Functional Polysilanes and their Optical, Chiroptical and Photoluminescence Properties

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Abstract: ‘Polysilanes’ is an important class of inorganic polymers having Si-Si σ-conjugation along the backbone. They exhibit extraordinary electronic and photophysical properties and find suitable optoelectronics applications. They are typically synthesized by Wurtz coupling reaction of dichlorodialkylsilane or dichlorodiphenylsilane or dichloroalkylphenylsilane and their combinations under drastic reaction conditions by using sodium dispersion in boiling toluene. In such a drastic condition, no functional groups sustain with polysilane polymer. In order to achieve such functional materials, researchers have been interested in synthesizing functional polysilane with a different functional group like a chiral group, azobenzene containing chromophore and other heteroatoms in their main chain or side chain. Therefore, it is a very challenging task to synthesize polysilanes having effective functionality integrated with their structures. However, the modern technological demand of materials leads to efforts to obtain polymers having functional and multifunctional activity in a single material. In this review article, we cover the synthesis of polysilane with functional activity via pre-polymerization and post-polymerization with a functional group.

Keywords: Chiral polymers, functional polysilane, optically active, photoactive properties, photo irradiation, silyl radical.

1. INTRODUCTION

Polysilanes are inorganic polymers which consist of two organic substituents on each silicon atom along with their backbone. It represents a novel class of material having unique electronic and optoelectronic properties, due to σ delocalization through their silicon backbone [1, 2]. Polysilanes and their copolymers, composed of organic-inorganic materials, have attracted the attention of inventors towards the hybrid materials. Homopolymers of polysilanes consist of single silylene unit (R₂Si) while copolymers consist of two or more silylene units. Most of the organic polysilanes are soluble in common organic solvents. However, highly crystalline polymers like (CH₃)₂Si, (C₂H₅)₂Si, (C₆H₅)₂Si are insoluble. These were found thermostable up to almost 300°C and weight loss begins around 350°C under vacuum. An extensive σ electron delocalization with Si-Si polymers makes these materials useful for optoelectronic devices as nonlinear optical and photoconductive materials [3-11]. The properties of polysilanes are influenced by the attached substituent to the polymer chain, like the degree of polymerization and polymer chain conformation. However, due to the strong absorption of polysilane in UV region makes these materials applicable for photo and X-ray photolithography [12, 13]. By the UV irradiation, polysilane produces silyl radical polymerization of vinyl monomers [14-16]. They have attracted great attention for their special electronic and optical properties as well as Si-C ceramic precursors [17]. They are also used in several techno-commercial applications in the field of polymers and composites, high and ultra-high temperature ceramic precursors and photore sist materials [18]. In this review study, we summarize the synthesis of polysilane and functional polysilanes having optical, optoelectronic and photophysical properties.

2. SYNTHESIS OF POLYSILANES

Polysilanes exhibit extraordinary electronic, optical and photophysical properties such as electroluminescence, UV-absorption, thermochromism (thermal study of polysilanes via UV-vis spectrophotometer within temperature range from -90 to +25°C) [19], solvatochromism, (is the property of polysilanes due to sudden change in the transition of solutions of the polymers in different solvent. This unrivalled change was observed due to hydrogen bonding of the fluoroo alcohol to the oxygen atom in the polymer side chains and this phenomenon was first observed by Yuan C.H. et al. in...
Poly[bis(4-propoxybutyl)silylene] (PPBS) [20]. It was due to σ-electron delocalization along their Si-Si backbone (Fig. 1) [21-24]. This imparts excellent conductive and luminescence properties induced in polysilane chain by the σ-electron delocalization [19, 25-29]. They were widely used in the field of material science such as semiconductor and optoelectronic, sensor materials and the precursor for Si-C ceramics [30, 31].

Synthesis of polysilanes was first reported in 1920 by Kipping S. via Wurtz coupling reaction of dichlorodiphenylsilane (monomer unit) with sodium dispersion in boiling toluene [32, 33]. The general method for the synthesis of polysilanes such as poly(dimethylsilane), poly(methylphenylsilane), poly(diphenylsilane), and poly(hexylmethylsilane) using Wurtz coupling reaction is shown in Scheme 1.

Later on, four common procedures were reported for the synthesis of polysilanes (Scheme 2) [34]. The most common method mentioned in the literature is Wurtz coupling reaction of dichlorodisilanes with sodium dispersion in refluxing toluene. The polysilanes were also synthesized by other routes such as anionic polymerization of masked disilenes, ring opening polymerization of strained cyclic oligosilanes catalytic dehydrogenation of primary silanes [35-39]. The readers can refer to a recent review [40] for in depth procedures as mentioned above.

However, all the above methods suffer from one or another drawback, such as the use of metal catalyst, poor yield of linear polymers etc. In order to overcome these problems, researchers used glycol ether or crown ether and other auxiliary additives [41]. They also modified sodium mediated surface using ultrasonic activation [42, 43]. The experiment showed that by the addition of a small amount of crown ether in sodium mediated Wurtz coupling reaction enables the synthesis of unimodal high molecular weight of polysilane (PDI=2.6) and yield obtained around 20%. The synthesized polysilanes have shown multiple applications such as semiconducting, photo-conducting, electroluminescent, and nonlinear optical materials. But, their mechanical properties were found relatively poor, that adversely affected their processability and posed a limitation in their exploitation. In order to obtain good mechanical strength, several attempts have been made to combine polysilane with organic polymers [44].

Copolymers of polysilanes were also synthesized by Wurtz coupling reaction by combining two diorganodichlorosilane monomers together. For example, poly(Dimethyl-co-Methylphenylsilane) P(DMS-co-MPS) was synthesized using Dichlorodimethylsilane (DDMS) and Dichloromethylphenylsilane (DMPS) in toluene medium using sodium metal (Scheme 3) [45].
3. PROPERTIES OF POLYSILANES

3.1. Optical Properties

Polysilanes belong to a class of heat stable inorganic polymers made up of entirely Si-Si bond along with two organic substituents. The pendant group can be hydrogen, alkyl and aryl groups. These polymers have excellent heat resistance properties which are not very susceptible to hydrolysis but photodegrade when exposed under ultraviolet light. They exhibit optical and electronic properties such as photoconductivity, photoluminescence, electroluminescence, and thermochromism, etc. They also have Nonlinear Optical (NLO) properties. The delocalization of σ-orbital with sili-

con backbone results in HOMO-LUMO band gap as low as 3 and 4 eV. The HOMO-LUMO band gap of polysilanes showed strong absorption in the UV region. The linear polysilanes showed good solubility in common organic solvents and they also exhibited potential applications in the field of electronic and optoelectronics. However, polysilane containing Si-Cl and Si-H group are air sensitive so their optical and conductive properties are unacceptable in comparison to other functional groups [58]. The linear structure of polysilane is given below in Fig. (4).

They have shown excellent optical properties, such as electromagnetic, nonlinear optical effects and photoconductivity [59-64]. It is worth mentioning that the optical properties of linear and nonlinear polysilane have potential applications in the field of optoelectronics [65-67]. It is additionally documented that the performance and properties of polysilanes change with the structures. In reported literature, Watanabe A. and Seki S, et al. have especially compared the optical properties between linear and branched polysilanes [68-70]. These polysilanes have various kinds of silicon skeletons, such as linear polysilane, branched polysilane, network polysilane, ladder polysilane, and polysilane dendrimer. Their properties are highly sensitive for their silicon backbone conformation; the optically active polysilane has another interesting type of relationship between their main chain or side chain conformational structures and inherent optical properties [68-72]. Fujiki M, et al. (2003) have reported 10 year progress of optically active polysilane, new polymers twisted for nanoscience and nanotechnology [73]. In their study, they reported that optically active polysilane comprises a helical main chain of Si-Si bond, chiral and achiral side groups. They exhibit unique absorption, circular dichorism and fluorescence spectra due to σ-conjugation around 300-400 nm. In optically active polysilane, helical conformation are induced by chiral side chain interaction or main chain, which showed intense UV, CD and FL due to σ-σ* transition at around 300-400 nm. The structure and conformational energy of polysilane as poly(dimethylsilane), H-(Si-H) 3-H have been studied by using full relaxation Empirical Force Field (EFF) method [74]. Weglikowska U.D, et al. (1997) have reported the structure of two dimensional planar polysilane. Wohler siloxene is responsible for their exciting luminescing properties. The single crystal siloxene was syn-

Scheme 3. Copolymer of polysilane synthesized by Wurtz Coupling reaction.

