

CHAPTER 1

**A SHORT REVIEW ON THE ORGANOTIN(IV)
COMPOUNDS**

1.1 Introduction

Tin (atomic number, 50; relative atomic mass, 118.69; electronic configuration $5s^2p^2$) is an element of group 14 of the periodic table, along with C, Si, Ge, and Pb. Tin as a metal, either as such or in the form of alloys and in its chemical compound has an astonishing amount of usefulness. Characteristically, for majority of its applications, only a small amount of tin are needed to see its effect. Tin exists in three allotropic modifications and it can form a variety of inorganic and organometallic compounds. This is generally true for organotin chemistry which is a subject of interest for years due to not only of its rich structural chemistry but also for its versatile applications. The use of organotin(IV) compounds in industry has risen dramatically during the last few decades as a result of their wide range of biocidal and industrial applications such as stabilizer for polyvinyl chlorides, industrial catalysts, wood preservatives and anti-fouling agents that has led to their accumulation in the environment and in biological systems [1,2]. At the present time, the industrial uses of non-toxic organotin compounds (R_2SnX_2 and R_3SnX_3 types) account for almost two third of the total world consumption, although the other major uses for these derivatives as selective biocides and pesticides (R_3SnX type) has increased rapidly in recent years. The estimated consumption of tin metal for chemical industry was large, the reason for this growth in tin chemicals are the diversity of tin applications in many cases, with their generally low toxicity [3]. The tetra organotins R_4Sn have no commercial outlets, but are important as intermediates in the manufacture of R_nSnX_{4-n} compounds from $SnCl_4$. So far, monosubstituted organotin compounds (R_3SnX_3) have had a very limited application, but they are used as stabilizers in poly (vinyl chloride) films.

Organotin(IV) compounds are characterized by the presence of at least one covalent C-Sn bond. The compounds contain tetravalent Sn centres and are classified as mono-, di-, tri- and tetraorganotin(IV)s, depending on the number of alkyl (R) or aryl (Ar) moieties. The anion is usually chloride, fluoride, oxide, hydroxide, a carboxylate or a thiolate [2].

1.2 Literature

The first organotin compound was prepared over 150 years ago. Way back, in 1849, E. Frankland in his paper described the reaction which occurred when ethyl iodide and zinc were heated together in a sealed tube [4]. Frankland described, the behaviour of ethyl iodide in contact with metal like tin at elevated temperatures (150 - 200 °C). Later, he showed that the crystalline mass diethyltin diiodide was obtained in this reaction (Eq.1)[5-7].



In an independent work, Löwig established that ethyl iodide when reacted with a tin/sodium alloy produced a compound which is now recognized as oligomeric diethyltin [8]. As an alternative to this so-called direct method, an indirect route was devised by Buckton in 1859, who obtained tetraethyltin by treating tin tetrachloride with Frankland's diethylzinc (Eq.2) [9].



In 1886, Letts and Collie were attempting to prepare diethylzinc and instead isolated tetraethyltin which was formed from tin (was present as impurity in the zinc). So they established that tetraethyltin could be prepared by heating ethyl iodide with a mixture of Zn and Sn powder (Eq.3) [10].



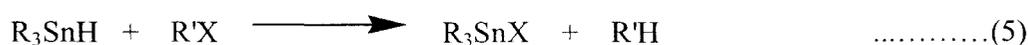
In (Eq.4), Frankland showed that the tin(IV) tetrachloride (which is used in Eq.2) could be replaced by tin(II) dichloride which is much more easier to handle and reacts in a more controllable fashion [11].



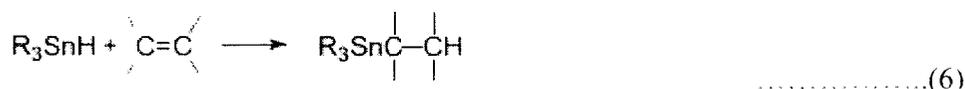
Up to 1900, some 37 papers were published on organotin compounds. In 1903, Pope and Peachey described the preparation of a number of simple as well as mixed tetraalkylstannanes and tetraphenyltin, from Grignard reagents and tin tetrachloride or alkyltin halides and reactions of this type soon became the standard route to alkyl- and aryl-tin compounds [12]. In 1937, Krause and von Grosse had summarized the early

work in *Organometallische Chemie* which is considered to be the first publication [13].

