

Synthesis of Functional Photoactive Polysilane Copolymers with Disperse Yellow 7 Methacrylate and Study of their Optical, Photophysical and Thermal Properties

KM. MEENU, DIBYENDU S. BAG* AND REKHA LAGARKHA^a

Defence Materials and Stores Research and Development Establishment
DMSRDE, P. O., Kanpur-208013, INDIA

^aDepartment of Chemistry, Bundelkhand University, Jhansi, INDIA

ABSTRACT

Functional photoactive polysilane copolymers of poly(methylphenylsilane) (PMPS) and disperse yellow 7 methacrylate (DY7MA) were synthesized using UV-technique. In the same manner functional polysilane copolymers of poly(methylphenylsilane-co-dimethylsilane) (CPS) and disperse yellow 7 methacrylate (DY7MA) were also synthesized. By the UV irradiation polysilanes (PMPS and CPS) give rise to silyl macroradicals which initiate the polymerization of photoactive monomer (DY7MA). The synthesized samples were characterized by FTIR, NMR, and UV-Vis spectroscopy. The molar mass of synthesized photoactive functional polysilane copolymers is of order of 10^3 gm/mol. They exhibited multimodal optical and photoluminescence functional properties. Optical absorbance was observed at 336 nm due to σ - σ^* transition of σ -conjugation of Si-Si main chain. The other absorbance at 276 nm is due to π - π^* transition of aromatic ring associated with polysilanes and DY7MA polymeric unit. The electronic absorption was observed at 367 nm for π - π^* and n - π^* transition of azobenzene chromophores of DY7MA. The photoemission spectra are observed at $\lambda_{em} = 405, 428$ and 454 nm for the excitation energy of 332 and 370 nm. Such functional polysilane copolymers exhibited two glass transition temperatures indicating the formation of block copolymers. The synthesized functional polysilane copolymers are thermally stable upto 300°C . Such functional photoactive block copolymers may find novel optoelectronic applications.

KEYWORDS: Polysilanes, Functional polysilanes, Disperse yellow 7 methacrylate, Photoactive polymers

J. Polym. Mater. Vol. **36**, No. 3, 2019, 275-292

© Prints Publications Pvt. Ltd.

Correspondence author e-mail: ds_bag@rediffmail.com

DOI : <https://doi.org/10.32381/JPM.2019.36.03.7>

1. INTRODUCTION

Now-a-days, functional and multifunctional materials have been attracted great attention to the materials scientists to fulfil the multi-mission objectives by a single material^[1-2]. Designing of such materials may be possible with a single chemical structure having different functional groups, and/or in the form of organic-inorganic hybrid materials in which each phase of materials performs different necessary function^[3]. The synthesis of functional materials having extraordinary functionality is a challenging task to the current demand of technological materials. Polysilanes, a class of inorganic polymers, exhibit unique electronic, optical, photo- and electroluminescence properties associated with the σ -conjugation of silicon-silicon backbone^[4-9]. Such unique properties have attracted great attention for their optoelectronic applications^[10-14]. Another important class of polymers which have attracted in the field of optoelectronic application is azopolymers (polymers having azobenzene chromophores as side chain or main chain) in which the orientation of azobenzene chromophores are changed by the irradiation of polarized light^[15-16]. Such polymers have also been reported to exhibit nonlinear optical properties, light-induced dichorism and birefringence^[17-27]. They are widely used in optical storage, optical switching and manipulation of information and other optoelectronic applications^[28-33]. Side chain azopolymers like poly (disperse red 1 methacrylate) (PDR1MA) and their copolymers were extensively investigated. Ding and Russell reported the photoluminescence (PL) properties of homopolymer of disperse red 1 methacrylate (DR1MA)^[29]. Copolymers of

DR1MA with chiral monomer, (S)-N-(1-phenylethyl)methacrylamide (S-NPEMAM) were reported by our group to exhibit both photoluminescence as well as chiroptical properties^[34]. Exciton splitting originated by the cooperative interactions between the pendant azobenzene chromophore of DR1MA and the benzene ring of the chiral monomer was observed because of the statistical disposition of the azobenzene moiety in a mutual chiral geometry of one prevailing handedness resulting asymmetric induction to the azobenzene moiety^[34]. We have also reported the copolymers of DR1MA and poly(methylphenylsilane) (PMPS)^[35]. In this investigation, we attempted to couple disperse yellow 7 methacrylate (DY7MA) monomer with polysilanes to obtain new multifunctional materials having special and multifunctional activity especially optical and photophysical properties. Another aspect of this investigation is as follows. The direct synthesis of functional polysilanes has been restricted due to drastic condition of high temperature refluxing of organodichlorosilane monomer along with sodium metal in toluene to the synthesis of polysilanes using the well established method of Wurtz coupling reaction^[36-38]. At this refluxing temperature no functional groups sustain with polysilanes. Hence it is very challenging for synthetic chemists to synthesize functional polysilanes as new technological materials^[3]. On the other hand, it is well known that polysilanes upon UV irradiation produce silyl radicals, which can initiate the radical polymerization of vinyl monomers^[39-40]. Following this synthetic methodology, we have recently reported the functional poly (methylphenylsilane) block copolymers with

optically active chiral vinyl monomer, (R)-N-(1-phenylethyl)methacrylamide [R-NPEMAM]^[41], with disperse red 1 methacrylate^[35] and with both R-NPEMAM and DR1MA^[42].

In this investigation, functional photoactive polysilanes of poly (methylphenylsilane) (PMPS) and poly(methylphenylsilane-co-dimethylsilane) (CPS) were synthesized along with disperse yellow 7 methacrylate (DY7MA) monomer. In this synthesis polysilane (PMPS and CPS) gives rise to silyl radicals upon UV-irradiation, which initiate the radical photopolymerization of DY7MA monomer producing poly (methylphenylsilane)-co-disperse yellow 7 methacrylate (PSDY) and poly (methylphenylsilane-co-dimethylsilane)-co-disperse yellow 7 methacrylate (CPSDY). The synthesized functional photoactive organic-inorganic block copolymers (PSDY and CPSDY) were purified and characterized by FTIR, NMR and GPC analysis. The optical and photophysical properties of the samples were measured using UV-vis spectroscopy and photoluminescence spectrophotometer respectively. The thermal properties of the polymers were also analysed by TGA and DSC.

EXPERIMENTAL

2.1 Materials

Poly(methylphenylsilane) (PMPS) from dichloromethyl phenylsilane and poly(methylphenylsilane -co-dimethylsilane) (CPS) from dichloromethylphenylsilane and dichlorodimethylsilane were synthesized following Wurtz coupling reaction in boiling toluene with sodium dispersion according to a reported literature^[40]. The synthesized and purified poly(methylphenylsilane) (PMPS) sample in Laboratory was used in this investigation^[41]. Its molecular weights are: $\bar{M}_n = 2,754 \text{ gm/mol}$, $\bar{M}_w = 5,484 \text{ gm/mol}$ and polydispersity index = 1.99. Synthesized poly(methylphenylsilane-co-

dimethylsilane) (CPS) was also used and its molecular weights are : $\bar{M}_n = 1,289 \text{ gm/mol}$, $\bar{M}_w = 3,905 \text{ gm/mol}$ and PDI 3.03 respectively. The yield of both the polymers (PMPS and CPS) was observed to be 40-44%.