Fig. (1). Structure of Linear Polysilane Chain.

It is also reported that polysilanes are a chain like polymers in rod form, which possess the semi-rigid segmented backbone of σ-conjugated chain and helical conformation [46-47]. Molecularly dispersed polysilanes and polysilane copolymers and their composites have attracted further great attention of scientists for preparation of (organic-inorganic) hybrid materials. The polar group-containing polysilane copolymers provide a fascinating potential of applications based on their networks with electronic and optical properties [48-51]. For the production of block and graft copolymers from inorganic and organic blocks it is generally pursued to exploit the best properties of the individual materials and to form new classes of compounds. Poly(methylphenylsilane)-poly(benzylmethacrylate) (PMPBzMA) block copolymer was prepared using photopolymerization of benzyl methacrylate (BzMA) monomer with PMPS as a macromolecular photo-radical initiator [52]. Polysilane-silica hybrid thin films were prepared from polysilane-methacrylic or acrylic block copolymers with alkoxysilyl or amide groups via the sol-gel process using Tetraethoxyorthosilicate (TEOS) [53-57]. The prepared film contained a different type of functionalities mixed with polysilane block with the silica component through covalent or hydrogen bonding [53, 56]. The polysilane block copolymer, (PMP-co-MPTES), was obtained using photopolymerization of Poly(Methylphenylsilane) (PMPS) along with 3(Methacryloxypropyltriethoxy) silane (MPTES) in which PMPS was acted as a macrophotoinitiator. Inorganic polymers generally possess properties that are different from carbon-based polymers due to catenation chain Si-Si backbone [34].
The synthesized via topotactic reaction using crystalline CaSi_2. The chemical composition was determined as [Si_6H_3(OH)_3]_n. Polysilane exhibit same structural properties as Wohler siloxene but different chemical composition [Si_6H_6]_n [75]. The PL spectrum of Wohler siloxene has maximum 2.30 eV and FWHM of 300 MeV as shown in Fig. (2).

They were synthesized as per following synthesis represented in Scheme 4 [76].

The circular dichroism is one of the basic techniques to understand the chirality of optically active compounds. The synthesized samples were characterized by GPC analysis, spectroscopic and chromatographic techniques. Further chiral-block-polysilanes were also characterized by CD spectropolarimeter for their chiral and optical properties as shown in Fig. (5). The cotton effect is observed at 276 nm due to the aromatic ring of chiral unit, [(R)-N-(1-phenylethyl) methacrylamide], which is obvious. But, cotton effect is also observed at 325 nm, due to association with the Si-Si conjugation. This induced circular dichoric signal appeared in the chiral-block-copolymer may be due to induction of chain helicity into the Si-Si chain by the presence of chiral chains at one or both the ends in chiral-block-copolymer of polysilane.

Further temperature effect on optical properties was also observed for chiral-block-PMPS (SCBC) as shown in Fig. (4). The absorbance at around 322 nm was observed due to Si-Si chain and changed with temperature continuously. But, the absorbance due to aromatic ring at about 270 nm did not change with temperature.

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Meenu et al. (2017) have reported optical properties of functional disperse red 1 methacrylate-block-polysilane copolymer (SCDR) which were studied in THF solution using UV-vis spectroscopy (Fig. 6) [78]. The absorbance at 276 nm can be assigned as π-π* transition of aromatic ring and absorption maxima at 325 nm was due to σ-σ* transition of Si-Si main chain. The electronic absorption in the visible region at 472 nm corresponds to the combined contribution of n-π*, first π-π* intermolecular charge transfer electronic transition of the azobenzene chromophore of DR1MA unit.

They also observed temperature effect on the optical properties of the synthesized polysilane-block-DR1MA (SCDR) copolymers. The UV-vis spectra of a synthesized...
Fig. (4). UV-Vis spectra SCBC-7 in THF (0.4 X 10^{-3}) at various temperature (a) normal and (b) expanded form showing clear variation.

Scheme 4. Representation of Synthesis of Chiral-Block-PMPS Copolymer (SCBC).

Fig. (5). CD spectra of SCBC-1 in THF (conc. 0.005 mg/dl).

photoactive block copolymer at different temperatures are shown in Figs. (7 and 8). The effect of temperature on the absorbance at around 276 nm due to aromatic ring is not observed effectively. However, the absorbance at around 325 nm due to Si-Si bond changed with temperature continuously and it decreased with the increase of temperature. The other combined n-π*, and π-π* electronic transition of azobenzene chromophore was appeared at 472 nm and increased with increase in temperature. The solution concentration effect was also observed by the same group of authors. They found the effect of different solution concentration of a synthesized polysilane block copolymers as shown in Fig. (9). The
Fig. (6). UV-vis spectrum of silane-co-disperse red 1 methacrylate (SCDR-1B) at 30°C (0.125 mg/dl in THF).

Fig. (7). UV-vis spectra of SCDR-1B measured with variation of temperature.

Fig. (8). Effect of temperature on the absorbance Si-Si $\sigma$-conjugation $n$-$\pi^*$ and $\pi$-$\pi^*$ electron transition of azobenzene chromophore at 472 nm.
absorbance both at 276 nm and also at 325 nm varies linearly due to the variation of solution concentration.

### 3.2. Photoluminescence Properties of Polysilanes

Photoluminescence (PL) is light emission from materials and polymers. The UV photoluminescence spectrum is originated from UV region. Generally, most of the polysilanes exhibit only UV luminescence spectra due to quasi-one-dimensional nature with σ-delocalized electron along the backbone [79-81], while other than linear polysilanes polymers, such as network polysilanes and branched polysilanes show luminescence in the visible region. The poly(methylphenylsilane) (PMPS) is an exception for this rule having one dimensional electronic states like other linear polysilanes but showed two luminescence band one in UV region and the other in the visible region [82-85]. The origin of such type of double luminescence bands is still controversial [82, 84-85]. The absorption spectra of poly(alkylarylsilane) derivatives such as poly(methyl-p-tert-butylphenylsilylene) (1), poly(methylphenylsilylene) (2), poly(ethylphenylsilylene) (3), poly(phenyltrimethylsilylene) (4), poly(n-hexylphenylsilylene) (5), and poly(n-pentyl-n-tolylsilylene) (6) exhibit photoluminescence (PL) and PL anisotropy in solution at room temperature and thin film was formed at 20-296 K range. The PL spectrum was always observed in the visible range for poly(alkylarylsilanes) 1, 2, and 3, and for sample no. 4, 5 and 6 PL band at room temperature to 20 K range was not visible. Toyoda S. and Fujiki M. (2001) have attributed the difference in the PL characteristics to the extended global shape with a spatially homogeneous local conformational in solution and in solid films [86]. Poly(methylphenylsilane), showed unusual dual bands in prepared films at low temperature. An intense broad, visible PL (V-PL) or EL band was observed around 2.7 eV and a sharp, near-UV PL (U-PL) or EL band at 3.5 eV [3, 6, 7, 82, 87-92]. The poly(alkylarylsilanes) derivatives exhibit dual PL band due to their chemical and electronic structure similarity. Meena, et al. (2017) have synthesized functional photoactive polysilane block copolymer (SCDR-2B) in THF solution. The properties of these polymers were studied as a photoluminescence shown in (Figs. 10 and 11) [78]. The PL properties of SCDR-2B were studied with the variation of concentration of polymer solution, and with variation of excitation energy (such as 275 nm, 325 nm and 475 nm). The optimum PL was observed at 2.7 eV D 307 nm and 415 nm for the excitation energy (λex) of 275 nm of π-π* transition of aromatic ring. An emission (λem) spectrum was observed at 415 nm for the excitation energy of 325 nm. The obvious multiple emission spectra were also observed at 510, 550 and 580 nm for the excitation at 475 nm shown in Fig. (11). This may be due to the exciton coupling between the azobenzene chromophore of DR1MA block and Si-Si σ-conjugation in association with the aromatic ring of PMPS block (Scheme 5). Such type of functional photoactive polysilane block copolymers (SCDR) having unusual photoluminescence properties may find novel optoelectronics application especially as UV-sensor, device for friend-and-foe identification, etc. [78].

