

Synthesis and characterization of a polyhedral oligomeric silsesquioxane-functionalized methyl red: A novel candidate for non-linear optical applications

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A Polyhedral Oligomeric Silsesquioxane (POSS) functionalized with methyl red azo dye was synthesized using the *Steglich Esterification*. The resultant organic-inorganic colorant was characterized using FTIR, ¹H NMR and elemental techniques. Change of acidic carbonyl groups to an esteric one was related to formation of functionalized dye. Differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) also confirmed that grafting was occurred, the result of which was observation of 12°C increase in thermal stability of the functionalized nano-structured dye. A 5 nm bathochromic shift revealed in UV-Visible spectra of the grafted dye was attributed to the covalent bonding of POSS and dye. Characterization techniques indicated that more dye is covalently grafted to POSS when the molar ratio of methyl red to POSS was 4:1. Studies of induced birefringence showed promising results confirming that aggregation of dye was significantly reduced due to incorporation of POSS to the dye chromophore.

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1. Introduction

Non-linear optical dyes have attracted enormous attentions during the last decade. Their advantage over the inorganic ones stems from their variety and structural versatility to be used in certain applications [1]. These advantages have made them suitable for various applications in the field of optical switches, telecommunications, data storage and processing [2]. A necessary condition to exhibit the second order non-linear optical properties is the central asymmetry of the molecules in both microscopic and macroscopic levels. Many of the donor-acceptor chromophores are in the form of a conjugated system with asymmetric charge distribution [3-4]. Besides the above properties, azobenzene chromophores have the ability to photoisomerize and consequently, photo reorient which made them suitable to be used in a wide range of applications [5]. Many of the organic molecules crystallize symmetrically and lose their second harmonic ability. Various physical and chemical methods have been performed to remove their symmetry. One approach is to place the guest chromophores into a host polymeric matrix. The guest-host system has some advantages such as applicability to a wide range of non-linear optical (NLO) chromophores, easy and inexpensive processing in low temperatures and also simple rescaling. However, disadvantages such as thermal instability, low activity due to limited solubility of dye in the matrix causes aggregation in high concentration and heterogeneity, leading to scattering of laser beam [1].

In this article, methyl red (C.I No. 13020) as an azo chromophore is bonded covalently to a nano structured material named polyhedral oligomeric silsesquioxane (POSS). POSS is an organic-inorganic nano compound containing an inorganic core made of silicone and oxygen surrounded by organic reactive or non-reactive ligands [6]. Furthermore, the inorganic core of POSS imparts hardness and stability to the system, while the organic ligands promote solubility, processability and compatibility with organic matrix [7].

Cheng et al. [8] synthesized electroluminescent POSS based material containing eight carbazole chromophores. Photoluminescence spectra of the synthesized hybrid showed decrease in aggregation due to prohibition of inter-chain interactions caused by POSS core. Pérez-Ojeda et al. [9] synthesized a dye-functionalized POSS for photostable photonic systems and studied degree of functionalization of POSS on the optical properties. They found out that functionalization of POSS with eight chromophores leads to dye aggregation and made the optical properties worse. Yan et al. [10] synthesized squaraine-containing POSS-based materials and showed that dipole-dipole and π - π interactions were decreased due to covalent bonding of POSS to the optical material, leading to inhibition of charge transfer between the adjacent chromophores. They reported an improvement in optical and chemical stability. A series of mono-, dis- and tris-azo dye grafted POSS compounds were also synthesized by Zhou et al. [11]. They proved that photo-isomerization of azobenzene chromophores depended on their molecular structure. Su et al. [12] synthesized nonlinear optical azobenzene

chromophores grafted POSS to study their structure and properties and observed thermal stability and good optical limiting properties.

We have previously synthesized [13] a guest-host disperse red 1 (DR1) dye-doped organic-inorganic nanocomposite via sol-gel process and analyzed the photo-induced properties. In reference [2] we studied the induced birefringence of a novel methyl red grafted epoxy silane coupling agent, which was hydrolyzed and condensed to form an organic-inorganic dye-containing hybrid. In both approaches, by increasing dye concentration, aggregation of the chromophores led to scattering of laser beam and reduced optical properties.

