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Synthesis and Characterization of Multifunctional Chiral and Photoactive Organic-Inorganic Block Copolymers of Poly(methylphenylsilane) with (R)-N-(1-phenylethyl)methacrylamide, Disperse Red 1 Methacrylate and Their optical and Photophysical Properties

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Abstract: Generally, polysilane synthesized by Wurtz coupling reaction in drastic reaction condition, in such condition, no functional group sustain. In our investigation, multifunctional polymers of poly(methylphenylsilane) (PMPS) with (R)-N-(1-phenylethyl)methacrylamide (R-NPEMAM) and disperse red 1 methacrylate (DR1MA) were synthesized in a quartz tube using UV-technique. This technique consumes less time and is easy to handle. The molecular weights of such synthesized polymers were of the order 10^3 . The optical absorbance was observed at 272 nm, 330 nm and 475 nm due to π - π^* , σ - σ^* and n - π^* with π - π^* transition respectively. The circular dichroism observed at 261 nm due to the chiral unit present in the polymeric chain. They also exhibited induced chirality at 330 nm and 470 nm due to associated with the Si-Si chain of PMPS and azobenzene chromophore of DR1MA unit, respectively. The Photoemissions (λ_{em}) were observed at 307 nm and 415 nm when excited at 275 nm and λ_{em} at 415 nm when excited by 325 nm. The multiemission spectra were observed at 500 nm, 550 nm and 590 nm when excited by 475 nm which may be due to exciton coupling between azobenzene chromophore and Si-Si σ -conjugation. Such multifunctional polysilanes may find novel chiroptical and optoelectronic application.

Keywords: Multifunctional polymeric materials; polysilanes; chiral polymers; photoactive polymers.

1. Introduction

Now-a-days, technological thrust area addresses the development of multifunctional materials to fulfill the multi-mission objectives by a single material [1-2]. Thus the developed multifunctional materials signify to embed multiple functional properties a single polymer material. This could be made possible with designing of materials where the single structures have different functional groups, and/or in the form of organic-inorganic hybrid of several distinct material phases in which each phase performs different necessary function [3]. The synthesis of new multifunctional materials having extraordinary and multifunctional, activity to support the current demand of technological materials is a challenging task.

Polysilanes consist of silicon backbone with organic substituents, which can exhibit

absorption, solvatochromism, thermochromism, electroluminescence etc. [4-6]. These properties of polysilane have attracted broad attention in academia and industry because of the delocalization of σ -electron along with the Si-Si chain. The functional materials used in field of semiconductors, precursor for Si-C synthesis, radical photoinitiator and sensors [7]. The direct synthesis of functional polysilanes restricted due to drastic reaction condition (high temperature refluxing of organodichlorosilane monomer along with sodium in toluene) of their synthesis via Wurtz coupling reaction [8-10]. At this refluxing temperature no functional groups sustain with polysilanes. However, functional polysilanes with special functional properties have attracted much more attention to the materials scientists. Hence various routes attempts for the synthesis of functional polysilanes [11]. The post functionalization of polymers is also an alternative way to introduce new functional groups into synthesized polysilanes [11-18]. Hydrosilylation reaction verified as an important approach for obtaining functional polysiloxane and the synthesis of functional polysilane [12]. Multihydroxy functional polysilane copolymer synthesized via acetal protecting group strategy [19]. The multifunctional polysilane synthesized by formation of Si-Cl intermediate and the substitution of Cl with hydroxy containing functional NLO chromophore [20]. We have reported functional polysilanes with optically active vinyl monomer, (R)-N-(1-phenylethyl) methacrylamide (R-NPEMAM) [21] and functional polysilanes with disperse red 1 methacrylate (DR1MA) [22] synthesized by UV-technique.

In this investigation, multifunctional polysilanes were synthesized by UV irradiation on poly(methylphenylsilane) (PMPS) along with two functional vinyl monomers which are optical active and photoactive. This technique is easy to handle and completes only in 5 min. In this synthesis, PMPS gives rise to silyl radicals upon UV-irradiation (for 5 min., Fusion by UV-curing Systems, 10 inch Fusion UV Electrodeless D-bulb, Wavelength=350-400 nm). which initiates the photopolymerization reaction of these functional vinyl monomers such as (R)-N-(1-phenylethyl) methacrylamide (R-NPEMAM) and disperse red 1 methacrylate (DR1MA) respectively. Thus multifunctional a PMPS-block-copolymer (SCDRDM) consists of PMPS block along with another block of a random copolymer of optically active and photoactive units of DR1MA. The synthesized multifunctional polysilanes were characterized by FTIR and NMR analyses. The molecular weights of the synthesized functional polysilanes were measured by GPC analysis. The optical, chiroptical and photoluminescence properties of synthesized materials were studied.