The origin of the broad visible emission has been claimed to be controversial and unclarified [6]. The luminescence spectrum of poly[methyl(phenyl)silylene] (PMPSi) thin films shows a strong absorption and narrow band at 353 nm due to σ-σ* transitions for their excitonic nature, and a broad emission peak with the maximum located at around 470 nm, due to polymer branching, charge-transfer transitions, and defect states (backbone scission) [93].

The poly(methylphenylsilane) (PMPS) exhibited a broad photoluminescent band in the visible region in addition to strong excitonic UV Photoluminescence (UPL) observed at 320 nm with associated σ-σ* transition of silicon backbone [85, 86, 93, 94-98]. Usually, the origin of a broad photoluminescent band is ascribed branch defect in polymeric chain, which is because of photodecomposition of polysilane chain and insertion of silyl radical in silicon backbone. The thermo-responsive PL spectra of PMPS exhibited emission band in the visible region due to polymer branching and σ-π* charge transfer transition [93, 97, 98]. The disappearance of the visible PL band in PMPS proposed that the steric effect
Fig. (10). PL spectra of SCDR-2B obtained with excitation energy of 275 nm.

Fig. (11). PL spectra of SCDR-2B obtained with excitation energy of 325 nm, and 475 nm.

Scheme 5. Schematic representation of the exciton coupling between delocalized $\sigma$-electron of the Si-Si chain in association with the aromatic ring of PMPS unit and azobenzene chromophore of DR1MA unit of the block copolymer.
favors the decomposition at the branching site of thermal reaction, which leads to a linear polysilane having minimum branching defect. The photoluminescence spectra of the narrow band were observed at 354 nm to 370 nm, which entails Visible Photoluminescence Region (VPL) with 500 nm edge. The intensity of the weak VPL band was observed from the excitation at 315 nm wavelength of $\sigma-\sigma^*$ transition in comparison to the excitation at 260 nm for $\pi-\pi^*$ transition. The multiple types of photolumiscence and electroluminescent polymers have received great attention for their photophysical properties [99-101]. Optoelectronic properties have limited applications for the fully saturated substituent of functional groups containing silicon backbone [102-104]. The polysilane silica hybrid materials, poly(methylphenylsilane-co-3-methacryloxypropyltrimethylsilane) (P(MPS-co-MPTMS)) were synthesized using poly(methylphenylsilane) with 3-methacryloxypropyltrimethylsilane via sol-gel method. Thin film was prepared using (P(MPS-co-MPTMS)) with solution of tetrahydrofuran having Diethylene glycol monomethyl ether and HCl with various feed ratio of tetraethoxysilane. Above prepared solution was mixed well and drop cast on a glass slide using the spin coated method. The prepared thin film of PMPs and hybrid material’s optical absorption and PL spectra were determined under excitation 3.76 eV at 298 K. The absorption peak appeared at ~3.70 eV and PL peak appeared at 3.54 eV due to one dimensional exciton of polysilane. In this spectrum, results reported that PMPS and (P(MPS-co-MPTMS)) hybrid thin films exhibit almost same PL spectra but the organic polysilane was embedded in inorganic silica matrix as described by A. Kobayashi.

The UV-vis spectra are strongly correlated with PL spectra for the study of structure identification of synthesized material [105]. In PL spectra of PMPS, there were observed two maxima first one at 333 ± 5 nm (due to $\sigma-\sigma^*$ transition) and the second at 277 nm (due to $\pi-\pi^*$ transition). In this spectrum, emission was observed only at 355 ± 5 nm which is sensitive towards UV degradation [106, 107]. Due to sensitivity, polysilane chain segments degraded under UV exposure, which corresponds to the distribution of absorption energy, lower absorption energy for longer segments. The fluorescent band of poly(methylphenylsilane) (PMPS) was observed at around 360 nm when excited at 313 nm, which was attributed to a fluorescence from their lowest excited state associated with the $\sigma-\sigma^*$ transition [108]. This sharp UV band in the photoluminescence was observed for exci-tonic nature which is associated with the Si-Si backbone of PMPS [99]. Broad Visible Photoluminescence (BVPL) band was also observed in the visible region at greater than 380 nm and their maximum was situated at about 415 nm [84, 101].

Scheme 6. Photolysis of Polysilane producing Silyl Radicals.

3.3. Photoinduced Process of Polysilanes

The photolysis of polysilanes gives rise to silyl macro-radicals which are capable to initiate radical polymerization of vinyl monomers (Scheme 6) [14, 39, 109-111]. The Si-Si main chains of polysilanes are degraded by UV-irradiation and silyl radicals are generated. The initial behaviour and efficiency of various polysilanes such as poly(methylphenylsilane), poly(di-n-hexylsilane), poly(methyl-n-propylsilane) and branched poly(p-butylphenylphenylsilane-co-phenylsilane) were observed and studied. By the UV irradiation of polysilane in the open atmosphere chain scission takes place and Si-Si bond is converted into Si-O-Si bonds selectively or efficiently, here siloxane bond products are flexible and show different refractive indexes. If photopolymerization is carried out in vacuum condition or in the absence of air then chain scission in Si-Si small chain takes place which is not converted into Si-O-Si, in which silyl radical is generated which is capable of initiating radical polymerization. The polysilane copolymers were prepared from photo radical polymerization with acrylic monomers [55]. The silyl radical reactivity observed towards various unsaturated compounds at room temperature [112]. By photodegradation of Si-Si backbone, a molar mass was observed to be decreased. In UV-vis spectrum shift of the absorbance maxima exhibited shorter wavelength (blue shift), for high molecular weight observed at a higher wavelength (red shift). In the reported literature, poly(methylphenylsilane) film irradiated at $\lambda_{inc}=347$ nm underwent transient absorption with strong absorption maxima at 460 and 370 nm. These two peaks are attributed to silyl radical of localized silyl radical and ordered localized cation radicals [113-117]. The kinetic studies reported lifetime of these radicals to be 4 and 260 $\mu$s, respectively.

4. CHIRAL POLYMERS

The chiral objects are not superimposable on their mirror images. They are enantiomers but not superimposable. Non-superimposability of left and right hand can be easily understood because gloves of the left hand cannot be used for the right hand (Fig. 12). About 97% of molecules of nature are chiral. Chiral molecules exhibit chiroptical properties and can rotate the plane polarized light clockwise or counter clockwise direction. Chiral polymers having asymmetric centers either at the main chains or side chains are optically active [118-125]. Optically active chiral polymers exhibit chiroptical properties i.e., optical rotation and circular dichroism. Optical rotation is observed using polarimeter. Chiroptical properties are investigating using circular dichroism (CD) spectroscopy. It is a spectroscopic technique, which can differentiate in the absorption of Left-Handed Circular (LHC) and Right-Handed Circularly (LHC) polarized light.
CD spectroscopy is extensively used to study chiral molecules and their polymers [126].

Fig. (12). Example of Enantiomers.

Chiral polymers are important polymeric materials, which have various applications in the field of separation of racemic compounds and asymmetric synthesis using catalyst [118]. They are also used in various other applications such as chiroptical switches, molecular switches, motors, and memories, etc. [46, 73, 127].

4.1. Synthesis of Chiral Polymers

The chiral polymers vary in terms of structure, synthetic method, property, and application and a variety of methods have been developed for the synthesis of chiral polymers.