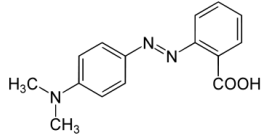
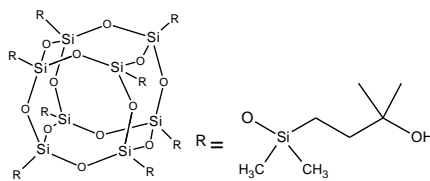
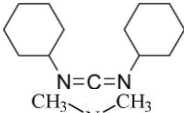
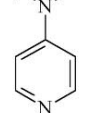
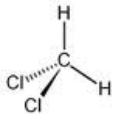
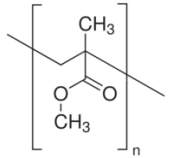
This work aims at synthesizing a novel methyl red-containing POSS hybrid to potentially reduce the aggregation of dye. This unique structure allows increasing the dye concentration by isolating the adjacent chromophores. This strategy also eliminates the disadvantages associated with sol-gel reactions such as large shrinkage due to gelation process, removal of undesirable residuals and presence of pores [14]. Structural, thermal and optical properties of the synthesized dye-POSS hybrid were elucidated.

2. Experimental

2.1. Materials

The NLO dye used in this study was 2-(4-(dimethyl-amino) phenylazo) benzoic acid, known as methyl red, purchased from Sigma-Aldrich as depicted in Table 1. Octa(3-hydroxy-3-methylbutyldimethylsiloxy) POSS, supplied by Hybrid Plastics Inc (USA), was used for grafting with the dye. The coupling agent and catalyst required for reacting the dye and POSS were 1,3-dicyclohexyl-carbodiimide (DCC) and 4-dimethyl-aminopyridine (DMAP) both obtained from Merck. Dichloromethane (CH_2Cl_2) and Hydrochloric acid (HCl 37%) were purchased from Merck. Sodium bicarbonate (NaHCO_3) was provided by Kiankaveh Inc. (Iran). Polymethyl methacrylate (PMMA) was supplied by Sigma-Aldrich. All materials were of analytical grade and used as received. The role, supplier and chemical structure of materials used are shown in Table 1.

Table 1. Chemical structure and role of materials used.

Name	Chemical Structure	Supplier	Role
O-methyl red (2-(4-(dimethyl-amino) phenylazo) benzoic acid)		Sigma- Aldrich	NLO chromophore
POSS (Al0136) Octa(3-hydroxy-3- methylbutyldimethylsil oxy)		Hybrid Plastics	Grafting
1,3-dicyclohexyl- carbodiimide (DCC)		Merck Co.	Coupling/activating
4-dimethyl- aminopyridine (DMAP)		Merck Co.	Catalyst
Dichloromethane		Merck Co.	Solvent
Hydrochloric acid 37%	H-Cl	Merck Co.	DMAP separator
Sodium bicarbonate	$\text{Na}^+ \text{ } ^-\text{O}-\text{C}(=\text{O})-\text{OH}$	Kiankaveh	Separator
Polymethyl metachrylate		Sigma- Aldrich	Polymeric matrix

2.2. Synthesis of dye-grafted POSS

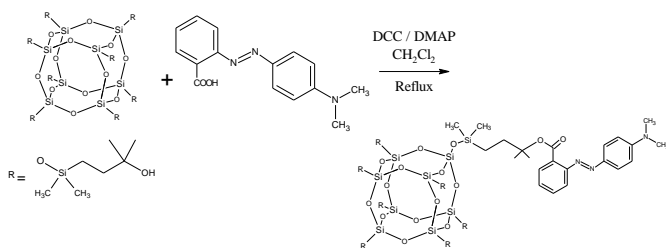
The purpose of this study was to graft methyl red to POSS via the Steglich reaction. The reaction involves esterification of carboxylic groups of the dye with hydroxyl groups of silsesquioxane compound [15]. To this end, 0.15 mmol of POSS was reacted with various molar ratios of methyl red in such a manner that the ratios of dye:POSS turned out to be 2:1, 4:1 and 8:1. The concentration of DCC and DMAP were equimolar of dye and 0.016 mmol respectively [16]. Table 2 dedicates the description of samples.

