Synthesis, Properties and Photochemistry of Organomodified Polymers

by

Amit Kumar

IISER, Pune, India

IISER PUNE

Advisor

Dr. Ashish Vaidya

Unilever R&D Bangalore, 64 Main Road, Whitefield,
Bangalore 560066, INDIA

Certificate

This is to certify that this dissertation entitled "**Synthesis, Properties and Photochemistry of Organomodified Polymers**" towards the partial fulfillment of the BS-MS dual degree programme at the Indian Institute of Science Education and Research, Pune represents original research carried out by ***Amit Kumar*** *at* ***Unilever R&D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, INDIA***" under the supervision of ***Dr. Ashish Vaidya, Research Scientist, Unilever R&D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, INDIA*** during the academic year 2012-2013.

Date: 30/March/2013

Signature: Ashish

Declaration

I hereby declare that the matter embodied in the report entitled "**Synthesis, properties and photostability of Organomodified Polymers**" are the results of the investigations carried out by me at ***Unilever R&D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, INDIA***" under the supervision of ***Dr. Ashish Vaidya, Research Scientist, Unilever R&D Bangalore, 64 Main Road, Whitefield, Bangalore 560066, INDIA*** and the same has not been submitted elsewhere for any other degree.

Date:

Signature:

Contents

Acknowledgements

It gives me immense pleasure to express my gratitude and respect for my advisor **Dr. Ashish Vaidya** for his expert and inspiring guidance throughout the period of my work. I am indebted to him for enlightening me on the finer skills of dealing with Polymeric chemistry and Photochemistry. It would have been impossible to achieve this goal without his constant support and encouragement. I consider myself fortunate to be associated with him who gave a decisive turn and a significant boost to my career.

I take this opportunity to thank my "**Prof. M. Jayakannan**" for his constant support during the course of this work.

I sincerely thank **Dr. Deeleep Rout, Dr. Janhavi Raut** and **Dr. Shilpa Vora** for supporting my project and **Dr. Vijay Gadgil** for the valuable discussions during the course of my project.

I sincerely thank D**r. Jyoti Seth** for the training on Polymer Rheology and **Mr. Balu K** and Mr. **Ravi Shukla** for the value additing discussion on photochemistry and synthetic chemistry.

I thank my friends **Nishant, Gaurav, Vasu, Ankur, Jeeten, Ravi, Harsh, Ankita, Ritesh, Rajkumar** for their help during the project work.

Abbreviations

PC	:	Personal care
DMMH-Co	:	Polly(dimethyl)-co-(methylhydrogen) siloxane
PDMS	:	Polydimethylsiloxane
HQ	:	1-hydroxyanthraquinone
1,2-HQ	:	1,2-hydroxyanthraquinone
Al-HQ	:	2-allyloxy-1-hydroxyanthraquinone
HQ-PDMS	:	Hydroxyanthraquinone modified Polydimethylsiloxane
OMPs	:	Organomodified Polymers
UVB	:	Ultra Violet Radiations (290 to 340 nm)
UVA	:	Ultra Violet Radiations (340 to 380 nm)
D_4	:	Octamethylcyclotetrasiloxane
DVDS	:	1,3-Divinyltetramethyldisiloxane
VTP	:	Vinylterminatedpolysiloxane
TMCTS	:	2,4,6,8–tetramethylcyclotetrasiloxane
D_5	:	Decamethylcyclotetrasiloxane
FTIR	:	Fourier Transform Infrared
NMR	:	Nuclear Magnetic Resonance
PHMS	:	Polymethylhydrosiloxane
TLC	:	Thin Layer Chromatography
PMMA	:	Polymethylmethaacrylate
ESIPT	:	Excited State Intramolecular Proton Transfer
g	:	Grams
mL	:	Millilitres
ppm	:	Parts per Million
M. Wt.	:	Molecular Weight
h	:	Hours
K_2CO_3	:	Potassium carbonate
nm	:	Nanometer
Ex	:	Excitation

λ_{max} : Maximum wavelength

M : Molar

$CDCl_3$: Chloroform D

$Ex\lambda_{max}$: Excitation wavelength maxima

$Em\lambda_{max}$: Emission wavelength maxima

HQ-gel : Hydroxyanthraquinone modified gel

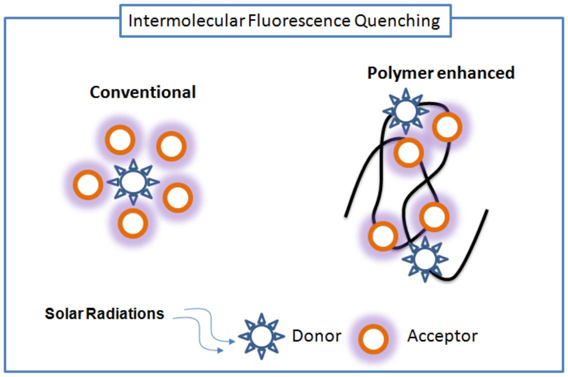
Ar : Aromatic

Min. : Minutes

Abstract

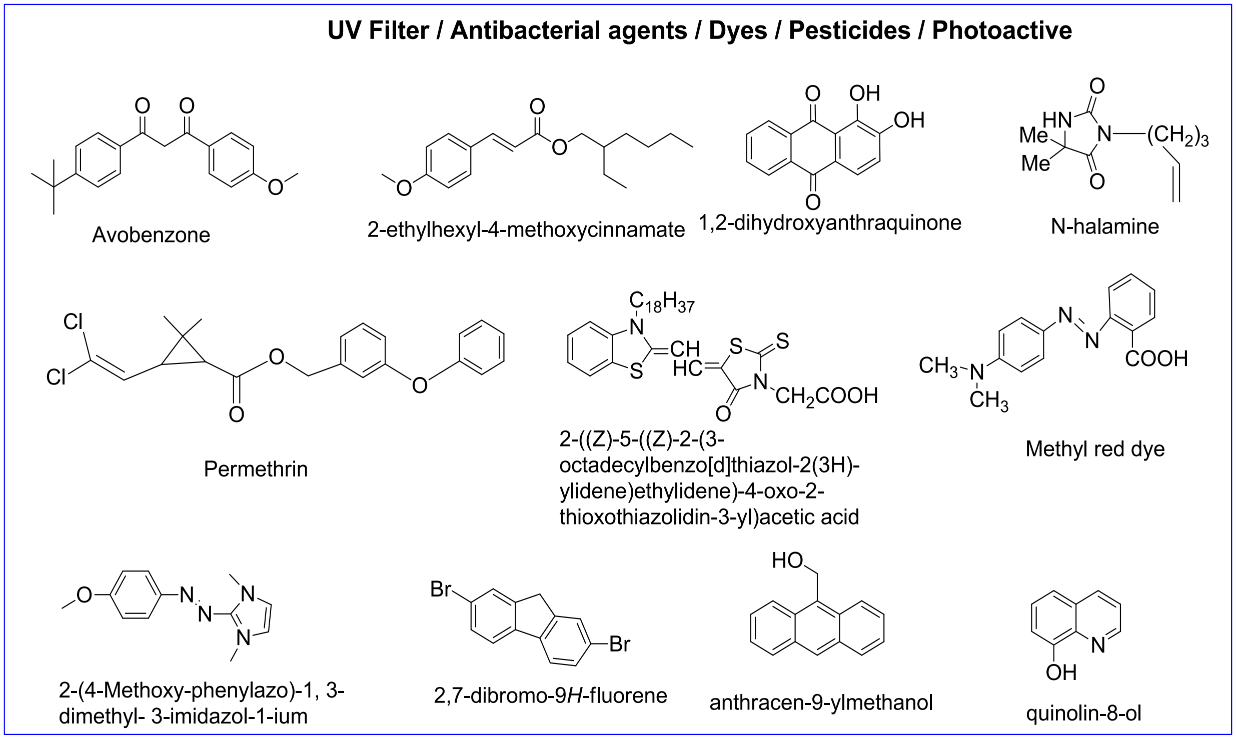
Photostable 1-hydroxyanthraquinone-tagged poly(dimethyl siloxane) (HQ-PDMS) were synthesized by reacting 2-allyloxy-1-hydroxyanthraquinone (Al-HQ) and octadecene with poly(dimethyl)-co-(methylhydrogen) siloxane (DMMH-co) in the presence of platinum catalyst. 2-allyloxy-1-hydroxyanthraquinone (Al-HQ) was synthesized by reacting 1,2 dihydroxyanthraquinone with allyl bromide in the presence of dry acetone/K_2CO_3. Al-HQ and HQ-PDMS showed absorption maxima (λ_{max}) at 420 nm. The extent of UV–Visible efficacy of HQ-PDMS was varied by changing the amount of HQ chromophore present on the polymer backbone.

The photoprotection efficacy of HQ-PDMS was found to be superior over free Al-HQ and 1,2-HQ chromophores. This was presumably to be due to effective molecular solubilization followed by uniform distribution of HQ chromophores on the substrate surface. HQ-PDMS also showed > 95% photostability when exposed to 3 hours of solar simulated sun exposure. Fluorescence measurements of HQ-PDMS and free Al-HQ were carried out using excitation wavelength of Exλ_{max} 420 nm. We observed enhanced fluorescence quenching between the HQ chromophores, only when tagged on the HQ-PDMS v/s free Al-HQ. Our study revealed potential use of chromophores-tagged polymers in enhanced fluorescence quenching, which demands effective intermolecular interactions between two chromophores. These enhanced intermolecular interactions between photo-excited donor and acceptor on the polymer backbone could play key role in the photo-stabilization.



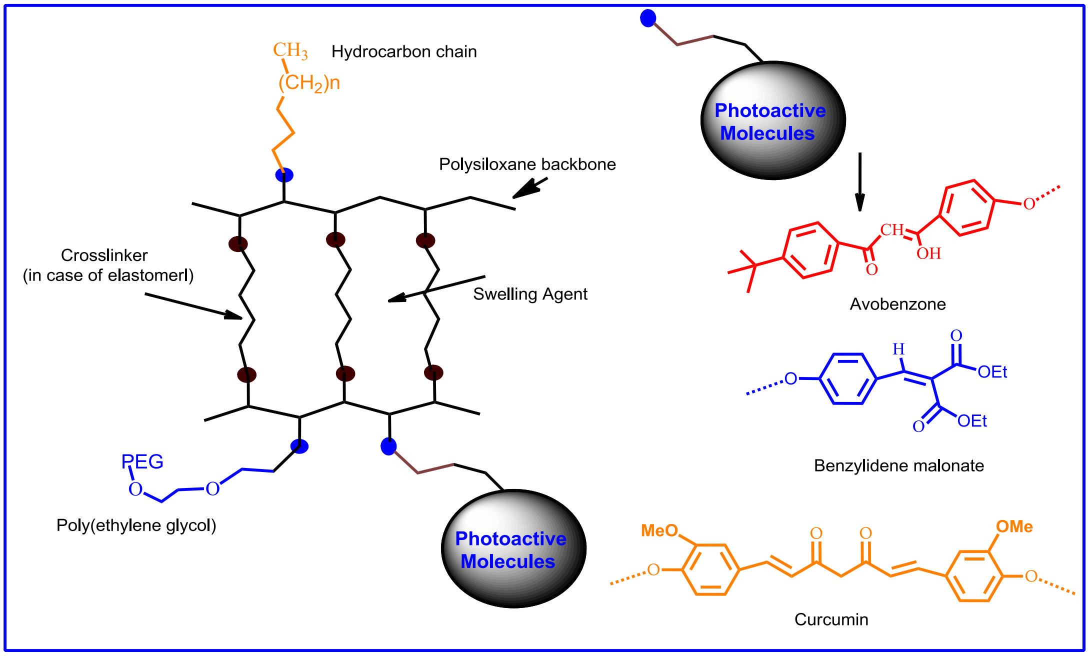
1. Introduction

Personal Care (PC) products thrive upon superior sensory and functional performance along with enhanced safety and minimum eco-toxicity. This functional performance is driven by superior deposition and distribution of organic actives, namely, sunscreens, dyes, antibacterial agents etc on the substrate surface. In addition various other organic actives such as pesticides, photo-harvesting, light emitting molecules also demand similar performance in agriculture, optical and solar applications.

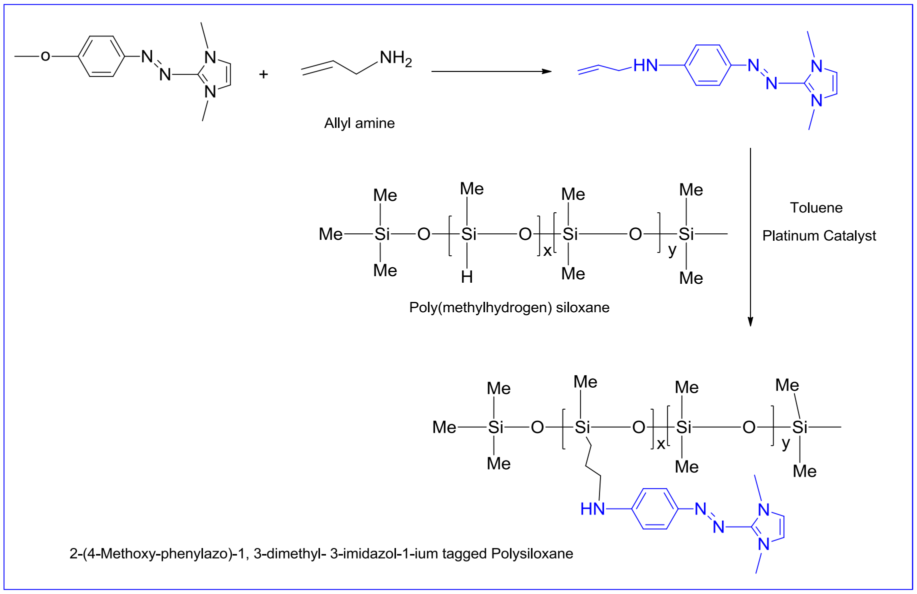


UV Filter / Antibacterial agents / Dyes / Pesticides / Photoactive

After all these organic actives could pose complex safety issues when they come in contact with skin / hair or ecotoxicity issues when they release into the environment. Ideally sunscreen molecules are expected to remain on the skin surface as a protective layer against sun radiation and not to penetrate into the underlying viable tissue. Similarly, dye molecules should effectively deposit and distribute evenly on the hair surface. However, substantial amount of applied sunscreens [1,2,3,4,5] are absorbed through skin [6] and also detected in human urine [7,8,9], gastro intestinal tract [10] and human milk [11]. A significant number of publications have reported case studies showing skin allergy due to commonly used sunscreens [12,13,14,15]. Hair dyes also showed significant toxicity [16,17,18] due to penetration through skin [19,20]. Recent studies revealed that parabens [21,22,23] showed toxicity due to permeation through skin. Studies also show that parabens are retained in the epidermis and dermis [24,25,29]. It has been indicated that risk due to such issues could be minimized if these molecules possess molecular weight (M. Wt) above 500 Dalton [26]. Superior deposition and distribution of above indicated organic actives can also be achieved when they are covalently anchored to the select polymers having low surface tension, for example polysiloxanes. Hence these molecules could perform at minimum required levels by reducing the toxicity and environmental impact. Organomodified polymers (OMPs) showing UV absorbing [27] and colorant [28,29,30,31] properties were developed for superior deposition and distribution of skin and hair surface. UV absorbing elastomer was synthesized using sunscreen molecules like 1-(4-(tert-butyl)phenyl)-3-(4-methoxyphenyl)propane-1,3-dione also known as avobenzone and 2-ethylhexyl-4-methoxycinnamate also known as MCX. Vinyl terminated polysiloxane was used as the cross-linker. The elastomer obtained was photostable and can be used as sunscreen actives.