4.1.1. Asymmetric Synthesis Polymerization

Asymmetric synthesis polymerization has attracted much more attention towards optically active polymer and precise control of the stereochemistry [128]. In this synthesis, optically inactive prochiral monomer affords a polymer having chirality in the main chain, due to enantioface selectivity of monomer based on the chiral catalyst. Natta, Farina, et al. (1961) have reported the synthesis of an optically active polymer by the asymmetric polymerization of β-styrylacrylates with a chiral anionic initiating system (Fig. 13) [129].

4.1.2. Enantiomer-Selective Polymerization

The enantiomer-selective polymerization has been achieved by the anionic polymerization of racemic methacrylates. Okamoto Y., et al. have reported that S-isomers were

![Diagrams and formulas related to asymmetric synthesis polymerization.](https://example.com/diagrams)

Fig. (13). Typical Example of asymmetric synthesis polymerization.

![Diagrams and formulas related to enantiomer-selective polymerization.](https://example.com/diagrams)

Fig. (14). (a) Enantiomer-selective polymerization of rac-α-methylbenzylmethacrylate using a cyclohexylmagnesium bromide/(-)-sparteine (b) different Enantioselective monomers.
first polymerized with a very high selectivity during the polymerization of rac-α-methylbenzylmethacrylate using a cyclohexylmagnesium bromide/ (−)-sparteine, as a result, enantiomeric excess (ee) of an optically active polymer 93% was obtained (Fig. 14) [130-134].

4.1.3. Chirality Induction

The chirality induction can be achieved by a reaction of an optically active homopolymer from 1-substituted and (1,1-disubstituted) olefins. In this synthesis, effective chirality regulation in the main chain based on a chiral template induced chirality in optically active homopolymers of styrene [135] and methyl methacrylate [136, 137]. The cyclopolymerylation of asymmetric bis[(4-vinylphenyl)borate] with sugar derivatives induced chirality in main chain through chiral vinyl polymer by the sugar moiety by the polymer precursors (Fig. 15) [138-141].

4.1.4. Chiral Polymer Preparation via Chiral Monomer

The polymerization of chiral moiety containing monomer definitely afford optically active polymer, in which chirality of synthesized polymer depends on their chiral structure and groups [142, 143]. Such type of chiral polymer synthesized by chiral catalyst and chiral separation techniques. Hu Q. S. et al. (1996) [144] have reported synthesis of optically active polyarylene, (R)-3 via sujuki cross coupling reaction of an optically active binaphthyl molecule, (R)-2,2′-bis(hexyloxy)-1,1′-binaphthal6,6′-diboronic acid, (R)-2, using palladium catalyst with 1,4-dibromobenzene. The molecular weight of synthesized polyarylene, (R)-3 $M_w$ 41000 and $M_n$ 20000 (PDI) 2.0 and its specific rotation $[\alpha]_D = -289.4^\circ$ (conc. = 0.5, THF) was observed. The optical absorbance of (R)-3 at $\lambda_{max}$ at 328 nm and $\lambda_{em}$ was observed at 388 and 407 nm in the fluorescence spectrum emit strong blue light in UV lamp. The polyarylene exhibited excellent resistance to oxidation, radiation, and thermal degradation and also used as electrode materials in electrochemical cells and in high energy density rechargeable batteries [145-146]. Itsuno S. (2005) [118] has reported repetitive asymmetric reaction between prochiral monomers using a chiral catalyst. In this reaction, repetitive asymmetric C-C bond forming reactions were performed in the presence of a chiral catalyst which gave optically active polymers and have configurational chirality in their main chain. Novel chiral polymers were prepared via asymmetric polymerization methods based on asymmetric reactions, such as asymmetric addition of allylsilane to aldehyde, asymmetric Diels-Alder reaction, and asymmetric Mukaiya-ma aldol reaction. Asymmetric polymerization is widely used to obtain chiral polymers with main-chain chirality. Iida H, et al. (2011) [147] have reported a chapter on synthesis and application of helical polymers with macromolecular helicity memory. They successfully described different type of optically active polymers with macromolecular helicity memory and applications were found in field of optically active helical polymers and enantioselective polymeric catalysts. Nolte and Okamoto have reported stable helical conformation and successfully synthesized poly(t-butyl isocyanide) into enantiomeric right- and left-handed helices by chiral liquid chromatography Fig. (16) [148]. It is difficult to prove that the optical activities were mainly derived from an excess of a one-handed helical conformation. Other polymerization methods were also reported such as helix-sense-selective polymerization, polymerization of optically active monomers, and memory of helical chirality. Nowacki B, et al. (2013) [149] have reported chiral photonics, which deals with enantioselective polarization control in nonlinear and linear function and also exhibit multiple application like optical signal processing, biosensing, and chiral bioimaging. The chirality was induced into polymeric chain by the helicity chiral monomer into their backbone. The chiral sensitivity could be controlled by solvent, temperature, pH, and solvent vapour [150-152]. The chiroptical properties changed in solid state can be induced by annealing of large macromolecules [153]. Islam M. R, et al. (2014) [154] have reported thiol-ene reaction of dithiol using two equivalents of cinchonidine afforded a thioetherified cinchonidine dimer. For the preparation of quaternary ammonium dimer, cinchonidine dimer was treated with benzyl bromide. Finally, chiral polymer was synthesized by quaternization polymerization using thioetherified cinchonidine dimer and dihalides which forms chiral polymers containing cinchoninium structures in their main chains. The synthesized chiral cinchoninium polymers exhibit excellent catalytic activity for asymmetric alkylation reactions and reused several times without loss of activity.

4.2. Chiral Polysilanes

Chiroptical properties of polysilane aggregates depend on the cosolvent and achiral side chain length [155]. The helical rods like polysilane arrangement on a layer of rubbed polymeid homogenous alignment were observed using Polarized Optical Microscopy (POM) and Atomic Force Microscopy (AFM) analyses [156]. Optical activity can be induced by
conformational or configurational chirality. Most of conformationally induced chirality of polymers in solution is obtained and stabilized by rigid structure [148, 157-159]. The synthesis of polysilanes with a highly optically active chirality control polymers attached as the main chain or side chain is advanced interest [40, 160-162], and of significant importance in a wide variety of functional group having different functional activity [69, 163]. Generally, most of the optically active polysilanes such as poly(alkylarylsilane)s, poly(dialkylsilane)s, and poly(diarylsilane)s were synthesized by the Wurtz coupling reaction using dichlorodimethylsilane with sodium in an inert solvent [164]. Optically active polysilane polymers were polymerized using enantiopure monomers. Helical conformation of optically active polysilanes can be induced by the presence of chiral side chain interactions with the main chain. The chromophore and fluorophore have exhibited intense UV, Circular Dichroism (CD) and Fluorophore (FL) bands in the main chain due to the Si-Si (σ-σ*) transition observed at around 300-400 nm. Optically active polysilanes were found suitable for chirooptical properties for intrinsic nature of a helical conformation itself. CD bands of chiral polysilane are referred to as either positive or negative Cotton effects. In the case of two adjacent chromophores, the coupling between the electronic dipole transition moments gave a bisignate CD signal which is the so-called exciton couplet signal [126, 165-167]. Matyjaszewski, et al. (1992) have reported about optical rotation, CD spectrum and chirooptical properties of optically active poly(dialkylsilane) copolymer of di-n-pentylsilane and di-(S)-2-methylbutylsilane repeating units in solution and in the solid film [168-170]. The helical chirality in a polysilane main chain can be introduced by the proton-metal exchange reaction using alkylolithium/chiral diamine complexes, which can control the conformation of polysilane. The helicity of polysilane can be regulated to a fixed direction, which depends upon the point chirality of the amines [171].
5. ORGANIC-INORGANIC HYBRID POLYMERS

Generally, hybrid materials are a mixture of two or more components, in which mostly half portion is inorganic and other half is organic. These two types of composites are intimately mixed at the nanolevel or molecular level forming the hybrid materials. Schematic representation of hybrid materials are given in Fig. (17) and the related materials were categorized as follows.

i. Composites: These are consisting of the organic matrix polymer in which inorganic particles are dispersed at the micron level.

ii. Nanocomposites: These are the sub-micron level mixture of similar kind of materials.

iii. Hybrids Materials: These are the sub-micron level mixture of different kinds of materials in which one component is organic and other is inorganic.

iv. Nanohybrids are an atomic or molecular level mixture of different materials combined with chemical bonds.