Table 2. Sample Labeling.

Sample Label	Molar ratio of MR to POSS
P2	2:1
P4	4:1
P8	8:1

The reactants were first dissolved in dichloromethane under stirring and kept under reflux for about 16 hours [17-18]. DCC activates methyl red to form O-acylisourea, which gives dicyclohexylurea (DHU) and the corresponding ester in a slow reaction with POSS.

DMAP, acting as an acyl transfer reagent, is a stronger nucleophile compared with POSS and reacts with protonated O-acylisourea to obtain an active ester. This reacts rapidly with POSS to give rise to the desired ester [15]. After being cooled to room temperature, DHU by-product was filtered out by a Buchner funnel. The residual solution was washed with two portions of 0.5 N hydrochloric acid to remove DMAP from the organic phase and two portions of saturated sodium bicarbonate solution. The hydroxide anion of the sodium bicarbonate reacts with carboxylic acid to form a water soluble carboxylate salt and removes the un-reacted methyl red from the grafted dye-POSS. Additional precipitated DHU was removed by filtration [19]. The organic layer was dried over silica gel and then in a vacuum oven to remove the residual solvent. Different amounts of methyl red were grafted to POSS according to the procedure described above. Scheme 1 represents the desired reaction.



Scheme 1. Grafting methyl red to POSS through Steglich esterification.

The synthesized methyl red grafted to POSS was aimed to form optically transparent films with PMMA.

3. Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Bomem Hartmann & Braun using KBr pellets with 4 cm^{-1} resolution. ^1H NMR spectra was obtained utilizing a Bruker Advance 300 NMR spectrometer using chloroform-d (CDCl_3). Elemental analysis of carbon, hydrogen and nitrogen were measured with a FOSS-Herues CHN-D-Rapid elemental analyzer.

Absorption of samples were recorded using a Jenway 6715 UV-visible spectrophotometer and a Gretag Macbeth Color-Eye 7000 Visible spectrophotometer using a 1 cm square quartz cell. Differential scanning calorimetry (DSC) was performed on a Mettler-Toledo DSC 1 under a continuous nitrogen flow at a heating rate of $10^\circ\text{C}/\text{min}$ within the temperature range of $25\text{-}300^\circ\text{C}$. Thermo gravimetric analysis was carried out on a Shimadzu 50 TGA at a heating rate of $10^\circ\text{C}/\text{min}$ under a nitrogen purge ($30\text{ ml}/\text{min}$).

In birefringence studies, methyl red grafted POSS (P4 sample) dissolved in PMMA and set between two crossed polarizers. A diode-pumped frequency doubled Nd:YAG laser (532 nm) was used to induce birefringence. He-Ne laser (632.8 nm) as the probe beam detected the material response. The setup is shown in Fig. 1.

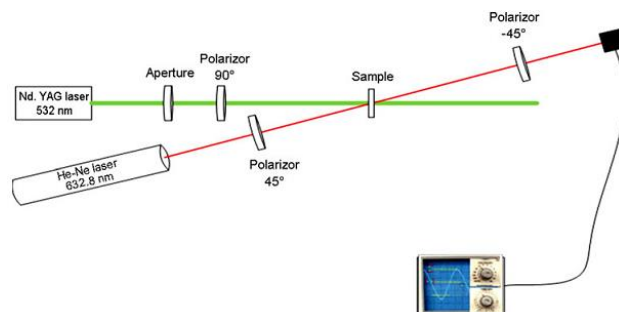


Fig. 1. Birefringence setup.