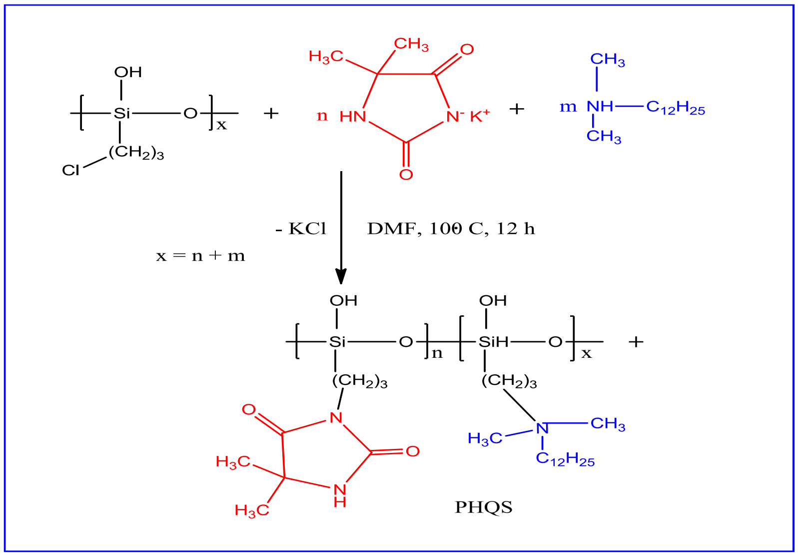


[32] Polysiloxane based 2-(4-Methoxy-phenylazo)-1, 3-dimethyl- 3-imidazol-1-ium dye was synthesized via platinum catalyzed reaction in toluene. The polymeric dye obtained showed long lasting properties on hairs.

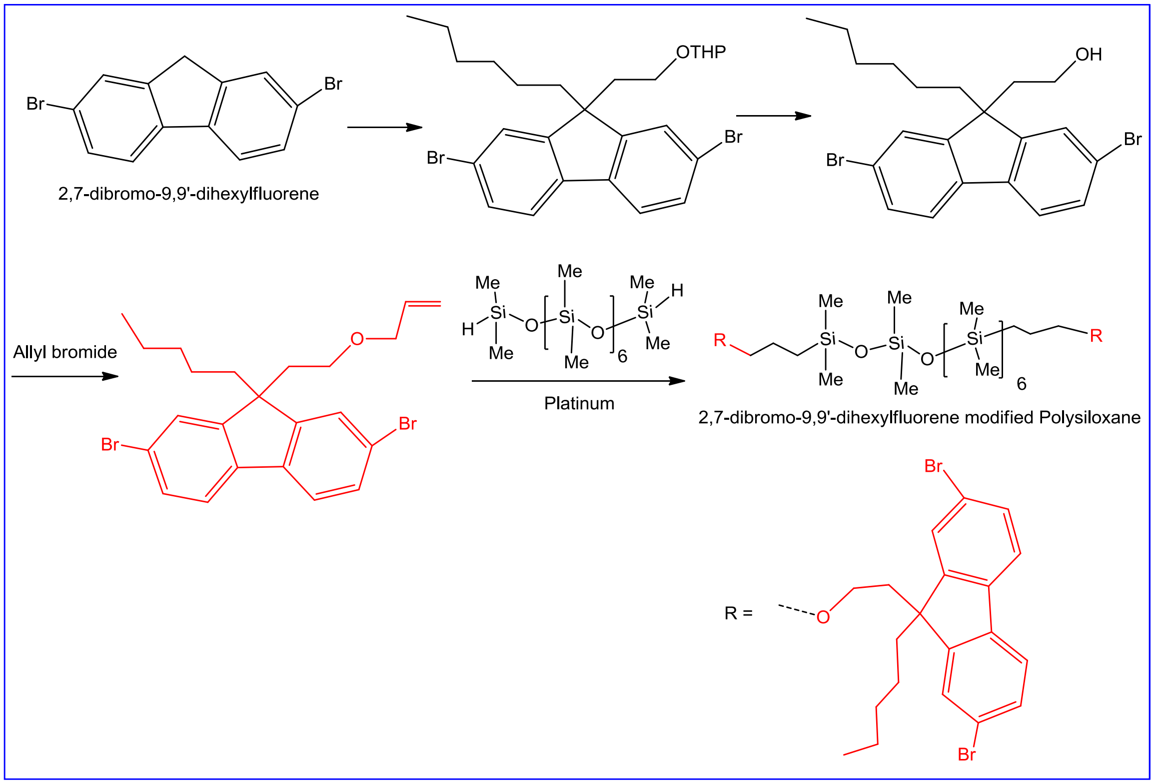


We recently [33,34] synthesized photo-stable broad spectrum UV absorbing OMPs by reacting 4-t-butyl, 4’-allyloxydibenzoylmethane (UVA chromophore), 4-allyloxy malonate class (UVB chromophore); with poly(methylhydrogen)-co-(dimethyl)siloxane copolymer in the presence of platinum catalyst. These polymers showed effective deposition on the skin and hair. Superior spreadable polymeric antimicrobials [35,36] have been designed to be effective against microorganisms.

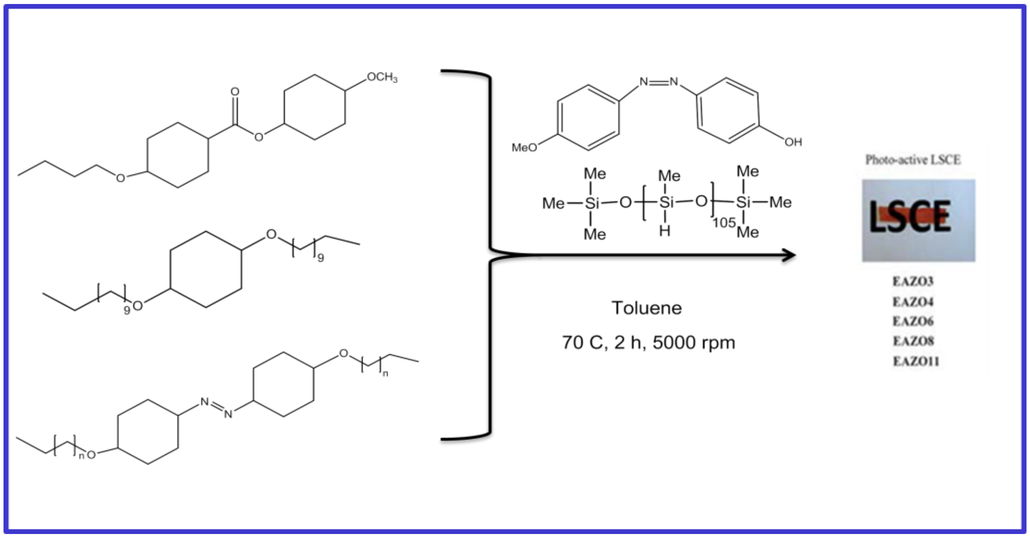
Recently, broad-spectrum antibacterials. Poly-(hexamethylen-guanidinium-chloride), poly-[2-(2-ethoxy)-ethoxyethyl)-guanidinium- chloride] [37,38,39,40], 3-trimethylammonium-2-hydroxypropyl-N-chitosan [41,42] have been developed as polymeric antimicrobials or antifungal agents. [43] Liang et al reported the synthesis of antimicrobial polymer by attaching 5,5-dimethylhydantoin and dimethyldodecylamine onto the poly(3-chloropropylsiloxane) backbone in DMF. The resulting polymer showed superior antimicrobial activity as compared to the monomer.



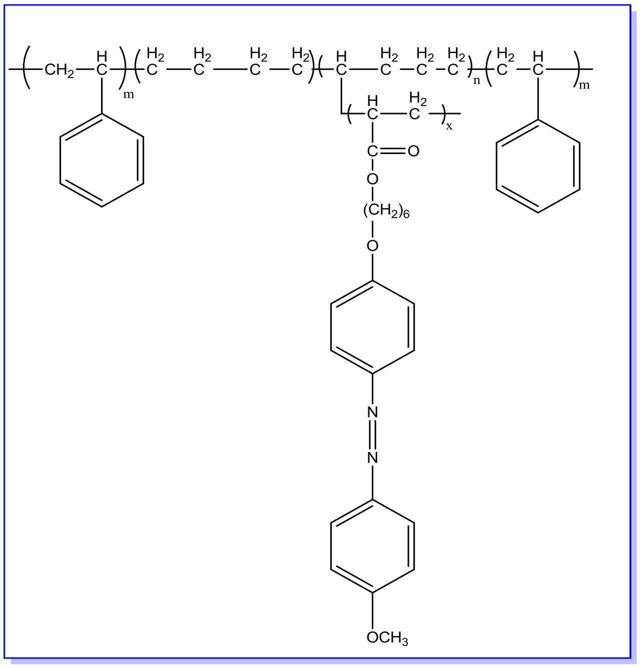
The blue light-emitting polyfluorenes [44] containing siloxane were synthesized by first alkylating 2,7-dibromo-9,9'-dihexylfluorene in series of reactions by using allyl bromide. The alkylation was then followed by Ni-mediated copolymerization of flourene molecule with hydride-terminated polysiloxane. The resulting polymer exhibited almost pure blue photoluminiscent emission and hence used for light emitting diodes.



Nematic liquid single crystal elastomers (LSCEs) [45] were synthesized by reacting 4,4'-diallyloxyazobenzene with Poly(methylhydrogen)polysiloxane in the presence of cross-linker.

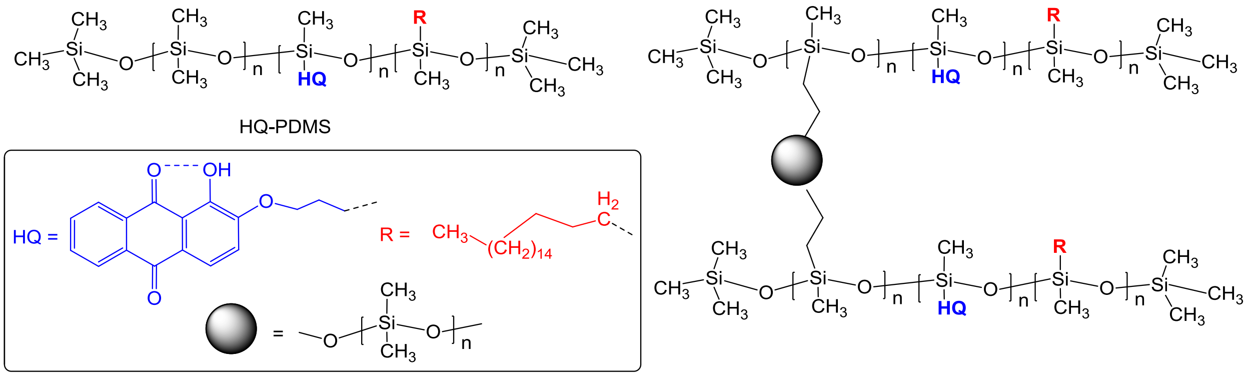


Zhao et al [46] has developed a photoactive elastomer which is used for holographic recordings. This elastomer is a liquid crystalline azobenzene polymer grafted onto a styrene-butadiene-styrene (SBS) triblock copolymer. All these polymers find useful in the optical and solar applications.



Most of the photostable molecules e.g. 1,2 hydroxyanthraquinones are difficult to solubilize, which results into poor photoprotective performance. This performance can be enhanced when they are liquid in nature or when they are molecularly solubilized in the polymers, having low glass transition temperature, for example polysiloxanes.

In this thesis, we report synthesis, characterization and properties of photo-stable UV absorbing 1-hydroxyanthraquinone-tagged poly(dimethylsiloxane) (HQ-PDMS) polymers and cross-polymeric elastomers.



2. Experimental Section

2.1. Materials

Poly(methylhydrosiloxane) [i.e. MHPS, molecular formula, $(CH_3)_3SiO-[(CH_3) HSiO]_n-Si(CH_3)_3$ where n = 35; and average M Wt. = 1700 - 3200, 15-40 cSt at 25 °C]; Octamethylcyclotetrasiloxane (D_4, 98%); 1,3-Divinyltetramethyldisiloxane (DVDS, 97%); 2,4,6,8–tetramethylcyclotetrasiloxane (TMCTS, 95%); Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution [$(O[Si(CH_3)_2CH=CH_2]_2Pt)$ 0.1 M solution in poly(dimethylsiloxane) vinyl terminated]; Octadecene (95 %); Allyl bromide (97%) ; 1,2-dihydroxyanthraquinone (1,2-HQ, 97%); and $CDCl_3$ (100%) were purchased from Sigma Aldrich. Decamethylcyclotetrasiloxane (D_5) [DC245, 95%] were kindly supplied by DOW Corning. Tulsion acid catalyst chemically known as sulfonic acid polystyrene resin was kindly supplied by Thermax India, T63MP. Polyalkylene glycol monoallyl ethers grades namely Polyglykol A 20 – 10, M Wt. 1500; Polyglykol A 20 – 20, M Wt. 2100 ; Polyglykol A 1100, M Wt. 1100; Polyglykol A 500, M Wt. 500; Polyglykol A 350, M Wt. 350; Polyglykol A 11 – 14, M Wt. 750, were procured from Clariant.