Disperse yellow 7 methacrylate (DY7MA) (96 %, Sigma-Aldrich) is a photoactive monomer which was purified by recrystallization from acetone: petroleum ether (60-90°C) (2:1) and stored at room temperature. Its appearance is yellow. Tetrahydrofuran (THF) was purified in two step processes as per our previous report^[35]. n - Hexane (AR, Samir Tech Chem. India), methanol (AR, Samir Tech. Chem., India), acetone (Spectrochem PVT. LTD., India) and petroleum ether (AR, Samir Tech Chem., India) were used as received.

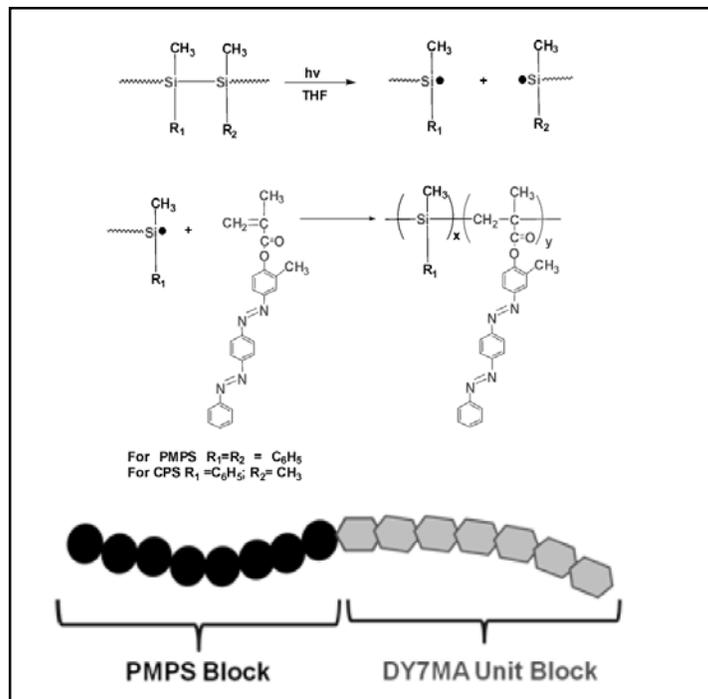
2.2 Synthesis of Functional Photoactive Polysilanes

Poly(methylphenylsilane) (PMPS) and poly (methylphenylsilane-co-dimethylsilane) (CPS) were used as a macrophotoinitiator. Polysilanes (both PMPS and CPS) copolymer upon UV-irradiation gave rise to silylmacroradicals which are capable to initiate radical polymerization of disperse yellow 7 methacrylate (DY7MA). Thus functional photoactive polysilanes like PMPS-co-DY7MA and CPS-co-DY7MA copolymers were synthesized using UV-technique (Scheme 1). In a typical synthesis, purified polysilane (PMPS or CPS) (0.5 gm) with photoactive monomer (DY7MA) (0.25 gm) were dissolved in 10 ml purified THF in a quartz tube and N_2 gas was flushed for 5 min. Then, the reactant mixture solution was sufficiently degassed using a vacuum pump and freeze thaw method. After sealing the tube under reduced pressure, it was exposed under UV light for different time for photopolymerization using Fusion UV-curing Systems having 10 inch Fusion UV Electrodeless D-bulb, wavelength=350-400 nm and light intensity = 8 W/cm².

After the UV-exposure, the reaction mixture was kept as such for overnight and then it was precipitated in hexane. Hexane and the reaction solvent (THF) were then removed by evaporation. The left out solid mass was dissolved in acetone then precipitated in methanol. However, a small portion was not dissolved in acetone which was unreacted PMPS or CPS. It was tested and observed to be soluble in toluene. The yellow colour precipitates were observed which were filtered and

collected. As the photoactive monomer, DY7MA is dissolved in both acetone and methanol; this precipitate must be free from the photoactive monomer. The precipitated samples are the synthesized poly(methylphenylsilane)-co-(disperse yellow 7

methacrylate)(PSDY) and poly(methylphenylsilane-co-dimethylsilane)-co-(disperse yellow 7 methacrylate) (CPSDY) copolymers which were dried under vacuum at 50°C (Table 1).



Scheme 1. Synthesis of functional photoactive polysilanes (Polymethylphenylsilane-co-(disperse yellow 7 methacrylate) (PSDY) and poly(methylphenylsilane-co-dimethylsilane)-co-(disperse yellow 7 methacrylate) (CPSDY)

TABLE 1. Synthesis of Functional Photoactive Polysilanes

| Sample Code | Reactant Ratios ^a PMPS or CPS: DY7MA] (wt/wt) | % Yield | \bar{M}_n (gm/mol) | \bar{M}_w (gm/mol) | PDI |
|-------------|--|---------|-------------------------|-------------------------|------|
| PSDY-1B | 2:1 [PS:DY7MA] | 28% | 2.71×10^3 | 3.52×10^3 | 1.30 |
| PSDY-2B | 1:1 [PS:DY7MA] | 22 % | 2.57×10^3 | 3.44×10^3 | 1.34 |
| CPSDY-1B | 2:1 [CPS:DY7MA] | 18 % | 1.32×10^3 | 1.36×10^3 | 1.03 |
| CPSDY-2B | 1:1 [CPS:DY7MA] | 26 % | 3.59×10^3 | 5.70×10^3 | 1.59 |

a. Solvent 10 mlTHF and in case CPSDY-1B 10 ml toluene; Time of UV exposure 4 min in all cases.

2.3 Characterization

The synthesized functional photoactive polysilanes (PSDY and CPSDY) were characterized by FTIR and NMR spectroscopy. The FTIR spectra of the synthesized samples were measured using KBr Pallet on a Perkin Elmer Spectrum 100 FTIR spectrophotometer. The ^1H NMR spectra were measured on a JEOL ECX-500 MHz FT-NMR spectrometer in CDCl_3 solvent and TMS was used as the internal reference. The samples were also tested for their solubility in different organic solvents.

The molecular weights of the synthesized functional polysilanes were measured by using a gel permeation chromatography (GPC) with a Waters 2414 RI detector, a Waters 1515 isocratic HPLC pump with 717 plus auto sampler in HSP RT MB-H, HSP RT 6.0 [Graft, linear, 500 Å, 100 Å] columns taking THF as a mobile phase. The column was calibrated with PS standards (Waters). Thermal properties of the samples were measured using a DSC Q200 (TA Instrument) and TGA Q500 (TA Instrument) at the heating rate of $10^\circ\text{C}/\text{min}$ under N_2 -atmosphere. The UV-Vis spectra were recorded on a CARY 5000 UV-Vis NIR spectrophotometer. The photoluminescence (PL) properties were studied for the synthesized functional photoactive polysilanes in their THF solutions with an F-2500 FL spectrophotometer (Hitachi).

3. RESULTS AND DISCUSSION

3.1 Synthesis of Functional Photoactive Polysilanes

In this synthesis of functional photoactive polysilanes, poly(methylphenylsilane) (PMPS) and poly(methylphenylsilane-co-dimethylsilane) (CPS) were used as a macrophotoinitiator and disperse yellow 7 methacrylate (DY7MA) as a photoactive vinyl monomer. By the UV irradiation, polysilanes produced silyl radicals which initiated the radical polymerization of DY7MA and thus functional photoactive polymers were obtained (PSDY and CPSDY). The purified samples were characterized by FTIR and NMR spectroscopy.

The molecular weights of PSDY and CPSDY samples were determined using GPC analysis. The optical and photoluminescence properties were also studied. The thermal properties were carried out using TGA and DSC analyses.