4. Results and discussion

During the attachment of methyl red to POSS, as can be seen in scheme 1, carboxylic acid group of methyl red reacts with hydroxyl groups of POSS and forms an ester. Decrease in intensity of the peak assigned to hydroxyl group appeared about 3391 cm^{-1} can be an evidence for the reaction progress. Generally, appearance of a peak in the range of $1000\text{-}1300\text{ cm}^{-1}$ can be used to distinguish esters [20] but here it is overlapped with Si-O-Si absorption band [21]. Monitoring the reaction mixture at the beginning of the reaction and after completion of the reaction can be helpful. A decrease in the width of the above peaks could be a sign of esteric bonds and C-O formation at 1275 cm^{-1} . On the other hand, esteric carbonyl appears at the higher frequencies in comparison with the acidic carbonyl [20], so the appearance of methyl red C=O at 1718 cm^{-1} at the

beginning of the reaction and then its shift to 1729 cm^{-1} at the end of the reaction could be assigned to grafting methyl red to POSS. After purification and separation of DHU and the un-reacted methyl red, esteric C=O and C-O are more evidenced. Fig. 2 shows the FTIR spectra of P4 during the reaction progress.

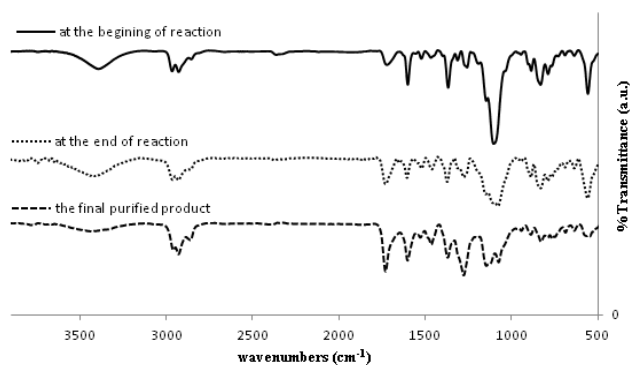


Fig. 2 FTIR spectra of the P4 reaction mixture during the reaction progress.

FTIR spectra of P2 and P8 were compared with P4 (as explained before) and the same trend was observed. So, only the spectra of the final product are shown in Fig. 3. The peak appeared at 1520 cm^{-1} corresponds to the azo group [5] and shows the presence of methyl red in the final product. In all samples, carbonyl absorption peak shifts to higher frequencies at the end of the reaction in comparison to the raw materials, which is a sign of converting acidic carbonyl to esteric carbonyl. Comparing the samples, increasing the C=O intensity and decrease in the O-H intensity are more obvious in P4 sample, then P8 and finally P2. Based on the FTIR results, the amount of methyl red attached to POSS seems to be $P4 > P8 > P2$. One can expect an increase in attachment with increasing the feed ratio. However, by increasing the concentration of methyl red, there will be a competition between the formation of the covalent bonds and hydrogen bonding due to presence of the hydroxyl, dimethylamine and carboxylic acid groups. This is why less amount of methyl red is grafted in P8 in comparison to P4.

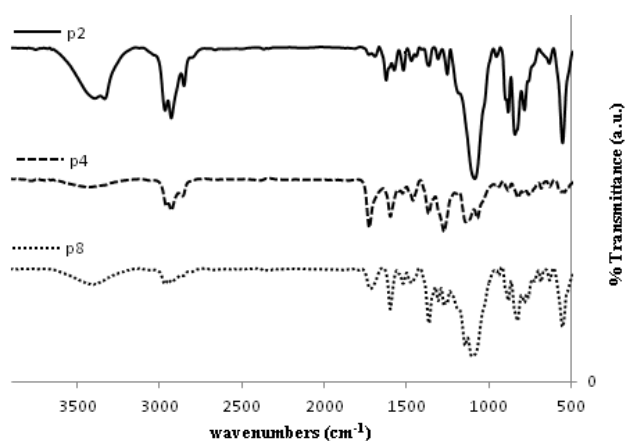


Fig. 3. FTIR spectra of P2, P4 and P8.

While FTIR spectroscopy reveals the functional groups presented in the sample, NMR can give more information on hydrogen skeleton of the molecule. The synthesized hybrids are soluble in many common organic solvents such as dichloromethane, dimethylformamide, THF, due to existence of organic molecules attached to silsesquioxane core [22]. NMR spectroscopy was done on the samples in the solution form.