2.2. Instrumentation

FTIR spectra were recorded on a Perkin Elmer FTIR/NIR spectrophotometer using carbon tetrachloride in the infrared region of 400-4000 cm^{-1}. Bruker NMR spectra were recorded on (200 MHz) spectrometer using $CDCl_3$ as a solvent. Fluorescence spectra were recorded on the Horiba Flouromax - 4 spectrophotometer using the slit width of 5. The excitation wavelength of $Ex\lambda_{max}$ 420 nm was used. UV-Visible absorption spectra were recorded on the Perkin Elmer Lambda 900 UV/Vis/NIR spectrophotometer. Viscosity of the polymers and gel were recorded using Rheometer AR 1000. Bruker Amazon SL mass spectrophotometer was used for the mass analysis. Analysis was carried out in both negative and positive mode with scan rage of 70 to 1500 m/z. Chemical shifts of various peaks in the spectra were reference with respect to $CDCl_3$ peak appearing at δ 7.26 in $CDCl_3$.

2.3. Synthesis of Monomers and Polymers

“Synthetic schemes”

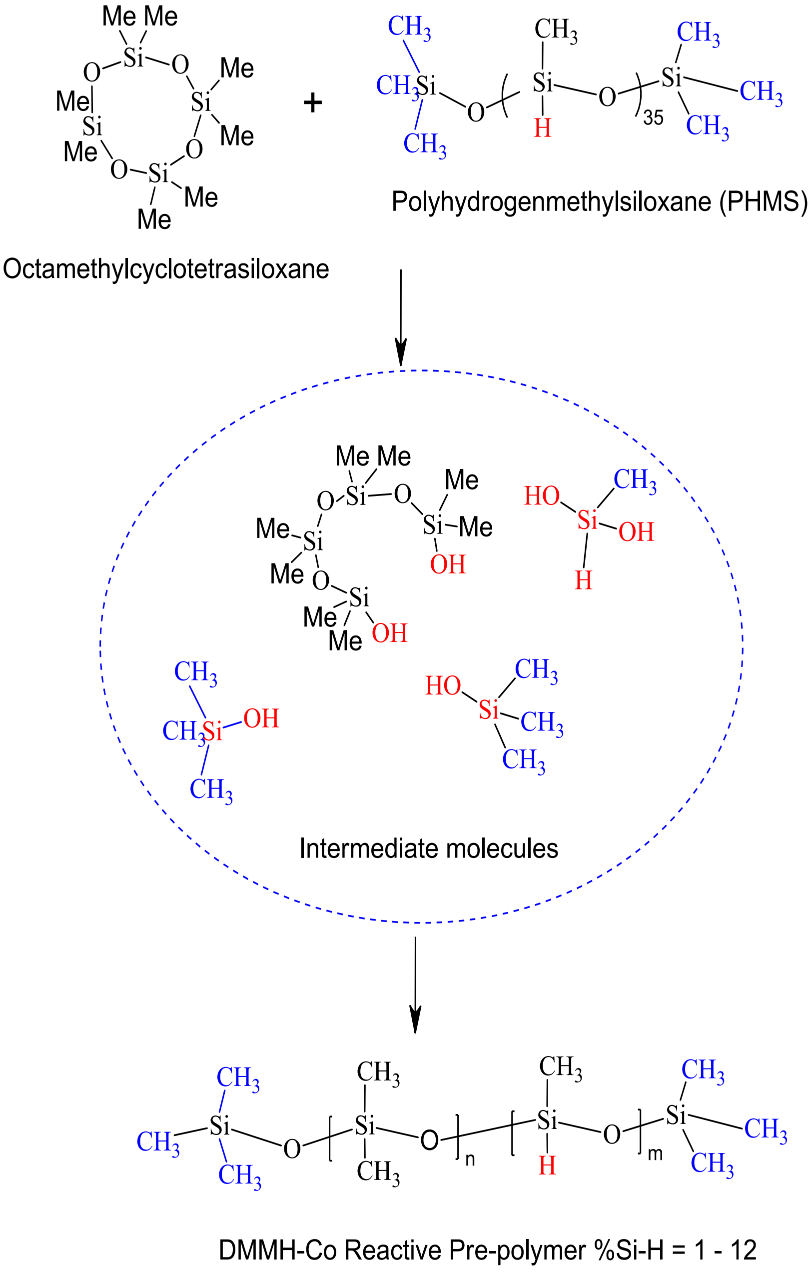


Figure 1: *Synthesis Poly(dimethyl)-co-(methylhydrogen) siloxane (DMMH-co) [%Si-H = 1 to 12]*

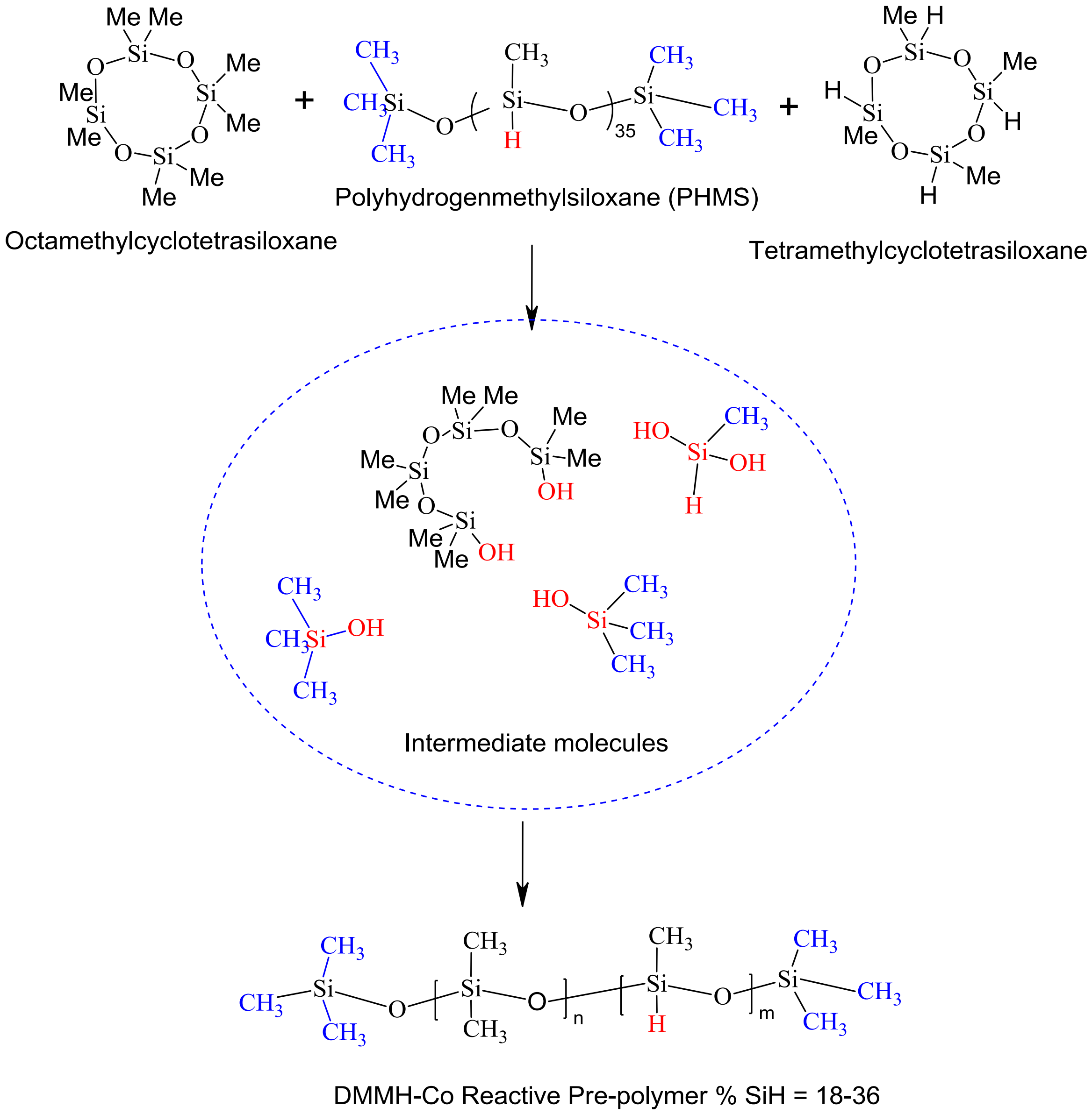


Figure 2: *Synthesis Poly(dimethyl)-co-(methylhydrogen) siloxane (DMMH-co) [%Si-H = 18 – 36]*

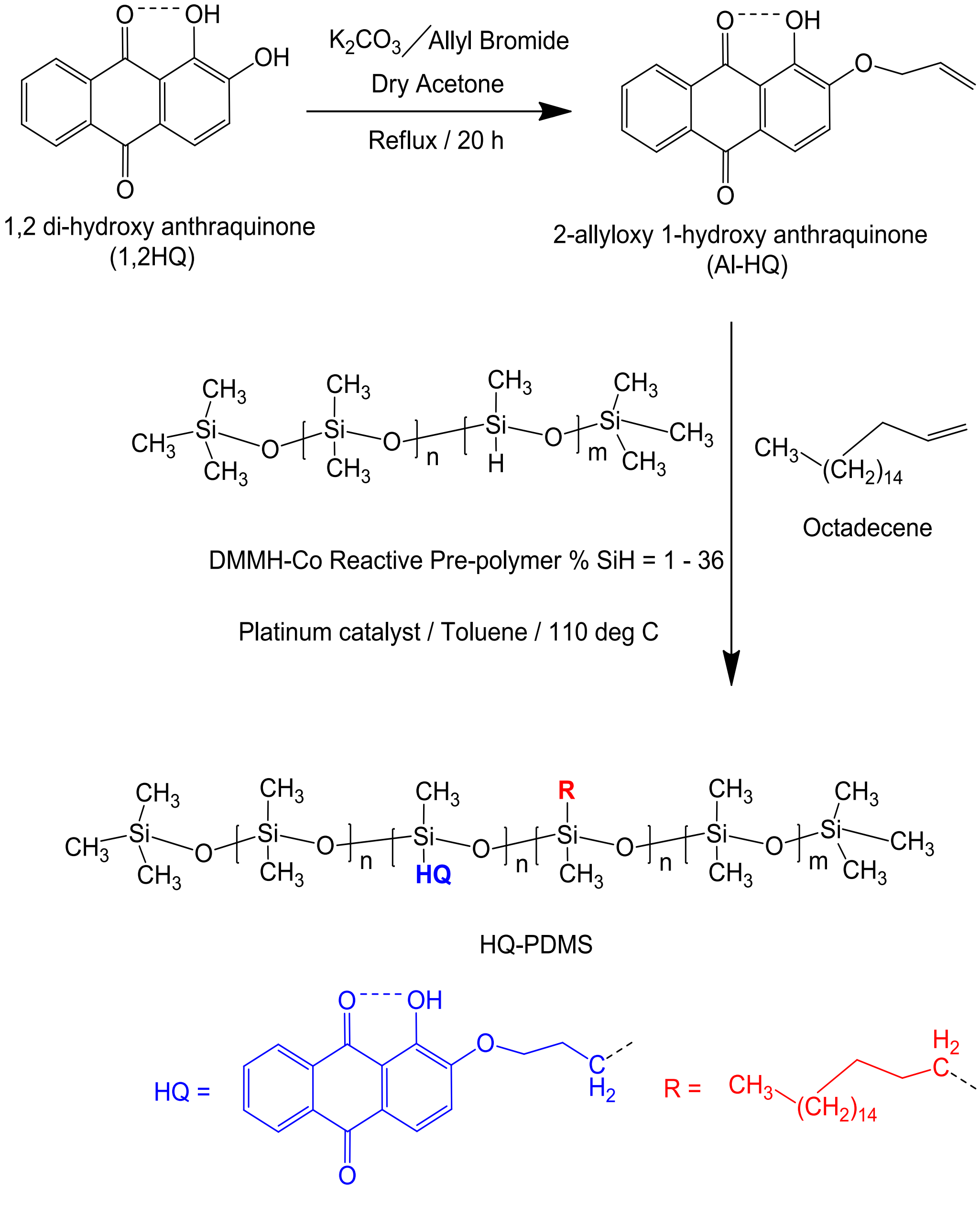


Figure 3: *Synthesis of Hydroxyanthraquinone modified Polydimethylsiloxane polymer (HQ-PDMS)*

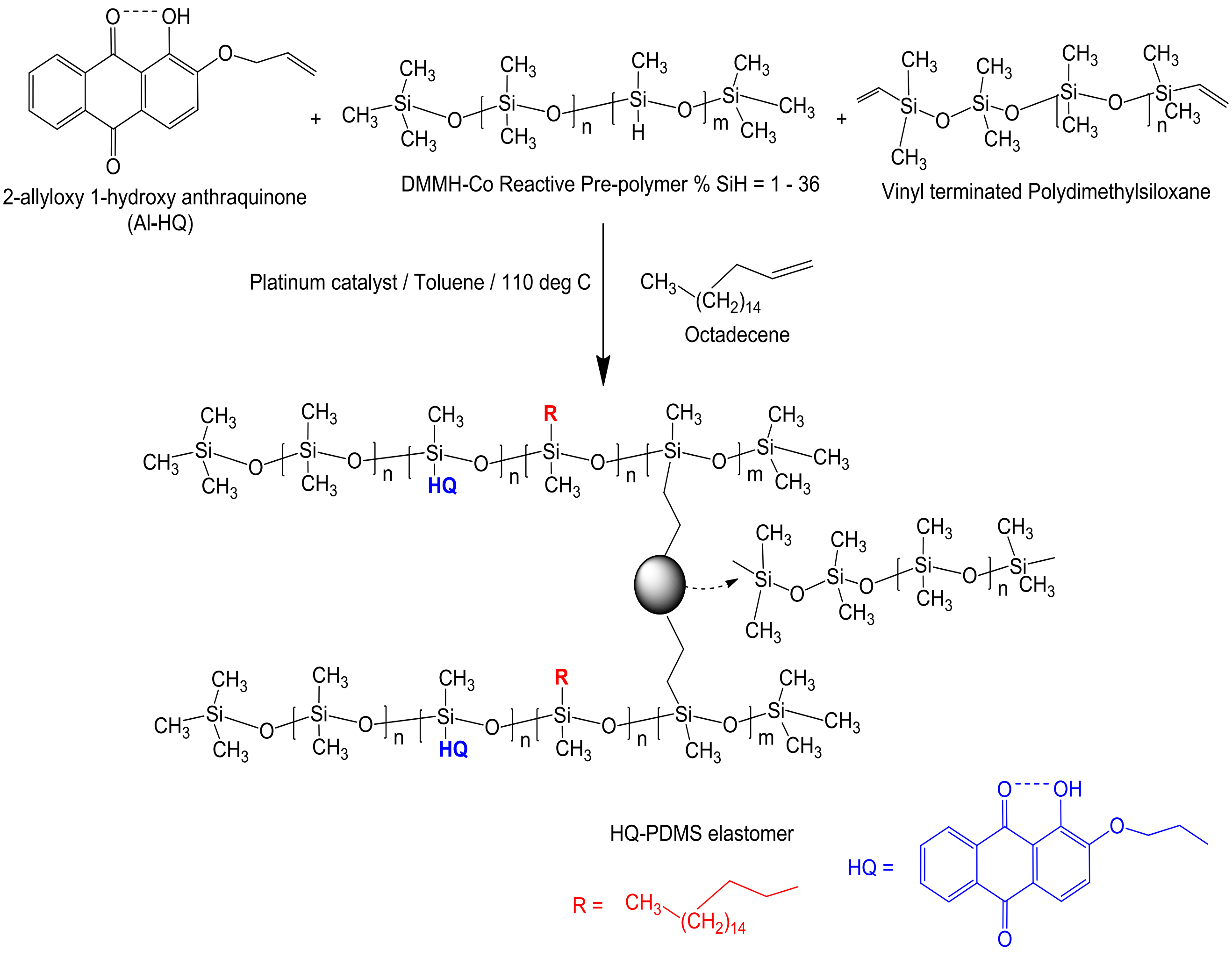


Figure 4: *Synthesis of Hydroxyanthraquinone modified Polydimethylsiloxane silicone elastomer (HQ-PDMS gel)*

