature contained no MCM classification of its own: MCMs were treated either as part of conventional monomers—based on the type of the appearing chain, nature of the multiple bond, types of substituents, etc.—or as belonging to organometallic compounds. Due to the fact that MCMs represent a special type of organoelement compounds, it is believed that their classification primarily should include the type of bond between the metal and the organic part of the molecule.[2,3] According to this principle, MCMs can be divided into the following major classes: covalent (I), ionic (II), donor-acceptor (III), chelate (IV), and π (V) types:



(I) (II) (III) (IV) (V)

where *M* is the metal; *n* is its valence; *X*, *Y*, and *Z* are the corresponding functional groups.

Moreover, along with monometallic single-atom complexes, MCMs can include heterometallic and cluster-type compounds for which the chemistry is at the early stage of development.

Covalent-type MCMs are responsible for a relatively small fraction. Primarily this pertains to true organometallic "metal-carbon" bond monomers, and a somewhat larger group incorporates "metal-oxygen" MCMs. Ionic-type monomers belong to the most widely spread group typical of both nontransition and transition metals. Donor-acceptor-type monomers, when the π-electrons of the multiple bond do not take part in complexing reactions, do not essentially differ from conventional (*nV*-type) complexes. They are most characteristic of transition metal halides. Chelate-type monomers represent a combined group of MCMs. They appear as a result of a covalent (ionic)- and *nV*-bonding. It was not until the last decade or so that researchers began studying these MCMs. While the functional groups in heteroatoms of the MCM ligands that give rise to donor-acceptor-type monomers provide lone electron pairs to form coordination bonds, in the event of π-type MCMs a π-electron system is involved in their formation. π-MCMs are characteristic exclusively of transition metals, predominantly of groups VIA, VIIA, and VIII of the Periodic Table.

Among the MCMs mentioned above, the greatest attention has been paid to π-type monomers. The syntheses, structure, polymerization, and copolymerization of these monomers (metallocene, cyclopentadienyl, styrene, and others) have been reviewed in excellent publications by U.S. authors.[4–7] For this reason as well as for consideration of space, this book does not describe these monomers.

The limited volume of this book also has prevented the authors from discussing polymerization conversions of "potential" MCMs with multiple bonds. The authors restrict themselves to MCMs with known polymerization properties. In addition, the same reason is responsible for the fact that the authors do not provide specific techniques suitable for performing polymerization conversions even with respect to the most important representatives of this class of monomers, as has been done in the enlarged Russian edition of the book.[3]

The order of presenting the material follows the above classification with respect to both MCMs and associated polymers. Within each class the material is presented in accordance with the position of a given metal in the Periodic Table.

It was our intent to give a well-balanced account of different viewpoints of the problems under discussion. Nevertheless, it is understood that in some cases the authors give preference to the opinions that reflect their own position as researchers.

Chapter 1

Production and Polymerization Conversions of Covalent-Type MCMs

Covalent-type metal containing monomers (MCMs) can include both true organometallic monomers containing an M—C bond and some of the M—O monomers. Knowledge about this class of compounds is rather limited. However, in the last few years the situation in this field has changed; this fact is corroborated by the appearance of new original works concerning both the synthesis and the polymerization conversions of these MCMs.

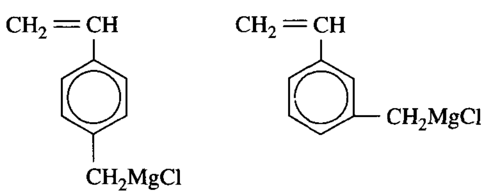
I. SYNTHESIS OF COVALENT-TYPE MCMs

It should be noted that monomers incorporating M—C and M—O bonds differ greatly in a large number of properties and the ways they can be synthesized, specifically the syntheses of true organometallic monomers.

A. SYNTHESIS OF TRUE ORGANOMETALLIC MONOMERS

These MCMs contain vinyl, allyl, styrene, and other groups directly associated with a metal. Extensive studies of their syntheses and properties date back to the development of preparative productions of organomagnesium compounds containing the corresponding radical (primarily a vinyl one, Normant's reagent).[8–10] The most convenient way for producing this reagent is via a reaction of vinyl halide with magnesium tetrahydrofuran (THF). The vinylmagnesium halides resulting from this reaction are interesting not by themselves but rather as intermediates used to synthesize unsaturated derivatives of some other metals.

Unsaturated organomagnesium compounds are rather unstable and sensitive to atmospheric oxygen, moisture, etc. Arylvinyl Mg(II)-containing species are more stable.[11] One of the best studied representatives of these MCMs, *p*- and *m*-vinylbenzenemagnesium halides:



were obtained through the interaction of magnesium with vinylbenzyl chloride in ether.

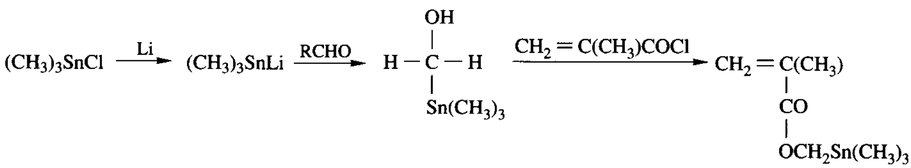
Among vinyl derivatives the greatest recognition for polymerization conversions has been gained, perhaps by metal compounds of Group IV of the Periodic Table. Vinyl compounds of Ge(IV) are synthesized by reacting the Normant reagent with alkyl- and arylgermanium in THF:[10,12]

$$R_{4-n}GeCl_4 + nCH_2 = CHMgX \rightarrow (CH_2 = CH)_n GeR_{4-n} + nMgXCl.$$

Vinyl derivatives of tin are obtained in the same way.[10] This metal is specific in that in this case the synthesis can be conducted, along with halides and with organotin oxides:[13]

$$(C_4H_9)_3SnOSn(C_4H_9)_3 + 2CH_2 = CHMgCl \rightarrow$$
$$\rightarrow 2(C_4H_9)_3SnCH = CH_2 + MgO + MgCl_2 .$$

Halogen-containing vinyl derivatives of tin have been conveniently synthesized via a redistribution reaction involving vinyl compounds of this metal and Sn(IV) tetrachloride.[14] In addition, this gives rise to such individual products as $(CH_2{=}CH)_3SnCl$ and $(CH_2{=}CH)_2SnCl_2$.