^1H NMR spectra and proton chemical shifts of the synthesized hybrids are shown in Fig. 4 and Table 3, respectively [20,23].

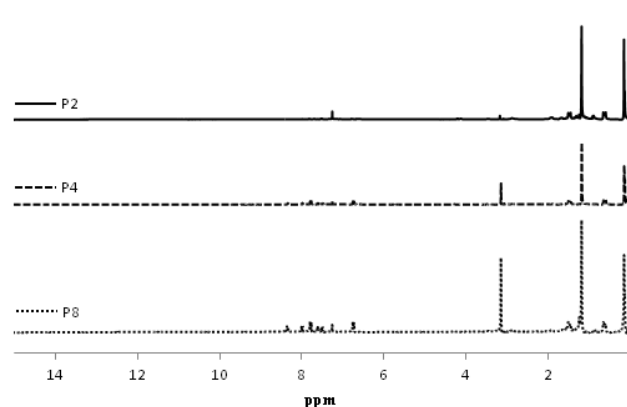


Fig. 4. ^1H NMR spectra of P2, P4 and P8.

Table 3. Proton chemical shifts of P2, P4 and P8.

Functional group	δ (ppm)
SiCH ₃	0.16
SiCH ₂	0.62
CH ₃	1.19
CH ₂	1.46
OH	2.89
NCH ₃	3.17
Benzene Ring	6.5-8.5

The proton of carboxylic acid group of methyl red resonances at 14.29 ppm due to both resonance and electronegativity effect of oxygen which withdraws electrons from the acidic proton (the ^1H NMR spectra of methyl red is not shown here) [20]. The protons of hydroxyl group of POSS have their resonance at 2.89 ppm. As can be seen in figure 4, the resonance peaks at 14.29 ppm are completely disappeared. This means that all the un-grafted methyl red molecules are most likely separated from the final product during separation and purification. It can be said that all dyes presented in the product are

attached to the POSS molecule. On the other hand, based on the integral of area under ^1H NMR peak at 2.89 ppm, the average number of hydroxyl groups of POSS presented in the sample could be calculated [24]. The less number of hydroxyl groups of POSS, shows greater methyl red molecules attached to POSS. According to reference [25], methyl protons attached to Si are appeared near 0 ppm. In order to calculate the number of methyl red molecules grafted to POSS, the peak appeared at 0.16 ppm assigned to OSiCH_3 [26], is assumed to be the reference peak because it has less shift and also is unchanged during the reaction progress. Considering the integral of the peaks attributed to the number of protons, in all synthesized hybrid samples, there are 48 protons assigned to OSiCH_3 . Accordingly, based on integral of the resonance peak at 2.89 ppm (related to OH of POSS), the number of unreacted hydroxyl groups can be calculated.

In P2, the integral of the peak related to OSiCH_3 is 8.7168 which is equal to 48 protons. The integral of OH peak is 1.0778 and number of the un-reacted hydroxyl groups is calculated to be 5.94 (*ca.* 6). POSS molecule has eight hydroxyl groups. So, in P2 two methyl red molecules are believed to have been attached to POSS.

By the same reasoning, in P4 sample the integral of peak corresponding to OSiCH_3 is 19.646 which is equal to 48 protons and the integral of the alcoholic protons is 2.016 equal to 4.93 (*ca.* five) un-reacted hydroxyls. So it seems that in P4, three methyl red molecules are attached to POSS. The same calculations show that between two and three methyl red molecules have been attached to POSS in P8 sample. As mentioned earlier, the competition between hydrogen and covalent bonding due to increase in methyl red concentration, may lead to more methyl red to be grafted in P4 compared to P8.

Based on ^1H NMR data, grafting of methyl red to POSS is confirmed by disappearance of COOH proton shift. Accordingly, the trend obtained by NMR shows that methyl red attachment to POSS is in the order of $\text{P4} > \text{P8} > \text{P2}$ which is in very good agreement with FTIR results previously shown.