(1) Synthesis of Poly(dimethy)-co-methylhydrogen) siloxane (DMMH-co) [%Si-H = 1-12]

D_4 was mixed with MHPS in a 50 mL two necked round bottom flask fitted with a water condenser. To this mixture 2% of tulsion catalyst was added. The reaction mixture was stirred at 120 °C for 14 h. The viscous DMMH-co obtained was cooled down to 25 °C. The copolymer was dissolved in hexane and the solution was filtered off to remove the catalyst. The hexane was evaporated from the filtered solution at 40 °C under vacuum (247 mm of Hg). The viscous copolymer was dried under vacuum for 4 h at 80 °C. The colorless, viscous liquid was obtained. As seen in table 3 and table 4 %Si-H and molecular weight of DMMH-co were tuned by varying amount of D_4 and MHPS.

Products Characteristics: FTIR peaks at 1040 cm^{-1} (Si-O-Si); 1260 cm^{-1} (broad peak) (Si-Me); 2160 cm^{-1} (Si-H). ^{1}H-NMR ($CDCl_3$) peaks at δ 0.09 (s, $Si(C\underline{\mathbf{H}}_3)_2$), 0.17 (s, $Si(C\underline{\mathbf{H}}_3)H$), 4.6 (m, $Si(CH_3)\underline{\mathbf{H}}$**).** ^{13}C NMR ($CDCl_3$) peaks at δ 1.02 ($Si(\underline{\mathbf{C}}H_3)_3$), δ 1.21 ($Si(\underline{\mathbf{C}}H_3)_2$) and δ 1.81 ($Si(\underline{\mathbf{C}}H_3)H$ and Refer figure 5, 6 and 7

(2) Synthesis of Poly(dimethyl-co-methylhydrogen) siloxane (DMMH-co) [%Si-H = 18 - 24]

MHPS was mixed with D_4 in a 100 mL round bottom flask fitted with a water condenser. To this mixture TMCTS was added followed by addition of 2 % of tulsion catalyst. The reaction mixture was stirred for 12 h at 120 °C. The viscous oil was cooled down to room temperature. The DMMH-co was dissolved in hexane and the solution was filtered off to remove the catalyst. The hexane was evaporated from the filtered solution at 40 °C under vacuum (247 mm of Hg). The viscous copolymer was dried under vacuum (0.1 mm) for 4 h at 80 °C. The %Si-H and molecular weight were tuned by varying the amount of D_4, MHPS and TMCTS during the synthesis. Details are described in table 3 and table 4.

Products Characteristics: FTIR peaks at 1040 cm^{-1} (broad peak, Si-O-Si); 1260 cm^{-1} (broad peak, Si-Me); 2160 cm^{-1} (broad peak, Si-H). ^{1}H-NMR ($CDCl_3$) peaks at δ 0.09 (s, $Si(C\underline{\mathbf{H}}_3)_2$), 0.17 (s, $Si(C\underline{\mathbf{H}}_3)H$), 4.6 (m, $Si(CH_3)\underline{\mathbf{H}}$). ^{13}C NMR ($CDCl_3$) peaks at δ 0- δ 0.7 ($Si(\underline{\mathbf{C}}H_3)_3$, $Si(\underline{\mathbf{C}}H_3)H$ and $Si(\underline{\mathbf{C}}H_3)_2$). Refer to figure 5, 6 and 7.

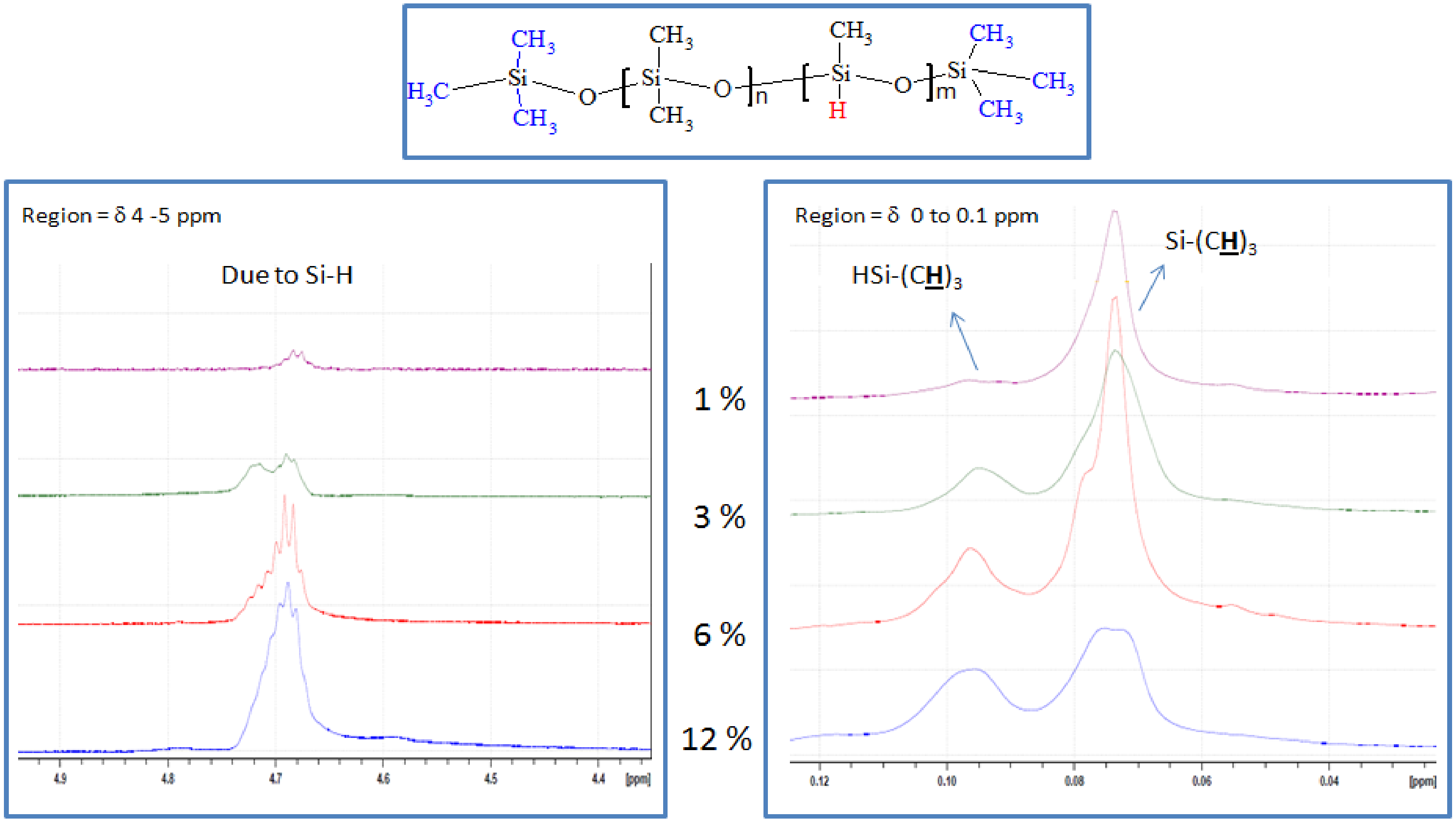


Figure 5: ^{1}H NMR of Poly(dimethyl)-co-(methylhydrogen) siloxane (DMMH-co) having different % Si-H (1 to 12 %) (a) Region = δ 4 -5 ppm and (b) Region = δ 0 - 0.1 ppm

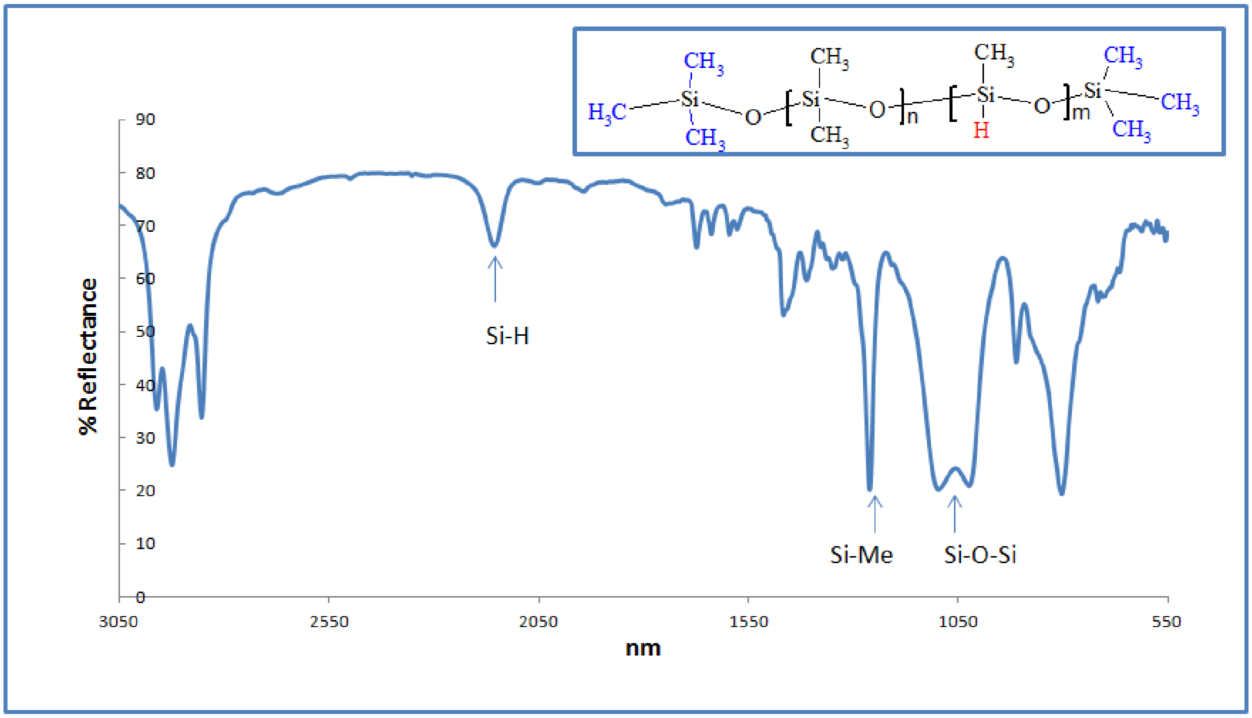


Figure 6: *FT-IR spectrum of Poly(dimethyl)-co-(methylhydrogen) siloxane (DMMH-co)*

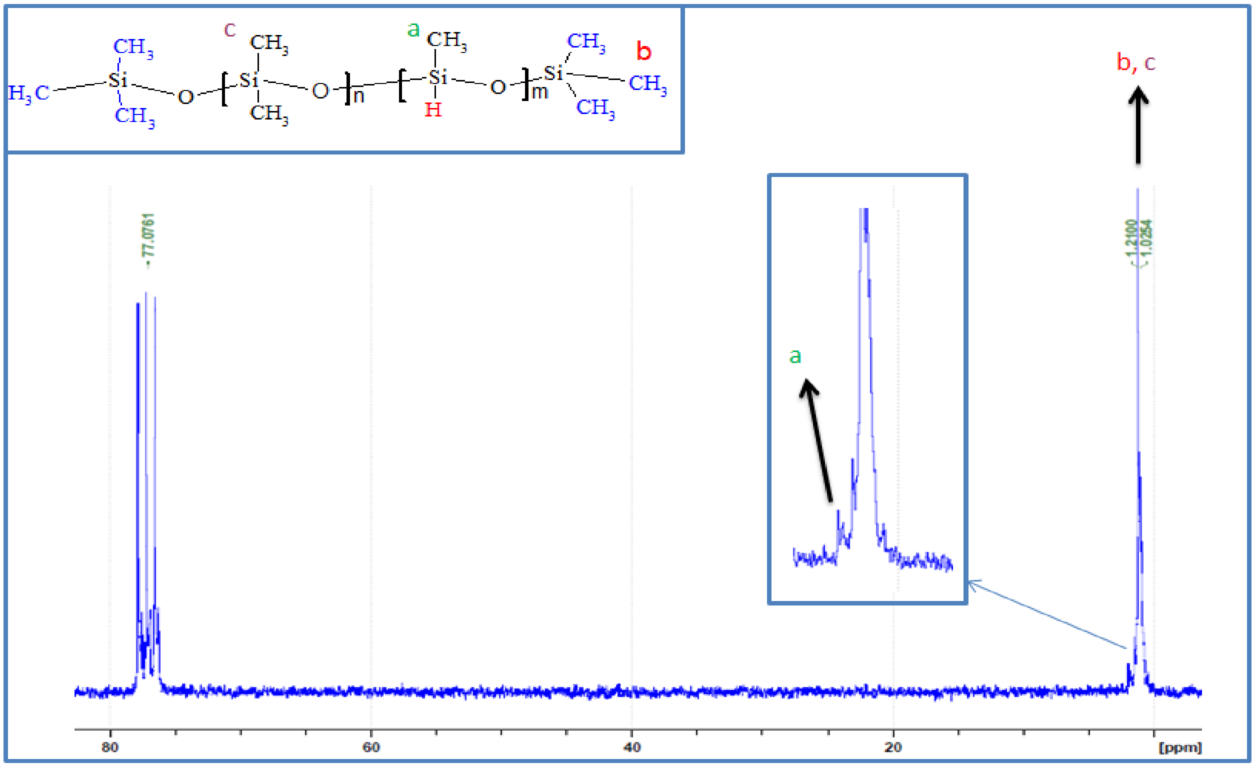


Figure 7: *^{13}C NMR of Poly(dimethyl)-co-(methylhydrogen) siloxane (DMMH-co)*

(3) Synthesis of 2-allyloxy-1-hydroxyanthraquinones

A 250 mL two necked flask was fitted with a reflux condenser. The flask was charged with potassium carbonate (2.8 g) and 200 mL dry acetone. 1,2-dihydroxyanthraquinones i.e. alizarin (5 g, 0.0208 mol, M Wt. = 240) was added to potassium carbonate-acetone dispersion. The reaction mixture was heated to 75-80 ^{o}C for 2 h. Allyl bromide (6 mL, 0.0694 mol, M Wt. = 121) was added using syringe and the heating was continued for 20 h. The reaction mixture was allowed to cool to the room temperature. Acetone was removed from the reaction mixture using rotary evaporator to obtain crude product under vacuum (417 mm of Hg) at 40 ^{o}C. 50 mL of water and 100 mg of K_2CO_3 were added to the crude product containing 2-allyloxy,1-hydroxyanthraquinone followed by addition of 25 mL of chloroform. The chloroform layer was separated and washed with 50 mL of water (3 times). The chloroform was evaporated using rotary evaporator at 40 ^{o}C at 355 mm Hg. Synthetic scheme is shown in figure 3. A crude product was obtained as reddish yellow coloured solid. This product was crystallized in hexane. The pure yellow crystals were dried under vacuum.