![Fig. (17). Schematic Representations of Hybrid Materials.](image)

Various approaches were used to prepare polymer-based hybrid materials. The most important and applied approach is in situ polymerization of organic polymer in the presence of inorganic unit as shown in Fig. (18). Organic-inorganic hybrid polymeric materials play an important role in the development of advanced functional materials that combine the advantages of organic polymers with inorganic polymers [172-175]. Hybrid polymers were also usually achieved by a different kind of chemical interaction such as van-der-Waals forces, coordinative or covalent bonds and hydrogen bonding between both (organic and inorganic) components [176]. Most of the hybrid materials are silicon-based, in which half portion is inorganic and another half is organic component. The side groups of the polymer control the properties such as solubility and resistance of solvent, nonlinear optical behaviour, and surface properties. Polysilane block copolymers with organic polymers are hybrid materials. They have been prepared by various methods, such as Poly(1,1-dimethyl-2,2-dihexylsilisilene)-b-poly(2-hydroxyethyl methacrylate) (PMHS-b-PHEMA) and Poly(1,1-dimethyl-2,2-dihexylylsilisilene)-b-poly(methacrylic acid) (PMHS-b-PMAA) prepared by anionic polymerization of masked disilenes method [177], such as poly(methylphenylsilane)-co-poly(benzylmethacrylate) (PMPS-PBzMA) were prepared by photopolymerization [52], poly(di-n-hexylsilane) (PDHS) dispersed in zirconia matrix and poly(di-n-hexylsilane)-co-2-(acetoacetoxy)ethylmethacrylate P(HMS-co-AAEM) by sol-gel method [178]. The poly(methylphenylsilane) were used as a macro-photo-initiator for photo-radical polymerization of methacrylates, acrylates and acrylamides to produce polysilane block copolymers [179].

The properties of hybrid polymeric materials are not only the sum of the individual contributions of both molecular phases, but the role of their inner interfaces could be predominant. Functional hybrid organic-inorganic materials have attracted growing interest of chemists, biologists, physicists, and materials scientists for the development of a new type of functional polymeric materials with remarkable resistance to heat and oxidation at high temperature. Organic-inorganic polymeric materials are intensively investigated for their multiple efficient applications such as electrolyte [180, 181], semiconductors [182], catalysts [183], biosensors [184], drug delivery systems [185], coatings for corrosion protection [186], fire retardant polymers [187], adsorbents of toxic compounds [188-196] and materials for telecommunications or information displays [197].

6. AZO POLYMERS

Azo polymers have been widely investigated for their interesting properties, which were arisen due to photoinduced isomerization of the azo (-N=N-) group. These polymers have shown wide applications in the field of optoelectronics and photonics such as in optical information storage, optical switching, diffractive optical element, and liquid crystal display technology [198-200]. Different types of azo-polymers have been described in literature such as polymers contain-
ing azo-dyes, polymers doping with azo-dyes, π-π interaction between polymers and the azo-dyes having a supramolecular system [201-204]. Azo polymers are interesting materials in the photochromic field because of the characteristic of cis-trans photoisomerization (Fig. 19). The novel pendant azobenzene chromophores were found an interesting type of organic materials, they are used in the field of optoelectronic and photonic application [205-210].

**Fig. (19).** Cis-trans photoisomerization of azobenzene chromophore.

Polymers having azobenzene chromophores were most extensively studied for their fundamental and applied research areas [211]. For the simplification of all complicated mechanism, light can be generated in azocompounds by optical anisotropy, due to reversible trans-cis photoisomerization. The cis-trans cycles of the azobenzene chromophore initiated by absorbed polarized laser light [212-214]. Azobenzene-containing chromophore and liquid crystalline polymers have optical and physical applications which are used in photocontrollable materials [215]. The azobenzene groups can be introduced into a polymer backbone or side chain by a different process [216-220]. Azo groups containing polyelectrolytes were used as a partner for the thin film electrostatic deposition of nonlinear optical films for their high optical responsivity, durability, and reversibility of the chromophore [221]. Most of the researchers have studied the dynamics of multilayers growth having thin film anisotropy and optical nonlinearity of azo-dye functionalized by layer-by-layer (LBL) films [222-227]. The azo-benzene chromophore containing block copolymer such as azo block copolymers have been restricted to grafted with di and triblock copolymers [228, 229]. The self-assembled nanostructures with azo-containing block-copolymers are especially attractive for phase segregation materials [230-234], which could be aligned to photoalignment effects [235-238]. The photoalignment of azo chromophores in block copolymers of poly(methylmethacrylate) (PMMA) with methacrylic azo monomer using a mesogen cyano azobenzene chromophores were reported for the synthesis of diblock-copolymers [239-240].

### 6.1. Photoactive Properties

Photoactive polymers have attracted much more attention using azobenzene chromophore for their potential application for optical and photonic device [241-247]. The photoisomerization of azobenzene chromophore exhibits cis-trans isomerization which exploited properties compared to other chromophores. A drastic change was observed in the shape of the molecule when switched between the stretched trans and contracted cis conformations. The photoactive property of azobenzene chromophore is an exploited area in diverse structures such as proteins [248], sol-gel materials [249], micelles [250] and dendrimers [251]. The photoactive azobenzenes chromophores have been covalently attached with the matrix, which remove the disadvantages of guest-host type systems.

### 7. FUNCTIONAL POLYSILANES

The properties of polysilane are extremely sensitive towards their attached substituents such as heteroatom attached to the silicon backbone. In this regards, functionalization of polysilanes became quite interesting with functional substituents and the substitution reaction of polysilane was found a powerful method for functionalization of polysilane. The synthesis of functional polysilanes is still the challenge for synthetic chemists in order to obtain new functional and multifunctional materials having special properties and multifunctional activity to support the current demand of new technological materials [252]. The direct synthesis of functional polysilanes with functional groups such as trimethylsilyl, dimethylamino, aryloxy group, and others has been restricted due to drastic reaction condition of high temperature reflowing of organodichlorosilane monomers along with sodium metal in toluene in the well known Wurtz coupling reaction [253, 254].

West, R. (1986) has reported that the chlorine-substituted polysilanes can be obtained using HCl and aluminium chloride, but practically in method polysilane also degraded [22]. Generally, chloromethylation is a post-functionalization process. The Friedel-Craft chloromethylation of aryl-containing polysilane by using chloromethylmethylether with stannic chloride as a catalyst was reported by Ban, H, et al. (1987) [216].

Kminek, I, et al. (1991) have reported that Poly(methylphenylsilane) (PMPSi) has been partly chloromethylated and formylated via the pyridinium salt and nitron (Kroehnke transformation) and aldehyde groups converted by condensation with aniline, 4-aminooazobenzene and 4-nitroaniline using Schiff bases [255]. All substituted polysilanes were found much less photolabile than the original PMPSi and the partly with chloromethylated PMPSi. Emission studies of PMPSi revealed that the fluorescence properties are strongly quenched by the attached chromophores [255].

Jones, R.G. et al. (1995) have reported that the chloromethylation of poly(methylsilane) can be achieved using chloromethylmethylether in a tin (IV) catalyst at 0°C in chloroform solution. The reaction of the chlorine substituted polysilanes with hydroxy-containing chromophores was performed in the presence of triethylamine as an acid acceptor in THF. A post-functionalization strategy was also adopted to obtain polysilanes with the different functional group reported in the literature [256].