2. Materials and Methods

Dichloromethylphenylsilane (97%, Sigma Aldrich, USA), sodium metal, THF (Aldrich, USA), n-hexane (Samir Tech Chem. Pvt. Ltd., India), methanol (SDFCL), dichloromethane and acetone (SRL) were used as received. Poly(methylphenylsilane) (PMPS) was synthesized by condensation reaction of dichloromethylphenylsilane with sodium metal dispersion in boiling toluene [23]. (R)-N-(1-phenylethyl) methacrylamide (R-NPEMAM) was synthesized by condensation reaction of methacryloyl chloride and (R)-N-(1-phenylethyl) amine as per the reported procedure [24]. It was further purified by crystallization from ethanol and water (1:1) mixture. The monomer appeared as white crystalline form. Disperse red 1 methacrylate (DR1MA) (95%, Sigma Aldrich, USA) was purified by crystallization from acetone/ petroleum ether (bp = 60-90°C) dried and stored at room temperature. Its appearance is red in color [25]. Tetrahydrofuran (THF) purification was mentioned in my published paper [22]. The purified THF was distilled and used immediately.

2.3. Synthesis of Multifunctional Polysilane Containing Optically Active and Photoactive Moieties

Poly(methylphenylsilane) (PMPS) was used as a macrophotoinitiator which initiated the radical polymerization of optically and photoactive vinyl monomers. In this photopolymerization reaction, PMPS (1.0g), R-NPEMAM (0.189g) and DR1MA (0.382g) were dissolved in 10 ml purified THF in a quartz tube and N₂ gas was flushed into it for 5 minute. Then reactant mixture was sufficiently

degassed using a vacuum pump and freeze thaw method. After sealing the tube under reduced pressure, photopolymerization was carried out by exposing it under UV light for 4 minute. (Fusion UV-curing Systems, 10 inch Fusion UV Electrodeless D-bulb, Wavelength=350-400 nm). After UV-exposure, the reaction mixture was kept as such for 24 hrs. The reaction mixture was then precipitated in hexane and initially dark orange colour was appeared. Now solvents (hexane and THF) were evaporated. The solid mass was dissolved in acetone and precipitated in methanol. Orange precipitates were observed that was purified by washing through methanol several times during the filtration. It is well known that DR1MA and R-N-PEMAM are dissolved in acetone. So this precipitate must be the synthesized functional polymer and block copolymer of PMPS and dispersed 1-methacrylate and (R)-N-(1-phenylethyl)methacrylamide (SCDRDM). It was dried under vacuum at 50°C (Scheme-1). The synthesized sample is SCDRDM-1B. Similarly, other functional polysilanes were synthesized having other composition of reactant ratios: PMPS/DR1MA/R-NPEMAM=1.00g/0.378g/0.764g and 1.00g/0.668g/1.026g respectively. The synthesized materials are designated as SCDRDM-1B, SCDRDM-2B and SCDRDM-3B. The yield of the synthesized materials was 30-35%.

2.4 Characterization

The synthesized multifunctional polysilanes (SCDRDM) were characterized by FTIR and NMR spectroscopy. FTIR spectra of the samples were measured with KBr Pallet on a Perkin Elmer FTIR Spectrum 100. The ^1H NMR measurements were carried out on a Bruker DRX-300 MHz FT NMR spectrometer in CDCl_3 solvent using TMS as the internal reference. The UV-vis spectra were recorded on an instrument from Analytek Jena Specord 200 PLUS spectrophotometer in THF solution of the samples. The UV-vis spectra were also taken with variation of temperature from 10°C to 60°C. The molecular weights of the synthesized multifunctional polysilanes (SCDRDM) were measured by using high temperature gel permeation chromatography (GPC) (ViscoTek, Malvern, model US make). DSC analysis was carried out using a DSC Q200 (TA Instrument) at a heating rate of 10°C/min under N_2 atmosphere. The photoluminescence properties were studied for the synthesized multifunctional polysilanes in their THF solutions with F-2500 FL Spectrophotometer (Hitachi). The circular dichroism (CD) of the synthesized polymer was measured on a JASCO J-810L CD spectropolarimeter.

3. Results and Discussion

3.1 Solubility of Synthesized Multifunctional Polysilanes

The synthesized multifunctional polysilanes were soluble in THF, chloroform, toluene and dichloromethane (DCM) but were insoluble in dimethylsulphoxide (DMSO), di-ethylether, acetone, petroleum ether, methanol and hexane.