Solubility of the Synthesized Samples

Poly(methylphenylsilane) (PMPS) was soluble in chloroform, THF, toluene and 1,4-dioxane, but was insoluble in acetone, diethyl ether, petroleum ether, methanol, hexane, dimethylsulphoxide (DMSO). Poly(methylphenylsilane-co-dimethylsilane) (CPS) was soluble in THF, chloroform, toluene and 1,4-dioxane. On the other hand, the synthesized functional photoactive polysilane polymers (PSDY and CPSDY) were soluble in acetone, chloroform, THF, toluene and 1,4-dioxane.

3.2 FTIR Analysis

The synthesized functional photoactive polysilane copolymers like PMPS-co-disperse yellow 7 methacrylate (PSDY-1B and PSDY-2B) and CPS-co-disperse yellow 7 methacrylate (CPSDY-1B and CPSDY-2B) were characterized by FTIR Analysis (Figures 1 to 3). The absorbance peak at $2894\text{--}2958\text{ cm}^{-1}$ is due to methyl ($-\text{CH}_3$) group and alkyl chain ($-\text{CH}_2-$) present in all the samples. The peak appeared at 1729 cm^{-1} is due to $\text{C}=\text{O}$ stretching of ester group present in DY7MA unit of the synthesized functional polysilanes. The characteristic $-\text{N}=\text{N}-$ (azo) stretching of DY7MA unit is observed at 1374 cm^{-1} and 1427 cm^{-1} [29, 34, 35, 43]. The strong absorption of $\text{O}-\text{CO}$ stretching of DY7MA unit is appeared at 1150 cm^{-1} . The other characteristic peak due to $\text{Si}-\text{CH}_3$ group is appeared at 1245 cm^{-1} . The characteristic band of $\text{C}=\text{C}$ stretching vibration

at 1638 cm^{-1} and C-H bending of vinyl group ($=\text{CH}_2$) at 949 cm^{-1} are absent in the synthesized functional polysilanes (PSDY-1B, PSDY-2B, CPSDY-1B and CPSDY-2B). The disappearance of these two peaks of photoactive vinyl monomer (DY7MA) indicated the formation of its polymers and the polymerization was initiated by the silylmacroradicals generated by the UV-irradiation of polysilanes (PMPS and CPS). Hence it also indirectly indicated the formation of functional photoactive polysilane block copolymers. The Si-Si stretching vibration in polysilanes usually appears at 457 cm^{-1} [35, 41, 42]. We also observed here the characteristic Si-Si peak which appeared at about 462 cm^{-1}

for the synthesized functional polysilanes. The CH_3 absorbance peak of Si-CH_3 is appeared at 1245 cm^{-1} in PMPS and 1259 cm^{-1} in functional photoactive polysilanes. The peak at 870 cm^{-1} is due to in Si-CH_3 group for wagging vibration appeared in copolymers^[41]. The aromatic C-C stretching is appeared at 1484 cm^{-1} in synthesized copolymers (PSDY-1B, PSDY-2B, CPSDY-1B and CPSDY-2B). The aromatic C-H out of plane bending is appeared at 731 cm^{-1} in PMPS and at about 764 and 799 cm^{-1} in synthesized functional polysilanes. However, the C-H bending in plane is appeared at 1100 cm^{-1} in PMPS and at about 1025 and 1103 cm^{-1} for the synthesized functional polysilanes.

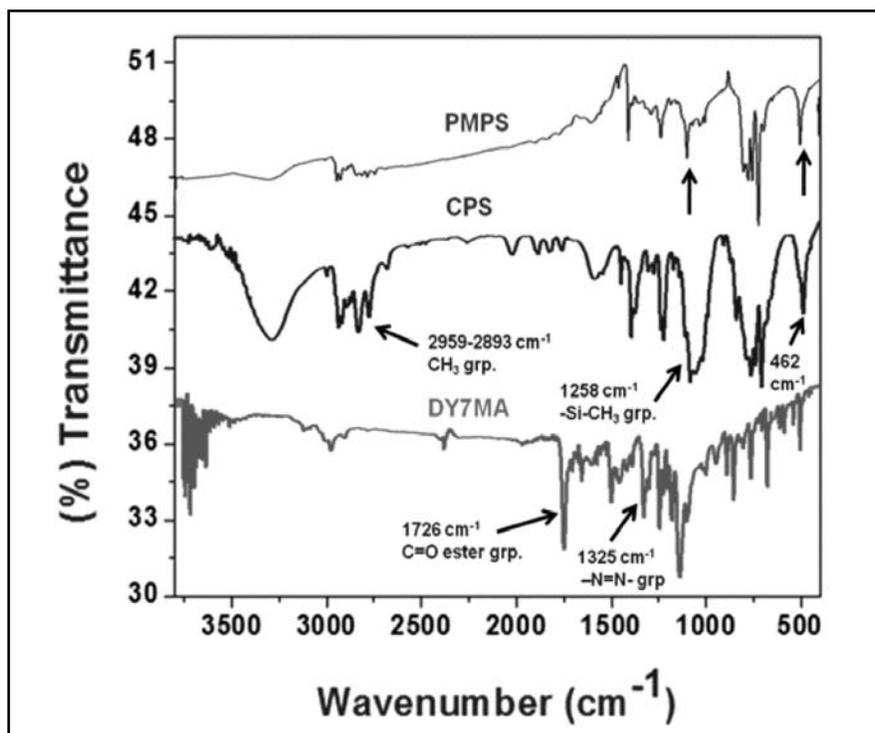


Fig. 1. FTIR spectra of PMPS, CPS and DY7MA

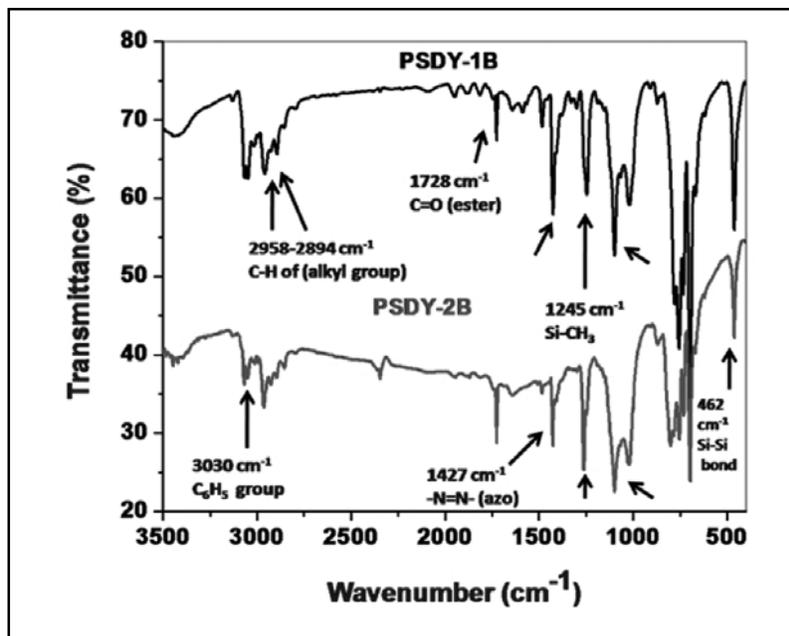


Fig. 2. FTIR spectra of functional polysilanes (PMPS-block-DY7MA copolymers)