Products Characteristics: FTIR peaks at 1592 and 793 cm^{-1} (aromatic region) and 1365 cm^{-1} (C-O-C); 1664 cm^{-1} (C=O); 3089 cm^{-1} (C=C); 3314 cm^{-1} (broad peak, OH. ^{1}H-NMR ($CDCl_3$) peaks at δ 4.75 (m, 2H, $CH=CH_2\text{-}C\underline{H}_2\text{-}O$); δ 5.32 & δ 5.43 (d, 2H, $C\underline{\mathbf{H}_2}=CH\text{-}CH_2\text{-}O$); δ 6.1 (m, 1H, $CH_2=C\underline{\mathbf{H}}\text{-}CH_2\text{-}O\text{-}$); δ 7.25 – δ 8.3 (s, 6$\underline{\mathbf{H}}$, aromatic protons); δ 13.1 (s, 1H, Ph-O$\underline{\mathbf{H}}$). Anal. Calcd for $C_{17}H_{12}O_4$: C, 72.85; H, 4.31; O, 22.83. Found: C, 72.71; H, 4.3; O, 22.79. M/z 280.3 found M/z 280.8. Refer figure 8, 9, 10, 11 and 12.

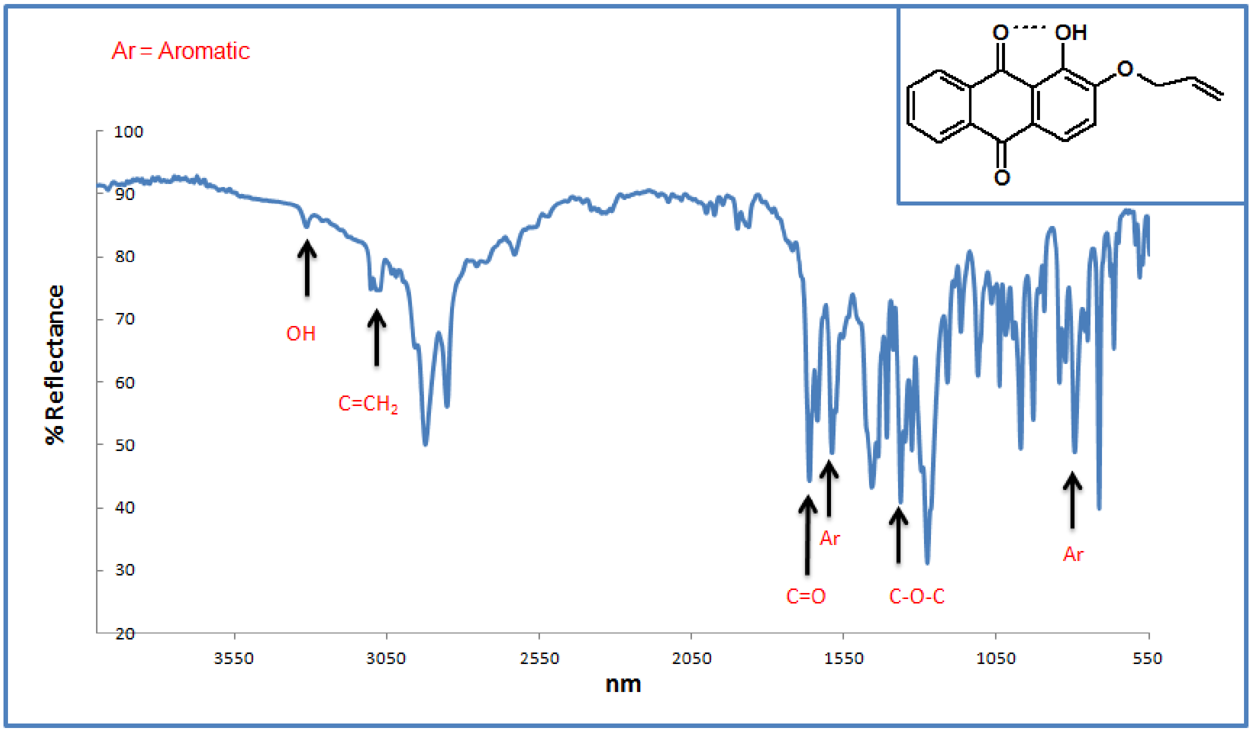


Figure 8: *FT-IR spectrum of 2-allyloxy-1-hydroxyanthraquinone*

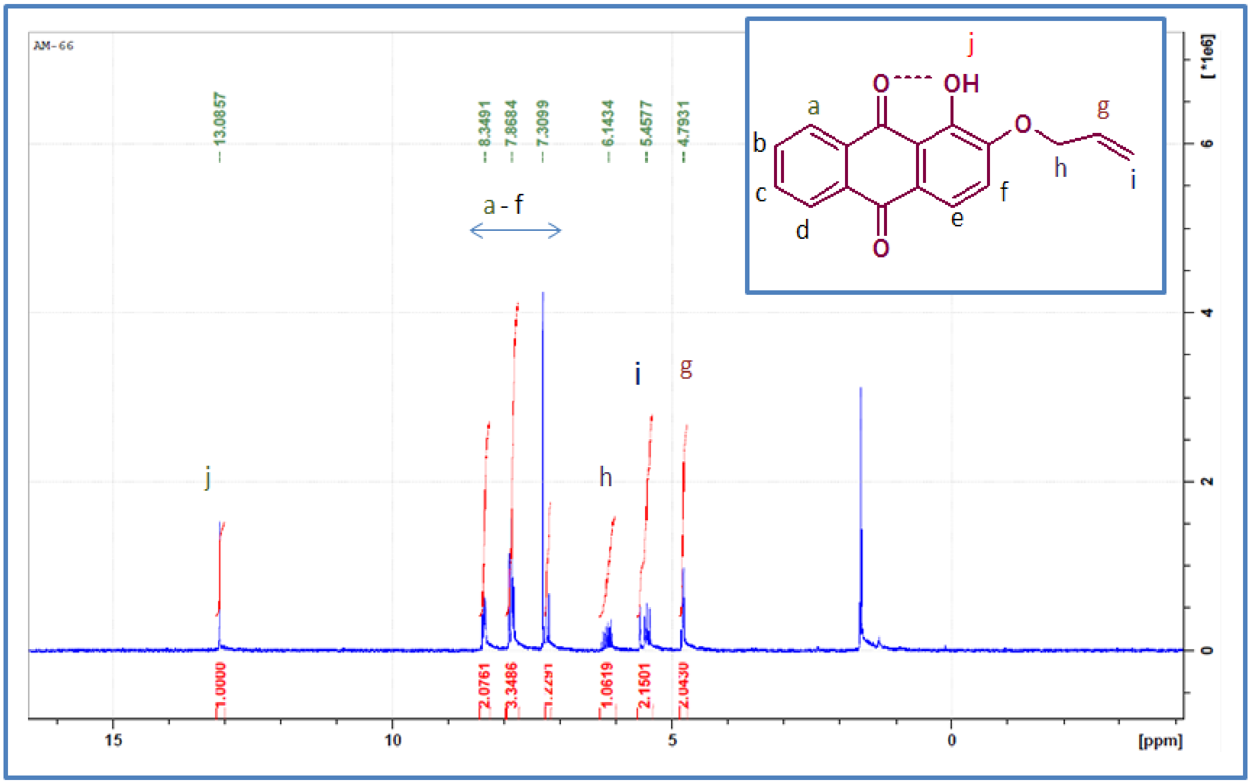


Figure 9: *^{1}H NMR of 2-allyloxy-1-hydroxyanthraquinone*

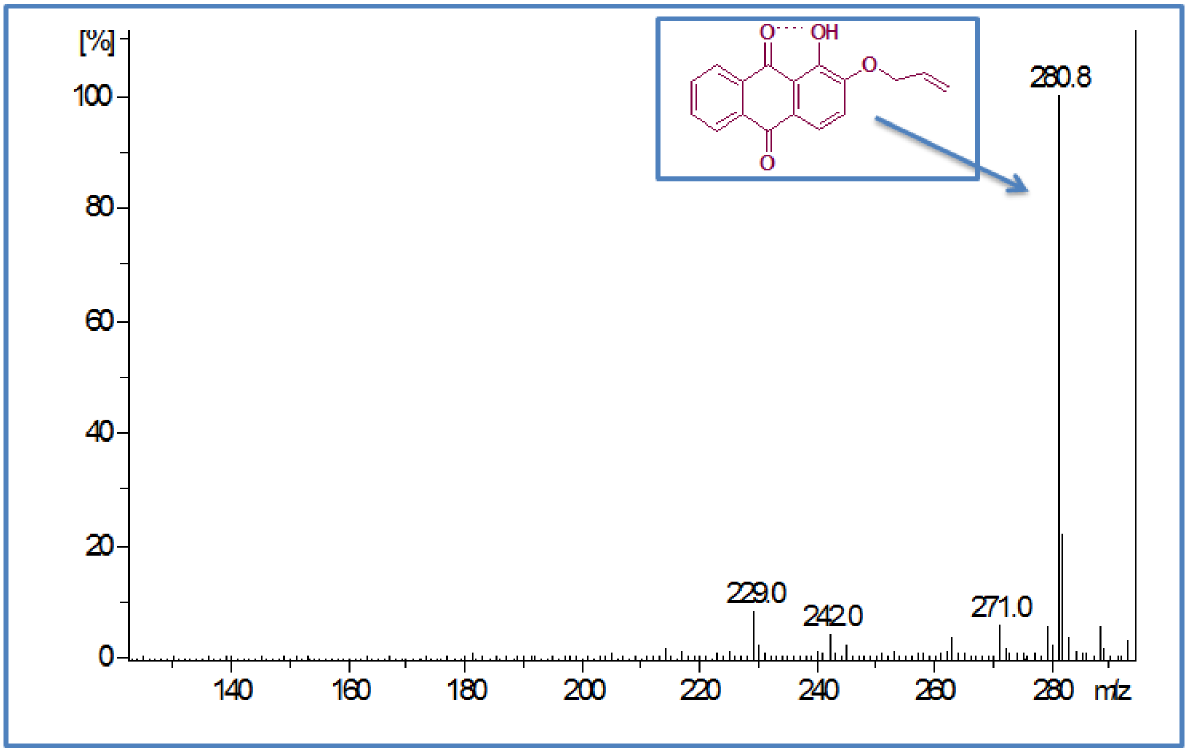


Figure 10: *GC-MASS of 2-allyloxy-1-hydroxyanthraquinone*

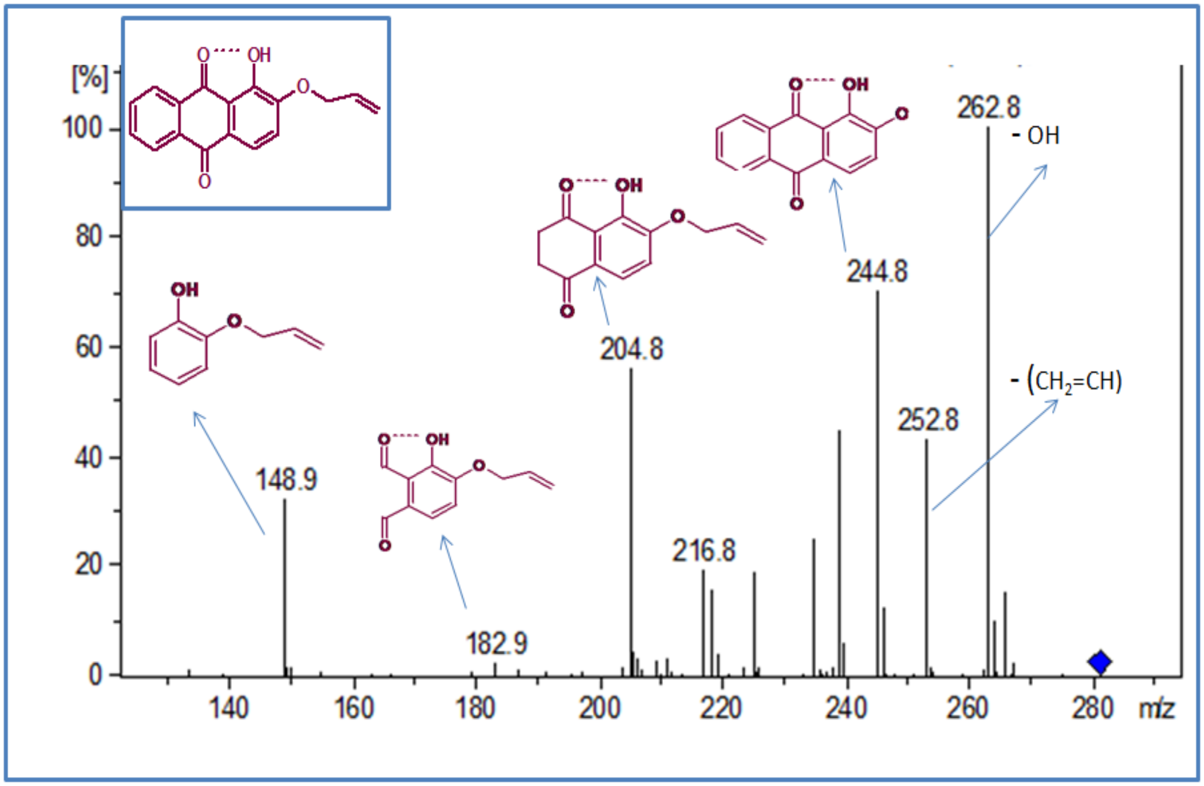


Figure 11: *GC-MASS fragmentation spectrum of 2-allyloxy-1-hydroxyanthraquinone*

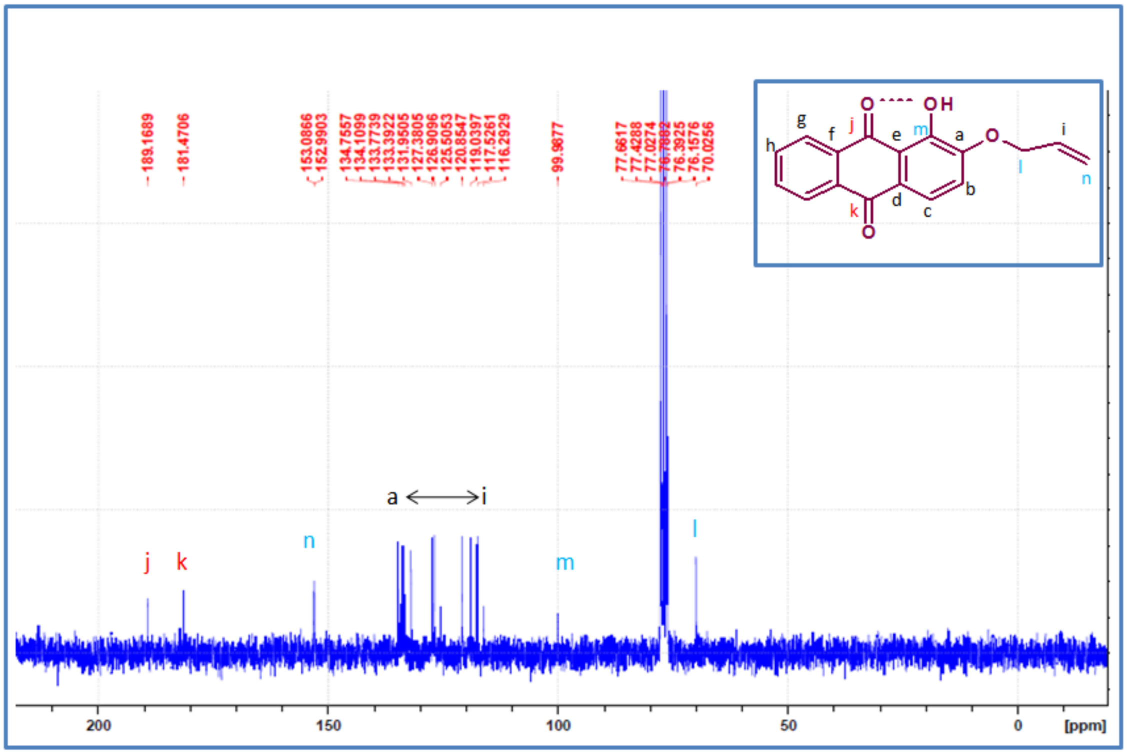


Figure 12: ^{13}*C NMR of 2-allyloxy-1-hydroxyanthraquinone*

(4) Synthesis of Hydroxyanthraquinone Modified Poly(dimethyl) siloxane (HQ-PDMS)

70 mL toluene was charged to a 3-necked flask fitted with a Dean and Stark set-up under nitrogen atmosphere. Traces of water present in toluene were removed by azeotropic distillation. 2-allyloxy-1-hydroxyanthraquinone and octadecene were added subsequently to dry toluene followed by addition of 100 ppm of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex. The mixture was stirred at 25 ^{o}C for about 0.5 h. The poly(dimethyl-co-methylhydrogen) siloxane (DMMH-co) was added to the 2-allyloxy-1-hydroxyanthraquinone-platinum-octadecene complex. The reaction mixture was stirred at 110 °C for 2 h. The progress of the reaction was monitored using Thin Layer Chromatography (TLC), FT-IR and NMR. Table 5 indicated various grades of HQ-PDMS containing different % loading of hydroxyanthraquinone.

Product Characteristics: FTIR peak at 1186 cm^{-1} (-Si-O-Si); 1260 cm^{-1} (Si-CH$_{3)}$. ^{1}H-NMR (CDCl$_3$) peaks at δ 0.09 (s, SiC$\underline{\mathbf{H}}_3$), 0.6 (t, -SiC$\underline{\mathbf{H}}_2$-), 1.57 (m, -SiCH$_2$C$\underline{\mathbf{H}}_2$-), 4.9 (m, -SiCH$_2$CH$_2$C$\underline{\mathbf{H}}_2$O-Ar), 12.8 (s, 1H, Ph-O$\underline{\mathbf{H}}$). Refer to figure 13 and 14.

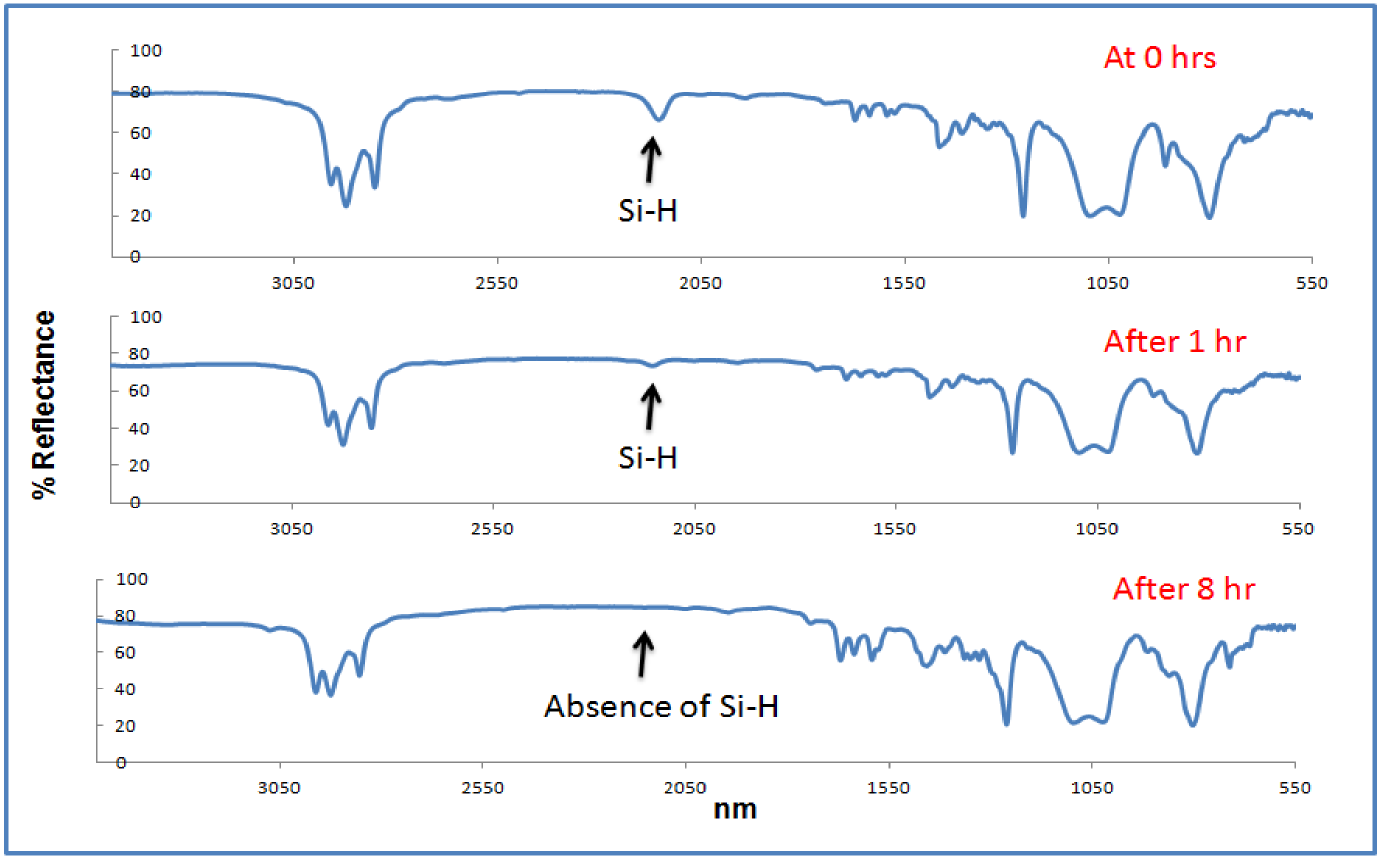


Figure 13: *FT-IR spectrum of 2-allyloxy-1-hydroxyanthraquinone modified Polydimethylsiloxane (HQ-PDMS)*

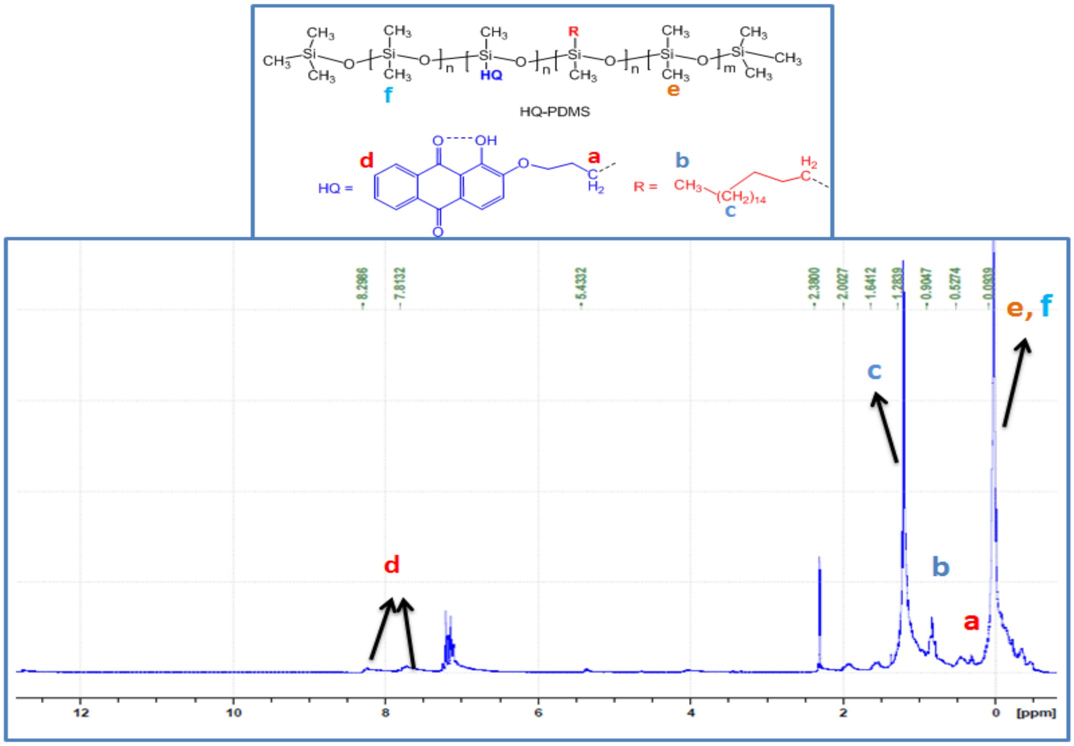


Figure 14: *^{1}H-NMR of hydroxyanthraquinone (HQ) modified Polydimethylsiloxane (HQ-PDMS)*

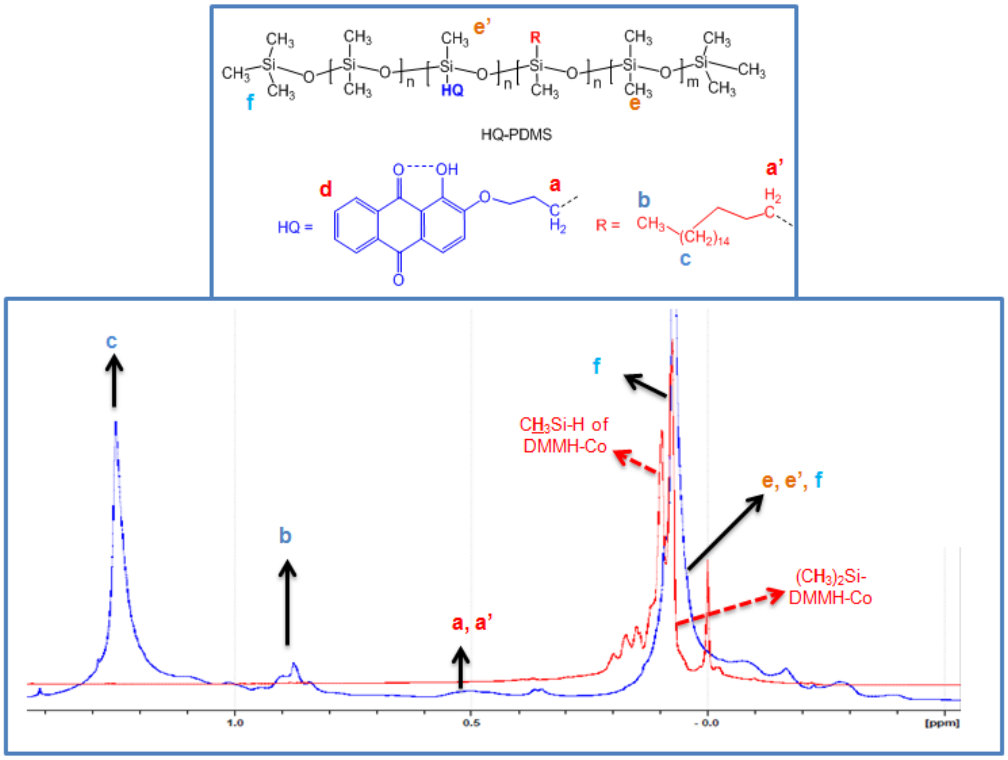


Figure 14-1: *^{1}H-NMR of hydroxyanthraquinone (HQ) modified Polydimethylsiloxane (HQ-PDMS)*

(5)Synthesis of Divinylpolydimethylsiloxane (VTP)

D_4 was mixed with DVDS in a 50 mL two necked round bottom flask fitted with a water condenser. To this 0.2 g of tulsion catalyst was added and the reaction mixture was stirred at 120 °C for 12 h. The polymer was dissolved in 15 mL of hexane and the solution was filtered off to remove the catalyst. The hexane was evaporated from the filtered solution at 40 °C under vacuum (247 mm of Hg). The viscous oil was dried under vacuum for 4 h at 80 °C. As seen in Table 1 the molecular weights of VTP were tuned by varying amount of D_4. The product was obtained as colorless, viscous liquid.