3.2 FTIR Analysis

FTIR spectra of SCDRDM samples are shown in Figure 1. A wide absorption peak at 3444 cm^{-1} to 3432 cm^{-1} are the characteristic of NH trans stretching vibration of secondary amide group of chiral mer unit. The narrow band at about 1638 cm^{-1} is due to C=O stretching vibration of -CONH- of the chiral monomer. On the other hand, the C=O of ester group of DR1MA is appeared at 1725 cm^{-1} in above series. The asymmetric stretching of NO_2 group is appeared at about 1481 cm^{-1} , whereas the symmetric stretching of the group is appeared at 1386 cm^{-1} . The characteristic azo (-N=N-) stretching is observed at 1427 cm^{-1} . The other characteristic peak at 1261 cm^{-1} is appeared due to O-CO of the ester group of DR1MA. The CONHR is appeared at 1527 cm^{-1} , but it is not observed as it is merged with C=O (amide) stretching vibration at 1654 cm^{-1} . The Si-Si bond of PMPS block is appeared at 462 cm^{-1} in all the synthesized samples. The peak appeared at around 1261 cm^{-1} is due to Si- CH_3 group. The Si- CH_3 wagging vibration is appeared at about 872 cm^{-1} for all the copolymers. The high intense peak appeared at 731 cm^{-1} is due to aromatic C-H out of plane bending. The peak appeared at 1021-

1100 cm^{-1} is due to C-H bending in plane. The C-H stretching of methyl group and the alkyl chain ($-\text{CH}_2-$) all appeared at 2852-2960 cm^{-1} . The C-H out of plane bending of aromatic near NO_2 resonated around at 876 cm^{-1} . On the other hand, the characterizing stretching frequency of double bond of vinyl ($\text{C}=\text{C}$) around 1614 cm^{-1} and the absorption band at 928 cm^{-1} due to the C-H bending of vinyl group ($=\text{CH}_2$) were absent in the spectra. So it clearly indicated the formation of polymer by photoinitiated radical polymerization.

3.3 NMR Analysis

The ^1H NMR spectrum of a multifunctional polysilane copolymer (SCDRDM-2B) is shown in Figure 2. The peak appeared at 1.4 ppm as a doublet is due to CH_3 of CH_3-CH group present in chiral unit and also present in photoactive unit. The peak appeared at 0.1 to -0.9 ppm is due to $\text{Si}-\text{CH}_3$ group. The signal between 0.77 to 0.92 ppm is exhibited by the proton of CH_3 group present in the main polymeric chain. The broad peak observed at 6.5 and 7.5 ppm corresponds to different aromatic protons in the multifunctional polymers present in PMPS, chiral unit (R-NPEMAM) and photoactive unit (DR1MA). The other aromatic peaks appeared at 7.6-7.7 ppm are due to C_6H_5 attached with $-\text{N}=\text{N}-$ (azo) group. The peak appeared at 4.23 due to $\text{COO}-\text{CH}_2-\text{CH}_2$ group of DR1MA unit. The appearance at 0.45 ppm due to $\text{Si}-\text{CH}_2$ clearly indicates the formation of block copolymers. The proton of aliphatic $-\text{CH}_2-$ of polymeric chain appeared in copolymer at 1.68 ppm which indicates the formation of the multifunctional polysilane block copolymers. The disappearance of two peaks at 5.30 ppm and 5.70 ppm of vinyl protons indicates the absence of residual vinyl monomer and formation of functional polymer.

3.3.1 Copolymer Composition of Multifunctional Polysilane

Copolymer compositions of synthesized multifunctional polysilane (SCDRDM) were determined accurately from ^1H NMR Spectrum. The composition of the chiral and photoactive polysilane were calculated with consideration of the internal peak area (I) of the $\text{Si}-\text{CH}_3$ of poly(methylphenylsilane), $\text{CH}-\text{CH}_3$ of $\text{Ph}(\text{CH}_3)\text{CH}$ of the chiral monomer and CH_2 of $-\text{COOCH}_2-\text{CH}_2$ of DR1MA unit. The mole fraction (F1) of $\text{Si}-\text{CH}_3$ for poly(methylphenylsilane) is 0.511, 0.436 and 0.510, chiral monomer is 0.372, 0.327 and 0.387 and photoactive monomer is 0.116, 0.236 and 0.102 in synthesized block copolymers for SCDRDM-1B, SCDRDM-2B and SCDRDM-3B respectively. The feed ratio of monomer composition is given in synthesis section 2.3.

3.4 Polymer Molecular Weight

The molecular weights of PMPS and SCDRDM were measured using gel permeation chromatography (GPC) instrument in THF (Figure 3). In this chromatogram we mentioned the measurement of molecular weight of a UV exposed PMPS sample PSUV-2B for comparison (reported in our previous paper) [21]. The molecular weight of PMPS is observed to be bimodal distribution which is obvious. Initially, UV exposed sample was observed the unimodal distribution, because of low molecular weight fraction is vanished due to degradation of PMPS chain and formed macroradical on which polymerization of vinyl methacrylate monomers obtained the SCDRDM block copolymer. In second case, the high molecular weight of SCDRDM slightly changed due to uniform Gaussian distribution MWD in comparison to PMPS. The number average molecular weight (\bar{M}_n) of PMPS and also the functional polymers were measured to be of the order of 10^3 (Table 1). On the other hand, the polydispersity indices of such polymers are 1.99, 1.08, 1.09, 1.09 and 1.10 for PMPS, SCDRDM-1B, SCDRDM-2B and SCDRDM-3B respectively. As a result of UV exposure on PMPS polydispersity indices (PDI) of synthesized SCDRDM is much narrower than PMPS polymer because of chain scission of PMPS, hence molecular weight decreased.