In 1962, Kuivila showed that the reaction of trialkyltin hydrides with alkyl halides (Eq.5) was a radical chain reaction involving short-lived trialkyltin radicals, $R_3Sn\cdot$ [14].



In 1964, Neumann showed that the reaction with non-polar alkenes and alkynes followed a similar mechanism and these reactions now provide the basis of a number of important organic synthetic methods (Eq.6) [15, 16].



A major development in recent years has been the increasing use of organotin reagents and intermediates in organic synthesis, exploiting both their homolytic and heterolytic reactivity [17].

In parallel with these developments, organotin compounds have found a variety of applications in industry, agriculture and medicine, though in recent years these have been circumscribed by environmental considerations. In industry, they are used for the stabilization of poly vinyl chloride, the catalysis of the formation of the polyurethanes and the cold vulcanization of silicone polymers and also as transesterification catalysts. Their biological properties are made use of in antifouling paints on ships, in wood preservatives, as agricultural fungicides as well as insecticides. Interestingly, in medicine, they are showing promise in cancer therapy and in the treatment of fungal infections [18].

In 1937, Krause and von Grosse published the first review of organotin chemistry [13]. In 1960, the field of organotin chemistry was reviewed by Ingham *et al.* with comprehensive tables of the known compounds [19]. In 1961, M. Dub compiled from Chemical Abstracts a non-critical compendium listing preparations, physical, chemical properties and literature surveyed from 1937 to 1959 [20]. Simultaneously, Weiss compiled an exhaustive list of organotin compounds which were reported between 1937 to 1964 [21]. A book namely, "Organotin Compounds:

New Chemistry and Applications", edited by J. J. Zuckermann (1976) was written based on lectures delivered at the centenary meeting of the ACS [22]. It is also noteworthy to mention that several famous books were written/edited describing the then progress of organotin research [1, 23-26]. A volume of Houben-Weyl deals particularly with preparative methods of organotin compounds [27]. In 1991, Guo Yushen reviewed the preparation, properties and applications of monoalkyltin compounds [28].

Structural aspects of organotin chemistry have been reviewed [29] and a comprehensive bibliography of X-ray diffraction studies is available from the International Tin Research Institute [30]. M.I. Bruce [31] who had written a comprehensive listing of organotin compounds (ca. 1500 entries) which have had their structure determined by electron diffraction or X-ray diffraction. The structural diversity of organotin compounds has been attracting the attention of a number of researchers and as a result a multitude of structural types have been discovered [32]. Gielen and Sprecher [33] included a discussion of organotin structure in which the coordination number of tin is greater than 4; the same topic was discussed in an article written by Okawara and Wada [34].

H. Ali and J. E. van Lier, have reviewed organotin compounds that react rapidly and chemo-, regio-, and stereo-selectively with a variety of reagents, and this have been exploited in the synthesis of pharmaceuticals with a radioactive label, particularly when the radioisotope has a short half-life [35]. A second review covering similar ground is included in Patai's volume [36].

J. J. Eisch and R. B. King have given tested experimental details for the synthesis of some 40 organotin compounds [37-39]. Synthesis, reactivity, structural aspects and applications of organotin(IV) complexes with phosphorous-based acids have been reviewed by V. K. Jain [40]. The applications of these complexes as catalysts, corrosion inhibitors and biocides were also discussed in this review. P.G. Harrison in 1989 has edited a multi-author book which has covered both inorganic and organic aspects of organotin chemistry [41].

S. J. de Mora in 1996 has edited a book in which chapters were written by various authors covering the different aspects of the problems associated with the use of tributyltin compounds in marine antifouling paints [42]. Nath *et al.* [43] have reviewed organotin (IV) complexes of the amino acids and peptides with special reference to their methods of synthesis, structural, thermal properties as well as their

solution studies and biological activity. The structures of these complexes were discussed on the basis of IR, electronic, multinuclear (^1H -, ^{13}C - and ^{119}Sn -) NMR, X-ray and ^{119}Sn Mössbauer spectral studies.