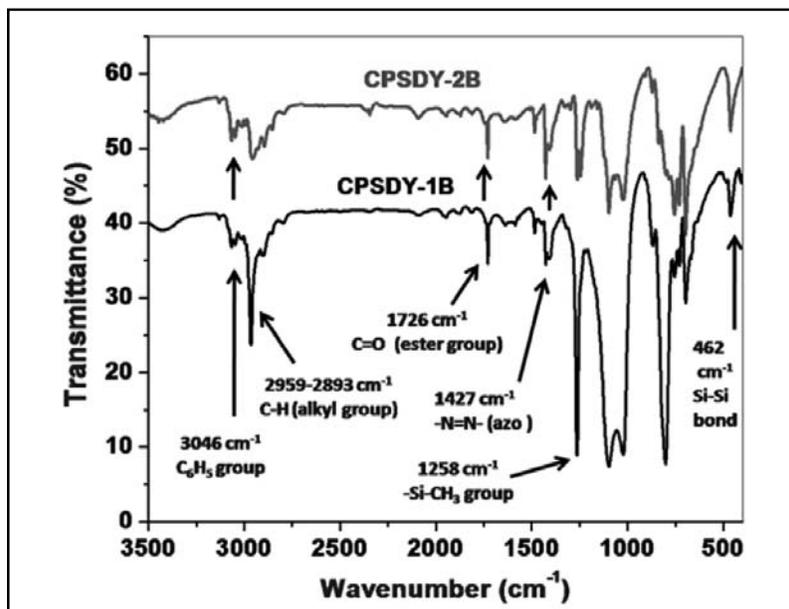


Fig. 3. FTIR spectra of functional polysilanes (CPS-block-DY7MA copolymers)

3.3 NMR analysis

The ^1H NMR spectra of the functional photoactive polysilanes (PSDY-1B and CPSDY-1B) are shown in Figures 4 and 5. The methyl proton of Si-CH_3 is appeared at 0.1 to -0.46 ppm in both synthesized photoactive polysilane copolymers (PSDY-1B and CPSDY-1B). The aromatic proton of $\text{Si-C}_6\text{H}_5$ of polysilane units are appeared at 6.4 to 7.5 ppm. The appearance of NMR signal at 8.1 ppm is due to aromatic protons surrounded by azo ($-\text{N}=\text{N}-$) group. The other aromatic protons are appeared at 7.8 and 7.9 ppm attached to the azo group at terminal position for both functional photoactive polysilane copolymers. The chemical shift appeared at 2.1 ppm is due to CH_2 of DY7MA main chain and 2.3 ppm for

CH_3 proton attached with benzene ring at the adjacent position of ester group. The appearance of NMR signal was at 1.54 ppm for Si-CH_2 group clearly indicate the formation of block copolymer [41,44-46]. The aliphatic polymeric chain $-\text{CH}_2-$ in the spectra is also appeared at 1.54 ppm [47-48]. The disappearance of two vinyl protons at 5.7 and 5.8 ppm clearly indicates the formation of functional photoactive polysilane polymers in both cases. The composition of synthesized functional azobenzene chromophore containing polysilane copolymers were determined from ^1H NMR analysis and calculated with the consideration of peak intensities of CH_3 of Ph-CH_3 of DY7MA unit and CH_3 of Si-CH_3 of PMPS and CPS unit using the following equations [34]:

$$F_1 = \frac{I_{\text{Ph-CH}_3}}{I_{\text{PhCH}_3} + I_{\text{Si-CH}_3}} \quad F_2 = \frac{I_{\text{Si-CH}_3}}{I_{\text{Si-CH}_3} + I_{\text{PhCH}_3}}$$

Where, F_1 is the mole fraction of photoactive comonomer in the copolymers. The 'I' corresponds to the NMR peak intensity of the respective protons. Thus the mole fractions of photoactive monomer unit (F_1) in the copolymers were estimated to be 20.71 mole%, 29.87 mole%, 62.50 mole% and 64.56 mole% for PSDY-1B, PSDY-2B, CPSDY-1B and CPSDY-2B respectively. The mole fractions of PMPS unit (F_2) in the copolymers were thus estimated to be 79.28 mole%, 70.12 mole%, 37.50 mole% and 35.43 mole% for PSDY-1B, PSDY-2B, CPSDY-1B and CPSDY-2B respectively.

3.4 GPC Analysis

The molecular weights of the synthesized functional polysilanes (PSDY and CPSDY) were measured using THF solvent in a GPC instrument. The weight average and number average molecular weights of the samples are given in Table 1. PMPS has bimodal molecular weight distribution synthesized by Wurtz coupling reaction, which we also reported earlier [41]. It was observed unimodal distribution upon UV-irradiation in which low molecular weight distribution of polysilanes was vanished and the high molecular weight distribution was

observed slightly different than to pure PMPS sample [41]. Here also we observed the similar effect. Although the molecular of PMPS and CPS decreased due to UV-exposure, the polymerization of DY7MA on the silyl macroradical leads to chain extension and further increase in molecular weight.

The number average molecular weights (\bar{M}_n) of PSDY-1B, PSDY-2B, CPSDY-1B and CPSDY-2B are measured to be 2.71×10^3 , 2.57×10^3 , 1.32×10^3 and 3.59×10^3 gm/mol respectively. On the other hand, the weight average molecular weights (\bar{M}_w) are 3.52×10^3 , 3.44×10^3 , 1.36×10^3 and 5.70×10^3 gm/mol respectively. The polydispersity index of such polymer are 1.30, 1.34, 1.03 and 1.58 respectively.

3.5 Optical Properties

The UV-vis spectra of PMPS, CPS and DY7MA are shown in Figure 6. In general, optical absorbances are observed for the photoactive monomer, disperse yellow 7 methacrylate at 276 nm due to the aromatic ring and other obvious absorption observed at 366 nm is due to $\pi-\pi^*$ and $n-\pi^*$ transition of azobenzene chromophores. On the other hand, polysilanes exhibited two optical bands at about 276 nm due to aromatic ring and 325 nm due to σ -conjugation of Si-Si main chain (Figure 6).

The UV-vis spectra of synthesized functional photoactive polysilanes of PMPS and CPS polymers are shown in Figure 7. The electronic absorption appears at 336 nm which is due to $\sigma-\sigma^*$ transition of σ -conjugation of Si-Si main chain of polysilanes. On the other hand, the absorbance at 276 nm due to $\sigma-\sigma^*$ transition of aromatic ring associated with polysilane and DY7MA polymer unit is also present in such

samples. The electronic absorption observed at 366 nm for $\pi-\pi^*$ and $n-\pi^*$ transition of azobenzene chromophore of DY7MA unit is present in all these synthesized functional polysilanes.

It is well known that the optical properties of polysilanes are dependent for their chain length and structural conformation [49-52]. The silicon backbone is sensitive towards external stimuli especially for temperature also [53]. The increasing in chain length of PMPS exhibits red shift of the absorbance of polysilane maxima[3].

3.6 Photoluminescence Properties

The photoluminescence (PL) properties of the synthesized functional photoactive polysilanes (PSDY-1B and CPSDY-1B) were observed in different solvents THF, chloroform, acetonitrile, methanol and 1,4-dioxane with different excitation energy such as 280, 332 and 370 nm (Figures 8 and 9). Among all the solvents, PL spectra are observed to be more prominent in THF solvent than that of the other solvents which might be because of the high solubility of the synthesized functional polysilanes in THF than the other solvents. The PL is observable clearly for all the solvents when excited at high energy 280 nm. However, it is apparent that PL is prominent in THF as well as in CHCl_3 solvent for the excitation both at 332 nm and 370 nm. The effect of solvent on the PL properties may be attributed to the good solubility of the synthesized functional polysilanes in these two solvents than the others.