Products Characteristics: ^{1}H-NMR ($CDCl_3$) peaks at δ 0.09 (s, $Si(C\underline{\mathbf{H}}_3)_2$), δ 5.5 - δ 6.2(m, $-C\underline{\mathbf{H}}_2=CH-Si-$, $-CH_2=C\underline{\mathbf{H}}-Si-$). Refer to figure 15.

Table 1: *Different Grades of VTP*

Expt. No.	DVDS (g)	D4 (g)	M. Wt
AM -11	2	10	1116
AM – 14	1.6	8.5	1116
AM – 22	4	20	1116
AM – 83	1.5	40	5146

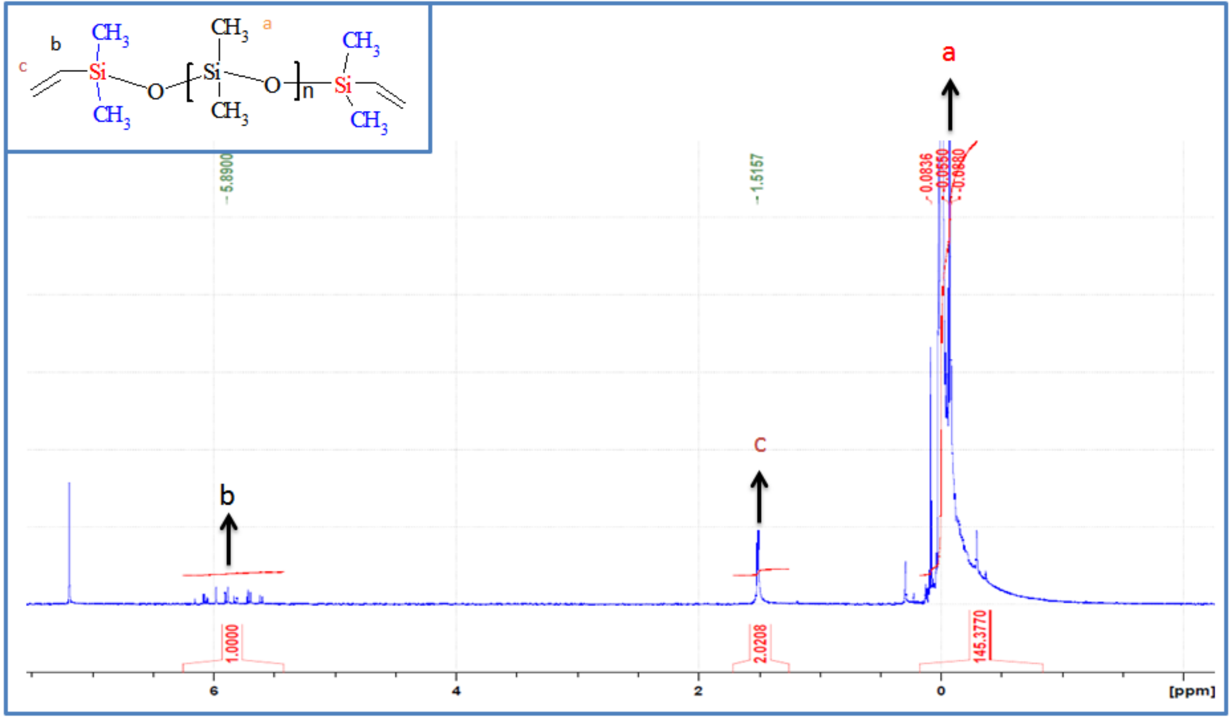


Figure 15: *^{1}H-NMR of 2-allyloxy-1-hydroxyanthraquinone modified Polydimethylsiloxane (HQ-PDMS)*

(6) Synthesis of Hydroxyanthraquinone Modified Silicone Elastomer Gel (HQ gel)

100 mL toluene was charged to a three necked flask fitted with a Dean and Stark set-up under nitrogen atmosphere. Traces of water present in toluene were removed by azeotropic distillation. 2-allyloxy-1-hydroxyanthraquinone and octadecene were added subsequently to dry toluene followed by addition of 100 ppm of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex. The mixture was stirred at 25 ^{o}C for 0.5 h. The poly(dimethyl)-co-(methylhydrogen) siloxane (DMMH-co) was added to the 2-allyloxy,1-hydroxyanthraquinones-platinum-octadecene complex. The reaction mixture was stirred at about 110 °C for about 2 h. The progress of the reaction was monitored using Thin Layer Chromatography (TLC) and FT-IR. The reaction was led to completion after 4 h at 110 ^{o}C by addition of divinyl terminated polysiloxane (VTP, molecular weight = 5000) copolymer-platinum complex in 10 mL toluene. Completion of reaction was confirmed by observing disappearance of FTIR peak due to Si-H at 2159 cm^{-1} (as seen in figure 13). The product was obtained in a gel form. Toluene was evaporated from the gel followed by subsequent washing with methanol to remove un-reacted 2-allyloxy-1-hydroxyanthraquinone and platinum catalyst. It was further swollen in decamethylcyclopentasiloxane (D_5). Synthetic scheme is shown in figure 4.

Product characteristics: FTIR peak at 1186 cm^{-1} (-Si-O-Si); 1260 cm^{-1} ($Si\text{-}CH_3$), ^{1}H-NMR ($CDCl_3$) peaks at δ 0.09 (s, $SiC\underline{\mathbf{H}}_3$), 0.6 (t, $\text{-}SiC\underline{\mathbf{H}}_2\text{-}$), 1.57 (m, $\text{-}SiCH_2C\underline{\mathbf{H}}_2$ -), 4.9 (m, $\text{-}SiCH_2CH_2C\underline{\mathbf{H}}_2O\text{-}Ar$), 12.8 (s, 1H, Ph-O$\underline{\mathbf{H}}$). HQ gel composition: Gel Solid Polymer content = 24%; chromophore content = 12 %; crosslinking density = 40 %.

2.4. Methods

(1) Quantification of Si-H using FT-IR spectroscopy

The reactive silanic hydrogen (Si-H) groups present in poly(dimethyl)-(methylhydrogen) siloxane copolymer (DMMH-co) were quantified using FT-IR. The stock solution (8000 ppm i.e. 200 mg in 25 mL) of MHPS was prepared in carbon tetrachloride. Test solutions having concentrations from 1000 to 6000 ppm were prepared. FTIR spectra were recorded for the test solutions. The peak due to Si-H was identified at 2160 cm^{-1} followed by the measurement of respective corrected areas and heights. Respective corrected areas or heights were plotted against concentration of Si-H mg/mL. The detailed grades of DMMH-co are shown in table 3 and table 4.

(2) In vitro Photostability Efficacy: Solution Study

The test solutions of 2-allyloxy-1-hydroxyanthraquinones (20 ppm i.e. 71.68 μM) and parsol (16 μM) in toluene were taken in two quartz stoppered cuvettes. The intensity of simulated solar atlas sun lamp was adjusted to 550 W/m^2. Both the solutions were exposed to solar simulated radiations for 30, 60, 90 and 120 minutes. The respective UV-Vis absorption spectra were recorded after each time interval using UV-Visible spectrophotometer (Lamda 900 Perkin Elmer).

(3) In vitro Photoprotection Efficacy: Transmittance Study

The test samples of HQ-PDMS/HQ-gel (~ 0.2 mg/cm^2) were applied on a polymethylmethaacrylate (PMMA) plate (6 micron roughness and 7x7 size) (3M) using standard procedure [47]. The intensity of simulated solar atlas sun lamp was adjusted to 550 W/m^2. The PMMA/HQ-PDMS or PMMA/HQ-gel was dried for 15 minutes prior to UV exposure. The transmitted energy/spectrum was recorded through the HQ-PDMS/HQ-gel film present on the PMMA using spectroradiometer (International Lights Model: RPS 900-R). The transmitted energy/spectrum obtained through the PMMA was used as the control. The control samples containing the mixture of free 2-allyloxy-1-hydroxyanthraquinones (Al-HQ, 17%) and DMMH-co were used for the study.

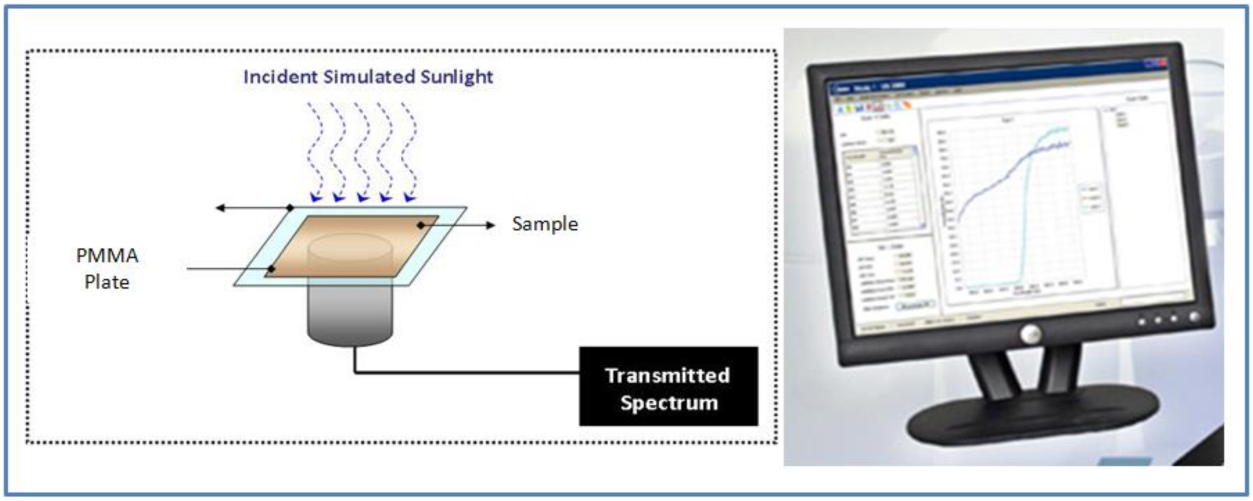


Figure 16: *In vitro Photoprotection Efficacy: Transmittance Study*

(4) In vitro Photostability Efficacy: Transmittance Study

Experimental procedure described in section 2.4.3 was followed. The PMMA/HQ-PDMS or PMMA/HQ-gel was exposed to solar simulated sun light for 30, 60, 90, 120, 150 and 180 minutes and respective transmitted energy / spectrum were recorded.

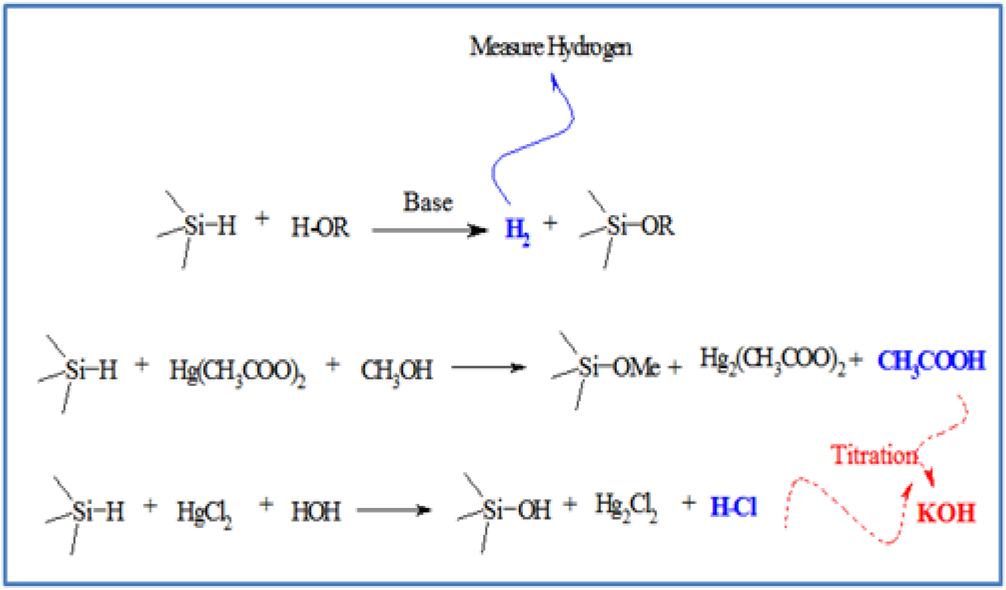
(5) Fluorescence measurement of 2-allyloxy-1-hydroxyanthraquinone (Al-HQ) and 2-allyloxy-1-hydroxyanthraquinone modified polymer (HQ-PDMS)

The stock solution of *2-allyloxy-1-hydroxyanthraquinone* (Al-HQ, 279 ppm ≈ 1000 μM) and HQ-PDMS (1000 ppm = 610 µM of Al-HQ) were prepared in toluene. The fluorescence spectra for Al-HQ test solutions (having concentrations ranging from 2.79 ppm ≈ 10 μM to 279 ppm ≈ 1000 μM) and HQ-PDMS (concentrations ranging from 16.4 ppm ≈ 10 µM of Al-HQ to 981.1 ppm ≈ 600 µM of HQ) were recorded using excitation wavelength of Ex$_{\lambda max}$ = 420 nm using Horiba Fluorometer. The fluorescence intensity obtained at emission wavelength of Em$_{\lambda max}$ = 600 nm with slit width 5 was plotted against concentrations of the hydroxyanthraquinones.

3. Results and Discussion

3.1 Synthesis & characterization of Poly(dimethyl)-co-(methylhydrogen) siloxane (DMMH-co)

Various grades of DMMH-co were synthesized by using different levels of MHPS, D_4 and capping agent (TMCTS). Detail synthesis procedures and reactions schemes are shown in section. The product was characterized using ^{1}H NMR, ^{13}C NMR and FT-IR and the data is shown in section 2.3.1 and 2.3.2. Previously [48] Si-H was determined by two methods such as (a) the base catalyzed reaction of silanes with alcohol and (b) via reaction of silanes with reducing substances like Hg (II) or Ag (II) salts as shown below.