A review by Beckmann and Jurkschat [44] was given with 140 references on the recent progress in the chemistry of *cyclo*-stannasiloxanes of different ring size and their potential in ring-opening polymerization reactions is critically evaluated and compared with that of related *cyclo*-borasiloxanes, *cyclo*-germasiloxanes, and *cyclo*-siloxanes. Pellerito and Nagy [2] in 2002, have written a review which deals with the organotin(IV) cations forming complexes with ligands containing (O), (N), (S), or {phosphorus(O)} donor atoms with various composition and stability. The emergence of new experimental techniques (EXAFS, multinuclear ^1H -, ^{13}C -, ^{119}Sn -NMR, ^{119}Sn Mössbauer, etc., spectroscopic techniques) provided useful information about the structure and stabilities of the complexes formed. They also have reviewed the literature on these types of complexes taking into account the biological aspects of the complexes. Chandrasekhar *et al.* [45] have written this review which deals with the recent progress in the area of organotin assemblies that contain Sn—O bonds. Various kinds of tri-, di- and monoorganotin compounds are described in terms of their preparation by methods such as hydrolysis of organotin halides, reactions of suitable organotin compounds with various kinds of substrates such as carboxylic acids, sulfonic acids, oxide transfer reagents etc. The structural characterization of these compounds by the use of ^{119}Sn -NMR, ^{119}Sn Mössbauer and X-ray crystallography was presented in considerable detail. The amazing structural diversity present in this family of compounds was discussed. Organotin compounds can be assembled by using various synthetic methodologies. Although in most instances, organotin oxides and hydroxides are the preferred starting materials for preparing organotin compounds, Sn—C bond cleavage reactions involving organotin compounds also offer a rational route. This review deals with the recent progress in this area and examines various reactions, where Sn—C cleavage occurs. A wide range of products are accessible from this approach and these were presented in this article [46]. Roy and Roy have reviewed details about making and breaking of Sn-C and In-C Bonds in situ; the cases of Allyltins and Allylindiums [47].

In 1985, two independently published reviews have demonstrated the utility of organotin(IV) derivatives of poly alcohols in regioselective manipulations involving

indirect acylation, alkylation and oxidation [48,49], while a work by Grindley deals with the applications of organotin(IV)-containing intermediates in carbohydrate chemistry [50]. Strong sugar-organotin(IV) cation complexation have been discussed by Burger and Nagy [51], Gyurcsik and Nagy [52], Verchere *et al.* [53] while Barbieri *et al.* [54] dealt mainly with the interactions of organotin(IV) cations and complexes with DNA and their derivatives.

The agricultural applications of organotin compounds in 1950's and early in 1960's were first explored by G. J. M. Vander Kerk and his coworker. They were the pioneer in the discovery of the high fungicidal activity of triphenyl- and tributyl- tin compounds [55-58]. Crowe [59,60] has reviewed the applications of organotin compounds in agriculture upto 1980 and published it in two parts. In part I, he discussed about the fungicidal, bactericidal, and herbicidal aspects of those compounds and the part II covered acaricidal, antifeedant, chemosterilant and insecticidal properties of organotin compounds. In 1989, Molloy surveyed in the wild field of bio-organotin(IV) compounds [61]. Detailed discussion of organotin(IV) compounds as wood preservatives had been published [62,63]. In 2008, Basu Baul reported a comprehensive review on antimicrobial activity of organotin(IV) compounds. After the review of Pellerito and Nagy it was an off beating review of biocidal activity of organotin(IV) compounds [64].

In 1973, Atsushi *et al.* [65] reported a very important piece of work, it was the high affinity of tin for tumours which was the highest among the group 14 elements. This finding was further confirmed by various workers who prepared tin labeled technetium complexes and used them as imaging agents for tumour localization [66]. Subsequently, two important reviews covering the literature of anti cancer activity of organotin(IV) compounds had been published [67,68]. In 2006, Tabassum and Pettinari have published substantial information on the mode of action of organotins in cancer chemotherapy [69]. Tsangaris and Williams published a paper on tin including organotin(IV) compounds in pharmacy and nutrition [70].

1.3 Bonding in organotin compounds

Tin has the electronic configuration $5s^2p^2$ in its valence shell which result the occurrence of two oxidation states +2 and +4. Its principal valence state is Sn(IV), though Sn(II) inorganic compounds are common. 3P is the ground state which is

derived from s^2p^2 configuration. In the ground state, there are only two unpaired electrons. Therefore, two covalence bond could be expected [71]. The 5S state of the tin is the first excited state. The Sn(II) state uses mainly the 5p orbitals for bonding otherwise Sn(IV) oxidation state occurs readily, where the tin is sp^3 hybridized.