When excited at 280 nm, a photoluminescence is significantly observed at $\lambda_{em} = 351$ nm for both PSDY-1B and CPSDY-1B samples which

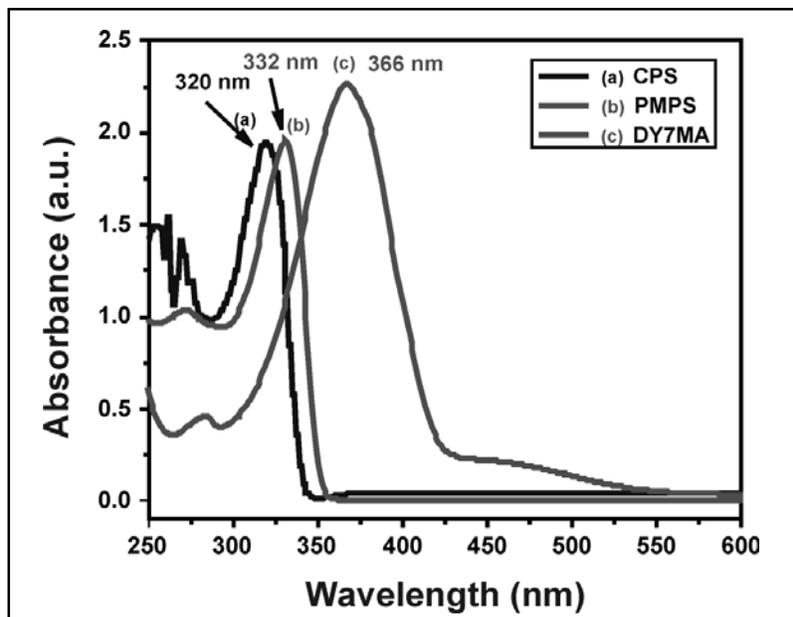


Fig. 6. UV-Vis spectra of (a) poly(methylphenylsilane) (PMPS) (Conc. = 0.4×10^{-2} gm/ml in THF) (b) Poly(methylphenylsilane-co-dimethylsilane) (CPS) (Conc. = 1.25×10^{-4} gm/ml in THF) (c) disperse yellow 7 methacrylate (DY7MA) (Conc. = 0.9×10^{-5} gm/ml in THF)

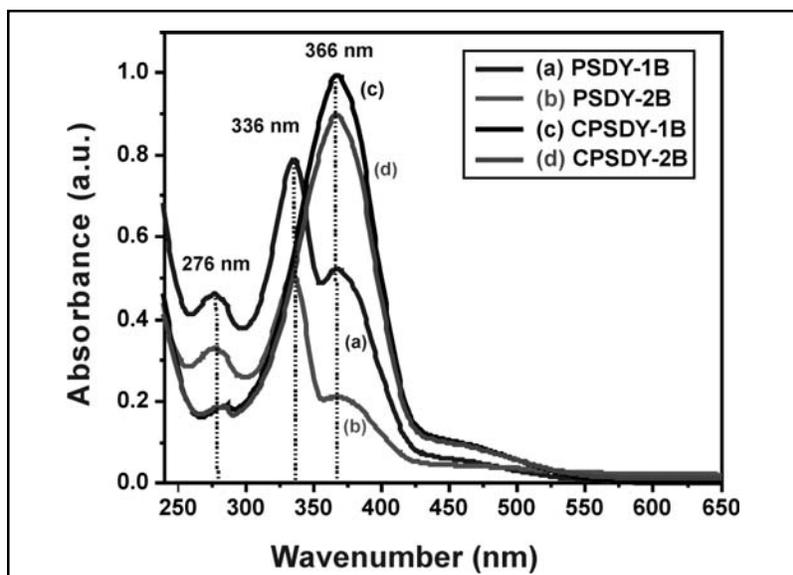


Fig. 7. UV-Vis spectra of synthesized functional polysilanes (PSDY-1B, PSDY-2B, CPSDY-1B and CPSDY-2B) (Conc. = 9.0×10^{-5} gm/ml in THF)

is corroborated with the fluorescence from the lowest excited state associated with the $\sigma\text{-}\sigma^*$ transition of the Si-Si chains. It is reported in the literature that the fluorescent band of poly(methylphenylsilane) (PMPS) was appeared at around 360 nm when excited at 313 nm. This was attributed to a fluorescence from their lowest excited state associated with the $\sigma\text{-}\sigma^*$ transition [54]. This sharp UV band in the photoluminescence is excitonic in nature which is associated with the polymeric Si-Si main chain [55]. In the region greater than 380 nm i.e., a broad visible photoluminescence (BVPL) band was observed at 415 nm [55-56]. Exciton photoluminescence (EPL) and broad visible photoluminescence (BVPL) bands were observed at around 307 nm and 415 nm respectively for the synthesized photoactive polysilane block copolymers of PMPS-disperse red 1 methacrylate when excited at 275 nm; also a multiemission band at 415 nm when excited at 325 nm [35]. Similarly, the optimum PL is observed to be multi-spectral emission at $\lambda_{em} = 405, 428$ (or 430) and 454 nm for both type of synthesized functional polysilanes (PSDY-1B and CPSDY-1B) due to the excitation energy of 332 nm for $\pi\text{-}\pi^*$ transition and $n\text{-}\pi^*$ transition associated with the pendant azobenzene chromophore. Similar multimodal photoemission is observed when excited at 370 nm also.

Photoluminescence properties of disperse red 1 methacrylate (DR1MA) monomer and its homopolymer were reported in which photoemission was observed at around 320 nm [29]. We also observed continuous blue shift (hypsochromic shift) from 240 to 280 nm with increasing excitation energy (λ_{ex}). The optimum photoluminescence was observed at

around 307 with excitation energy at 270 nm for the copolymers of DR1MA with a chiral monomer [34]. The synthesized block copolymers reported in this investigation is associated with disperse yellow 7 methacrylate (DY7MA) monomer unit. We observed multiple emission spectra at $\lambda_{em} = 408, 430$ and 454 nm for the excitation energy 332 nm and 370 nm for both type functional polysilane copolymers which might be due to exciton coupling between azo-benzene chromophore of DY7MA block with Si-Si $\sigma\text{-}\pi$ conjugation attached aromatic ring of PMPS block and/or CPS block. Such synthesized functional photoactive polysilanes having unique photoluminescence properties may find optoelectronic applications for UV light sensor, device used for friend and foe identification etc.

3.7 Thermal Properties

Glass Transition Temperatures

The glass transition temperatures (T_g) of functional photoactive polysilane copolymers (PSDY and CPSDY) were measured using DSC analysis (Figures 10 and 11). The synthesized photoactive polysilane copolymers, PSDY-1B, PSDY-2B exhibited two glass transition temperatures (T_g): first T_g at 66°C and 67°C respectively which are associated with the polysilane block and the second T_g at 127°C and 119°C respectively for the block of photoactive DY7MA unit. The synthesized photoactive polysilane copolymer, CPSDY-1B, CPSDY-2B exhibited two glass transition temperatures (T_g): first T_g at 56°C and 59°C are associated with the polysilane block and the second T_g at 94°C and 89°C for the block of photoactive DY7MA unit.