3.5 Glass Transition Temperature

Glass transition temperatures (T_g) of the synthesized multifunctional polysilane block copolymers were measured using DSC analysis (Figure 4). The T_g of homopolymer of DR1MA was reported to be 105.6°C [26], and that of chiral polymer (PR-NPEMAM) was reported to be 100.6°C [27]. The observed two glass transition temperatures indicated that the synthesized polymers are block copolymers. First block was observed for polysilane block and second block is due to random copolymer of R-NPEMAM and DR1MA functional monomer units. On the other hand, the T_g of our synthesized PMPS is 62°C (Figure 5). The synthesized multifunctional polysilane, SCDRDM-1B exhibits two glass transition temperatures at 54.41°C and 92.82°C. First T_g is associated with the polysilane block and second for the random block of photoactive DR1MA unit and chiral unit. Two glass transition temperatures for SCDRDM-3B sample are observed to be 60.47°C and 98.03°C. The higher value of this block copolymer with respect to first one (SCDRDM-1B) may be due to higher molecular weights. The reported glass transition temperatures of the chiral homopolymer and photoactive homopolymer are more than the random copolymer blocks in this synthesized multifunctional polysilanes. This may be due to different method of synthesis: In the first cases it was radical polymerization and the second case is the UV initiated radical polymerization by silyl macroradical where low \overline{M}_w block was formed.

3.6 Optical properties

The optical absorbance spectra of functional polysilane copolymers (SCDRDM) were studied in THF solvent using UV-vis spectroscopy in Figure 6. The electronic absorption maxima which appeared at 330 nm is due to σ - σ^* transition of the σ -conjugation of Si-Si main chain. The absorbance at 272 nm can be assigned to the π - π^* transition of aromatic ring. The electronic absorption in the visible region at 475 nm corresponds to the combined contribution of n - π^* , first π - π^* intermolecular charge transfer electronic transition of the azobenzene chromophores of DR1MA unit. The absorbance of this azobenzene chromophore is in corroborated with the reported results [25, 28]. The π - π^* transition and n - π^* intermolecular charge transfer electronic transition of azobenzene chromophores was reported for photoactive DR1MA monomer [26]. In case of polysilane, optical properties are dependent on their conformations and chain lengths. The Si-Si backbone of polysilane is sensitive towards external stimuli especially for temperature. The effect of temperature on such properties of the synthesized functional polysilanes was also studied. The temperature effect on the absorbance at 272 nm due to aromatic ring, at 475 nm due to DR1MA unit and on the absorbance at 330 nm due to Si-Si σ -conjugation is shown in Figure 7 to 9. The absorbance of flexible Si-Si bond which appears at about 330 nm was decreased marginally with increase in temperature (10°C-60°C).

3.7 Chiroptical Properties

3.7.1 Circular Dichroism (CD)

The chiroptical properties of functional optically active and photoactive polysilanes were determined using circular dichroism in THF solution in the spectral range of 200 to 700 nm (Figure 10 and 11). The cotton effect observed at 261 nm is due to aromatic ring associated with the chiral unit, (R)-N-(1-phenylethyl)methacrylamide and it is obvious [24]. Moreover, we also observed the cotton effect at 330 nm and 470 nm, which are associated with the Si-Si conjugation of PMPS block and azobenzene chromophore of photoactive monomer unit. Hence these induced circular dichroism signals appeared in case of functional polysilane block copolymers may be due to the presence of chain helicity into Si-Si chain and also other interaction with the azobenzene chromophores of the photoactive DR1MA unit. Thus the synthesized multifunctional polysilanes have tunable chiroptical properties. Polysilanes have one handed helical-screw conformation with chiral alkyl substituents [29-32].

Chain helicity induced in oligosilane by the terminal substituents of chiral unit was also reported [33-34]. Thus polysilane can take a stable conformation in one handed helix sense as a result of chiral

stimuli [35-37]. Polysilane-b-poly-(triphenylmethyl methacrylate) was also reported to exhibit helical conformation of polysilane block due to helical induction of poly(triphenylmethyl methacrylate) block [38]. It was reported to have cotton effect at 340 nm below -20°C. The helical sense of one polymer chain could induce helical sense in another polymer chain throughout block copolymer system in response to an external stimuli such solvent, pH and temperature. It was also reported that polysilane exhibited optical activity with (+) or (-)-menthoide group at the terminal position due to adoption a preferential helical sense [39]. The chiral solvent influenced the behaviour of polymerization and polymers which affect the molecular distribution of a helical polymer [40-41]. The polymer chains of poly(methylphenylsilane) and poly(hexylmethylsilane) were adopted preferred helical screw senses through such chiral salvation [41]. In our earlier investigation we observed the circular dichroism due to induction of chain helicity in poly(methylphenylsilane) chain as a result of the presence of chiral block at one or both the ends of chiral-block polysilanes [21]. In this investigation also we observed the induced optical activity both in Si-Si chain of PMPS and in azobenzene chromophore of photoactive monomer (DR1MA) due to the presence of chiral unit in the synthesized multifunctional polysilanes (SCDRDM).