Elemental analysis was also done to determine the quantitative amount of methyl red grafted to POSS. In this method, the weight percent of carbon, hydrogen and nitrogen atoms were examined. P4, as the highest grafted sample, and P2, as the lowest one, were tested. The analysis was also done on methyl red itself. It is assumed that all the methyl red molecules present in the samples are grafted to POSS, as confirmed by ^1H NMR. The results are shown in Table 4.

Table 4. Carbon, Hydrogen and Nitrogen contents of P4 and P2.

Sample	%C	%H	%N
methyl red	67.1	5.5	3.7
P4	47.3	7.3	4.7
P2	48.6	7.8	3.3

According to calculations, each methyl red molecule has 3 nitrogen, 15 carbon and 15 hydrogen atoms which is to be expected from dye general formula ($\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_2$). POSS molecule ($\text{C}_{56}\text{H}_{136}\text{O}_{28}\text{Si}_{16}$) has 56 carbon, 136 hydrogen and no nitrogen atoms. Due to the absence of nitrogen atom in POSS, %N could be the criteria for methyl red presence in the sample. Comparing %N of P2 and P4, it is observed that in P4 more methyl red is grafted to POSS, which is in agreement with FTIR and ^1H NMR results.

Based on CHN analysis in P2, two molecules of methyl red and in P4 three molecules are attached to POSS. These results are in a good agreement with results of ^1H NMR studies.

Fig. 5 shows the UV-visible spectra of methyl red and P4 sample. The samples were completely dissolved in dichloromethane at the same concentration. As it is shown, P4 shows a decrease in absorption intensity in comparison to methyl red in both UV and visible regions. These arise from $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively [20]. Grafting methyl red to POSS makes the non bonding oxygen electrons of methyl red to be interacted with POSS. So absorption intensity in the UV region decreases. The main reason for loss of the intensity in the visible region might due to decrease of concentration of methyl red in the synthesized hybrid in comparison to the dye, itself. The maximum absorption wavelength (λ_{max}) of methyl red and P4 are *ca.* 482 nm and 487 nm, respectively. A 5 nm bathochromic shift is observed due to grafting of dye to POSS. This slight shift can be explained by larger electron delocalization [27]. Band width has also been increased in P4 due to loss of purity of P4 in comparison to methyl red.

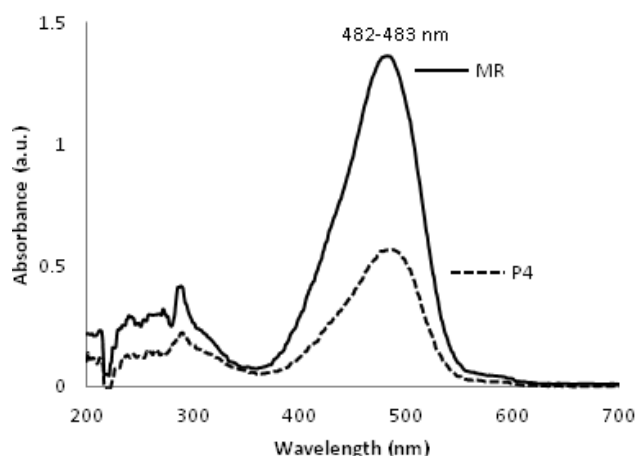


Fig. 5. UV-Visible absorbance spectra of methyl red and P4.

Visible absorption spectra of P2, P4 and P8 are shown in Fig. 6. The samples were dissolved at the same concentration in dichloromethane. Since the absorption in the visible region is due the $\pi \rightarrow \pi^*$ transition in methyl red, higher absorbance may correspond to greater attached dye to POSS [24,28]. Again, these results show that P4 has more absorbance due to higher dye molecules attached to the siliceous structure.