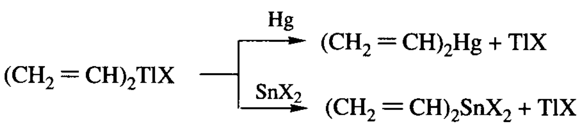
Also, mention should be made of a recently synthesized new group of organotin monomers, namely, 1-(trimethylstannyl) alkyl acrylates:[15]

Vinyl Tl(III) derivatives have been effectively synthesized using the Normant reagent:[16]

$$CH_2 = CH\,MgX + TlX_3 \rightarrow Tl(CH = CH_2)_2\,X$$

where X = Cl or Br.

The resulting products can then be used for producing the corresponding Hg(II) and Sn(IV) derivatives:



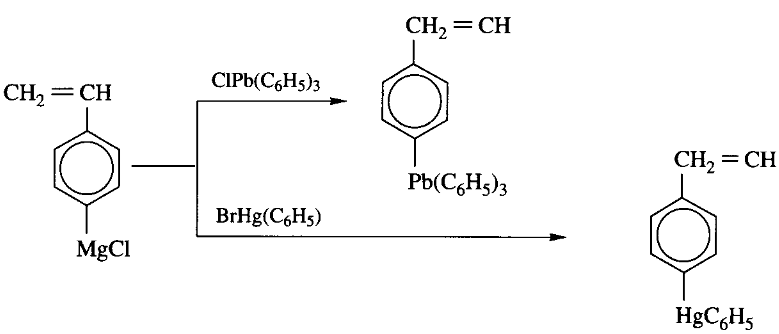
Divinylmercury is in turn a good vinylating agent for the synthesis of the corresponding Al(III) derivatives.[17]

Normant's reagent also can be applied to the synthesis of vinyl Pb(IV) derivatives:[18]

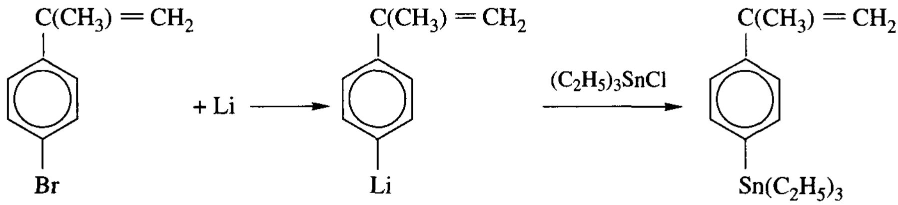
$$4CH_2 = CHMgX + 2PbY_2 \rightarrow Pb(CH = CH_2)_4 + 2Pb + 4MgXY,$$

where X = Cl or Br, and Y = Cl, I, or CH_3COO.

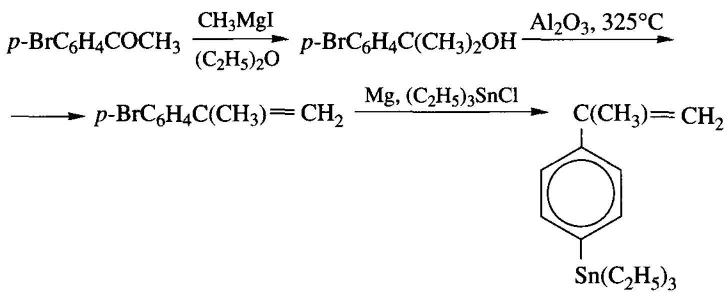
Among covalent-type MCMs there is a very interesting group of organometallic styrene derivatives based on germanium, mercury, tin, and lead. Their synthesis has been well studied elsewhere:[19–21]



α-Methylstyrene derivatives can be produced using both organolithium synthesis:[22]



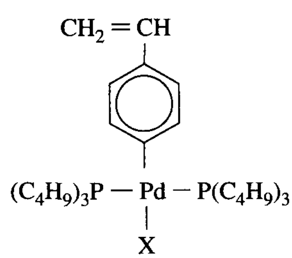
or the Normant reagent:[23]



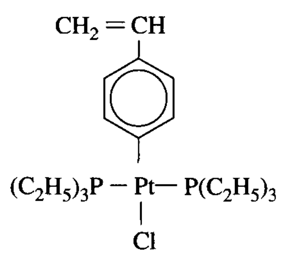
Similar methods are used to prepare styrene derivatives of other metals.

Among transition metal-containing acetylene derivatives that are few in number one can mention only bis(1,3-pentadiinyl)mercury[24] $H_3C—C\equiv C—C\equiv C—Hg—C\equiv C—C\equiv C—CH_3$ since the polymerization properties of other representatives of these compounds have not been studied.

Concerning transition metal-containing organic compounds, the corresponding vinyl derivatives are usually very unstable, which complicates their application to polymerization processes. At the same time, it has been possible to obtain the following stable Pd(II) and Pt(II) compounds:[25]



and



where X = Cl, Br, CN, or C_6H_5.