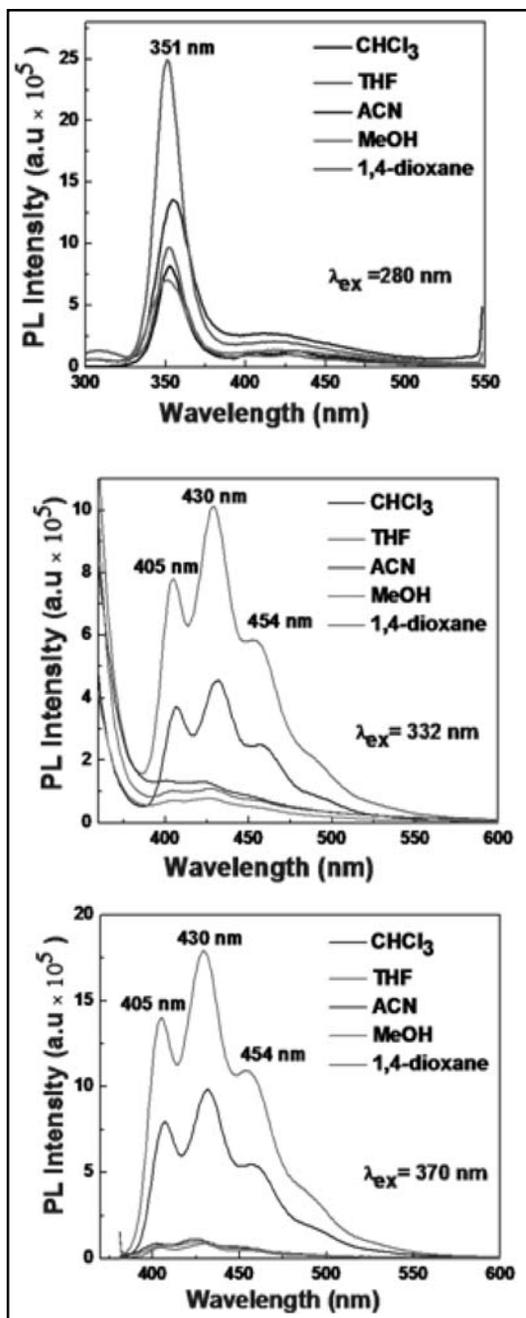


Fig. 8. PL spectra of functional photoactive polysilanes (PSDY-2B)

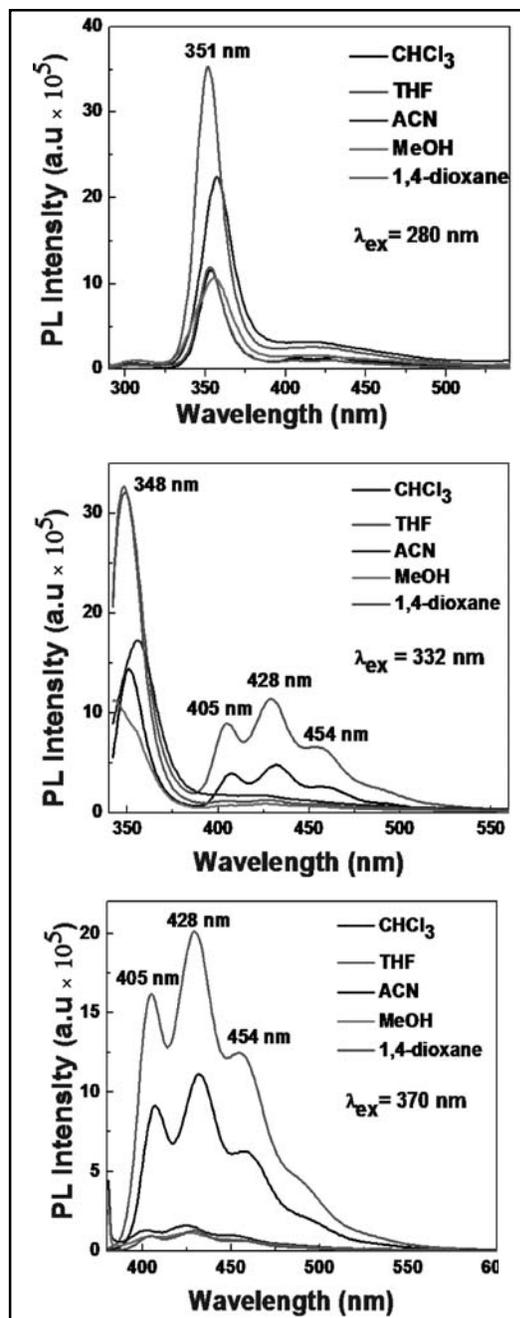


Fig. 9. PL spectra of functional photoactive polysilanes (CPSDY-1B)

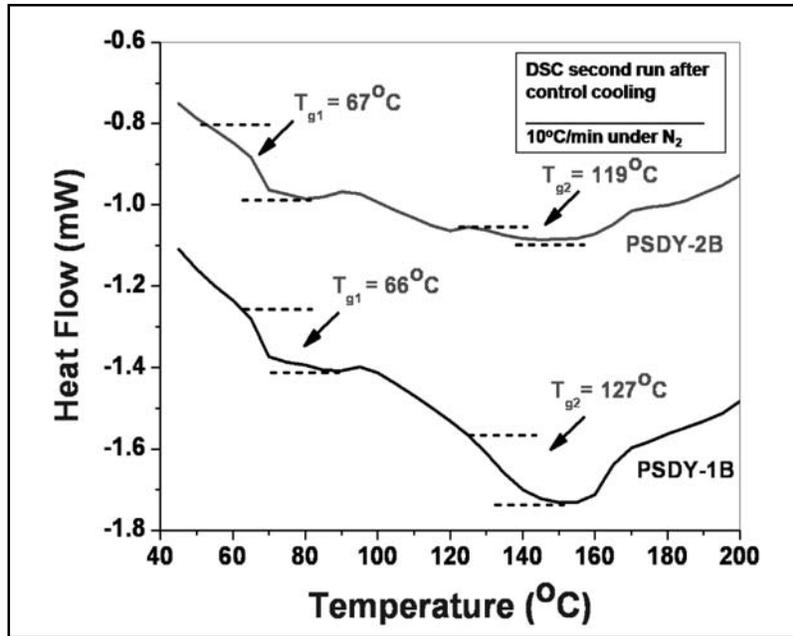


Fig. 10. DSC thermograms of Photoactive-block-polysilane copolymer

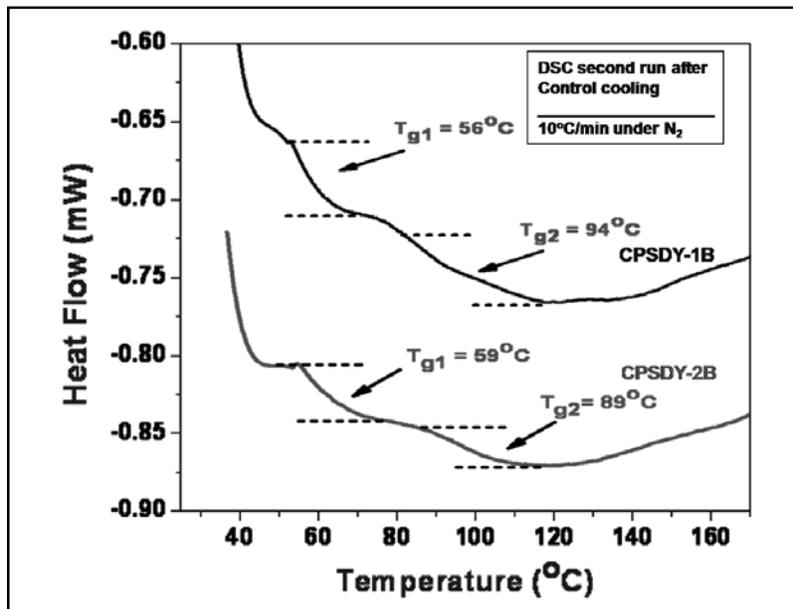


Fig. 11. DSC thermograms of Photoactive-block-polysilane copolymer

Thermal Stability

The thermal properties of the synthesized functional photoactive polysilanes (PSDY and CPSDY) were evaluated using TGA analysis (Figures 12, 13 and 14). The TGA thermograms of functional photoactive polysilane copolymer (PSDY) are shown in Figure 12 (a) and derivative curve in 12 (b). The TGA thermograms and derivative curves of CPSDY are shown in 14 (a) and 14 (b). The results of thermal analysis of synthesized functional photoactive polysilanes are given in Table 2 and 3. The decomposition of PMPS and CPS was started