3.8 Photoluminescence Properties

The photoluminescence (PL) properties of the synthesized multifunctional polysilane were observed in THF with excitation energy such as 275 nm due to aromatic ring, 325 nm for Si-Si chain and also 475 nm for azobenzene chromophore (Figures 12, 13 and 14). The optimum PL is observed at $\lambda_{em} = 307$ nm for the excitation energy of 275 nm. Another photoemission is observed at $\lambda_{em} = 415$ nm for the same excitation energy. The same emission is also observed at 415 nm for the excitation at 325 nm. The PL intensity is enormously increased due to decrease in the solution concentration. But there is no shift of emission wavelengths due to change in concentration of the solution.

Other than the obvious emissions as mentioned above, a multiple emission spectra are also observed at 500 nm, 550 nm and 590 nm due to excitation at 475 nm. This may be due to the exciton coupling between the azobenzene chromophore of DR1MA and benzene ring of R-NPEMAM block with Si-Si σ -conjugation in association with the aromatic ring of PMPS block (Scheme 2). Such synthesized functional polysilanes having unusual photoluminescence property may find novel optoelectronics application. The appearance of fluorescent band was reported at around 360 nm, which is assigned to a fluorescence from their lowest excited state $\sigma-\sigma^*$ transition of Si-Si chain [42]. This sharp photoluminescence UV band is of excitonic nature, which is associated along with the Si-Si backbone [43]. A broad visible photoluminescence (BVPL) band is also reported at 380 nm regions and its maximum is situated at about 415 nm [43-44]. The contribution of PMPS block of the copolymers and both exciton photoluminescence (EPL) and broad visible photoluminescence (BVPL) band are observed at around 350 nm and 415 nm in functional polysilane block copolymers (SCDRDM) when excited at 325 nm (Figure 13). The photoluminescence of DR1MA monomer and its polymer was reported in which photoemission was observed at around 320 nm [26]. Photoluminescence behavior of copolymers of DR1MA with a chiral monomer was reported that exhibited optimum photoluminescence at around 307 nm due to excitation from 275 nm. A blue shift of 10-12 nm was observed for the copolymers of DR1MA [25]. It is true that the $\pi-\pi$ stacking arising for two azobenzene moieties was minimized due to second monomer introduction (chiral monomer) in the copolymers. This blueshift may not have only due to $\pi-\pi$ stacking of a similar kind of moiety, such as, azobenzenes, but also to the randomly distributed $\pi-\pi$ stacking of the benzene ring of the chiral comonomer and azobenzene chromophore of DR1MA [25]. In this investigation when excited from 275 nm, we also observed emission at 307 nm due to DR1MA block along with PMPS block at around 415 nm (Figure 12). Other than the obvious multiple emissions spectra are also observed centred at 550 nm due to excitation at 475 nm (Figure 14). 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 2). Such synthesized functional photoactive polysilane block copolymers having unusual photoluminescence property may find novel optoelectronics application.

3.9 Figures, Tables and Schemes

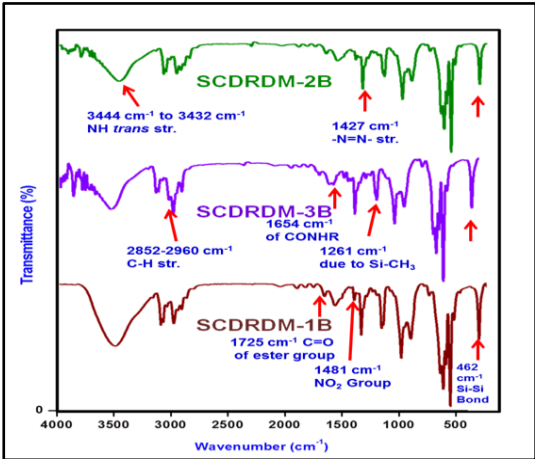


Figure 1 FTIR spectra of multifunctional polysilanes

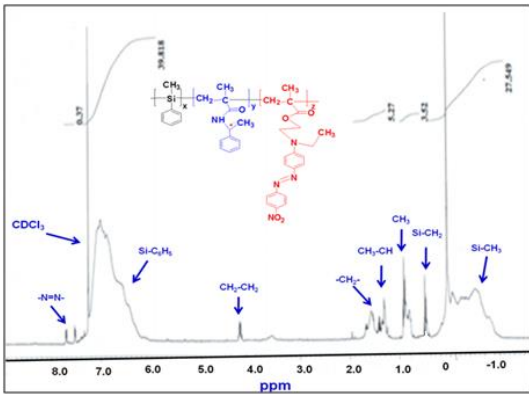


Figure 2 NMR analysis of multifunctional polysilane (SCDRDM-2B)