Tin(II) compounds are mostly bent, pyramidal or distorted due to the presence of an electron pair that does not participate in bonding and displays stereochemical activity, tin(IV) compounds adopt regular geometries as tetrahedral, bipyramidal and octahedral depending upon the coordination number, the electronegativity of tin change with its oxidation number. Tin(II) compounds are more ionic compared to corresponding tin(IV) derivatives. The marked increase in the stability of R_4Sn compounds over R_2Sn types demonstrates the effect of increased hybridization. So most of the organometallic tin compounds are of tin(IV) type [72]. The Sn-C bond should be polar since Sn is electropositive with respect to C. But the polarity is so low as in the tetraalkyls and aryl derivatives of tin so these are not hydrolysed by water. It is possible that the d orbital of tin are used for $(d\pi-p\pi)$ bonding.

1.4 Structure of organotin compounds

The principal valence state Sn(IV), is remarkable capacity to expand its coordination number from anywhere between four to seven. Therefore, the structure of organotin(IV) compounds are tetrahedral, trigonal bipyramidal and octahedral depending upon the coordination number. Tin(II) compounds are bent, pyramidal or distorted in structure [73-75].

Simple tetraalkyl- and tetraaryl-tin(IV) compounds exist under all conditions as tetrahedral monomers, but in derivatives R_nSnX_{4-n} ($n = 1$ to 3), where X is an electronegative group (halide, carboxylate *etc.*), the Lewis acid strength of the tin is increased, and Lewis bases form complexes with a higher coordination number. The compounds R_3SnX usually give five-coordinate complexes R_3SnXL which are approximately trigonal bipyramidal, and the compounds R_2SnX_2 and $RSnX_3$ usually form six-coordinate complexes $R_2SnX_2L_2$ and $RSnX_3L_2$ which are approximately octahedral. The groups X, however, usually carry unshared electron pairs, and can themselves act as Lewis bases, resulting in intermolecular self-association to give dimers, oligomers, or polymers. This self-association is governed by the nature of the ligands L and also by the steric demands of R, X, and L, and it is common for the

degree of association to increase in the sequence gas < solution < solid. If R or X carries a functional substituent Y beyond the α -position, the alternative of intramolecular coordination can occur leading to the formation of monomers with 5-, 6-, 7-, or 8-coordinated tin [11]. The structures of these intramolecularly self-associated monomers, oligomers, and polymers are seldom those of regular polyhedra, and the determination of their structures, and the steric and electronic factors which govern them, has been an important feature of organotin chemistry since the early 1960s [23,24,76].

1.5 Reactivity of organotin compounds

In the periodic table group 14 elements are Si, Ge, Sn, Pb. In Sn-C bond, Sn is electropositive with respect to C and it is represented by $C^{\delta-}-Sn^{\delta+}$. Therefore, it should be polar. The polarization of Sn-C bond makes tin atom more electrophilic and carbon atom which is attached to tin more nucleophilic. So the reactivity of organotin compounds towards nucleophilic and electrophilic both. But the polarity of tetraalkyl and aryl derivatives of tin is low that is why these are not actually hydrolyzed by water. In group 14 elements, reactivity of M-C bond in tetra-alkyl and aryl increases progressively from Si to Pb [77]. A bond between M-C, where M is C, there is possibility of forming double bond ($p\pi-p\pi$). When M substitutes other element of group 14 of the periodic table, there is enough evidence that the d orbitals of these elements are used for bonding ($d\pi-p\pi$). In bonding, the tendency for using d orbital decreases from Si to Sn. In $(GeH_3)_2S$ and $(GeH_3)_2O$, the Ge-S-Ge and Ge-O-Ge appears to be highly bent [78] whereas in $(SiH_3)_2O$, the Si-O-Si bond angle is around 150° [79]. Bond energy and thermal stability decreases in the same sequence Si to Pb. Expanding of the coordination number of the metal, it becomes easier with the increasing atomic size [80].