Zhang, Y. (1996), Peng, Z. (1994), Peng, Z. (1996) et al. have shown great interest in functional polysilanes, that was attached with NLO chromophores as a pendant group for the origin of functional polysilanes photorefractive effect [257-259]. The photorefractive effect has major applications in the
field of optical image processing, high-density optical data storage, dynamic holography, phase conjugated mirrors and lasers, pattern recognition, optical computing, etc. The significant developments have been made in the field of photo-refractive polymers and composite materials in the last few years [257-259]. It is well known that photo-refractive materials are multifunctional materials which combine the Electro-Optic (EO) effect and produced photoconductivity. Herjog, U, et al. (1997) have reported that the methyl phenyl substituted oligosilanes were synthesized using oligosilanes like, disilanes SiX₂-SiXMe₂-i (i = 0, 1, 2; X=C₁, Br), trisilanes SiX₃(SiXMe₂-i) (i = 0, 1) and branched tetrasilanes SiX(SiXMe₂-i) and their behavior towards the Lewis-base catalyst in which hydrogenation is completed by stannanes [260]. In this study, methylchlorodisilanes SiCl₂-SiClMe₂-i Si-Si bond cleavage competes with the hydrogenation reaction [260].

Herzog U, et al. (1999) have also reported the preparation of Si-Cl substituted polysilane without the change in its molecular weights, substituted polysilane were further synthesized with hetero substituted like lower alcohol or mercaptans [261]. The polysilane reaction with amines gave polymers having ammonium substituent to prepare Langmuir Blodgett (LB) films. Polysilane block copolymers have been prepared by anionic polymerization. Cationic polymerization of vinyl ether opened a new way of generating an interpenetrating structure with the prospect of improving materials properties. The photochemical initiation efficiency of the allylic type onium salt in conjugation with poly(methylphenylsilane) (PMPS) was used as a radical source for the cationic polymerization of appropriate monomers.

Tang H, et al. (2001) has reported multifunctional polysilanes, synthesized via Si-Cl containing intermediate by Friedel-Craft reaction [262].

Extensive literature is available on functionalization of polysilanes. However, the methods reported in Journal of Organometallic Chemistry (2003) make a sense as it has completed a half century. Few details are described below.

Fujiki M. (2003) have reported switching handedness in optically active polysilanes of Si-Si single bond due to chiral or achiral side groups. They exhibit circular dichroism, and at around 300-400 nm due to the σ-conjugation [263]. They included various optically fluorescence spectra active homo-polymers and copolymers such as of poly(dialkylsilane), poly(dialkoxysilane), poly[alkyl(aryl)silane], and poly(diarylsilane). They focused switching handedness of optically active polydiaryl silane which among all optically active polysilane and also studied chiroptical properties, Kuhn dis-symmetry ratio, chiroptical switch and memory, and capability of screw-sense inversion, and external stimuli [263].

Oh H.S. et al. (2003) have reported novel synthesis of naphthylphenyl-substituted optically active oligosilanes and their chiroptical properties of α,ω-chiral silicon centers. The configuration of (1R, 2R)-1, 2-dimethyl-1, 2-di(1-naphthyl)-1,2-diphenylsiloxane (R, R)-3, was determined by X-ray diffraction, which gave direct proof for retention and inversion of attacking silylation and attacked chlorosilane [264]. The absolute configuration and conformation of optically active oligosilanes were possible due to intense π-π interaction of aryl substituted chiral silicon centre enhanced σ-π conjugation with oligosilanes [264].

Motonaga M. et al. (2003) have reported first optically active polygermanes which have screw sense helicity due to enantiopure chiral-substituents of aryl groups and comparative study with derivatives of polysilanes. They studied circular dichroism (CD) and ultraviolet (UV) spectroscopy of meta and para (chiral substituted) poly[methyl[(S)-2-methybutylphenyl]germane]s exhibited induced sense helical conformations and Kuhn dis-symmetry ratio (gabs = Δε/ε) at -70°C were evaluated as -0.34 x 10⁻⁴ for (meta) and -0.38 x 10⁻⁴ for (para) substituted polymers. The polysilane derivatives have gaps, values of -0.76 x 10⁻⁴ and -0.8 x 10⁻⁴, which indicate greater screw sense selectivity than polygermanes shown in Fig. (20) [265].

Sanji T. et al. (2003) have reported functional transformation of poly(dialkylaminotrimehtyldisilene) synthesized by anionic polymerization masked disilenes [266]. The amino substituted polysilanes Si-N bond of poly[1,1,2-trimethyl-2-(dibutylamino)disilene] yielded chloro-substituted polysilanes. The substitution reaction can be performed by some nucleophiles such as hydrides, Grignard reagents, organolithium reagents, and alcohols for the preparation of new type of polygermanes [266].

Uhlig W. (2003) has reported tailor-made synthesis of functional oligo- and polysilanes substituent from silyl triflates and (aminosilyl)lithium compounds. The diethylamino substituted silyllithium compounds synthesized in-situ from phenylchlorosilane and lithium. The reagents triflate derivatives of silanes and oligosilanes undergo coupling reaction [267]. The bond cleavage of Si-Si and exchange derivatives of metal-halogen exchange, in which side reaction of chlorosilane was not observed. The synthesis of functionalized tri-, tetra-, penta- and hexasilanes was performed by the coupling reaction of amino-to-triflate transformation. The synthesized compounds are useful building blocks for new organosilicon polymers [267].

Kim B.H. et al. (2003) have reported one-pot synthesis of poly(alkoxysilanes) by dehydrocoupling reactions (Si-Si and Si-O) of silanes (PhCH₂SiH₃, and (PhSiH₂)₂) with alcohols (MeOH, EtOH, iPrOH, PhOH, and CF₃(CH₂)₂CH₂OH) were catalyzed by Cp₃MCl/Red-Al (M=Ti, Zr) and Cp₂M’ (M’ = Co, Ni). The phenylsilane with ethanol (1:1.5 mole ratio) using Cp₃HfCl₃/Red-Al and phenylsilane with ethanol (1:3 mole ratio) using Cp₂TiCl₃/Red-Al gave only triethoxyphenylsilane as a product as shown in Fig. (21) [268].

Rosenberg L. and Kubos D.N. (2003) have reported synthesis of primary alkyl silanes (R₃SiH), where R=n-C₁₂H₂₅ or n-C₆H₁₃) undergo dehydrogenative coupling in the presence of (P₅H₃)RhCl (1) to give oligomeric silicone. In this synthesis 5-6 silicon atoms are attached to each other, it was confirmed by ²⁹Si and gel permeation chromatography (GPC) [269].

Watanabe A. (2003) has reported polysilanes optical properties with various silicon backbones, branched poly-
silanes such as network polysilanes (polysilylene), polysilane dendrimer, and organosilicon nanocluster (OSI) etc. The branched polysilanes have higher dimensionality in comparison to linear polysilanes. The optical properties of polysilanes are influenced by the structure of silicon backbone [270]. The emission spectra of branched polysilanes were exhibit dual in UV and Vis region due to large stock shift between absorption and emission spectra [270].

Wakahara T, et al. (2003) have reported the reaction of fullerenes (C60 and C70) with active species in photolysis of disilane and polysilanes. The synthesized attractive materials has simplified the chemical and electronic properties of fullerenes. The recent advances in the chemistry of mono- and bis-silylation of fullerenes with silylene and silyl radical is to afford the corresponding new fullerene-based organosilicon materials. This is a new route for the synthesis of fullerene derivatives [271].

Villegas A, et al. (2003) have reported photo polymerization reaction of poly(ferrocenylmethylsilane-co-phenylmethyilsilane), [(FcMeSi)(PhMeSi)n]m, (Fc-ferrocenyl- (η⁵-C₅H₅)Fe(η²-C₂H₄)) in solution via coupled gel permeation chromatography/light scattering method. The presence of the ferrocenyl substituent indicated that photo-scission of Si-Si bonds occurred at the polymer chain termini. The process has been monitored in terms of changes in the percent of initial mass and after scission of Si-Si bonds [272].