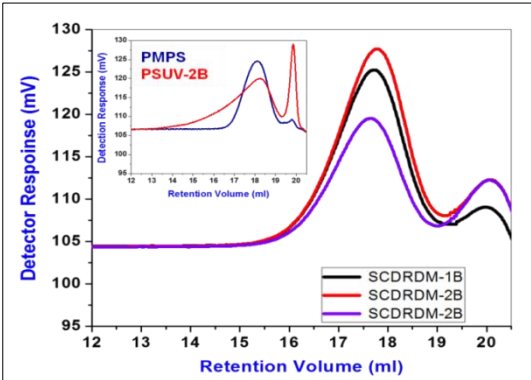


Figure 3 Combined GPC chromatograms of PMPS, UV-exposed PMPS and SCDRDM copolymers

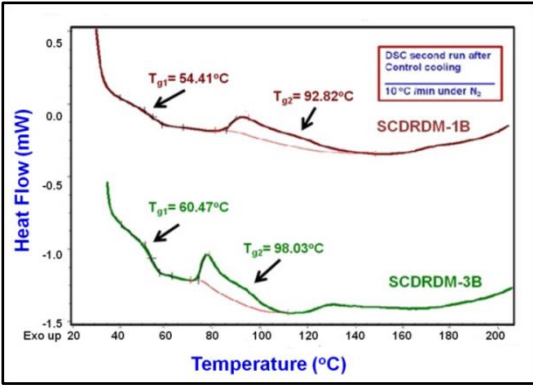


Figure 4 DSC Thermograms of functional polysilane block copolymers

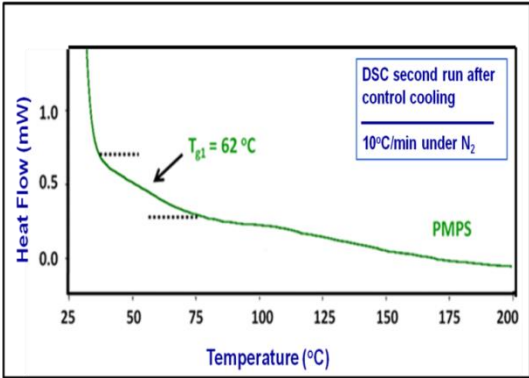


Figure 5 DSC Thermograms of poly(methylphenylsilane) (PMPS)

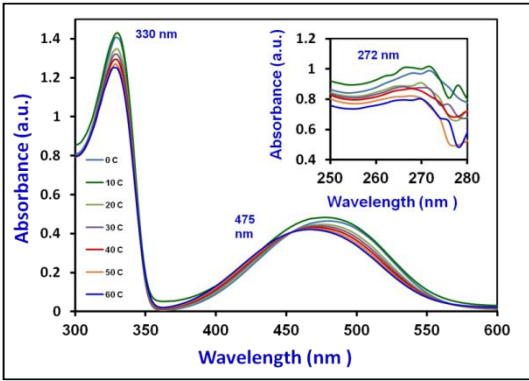


Figure 6 UV-vis spectra of a functional polysilane (SCDRDM-3B) in THF (conc. 0.125mg/dl)

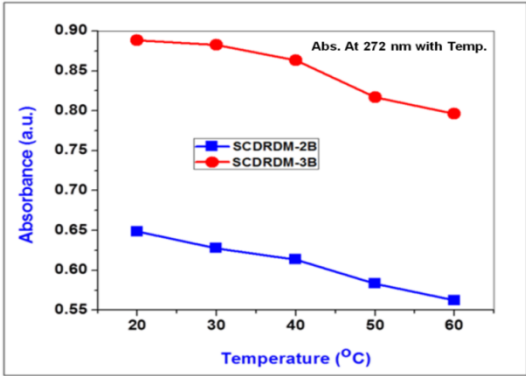


Figure 7 Temperature versus optical absorbance (at 272 nm due to benzene ring)

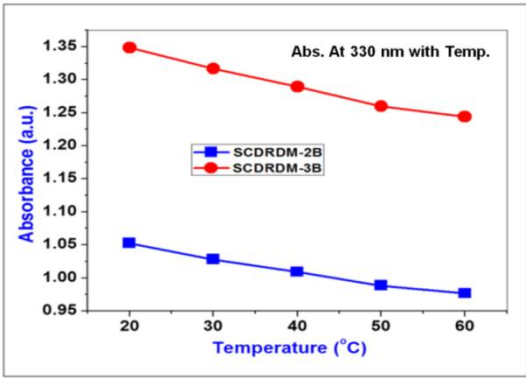


Figure 8 Temperature versus optical absorption (at 330 nm due to Si-Si bond)

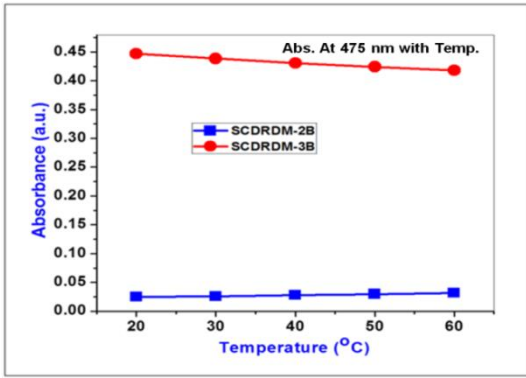


Figure 9 Temperature versus optical absorption (at 475 nm due to azobenzene group)

