SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF DIORGANOTIN(IV) COORDINATION POLYMERS DERIVED FROM PHOSPHITE/PHOSPHONATE ESTERS

MEENAL ASIJA

DEPARTMENT OF CHEMISTRY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

MEENAL ASIJA

Department of Chemistry

Submitted

In fulfillment of the requirements of the degree of

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Dedicated to My Family

CERTIFICATE

This is to certify that the thesis entitled "***Synthesis, characterization and reactivity of diorganotin(IV) coordination polymers derived from phosphite/phosphonate esters***" being submitted by **Ms. Meenal Asija** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her.

Meenal Asija has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

Prof. Ravi Shankar

Department of Chemistry,
Indian Institute of Technology Delhi,
New Delhi-110016, India.

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ABSTRACT

The work presented in the thesis is devoted to synthesis, structural aspects and reactivity behaviour of two distinct class of diorganotin(IV) coordination polymers derived from phosphite ester and phosphonate ester based ligands. The content of the thesis is divided into five chapters. The introductory chapter deals with a brief survey of literature highlighting recent advances on metal organic frameworks/ infinite coordination polymers. The experimental details including synthetic procedures and spectroscopic methods for the characterization of new compounds are presented in chapter II. The results and discussion are embodied in chapters III-V.

The synthesis of dialkyltinbis(*O*-alkylphosphite)s, $R_2Sn\{OP(O)(OR^1)H\}_2$ as well as dialkyltinbis(*O*-alkylalkylphosphonates)s, $R_2Sn\{OP(O)(OR^1)R^1\}_2$ [R = Me, Et, *n*-Bu; R^1 = Me, Et] has been achieved by a one-pot reaction between an appropriate diorganotin dichloride and dialkylphosphite, $HP(O)(OR^1)_2$ or dialkylalkylphosphonate, $R^1P(O)(OR^1)_2$ under ambient conditions (120 °C, 18 h) in a solvent free medium. Each class of compounds obtained herein are isostructural and adopt one dimensional polymeric motif by virtue of bridging bidentate character of the phosphite-/phosphonate monoester ligands. The diorganotin(IV) phosphite esters (chapter III) readily undergo tranesterification and de-esterification of the P-OR bonds and thus allow chemical modification of the pre-formed polymers. For example, isolation of mixed-ligand coordination framework, $[n\text{-}Bu_2Sn\{OP(O)(OEt)H\}_{1.5}\{OP(O)(OCH_2CCl_3)H\}_{0.5}]_n$ as well as $R_2Sn\{OP(O)(OH)H\}_2$ has been achieved by following this approach. The later family of polymers are found to be important candidates as materials for proton conduction under humid conditions. The results obtained from impedance plots suggest conductivity values, σ of the order of 10^{-4} - 10^{-6} Scm^{-1}. The Arrhenius plots obtained from impedance

data at variable temperatures (40-80 °C) provide an estimate of activation energy, E_a. The values obtained are of the order of 0.33-0.42 eV and suggest Grotthus mechanism.

Contrary to these results, diorganotin(IV)-phosphonate esters (chapter IV) are inert towards tranesterification and de-esterification of the P-OR bonds. The difference in the reactivity behaviour is attributed to arise from difference in the electrophilicity of phosphorous centre amongst two classes of ligands. During crystallization process of the polymer, *n*-$Bu_2Sn\{OP(O)(OMe)Me\}_2$ from a solution in chloroform we have isolated fibre like structures of several microns in length with unique bending features. Based on recent reports, it is speculated that the presence of weak secondary interactions act as structural buffers for such deformation. The crystal growth behaviour of this polymer in presence of trace amount of iodine in chloroform solution however resulted in the isolation of cubic shaped crystals suitable for X-ray crystallography. The real time growth phenomenon has been monitored by UV-Vis and SEM studies, suggesting the role of charge transfer complexation between the polymer and iodine in modulating the growth process.

The content of chapter V provides an insight into the versatility of dialkylphosphites in synthetic organotin(IV) coordination polymers bearing phosphite monoester and sulfonate ligand sets. The isolation of a series of polymers of composition, $R_2Sn\{OP(O)(OR^1)H\}(OSO_2Me)$ [R = Et, *n*-Bu; R^1 = Me, Et] suggest generality of this synthetic protocol. All the coordination polymers thus obtained have been characterized by elemental analysis, IR and multinuclear [^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$ and $^{119}Sn\{^1H\}$] NMR spectral studies. An examination of the reactivity behaviour of *n*-$Bu_2Sn\{OP(O)(OEt)H\}(OSO_2Me)$ towards methanol has led to the isolation of transesterified product, *n*-$Bu_2Sn\{OP(O)(OMe)H\}(OSO_2Me)$.

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GLOSSARY OF SYMBOLS AND ABBREVIATIONS

%	percent
°	degree
°C	degree centigrade
Å	angstrom
AFM	atomic force microscopy
ATR	attenuated total reflectance
br	broad signal
b.p.	boiling point
CH_2Cl_2	dichloromethane
$CHCl_3$	chloroform
cm	centimeter
d	doublet
D	dimensional
DMSO	dimethyl sulfoxide
DEF	diethyl formamide
ε	molar absorptivity
e.g	for example
EDX	Energy Dispersive X-ray
eq.	equation
ESI	electrospray ionization
Et	ethyl
Et_2O	diethyl ether
FT	fourier transform
g	gram
h	hour

Hz	hertz
ICP	infinite coordination polymer
i.e	that is
IR	infrared
J	coupling constant
λ	wavelength
μ	micro
m	multiplet
m.p.	melting point
Me	methyl
MeOH	methanol
MHz	mega hertz
mL	milliliter
Mmol	millimole
mol	mole
MOF	metal organic framework
n-Bu	*n*-butyl
nm	nanometer
NMR	nuclear magnetic resonance
ORTEP	Oak Ridge Thermal Ellipsoid Plot
Ph	phenyl
q	quartet
RT	room temperature
Σ	sum
SEM	scanning electron microscopy
t	triplet

t-Bu	*t*-butyl
TGA	thermogravimetric analysis
TMS	tetrametylsilane
UV	ultraviolet
δ	chemical shift
ν	frequency