Sacarescu G, et al. (2003) have reported polycodensation reaction of α,ω-bis(chloromethyl)-polymethylphenylsilane with the Ni(II) complex of bis(salicylidene)ethylendiamine (salen). This is a new method for chloromethylolation of polysilanes and was obtained through a modified Wurtz coupling technique in THF solvent as shown in Scheme 7 [273]. ¹H-NMR of chloromethyl-polysilane showed the characteristic peak at δ-/2.93 ppm due to -CH₂-Cl group in (Fig. 22) [273].
Hatanoaka Y. (2003) has reported synthesis, structures, and electronic properties of polysilanes which have hypervalent silicon moieties, polar substituents, or transition metal moieties. They exhibit unusual spectral properties of UV-visible spectra of polysilanes substituted with (alkoxycarbonyl)methyl groups at around 400 nm with temperature and solvent effects [274].

Matsuura Y, et al. (2003) have reported polysilane-titania hybrid thin films by sol-gel method of titanium alkoxides with poly(methylphenylsilane)/3-methacyryloxypropyltriethoxysilane block copolymer (P(MPS-co-MPTES)) as shown in Scheme 8 [275]. In this method, polysilane block copolymer was bonded to titania component via Si-O-Ti by the hydrolysis/condensation of P(MPS-co-MPTES) and Ti(O-n-C4H9)4. As a result, polysilanes dispersion in titania components (10 nm) was observed by Atomic Force Microscopy (AFM) as shown in Fig. (23) [275].

Kamata N, et al. (2003) have reported a mini review for the observation of an efficient energy transfer between polydihexylsilane and polydiphenylsilane. The soluble polysilanes synthesized were enabled to prepare such type of thin films via spin coating techniques. The conductive poly(m-hexoxyphenyl)phenylsilane was utilized for Electroluminescence (EL) of coumarin 6 (green), perylene (blue), Zinc tetra-phenylporphyrin (red), and 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran [276]. The white Electroluminescence (EL) property was also observed for four molecules of dye after mixing. The synthesized water-soluble polysilanes suppressed the ultraviolet light by

![Diagram](image-url)
photo-oxidation and it was also embedded sol-gel glass matrices. As a result, polysilanes have the possibility of new optical applications. The polysilanes trans conformations correspond to a unit along <110> direction in the crystalline silicon as shown in Fig. (24) [276]. One dimensional polysilane configuration gave direct energy band structure and excitonic Photoluminescence (PL).

A novel functional polysilane was synthesized using a high content of hydroxy containing chromophore as side chains by the replacement of chlorine substituents. J. Li, et al. (2003) have reported mainly synthesis and characterization of polysilane functionalized by NLO chromophore in side chain by below-mentioned synthesis routes such as Friedel-Craft reaction, Hydrosilylation, chlorine substituted polysilane, Wurtz coupling reaction [252].

**Method 1:** Ban, H, et al. (1987) have reported chemical modification of aryl containing polysilane via Friedel-Craft chloromethylation using chloromethylmethylether with stannic chloride catalyst as shown in Scheme 9 [216]. It is notable that chlorine substituted polysilane is a good intermediate for further polymerization, because chloromethyl group are very much reactive and gives fast nucleophilic displacement reaction under mild condition of temperature and pressure [216].

**Method 2:** West, R. (1986), Hasiao, Y.L. (1994), et al. have reported hydrosilylation reaction of polysilane with NLO chromophores. Such synthesized compounds are useful for preparation of functionalized polysiloxanes. Other researchers have also used the same method of synthesis by using different catalyst such as platinum [217] and H2PtCl6 [218]. Li, J. et al. (2003) have also used a similar method of synthesis by using NLO group with polysilane, overall yield was observed approximately 16% as shown in Scheme 10 [217]. Hydrosilylation of poly(phenylhydrosilane) was reported with nonlinear optical chromophore using platinum-transition metal complexes to obtain functional polysilane [219].

**Method 3:** Herzog, U. and West, R. (1997) have reported functionalization of polysilane via chloride substituted polysilane with acetyl chloride/aluminium chloride resulted intermediate chlorine substituted polysilane [217]. In reported process, Si-Ph bond is much more reactive towards acetyl chloride than Si-Me bonds [220]. The reaction intermediate is air sensitive so they were directly used for further functionalization without purification and characterization. In this process, hydroxyl containing chromophores were used in the presence of triethylamine as acid acceptor in THF solvent as shown in Scheme 11. The synthesized reaction product was precipitated in methanol and recovered after filtration and drying [218].

**Method 4:** Li, J, et al. (2003) have reported polysilane containing 3-(N-ethyl, N-phenyl)aminopropyl group which was synthesized by Wurtz coupling reaction and further functionalization with NLO chromophore with P-nitrobenzenediazonium fluoroborate as a azo coupling agents (Scheme 12) [252, 270]. The polysilane containing 3-(N-ethyl, N-phenyl) aminopropyl was also post functionalized by tricyanovinylation with tetracyanoethylene (TCNE) oxidant [252].
Sanji, T, et al. (2004) have reported that the polysilanes bearing an optically active terminal (-)-methoxy groups were synthesized by the anionic polymerization of masked disilene, which adopted a preferential helical-sense conformation in the solid state at room temperature and also in solution at low temperature [277].

Matsuura, Y, et al. (2004) have reported the synthesis of a block copolymer of poly(methylphenylsilane) (PMPS) and 2-(methythio) ethyl methacrylate (MTEM), P(MPS-co-MTEM), by photpolymerization. In this synthesis PMPS was used as a macrophotoinitiator and the prepared a bilayer structure of P(MPS-co-MTEM)/Au in which the copolymer adsorbed on gold layer [179].

Sacarescu, L. et al. (2007) have reported the synthesis and characterization of new polysilanes with functional pendant metal complex and their applications in organic electro-conductive devices [278].
Shankar, R, et al. (2008) have reported the synthesis and characterization of functional polysilanes \([RMe_2Si(CH_2)_x\phantom{\text{Si}}R'^{\text{Si}}]_n\phantom{\text{Si}}(R=2-Fu, 5-Me-2-Fu, 2-Th, 4-Me-2-Th; x = 2, 3)\) with functional furyl/thienyl groups on the carbosilyl side chains and its application in field of generation and stabilization of palladium nanoparticles. The chemical reactivity of polysilane 2 \((2-C_4H_3O)Me_2Si(CH_2)_3SiMe\phantom{\text{Si}}R'^{\text{Si}}]_n\phantom{\text{Si}}(R=2-Fu, x=3)\) toward palladium acetate group was explored [279]. However, they have also reported the reduced catenated silicon backbone and explained the role of furyl substituents for the stabilization of generated palladium nanoparticle [279].

Kim, M.H, et al. (2010) have reported hydroxilolation reaction of Si-H group with different polysilanes by dehydrocoupling of organometallic promoters. The catalytic activity of Si-Si/Si-O coupling of hydrosilanes with alcohols, and lactones were also studied for the preparation of silicon based polymers and this synthesized material can be used in fabricating electronic devices [280].

Ishifune, M, (2012) have reported electroreductive synthesis of polysilanes having a variety of hydroxyl functional groups. The electroreduction polymerization of reaction mixture 3a and 3d-g with Mg electrode afforded the corresponding copolymers 16 (16 (d), (e), (f), (g), Scheme 13) [281].

Shankar, R, et al. (2012) have reported that Wurtz coupling and catalytic dehydrocoupling methods for the synthesis of functional polysilanes like \[RR'Si\]n (linear), \[(PhMe-Si)_x-co-(RSi)_y\]n (branched) and \[RSi\]n (network) \([R = Et_3SiCH_2CH_2, 2-Fu/2-ThMe_2SiCH_2CH_2 (Fu = Furyl, Th = Thienyl), n-Hex or Ph; R' = H or Me]\) [301]. Further, by the \(\sigma\)-delocalization of silicon backbone polymer and HOMO-LUMO band gap energy variables were found a promising candidate of reducing agent for Ag(I) in toluene and cyclohexane [282]. This method was simply used for size controlled silver nanoparticles and also in fluorescent polymer silver nanocomposite [282].