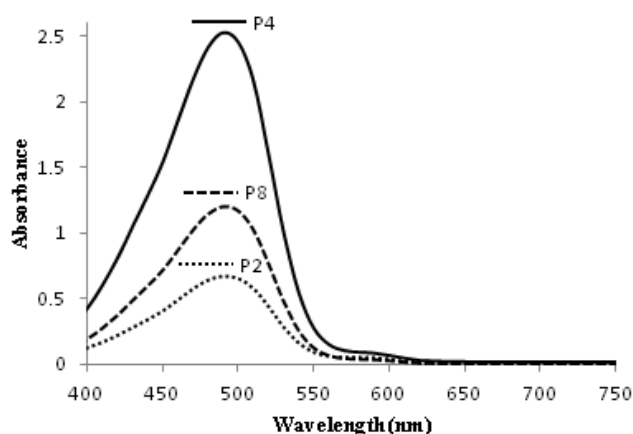


Fig. 6. Visible absorbance spectra of P2, P4 and P8.

To examine the thermal behavior of methyl red grafted to POSS, thermal behavior of components were studied using DSC and TGA as shown in Figs. 7 and 8.

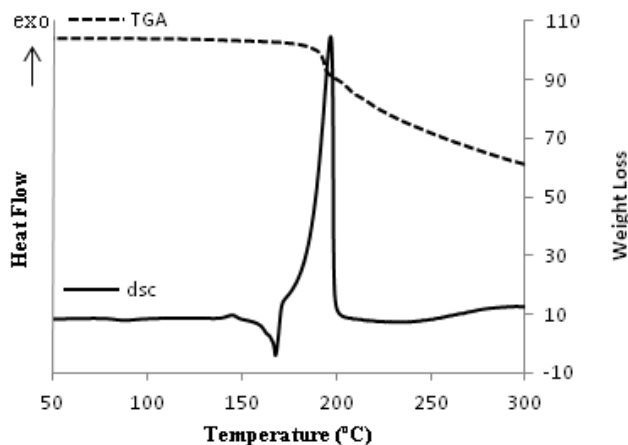


Fig. 7. DSC and TGA thermograph of methyl red.

As can be seen, an exothermic peak is observed at 144 °C, which can be related to Cis-trans isomerization cycle of azo compounds. By increasing the temperature, at 167°C an endothermic peak is appeared without any weight loss due to dye melting. Finally, at 196°C methyl red starts to degrade, showing an exothermic peak accompanied by an intense weight loss [2,29].

DSC and TGA results of POSS are shown in Fig. 8. There is an endothermic peak at 122°C without any weight loss, which could be related to melting of organic groups attached to the inorganic core of POSS. By increasing the temperature, a broad endothermic peak accompanied by weight loss is observed at 274°C due to degradation of the mentioned organic groups.

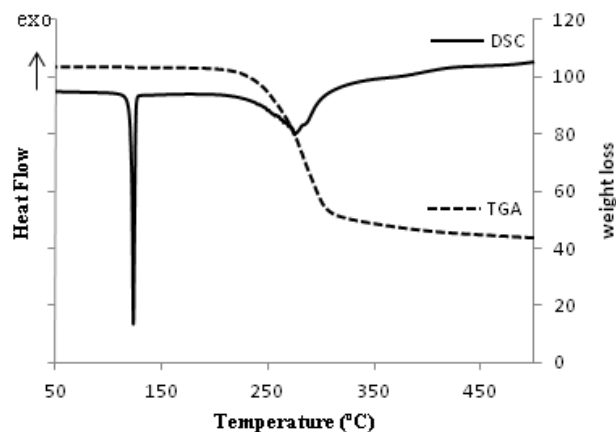


Fig. 8. DSC and TGA thermograph of POSS.

In Fig. 9, the DSC thermograph of P4 and a physical blend of dye : POSS at a similar ratio is represented. The reason to compare these two samples is to distinguish the effect of chemical attachment of dye to POSS.

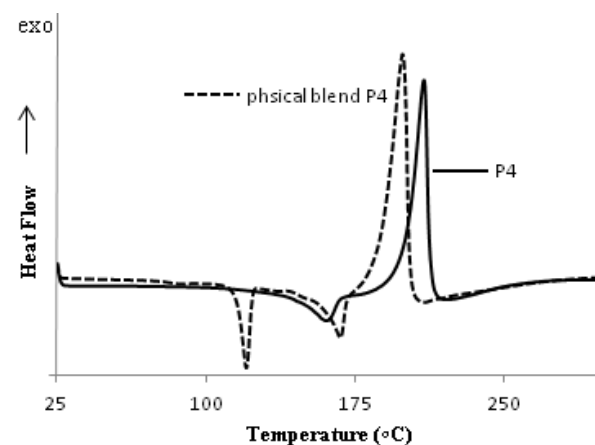


Fig. 9. Thermographs of physical and chemical blends of P4.