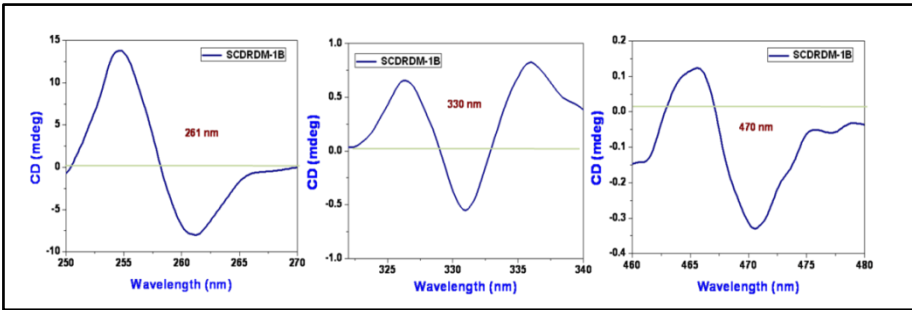


Figure 10 CD spectra of SCDRDM-1B in THF (conc. 0.0005 gm/dl)

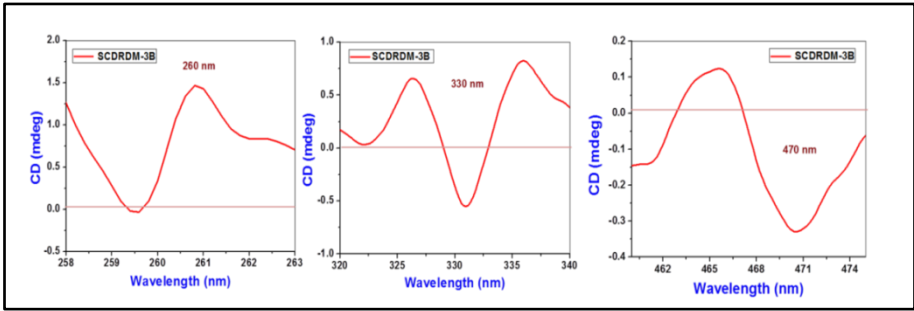


Figure 11 CD spectra of SCDRDM-3B in THF (conc. 0.0005 gm/ml)