at 260°C and 240°C respectively. On the other hand, thermal decomposition of PSDY-1B, PSDY-2B, CPSDY-1B and CPSDY-2B was started at 340°C, 325°C, 315°C and 327°C respectively. Thermal stability of synthesized photoactive polysilane copolymers, PSDY and CPSDY is higher as compare to PMPS homopolymer and CPS copolymer. The char residues of PMPS, CPS and functional photoactive polysilane copolymers (PSDY-1B, PSDY-2B, CPSDY-1B and CPSDY-2B) are observed at 600°C to be 15, 7, 17, 33, 40 and 15 respectively.

TABLE 2. Thermal Properties of PMPS and Functional Photoactive Polysilane Copolymers (PSDY and CPSDY)

| Samples | T _{di} (°C) | T _{d peak} (°C) | T _{dt} (°C) |
|----------|----------------------|--------------------------|----------------------|
| PMPS | 260 | 407 | 450 |
| PSDY-1B | 340 | 420 | 576 |
| PSDY-2B | 325 | 426 | 470 |
| CPS | 240 | 375 | 450 |
| CPSDY-1B | 315 | 449 | 650 |
| CPSDY-2B | 327 | 410 | 650 |

TABLE 3. Weight Loss and Char Residue of PMPS and Functional photoactive polysilane copolymers

| Samples | Weight Loss (%) at | | | Char Residue (wt%) at 600°C |
|----------|--------------------|-------|-------|-----------------------------|
| | 300°C | 350°C | 450°C | |
| PMPS | 3.9 | 15.8 | 88.8 | 15 |
| PSDY-1B | 2.8 | 10.5 | 78.7 | 17 |
| PSDY-2B | 2.7 | 11.6 | 66.4 | 33 |
| CPS | 6.2 | 28.3 | 92.4 | 7 |
| CPSDY-1B | 2.3 | 5.4 | 38.1 | 40 |
| CPSDY-2B | 3.9 | 10.7 | 70.4 | 15 |

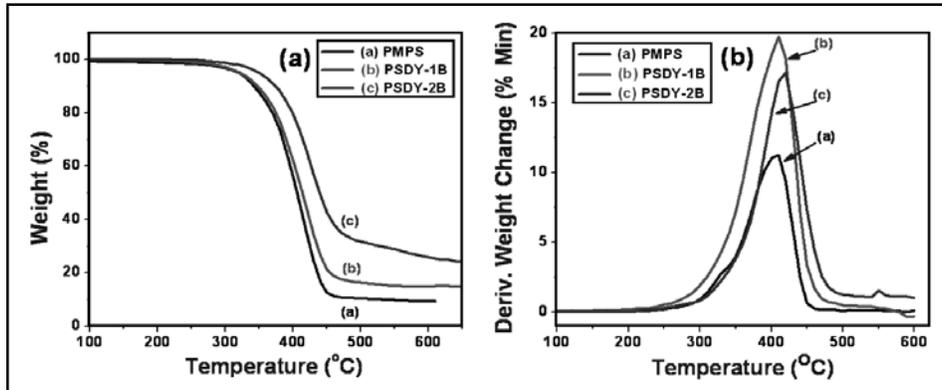


Fig. 12. TGA and DTGA thermograms of synthesized functional polysilanes (PSDY) and PMPS

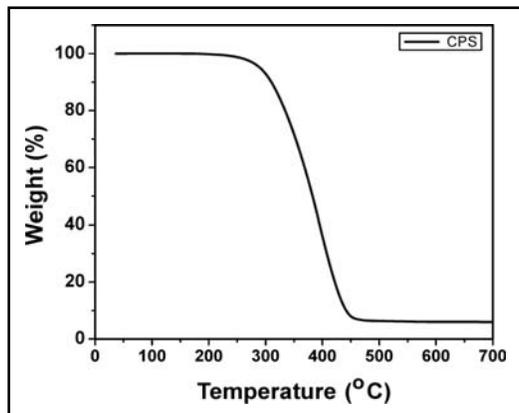


Fig. 13. TGA thermogram of synthesized polysilane copolymer (CPS)

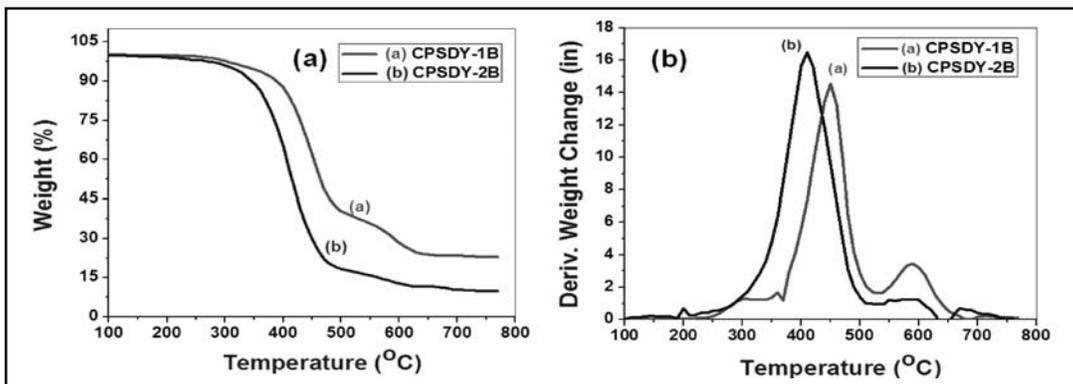


Fig. 14. TGA and DTGA thermograms of synthesized functional polysilanes of CPS

4. CONCLUSIONS

Functional photoactive polymers of poly(methylphenylsilane) (PMPS) and poly(methylphenylsilane-co-dimethylsilane) (CPS) were synthesized along with disperse yellow 7 methacrylate by UV technique. Polysilanes (PMPS and CPS) give rise to silyl radicals upon UV-irradiation which initiate the radical polymerization of photoactive azo monomer (disperse yellow 7 methacrylate). These synthesized functional polysilanes (PSDY and CPSDY) were characterized by FTIR and NMR spectroscopy. The molecular weights of PSDY and CPSDY samples were measured to be of the order of 10^3 gm/mol. The optical and photoluminescence properties were also studied. These functional polymers exhibited optical absorbance at 276 nm due to aromatic ring, at 336 nm due to Si-Si σ -conjugation and at 366 nm due to azobenzene chromophore of disperse yellow 7 methacrylate unit. The synthesized functional photoactive polysilanes exhibited good multi-emission photoluminescence properties at 405, 428 and 454 nm when excited at 332 nm. These synthesized polymers are stable upto 315°C. They may find novel optoelectronic applications.