The alkyl groups are usually introduced to tin by complete alkylation of tin tetrachloride with an organometallic reagent, then the various alkyltin chlorides, R_nSnCl_{4-n} , are prepared. Other functional groups are then introduced by nucleophilic substitution of the chloride. Reaction of the alkyltin chlorides with the appropriate nucleophiles gives the alkyltin alkoxides, amides, thioalkoxides, carboxylates etc. The presence of these electronegative groups on the tin renders the metal susceptible to coordination by Lewis bases and simple tetrahedral four-coordination is the

exception rather than the rule. Hydrolysis of the organotin halides gives the organotin oxides, and in the case of the dihalides and trihalides, the reaction proceeds through a series of well-characterized intermediate hydrolysis products [26, 81].

Cleavage of the carbon-tin bond by heterolytic reaction is usually dominated by electrophilic attack at carbon, although nucleophilic assistance may be provided at the centre and this can sometimes predominate (Eq. 7) [82-84].



The most important electrophiles which are involved are protic acids, particularly carboxylic acids, metallic halides such as tin chlorides, and the halogens, particularly bromide. The cleavage of the alkyl-tin bond by sulphur dioxide is similar. Homolytic attack at carbon to break the carbon-tin bond has not yet been identified, but attack at hydrogen on the β -carbon may sometimes result in cleavage of the carbon-tin bond through a subsequent fragmentation process [85].

1.6 Analytical techniques applied to determination the structure of organotin compounds

The basic studies in the field of organotin compounds have been developed due to the success of a large number of modern analytical techniques applied to organotin compounds. Investigations can be performed by general techniques such as UV-Vis [24], IR [24, 81], 1H -NMR [86], ^{13}C -NMR [87], mass spectroscopy [88] and also by specialized techniques such as ^{119}Sn Mössbaure spectroscopy [24,26] and ^{119}Sn -NMR spectroscopy [89]. The ^{119}Sn Mössbaure and ^{119}Sn -NMR spectroscopy provide complementary information on the structure of the organotin molecules in the solid state and in solution respectively.

1.7 Applications of organotin compounds

Organotins are currently one of the most studied groups of organometallic compounds; their novel and often unique chemical properties have intrigued chemists for over 100 years and, today, many of these compounds find extensive use in

agriculture and industry [90]. As the world of organotin chemicals is quite extensive and diverse which are discussed briefly here. The majority of organotin uses are comprised of five major commercial applications: PVC Heat Stabilizers, Biocides, Catalysts, Agrochemicals, and Glass Coatings. These applications divided into two groups: biological applications and non biological application.

1.7.1 Biological applications

At the Institute for Organic Chemistry TNO, Utrecht, Holland, in early 1950s, Vander Kerk and Lujten, systematically discovered the high fungicidal activity of tributyl- and triphenyl-tin compounds [55, 56, 57]. It was not until 1925 that the first commercial application of an organotin was recorded (as a mothproofing agent). Seven years later, tetra-alkyltins found to have an industrial application as hydrogen chloride scavengers in chlorinated hydrocarbons used as insulators in heavy-duty transformers and capacitors. This was taken to mark the beginning of the more generalized biological commercial applications of organotin compounds [90]. The first organotin compound to reach commercialization in agriculture in the early 1960s were triphenyltin acetate (Brestan*, Hoechst A.G) and triphenyltin hydroxide (Duter*, Philips Duphar N.V), both of which were widely used [91] to combat a number of fungal diseases in various crops, like potato blight, leaf spot on sugar beet and celery, rice blast as well as coffee leaf rust. A further interesting property of chemosterilant [92,93]. A third triphenyltin compound, the chloride (fentin chloride: Brestanol) which was also produced by Hoechst is now used, although to a lesser extent [94]. A few years later Dow introduced the tricyclohexyltin hydroxide (cyhexatin: Plictran) which was highly effective in the control of phytophagous mites. Subsequently, two further organotin miticides were introduced; bis(trineophyltin)oxide (fenbutatin oxide: Vendex or Torque) by Shell and tricyclohexyltin- 1,2,4-triazole (azocyclotin: Peropal) by Bayer [91]. Activity of fungi was also influenced by the nature of the organic group. The tributyl compounds Bu_3SnX , was shown fungicidal activity was largely independent of the group X [95]. The fungicidal activity of a group of these triphenyltin fungicides was that they were function as antifeedants in which they deterred insects from feeding, and they also acted as insect Ph_3SnX compounds were shown to be highest when $X = NCO$ or NCS [96]. The trimethyl- and triethyl-tin