Simionescu, M, et al. (2012) have reported the synthesis of functional polysilanes via microwave assisted chemistry in which Si-H groups of polyhydrosilanes allows obtaining a different functional polysilane structure with various functionalities by catalytic addition of unsaturated compounds as shown in Scheme 14 [283]. Comparative study of micro-wave assisted functional polysilanes demonstrates advantages of milder reaction conditions, shorter reaction times, better reaction yields, and better protection of polysilane chemical structure.

Lee, P.T.K, et al. (2013) have reported that dehydrocoupling and hydrosilation reactions of poly(phenylsilane), in which Si-H bonds is catalyzed by B(C_6F_5)_3 catalyst for the preparation of new polymers containing both Si-H and Si-SR functional groups as a side chains [284]. This is the post-polymerization modification of polysilanes which takes place without any other Lewis acid, transition metal, or radical mediated routes for the observation to compete Si-Si bond cleavage [284].

Shankar, R, et al. (2013) have further reported the synthesis of functional polysilanes with the relevance of Au and Au-Pd nanoparticle assemblies and studied the role of polymer supported by thioether side chains [285], where they have described the role of thioether groups in polysilane support. This was the first report on ensembles of AuNPs structures. This method is found very interesting as it proceeds \(\text{via}\) a one-pot reaction between the gold precursor, HAuCl_4-3H_2O and the polymer without an external reducing agent [285]. Whereas the developed waterborne polysilane photoinitiator reported by Liang, Q, et al. (2015) finds the interesting type of environmental friendly photopolymerization applications [286]. The polysilane-co-poly(polyethylene glycol acrylate) was synthesized by the UV-irradiation of water-soluble polysilane photoinitiator in which photodecomposition of poly(methylphenylsilane) takes place in the presence of acrylate functionalized polyethylene glycol [286].

Ekhorutomwen, S.A, et al. (2015) have reported the synthesis of hydro polysilane copolymers by the Wurtz-type reductive coupling of mono and diorganodichlorosilane comonomers in a refluxing toluene medium with sodium dispersion [284]. For the improvement of photosensitivity of hydro polysilane copolymers, post-synthetic modifications were carried out by the substitution of electron withdrawing groups such as acetate (from mercuric acetate), p-nitrophenol, p-cyanophenol, and p-chloroanmonic acid [287].
Meenu, et al. (2016) have reported that chiral block functional polysilanes were synthesized by UV irradiation of poly(methylphenylsilane) (PMPS) with a vinyl chiral monomer, (R)-N-(1-phenylethyl)methacrylamide (R-NPEMAM). Such synthesized functional polysilane polymers have tunable chirality which may find potential application in the field of optoelectronics [76]. Same group of authors have also reported, in 2017, the synthesis of functional photoactive organic-inorganic block copolymers of poly(methylphenylsilane) (PMPS) and disperse red 1 methacrylate (DR1MA) were synthesized in a quartz tube using UV-technique. Such type of synthesized copolymers were found thermally stable up to 260°C and find novel optoelectronic application [78].

Lee, P.T.K. et al. (2017) have reported postpolymerization of poly(phenylsilane) Si-H group using borane catalyst. In this reaction, B(C₆F₅)₃-catalysed heterodehydrocoupling, hydrosilylation, and demethanative coupling reactions in poly(phenylsilanes) of Si-H group which induced 10-40% side chain in this polymer [288]. The synthesized polymer contains a wide variety of functionalities like Si-C, Si-N, Si-S, Si-O bonds, which are confirmed by NMR and FTIR spectroscopies. UV-vis spectroscopy is sensitive towards the new functional groups [288].

Okamura, H. et al. (2017) have reported the fabrication of photocrosslinked polymerization of polysilanes blends with diarylfluorene epoxy and oxetane moieties in the presence of a photoacid generator by UV irradiation (405 nm). The photodecomposition of Si-Si bonds of polysilanes was suppressed by the UV-vis irradiation [289]. The prepared blends cationic photocrosslinking properties were affected by the post-exposure-bake conditions and irradiation dose. The polysilanes unit was incorporated into films by the terminal OH groups [289].

Nakagawa, J. et al. (2017) have reported that spin-coated polysilane thin films can be modified with n-type and p-type semiconductors. The microstructures of dimethyl-polysilane (DMPS), deca(phenylpenta)silane (DPPS), and poly(methylphenyl)silane (PMPS) thin films were studied by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The doping of PMPS thin films with (P) became amorphous after annealing at 300°C, but DMPS, and DPPS thin films doping with (P) exhibited crystalline structures [290]. PMPS and DMPS thin films showed decreased electrical resistances doping with (P). The energy band gaps were observed 3.9, 3.8, and 3.5 eV for DMPS (P), DPPS (P), and PMPS (P) respectively. Photoluminescence properties also decreased after doping with (P) [290].

Sanji, T. (2018) has reported a book chapter of materials containing homocatenated Polysilanes. In this chapter, they described a unique ability of homocatenated polysilanes such as long linear stable chain formation similar to carbon. Polysilane composed of Si-Si bond with σ-conjugation in their backbone results in HOMO-LUMO band gap at about 3-4 eV having a unique photo and electronic properties. The polysilanes also exhibit chromism in electronic spectra of temperature dependent conformation [291].

Folster, C.P. et al. (2018) have reported dehydrocoupling polymerization of Poly(cyclosilanes), with metalloocene, (Ti, Zr, or Hf) dichloride (C₉₂ZrCl₂) and butyllithium (n-BuLi), to initiate stepgrowth polymerization. In this method, poly(cyclosilane) backbone was capped with SiMe and SiH groups, although end group polymers (Si₃SiH₃) are secondary silanes. The synthesized novel conjugated inorganic polymers were sensitive towards the optical properties of structural perturbations [292].

Miyamura, H. et al. (2018) have reported hydrogenation of arenes, which is an important reaction for the synthesis of functional polysilanes not only useful for hydrogen storage and transport but also pharmaceuticals and biologically active compounds. In this study, heterogeneous Rh-Pt bimetallic nanoparticle was used as catalysts for the hydrogenation of arenes with low-cost polysilane [293]. The catalytic performance was strongly durable in flow system, that was demonstrated (>50 days continuous run; turnover number >10⁸).

7.1. Defence Application

Functional optically active polysilane having good optical and chiroptical properties finds application in an electronic device, an optoelectronic device, light switches, and
optical storage devices. Functional photoactive polysilane exhibited optical and photoluminescence properties and its application in the field of optoelectronic and photonics such as optical waveguide, friend and foe identification, secretive code identification (Fig. 25), variable UV-light sensors, situational awareness and thermal sensors find a place in defense applications.

CONCLUSION

The aim of this review article is to evaluate novel functional and/or multifunctional optically active and photoactive polymers and copolymers for potential optoelectronics application. Although polysilanes is a class of inorganic polymers having potential optoelectronics properties, yet they have their own limitations to obtain the functional polysilanes (having attractive derived properties) because of the drastic reaction condition for their synthesis. Under the drastic conditions, no functional groups sustain. Hence, it is a major challenge for chemists to synthesize polysilanes having various effective functional groups along with integrated molecular structure. On the other hand, chiral and azopolymers are two classes of optically active and photoactive polymers, which may provide good optically active and optoelectronic properties. In addition to above, organic-inorganic hybrid materials are the recent attraction of materials scientists to achieve combined properties as well as novel functionality and thermal stability. In this review article, we have summarized various functional polysilane materials which may have novel functional properties having optically activity, photoactive and nonlinear optical properties. Functional optically active polysilanes showed good optical and chiroptical properties as an electronic device, an optoelectronic device, light switches, and optical storage devices. Functional photoactive polysilane exhibited optical and photoluminescence properties and its application in the field of optoelectronic and photonics such as optical waveguide, friend and foe identification, secretive code identification, variable UV-light sensors, situational awareness and thermal sensors in defense applications. Although extensive researches have been carried out by various groups of scientists, stillmore intensive research needs to be done in this area.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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