REFERENCES

1. S. Nemat-Nasser, T. Plaisted., A. Starr and A. V. Amirkhizi "Multifunctional Materials" in *BIOMIMETICS: Biologically Inspired Technologies*, Yoseph Bar-Cohen (Ed.), CRC Press Ch.12 (2005) 309-341
2. D. S. Bag, "Functional Polymers" in *Principles of Polymers-An advanced Book*, D. S. Bag, Nova Science Publishers Inc., New York, Ch.11 (2013) 497-590
3. J. Li, Z. Li, H. Tang, H. Zeng, J. Qin, *J. Organomet. Chem.* 685 (2003) 258
4. R.D. Miller, J. Michl, *Chem. Rev.*, 89 (1989) 1359
5. S. Nespurek, A. Eckhardt, *Polym. Adv. Tech.*, 12 (2001) 440
6. S. Kashimura, M. Ishifune, *J. Synth. Org. Chem. Jpn.*, 58 (2000) 966
7. R. West, *J. Organomet.* 300 (1996) 327
8. M. Fujiki., *J. Organomet. Chem.*, 685 (2003) 15
9. S. Hayase, *Prog. Polym. Sci.*, 28 (2003) 359
10. H. Tang, J. Qin, X. Deng, Y. Cao, *Organomet.*, 23 (2004) 6070
11. F. Kajzar, J. Messier, C. Rosillio, *J. Appl. Phys.*, 60 (1986) 3040
12. Y. Chen, C. Liao, T. Wu, *Polymer* 43 (2002) 4545
13. P. K. Bhowmik, R. A. Burchett, H. Han, J. Cebe, *J. Polym.*, 43 (2002) 1953
14. L. Akcelrud, *Polymer* 46 (2005) 2452
15. S. K. Yesodha, C. K. S. Pillai, N. Tsutsumi, *Prog. Polym. Sci.*, 29 (2004) 45
16. A. Nathansohn, P. Rochon., *Adv. Mater.*, 11 (1999) 1387
17. N. Tirelli, R. A. Solaro, F. Ciardelli, S. Follonier, C. H. Bosshard, P. Gunter, *Polymer* 41 (2000) 415
18. N. Tsutsumi, M. Morishima, W. Sakai, *Macromolecules*, 31 (1998) 7764
19. T.Y. Luh, R.M. Chen, T.Y. Hwu, S. Basu, C.W. Shiao, W.Y. Lin, B. Y. Jin, C.C. Hsu, *Pure Appl. Chem.*, 73 (2001)243
20. M. Chen, L. Yu, L. R. Dalton, Y. Shi, W. H. Steier, *Macromolecules*, 24 (1991) 5421
21. Z. S. Xu, V. Drnoyn, A. Natansohn, R. Rochon, *J. Polym. Sci. Part A: Polym. Chem.*, 38 (2000) 2245
22. C. Zhang, C. Wang, J. Yang, L. R. Dalton, G. Sun, H. Zhang, W. H. Steier, *Macromolecules*, 34 (2001) 235

23. N. Nemoto, F. Miyata, Y. Nagase, J. Abe, M. Hasegawa, Y. Shirai, *Macromolecules*, 29 (1996) 2365
24. H. Xie, Z. Liu, X. Huang, J. Guo., *Eur. Polym. J.*, 37 (2001) 497
25. J. D. Stenger-Smith, P. Zarras, R. A. Hollins, A. P. Chafin, L. H. Merwin, R. Yee, G. A. Lindsay, W. N. Herman, R. F. Gratz, E. J. Nickel, *J. Polym. Sci. Part A: Polym. Chem.*, 38 (2000) 2824
26. Y. Aoshima, C. Egami, Y. Kawata, O. Sugihara, M. Tsuchimori, O. Watanabe, H. Fujimura, N. Okamoto, *Opt. Commun.*, 165 (1999) 177
27. E. Gubbeldmans, T. Verbiest, M. V. Beylen, A. Persoons, C. Samyn, *Polymer*, 43 (2002) 1581
28. E. Hendrickx, D.V. Steenwinkel, A. Persoons, *Macromolecules*, 32 (1999) 2232
29. L. Ding, T. P. Russell, *Macromolecules*, 40 (2007) 2267
30. S. Xie, A. Natansohn, P. Rochon, *Chem. Mater.*, 5 (1993) 403
31. P. Uznanski, M. Kryszewski, E. W. Thulstrup, *Eur. Polym. J.*, 27 (1991) 41.
32. A. Natansohn, P. Rochon, *Adv. Mater.*, 11 (1999) 1387
33. S. K. Yesodha, C. K. S. Pillai, N. Tsutsumi, *Prog. Polym. Sci.*, 29 (2004) 45
34. D. S. Bag, S. Alam, *J. Appl. Polym. Sci.*, 125 (2012) 2595-2603
35. Km. Meenu and D. S. Bag, *J. Macromol. Sci.: Pure and Appl. Chem.*, 54 (6) (2017) 418
36. L. A. Harrah, J. M. Zeigler, *Macromolecules*, 20 (1987) 2037
37. T. J. Cleij, J. K. King, L.W. Jenneskens, *Macromolecules*, 33 (2000) 89
38. S. H. Yi, N. Maeda, T. Suzuki, H. Sato, *Polym. J.*, 24 (1992) 865
39. S. Mimura, H. Naito, Y. Kanemitsu, K. Matsukawa, H. Inoue, *J. Organomet.*, 611 (2000) 40
40. K. Matsukawa, S. Fukui, N. Higashi, M. Niwa, H. Inoue, *Chem. Lett.*, 28 (1999) 1073
41. Km. Meenu, D. S. Bag, A. K. Saxena, *J. Polym. Sci. Part A: Polym. Chem.*, 54 (2016) 3626
42. Km. Meenu, D.S. Bag, R. Lagarkha, R. Tomar, A. K. Gupta, *Current Organocatalysis*, 6 (2019) 193
43. T. Buffeteau, A. Natanshon, P. Rochon, M. Pezolet, *Macromolecules*, 29 (1996) 8783
44. A. Ranjan, C.S. Bisaria, A.K. Saxena, *Int. J. Technol.*, 31 (1993) 666
45. M. Nasim, A.K. Saxena and L. M. Pande, *Polyhedron*, 7 (1998) 2189
46. K. Saxena, Bissaria C.S. Bisaria A.K. Saxena, *Appl. Organomet. Chem.*, 24 (2010) 251
47. S. K. Sukla, R. K. Tiwari, A. Ranjan, A. K. Saxena, G. N. Mathur, *Thermochem. Acta*, 424 (2004) 209
48. D. S. Bag, T. C. Shami, K. U. B. Rao, *J. Polym. Mater.*, 25 (2008) 51
49. B. M. Klemann, R. West, J. A. Koutsky, *Macromolecules*, 26 (1993) 1042
50. H. Kishida, H. Tachibana, K. Sakurai, M. Matsumoto, Y. Tokura, *Phys. Rev. B*, 54 (1996) R14254
51. B. M. Klemann, R. West, J. A. Koutsky, *Macromolecules*, 29 (1996) 198
52. B. Jambe, A. Jones, J. Devaux, *J. Polym. Sci. Part B: Polym. Phys.*, 35 (1997) 1533
53. H. F. Mark, *Encyclopaedia of Polymer Science and Technology*, Vol 7 (2003) 625
54. H. Nakashima, M. Fujiki, *Macromolecules*, 34 (2001) 7558
55. S. Nespurek, A. Kadeshchuk, Yu. Skryshevski, A. Fujii, K. Yoshino, *Journal of Lumin.*, 99 (2002) 131
56. O. Ito, M. Terajima, T. Azumi, N. Matsumoto, K. Takeda, M. Fujino, *Macromolecules*, 22 (1989) 1718

Received: 12-07-2019

Accepted: 12-09-2019