derivatives had a high toxicity to insects and mammals, [97,98] the tripropyltins to gram-negative bacteria, and the tributyltins to the gram positive bacteria and fungi [99]. The tricyclohexyl- and trineophyl- tin compounds are effective acaricides [100,101]. The toxic triorgano-tin compounds are able to inhibit mitochondrial oxidative phosphorylation and their biological activity pattern is probably due to their ability to bind certain proteins. The exact nature of the binding sites on the proteins is not known. The biological effect of the tetra organotin compounds R_4Sn appear to be caused entirely by the R_3SnX derivative, which is produced by their fairly rapid dealkylation *in vivo* [102, 103]. The dialkyltin compounds show a toxic behavior which is quite different from that of the R_4Sn and R_3SnX compounds. They combine with co-enzymes or enzymes possessing dithiol groups, e.g. reduced lipoic acid and thereby inhibit α -ketoacid oxidation. As with trialkyltin compounds, the mammalian toxicity of the di-n-alkyltins decreases with increasing length of the alkyl chain [102,104]. A series of diorganotin complexes were modeled for the antitumour agent like cisplatin showed antitumour activity. These compounds exert a selective cytotoxic action on T- lymphocytes and therefore hold potential as anti-T-cell tumor agents [105]. Organotin compounds have been used as anthelmintic agents e.g. dibutyltin dilaurate which is one of the constituents of the commercial product that has been used as formulation for treating poultry in combination with piperazine and phenothiazine [101]. Tin(II) fluoride is used in toothpastes as an antidecaying agent and applied to children's teeth [106]. Di-n-butyltin dilaurate and tin(II) acetate have been used as catalyst in vulcanizing silicon rubbers used for the protection of the dental prosthetic devices.[107]. Trialkyltin compounds are used in organic solvent-based wood preservative formulations. Tributyltin oxide at concentration up to 3% in a solvent like kerosene has been used for the pretreatment of the wood to protect it from insect attacks [108]. In the early 1960s, triorganotin compounds were used for antifouling paint and regular consumption of these compounds increases with the time [109].

1.7.2 Non biological Applications

There is considerable industrial activity in organotin chemistry because of its large-scale applications in the fields of polymer stabilization, organic synthesis and

catalysis. The PVC is the second most plastic after polyethylene. Certain organotin compounds are amongst the most effective stabilizers for plastic. Carboxylates and mercaptide tin salts can replace labile chlorine atoms; with more thermally stable C-O or C-S bond ligands. Organotin-based stabilizers are the efficient and widely used PVC stabilizers [110]. Certain monobutyl- and mono-octyl-tin compounds, e.g. $[\text{BuSn}(\text{O})\text{O}]^- \text{Na}^+$, are active hydrophobic agents for cellulosic materials, such as cotton textiles, paper and wood but have not reached commercialization for this application. These have been tested on building materials (limestone) bricks and concrete and on cellulosic substrate (cotton, paper and wood) as well [111,112]. Tin(II) chloride, ammonium hydrogen fluoride isopropanol and polishing agents are used to protect the sheepskin wool in the spray treatment process. The K_2ZrF_6 , tin(II) chloride and hydrochloric acid have been used for protection purposes in treatment process [113]. The most commonly used compounds in electroplating are tin(IV) sulphate, tin(II) chloride, tin(II) fluoroborates and sodium/potassium stannates [114]. Thin coatings of tin(IV) oxide on glass have a number of applications. The precursor of these tin(IV) oxide films was originally tin(IV) chloride, which is applied in the vapour phase at 500-600°C to hot glass surface where it is pyrolysed to tin(IV) oxide [114]. Tin(IV)oxide electrodes are used in the manufacture of lead-containing crystal glass by electric melting. The tin(IV) oxide electrodes are more preferably used as compared to the conventional molybdenum or graphite rod, because the electrical conductivity of tin(IV) oxide increases with increasing temperature [115]. The most widely used catalysts are stannous octoate [tin(II)2-ethyl hexoate] and various mono- and diorganotin compounds. These catalysts play an important role in the formation of polyurethane foams in the production of polyesters and in the curing of certain types of silicone resins. Dibutyltin dilaurate, dibutyltin diacetate are used as homogeneous catalyst in the manufacture of polyfoams and cross linking agents at room temperature for olefinic polymerization [116].

1.8 References

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