In the DSC thermograph of the physical blend, the first endothermic peak at 120°C is related to the melting point of methyl red and the second one at 167°C is due to that of POSS. The degradation temperature seems to have not changed in this sample.

Interestingly, in P4 sample, instead of two independent separated melting points, there is one at 160°C, which lies between those of methyl red and POSS. This may imply that dye is chemically attached to POSS.

The onset of degradation is observed at 209°C, which is higher than that of methyl red degradation temperature. This confirms the enhanced thermal stability of the synthesized hybrid.

5. Birefringence studies

The effect of concentration of P4 in PMMA on the induced birefringence was studied. The pump power was 36 mw. The maximum induced birefringence of different concentrations is shown in Fig. 10.

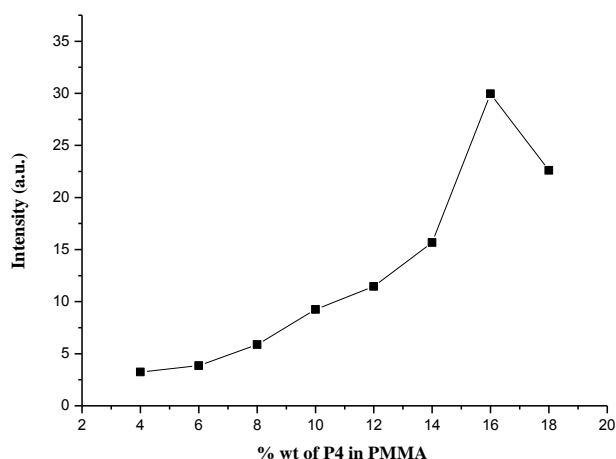


Fig. 10. Maximum induced birefringence of P4 in PMMA.

As can be seen in Fig. 10, increasing the optical material concentration leads to increased induced birefringence. This trend continues to % 16 after which the birefringence response decreases. This effect might be due to aggregation of the synthesized hybrid. At high concentrations, increasing of dipole-dipole interactions of the chromophores causes aggregation and leads to scattering of laser beam and worsening the optical properties.

The induced birefringence of methyl red in PMMA was also studied. The results showed that the maximum possible concentration of methyl red is at 4%. Absorption amount in the visible region could be a criterion of dye present in the system. To compare the effect of bonding POSS to dye, the visible spectra of methyl red and methyl red-grafted POSS (P4) at different concentrations were examined (not shown here). According to the results, % 16 P4 shows higher absorption than %4 methyl red. This confirms that grafting methyl red to POSS makes it possible to increase the dye concentration in matrix. In other words, rigid core of POSS prohibits the interactions of adjacent chromophores, leading to better dispersion of dye in the matrix.

6. Conclusion

Reaction of methyl red to POSS was performed at different concentrations of dye. FTIR, ^1H NMR, CHN elemental analysis, UV-Visible spectroscopy and thermal analyses confirmed that the grafting methyl red to POSS was accomplished. According to FTIR spectroscopy

increasing C-O intensity and shifting carbonyl frequency to higher frequencies revealed the esterification reaction. In ^1H NMR spectroscopy results, complete disappearing of peak related to acidic proton of methyl red, is a sign of removing the un-grafted dye. Based on CHN elemental analysis, presence of nitrogen confirms the existence of methyl red in the synthesized hybrids. Bathochromic shift in the UV-Visible absorption spectra of the hybrid also verified attachment of dye to POSS. Finally according to DSC data, existence of a single melting point and also the shift in degradation to higher temperatures approved the occurrence of grafting. This novel grafting approach had a marked effect on induced birefringence properties due to depreciation of aggregation.

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