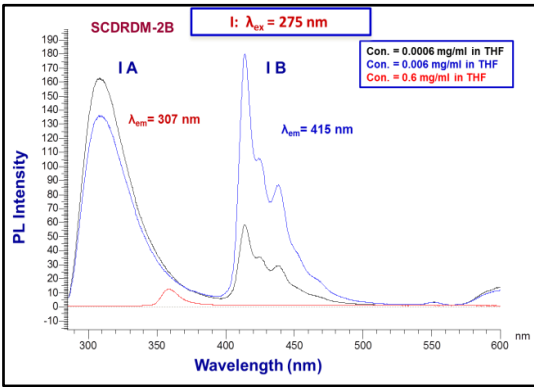


Figure 12 PL spectra of SCDRDM-2B with excitation energy of 275 nm

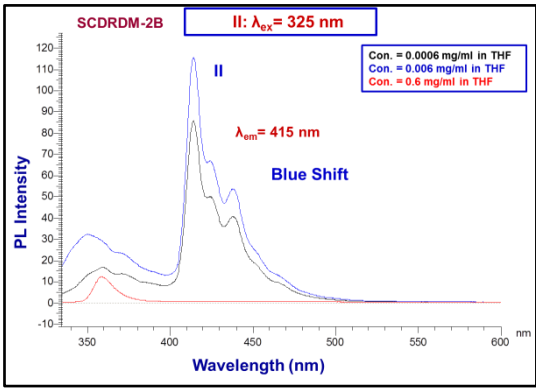


Figure 13 PL spectra of SCDRDM-2B with excitation energy of 325 nm

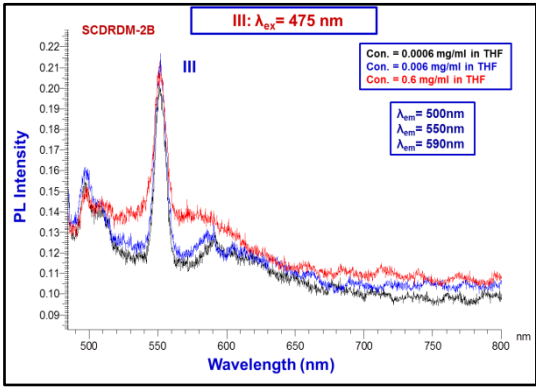


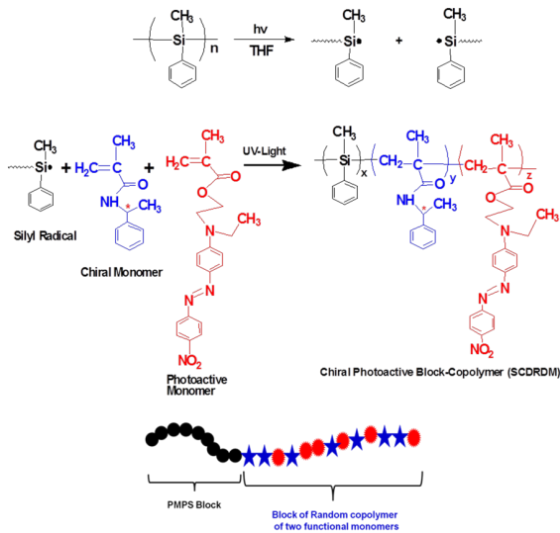
Figure 14 PL spectra of SCDRDM-2B with excitation energy of 475 nm

Table1: Molecular Weights of Synthesized Multifunctional PolysilaneCopolymers

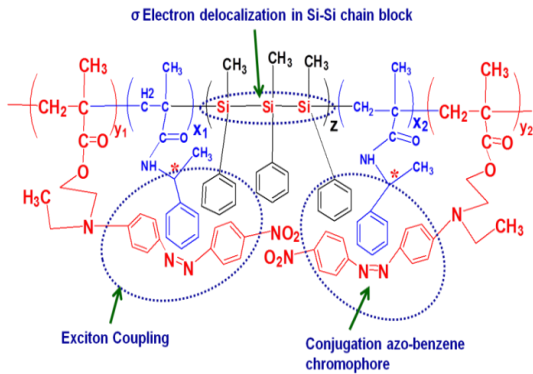
Sl. No.	Sample Name	\overline{M}_n	\overline{M}_w	\overline{M}_z	$PDI = \overline{M}_w/\overline{M}_n$
1.	PMPS	2754	5484	12049	1.991
2	SCDRDM-1B	2202	2408	2783	1.094
3.	SCDRDM-2B	2282	2498	2867	1.094
4.	SCDRDM-3B	2095	2314	2690	1.104

Table2: Results of PL Analysis of Photoactive Polysilane Block Copolymer (SCDRDM-2B)

Conc. of Polymer Solution (mg/ml)	Excitation ($\lambda_{ex} = 275\text{ nm}$)		Excitation ($\lambda_{ex} = 325\text{ nm}$)	
	$\lambda_{em}(\text{nm})$	PL intensity (au)	$\lambda_{em}(\text{nm})$	PL intensity (au)
6×10^{-4}	307	163	352	32
6×10^{-3}	307	136	359	17
6×10^{-4}	415	180	415	116
6×10^{-3}	415	57	415	86



Scheme 1 Synthesis of multifunctional polysilanes having optically active and photoactive Moities



Scheme 2 Plausible interaction of functional moieties in synthesized functional polysilanes (SCDRDM)

4. Discussion

Multifunctional polysilanes were synthesized along with a chiral monomer, R-NPEMAM and a photoactive monomer, DR1MA. By the UV irradiation, PMPS gave rise to silyl radical, which initiated by radical polymerization with (R)-N-(1-phenylethyl)methacrylamide (R-NPEMAM) and disperse red 1 methacrylate (DR1MA) monomers. The number average molecular weights (\overline{M}_n) of PMPS and SCDRDM-1B, SCDRDM-2B, SCDRDM-3B were measured to be 2.75×10^3 , 2.20×10^3 , 2.28×10^3 and 2.09×10^3 respectively. In the UV-vis spectra, peak appeared at 272 nm is due to presence of aromatic ring. The absorption due to Si-Si σ -conjugation appeared at 330 nm. The electronic absorption in the

visible region at 475 nm corresponds to the combined contribution of $n-\pi^*$, first $\pi-\pi^*$ intermolecular charge transfer electronic transition of the azobenzene chromophores of DR1MA unit. These synthesized multifunctional polymers not only exhibited circular dichroism due to the chiral unit (at 261 nm) present in the polymeric chain, but also exhibited induced circular dichroism at 330 nm and 470 nm associated with the Si-Si chain of PMPS and azobenzene chromophore of DR1MA unit, respectively. This type of tunable optical activity may find novel application. These synthesized functional polysilanes exhibited good photoluminescence properties. They emitted 307 nm when excited at 275 nm. Another photoemission is observed at λ_{em} = 415 nm for the same excitation energy. The same emission at 415 nm is also observed for the excitation at 325 nm. Other than, the obvious emissions, multiple emission spectra are also observed at 500 nm, 550 nm and 590 nm for the excitation at 475 nm. This might be due to exciton coupling between azobenzene chromophore, benzene ring and Si-Si conjugation present in the multifunction polysilanes. Such synthesized multifunctional polysilanes having unusual optical activity as well as photoluminescence property may find novel optoelectronic applications.

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