Due to high toxicity of Hg (II) salts we developed a new method for the characterization of Si-H using FT-IR. As described in the experimental section, stock solution of MHPS (8000 ppm) was prepared. The test solutions were subjected to FT-IR followed by measurement of corrected peak areas and corrected peak heights at 2159 cm^{-1}. Table 2 shows respective corrected heights obtained from test solutions having different concentration of Si-H. These concentrations (SiH ppm) were then plotted against the corrected heights in figure 17.

***Table 2**: Calibration data for SiH MHPS (% SiH - 45)*

Sample	Test volume (ppm)	SiH (ppm)	Total Height	Corrected Height
AM4-1	6000	2700	0.3110	0.3089
AM4-2	4800	2160	0.3062	0.3047
AM4-3	4000	1800	0.2233	0.2221
AM4-4	2000	900	0.1121	0.1109
AM4-5	1000	450	0.0594	0.0590
AM4-6	500	225	0.0288	0.0285

This result was validated with known %Si-H i.e. 45% present in the MHPS. As a result, the avg. % Si-H observed after the characterization was 43.99%.

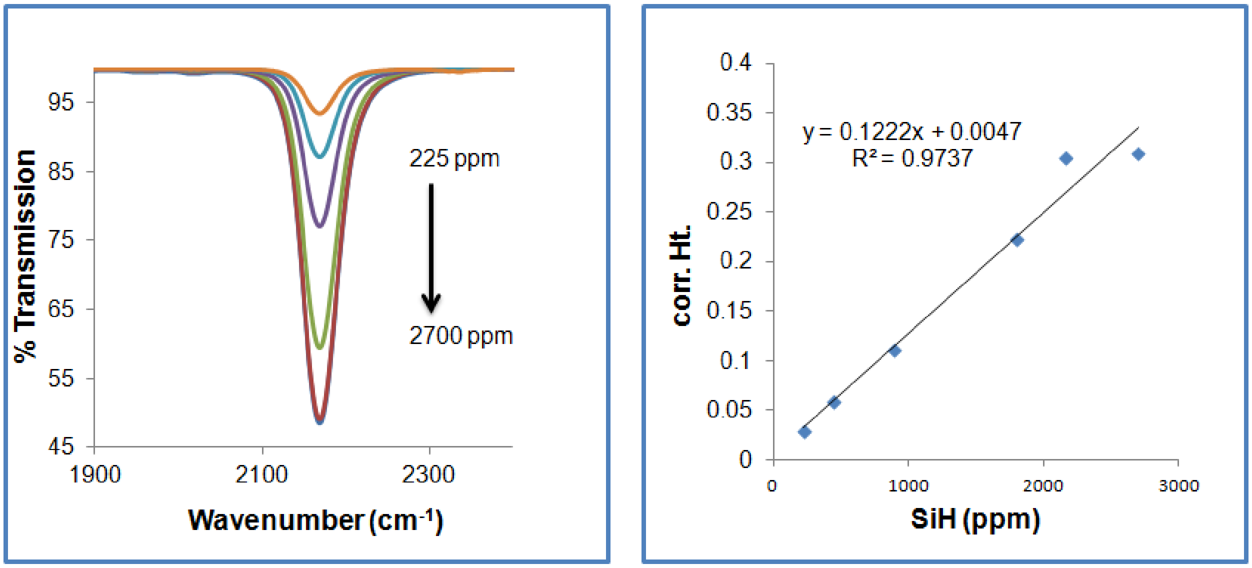


Figure 17: *Peak Height at* 2159 cm^{-1} with respect to e*ffective Si-H (mg/mL) and Correlation of Peak Height v/s Effective Si-H (mg/mL)*

Peak heights obtained at various concentrations (ppm) of SiH were plotted in figure 17. The linear equation $y = 0.1222x + 0.0047$; $R^2 = 0.9737$ was obtained, where y is peak height and x is concentration of SiH (ppm). Based on the calibration, unknown Si-H was quantified from various grades of synthesized DMMH-co. Following table describes various grades of DMMH-co. Theoretical % Si-H present in each sample was calculated as shown in the table 4.

Table 3: *Various grade of DMMH-co % SiH ranging from 1% to 36 %*

Sample	MHPS (g)	D_4 (g)	TMCTS (g)	Calculated M. Wt
AM-14	0.8	20	-	87061
AM-13	2	20	-	31042
AM-2	5	35	-	16932
AM-1	10	30	-	9877
AM-43	8	20	5	11641
AM-38	10	20	10	11288
AM-45	8.5	10	12	10292

Temperature = 120 °C; Tulsion Catalyst = 2%

Various test solutions of DMMH-co were prepared followed by measurement of the peak height.

Table 4: *Various grade of DMMH-co % SiH ranging from 1% to 36 %*

Sample	Test solution (ppm)	Peak height	Theoretical % Si-H	Exp. % Si-H	Calculated M. Wt
AM-14	50000	0.1283	1	1.18	87061
AM-13	45000	0.5117	3	3.45	31042
AM-2	8000	0.0379	6	7.32	16932
AM-1	6000	0.0314	12	11.98	9877
AM-43	4500	0.1773	18	18.58	11641
AM-38	4000	0.2474	24	24.8	11288
AM-45	1000	0.0854	31	33.01	10292

3.2. Synthesis & Photostability of Allyloxy Hydroxyanthraquinone (Al-HQ)

We selectively carried out allylation of ortho hydroxyl group present on 1,2-di-hydroxyanthraquinone to form 2-allyloxy-1-hydroxyanthraquinone. The reaction scheme is shown in figure 3 and synthetic procedure is described in the experimental section.

The product was characterized using ^{1}H NMR, ^{13}C NMR, FT-IR and GC-MASS. The data is shown in section 2.3.3. UV absorption efficacy and the photostability of 2-allyloxy-1-hydroxyanthraquinone (Al-HQ) were studied in toluene. The detail procedure is described in the experimental section 2.4.2. Figure 18, shows UV-Visible spectrum of 2-allyloxy, 1-hydroxyanthraquinone in toluene having λ_{max} of 415 – 420 nm, before and after exposure to 30, 60, 90 and 120 minutes of solar simulated sunlight. All the spectra were compared with the spectrum obtained before exposure (0 minutes). As seen in figure 18, marginal change in UV-Visible efficacy of 2-allyloxy-1-hydroxyanthraquinone solution was observed after exposure to 120 minutes of solar simulated radiation. This indicated the superior photostability of 2-allyloxy-1-hydroxyanthraquinone (Al-HQ).

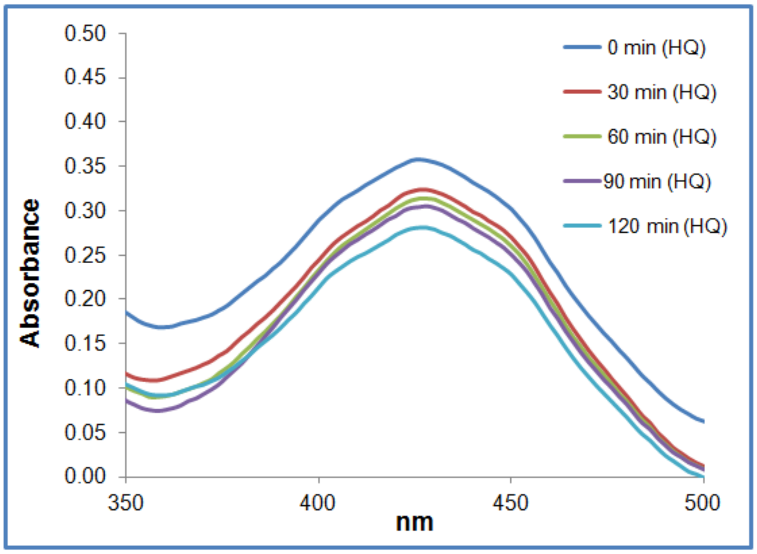


Figure 18: *UV-Visible absorbing efficacy of 2-allyloxy-1-hydroxyanthraquinone (20 ppm) before (0) and after the 30, 60, 90 and 120 minutes of exposure to solar simulated sunlight (In toluene)*

3.3 Synthesis & Photostability of Hydroxyanthraquinone Modified Silicone polymer (HQ-PDMS)

2-allyloxy-1-hydroxyanthraquinone (Al-HQ) and octadecene were reacted with DMMH-co in the presence of platinum catalyst and toluene. The reaction scheme is shown in figure 3 and synthetic procedure is described in experimental section 2.3.4. The reaction was monitored by disappearance of FTIR peak due to Si-H at 2159 cm^{-1} (figure 13). Covalent attachment of 2-allyloxy-1-hydroxyanthraquinone (Al-HQ) to DMMH-co backbone was reconfirmed using ^{1}H-NMR in figure 14. The appearance of peak at δ 0.6 indicated formation of [-Si-C$\underline{\mathbf{H}}_2$CH$_2$CH$_2$-O-hydroxyanthraquinone] linkage shown ibn figure 14-1. % hydroxyanthraquinone present on the HQ-PDMS was determined by using UV absorption spectroscopy.

The stock solution of Al-HQ (279 ppm) was prepared in toluene. Various test solutions of Al-HQ having concentrations ranging from 5 - 40 ppm were prepared. As seen in figure 19, The absorbance at λ_{max} = 420 nm was plotted against the test concentrations of Al-HQ.

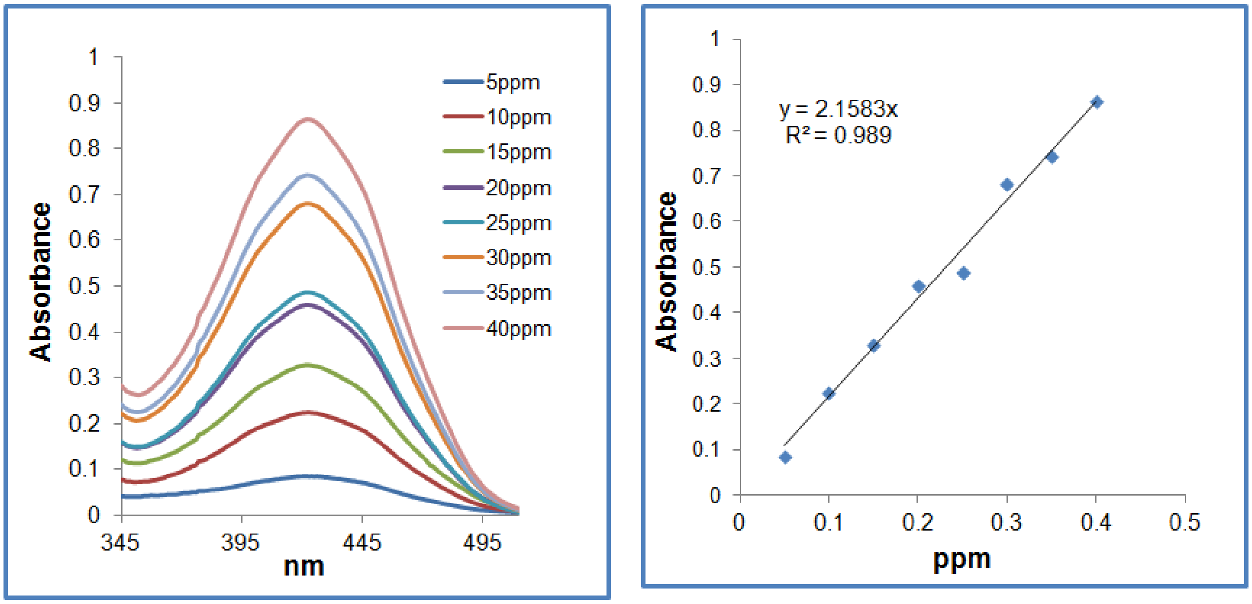


Figure 19: *Absorption spectra of Al-HQ*

Similarly, the stock solution of HQ-PDMS (1000 ppm) was prepared in toluene. Various test solutions of HQ-PDMS having concentrations ranging from 15 - 120 ppm were prepared. As seen in figure 20, the absorbance at λ_{max} = 420 nm was plotted against the test concentrations of HQ-PDMS. The linear equation obtained in figure 19, i.e. $y = 2.1583x; R^2 = 0.989$ was used to calculate unknown levels of hydroxyanthraquinone loaded in HQ-PDMS, where y is absorbance obtained at any given concentration of HQ-PDMS and x is concentration effective HQ (ppm) present in HQ-PDMS.

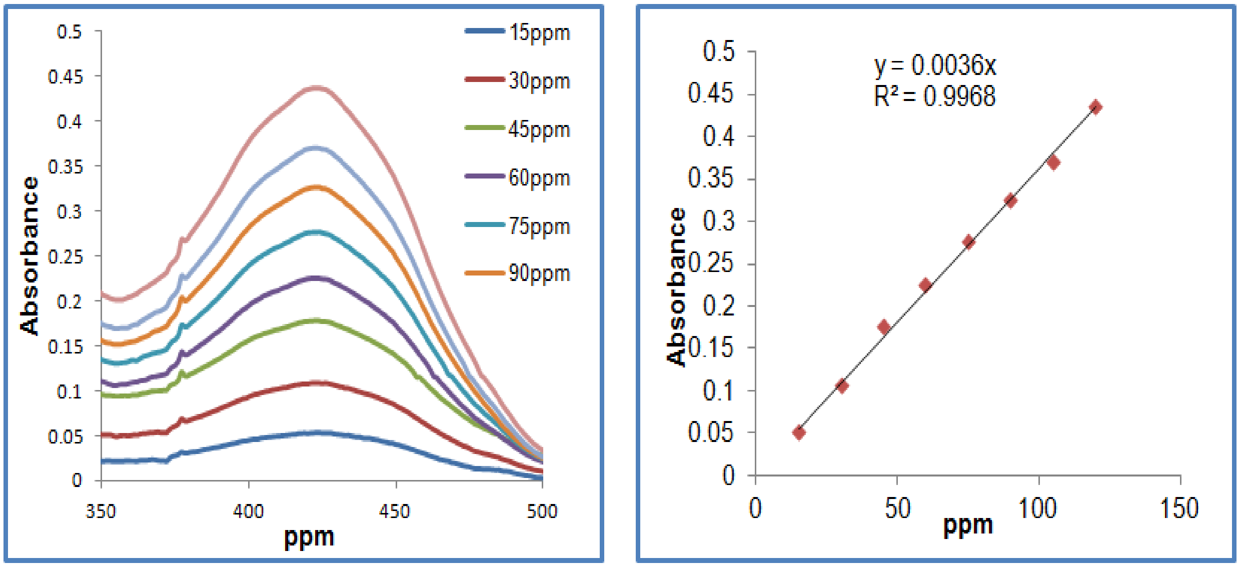


Figure 20: *Absorption spectra of HQ-PDMS*

Table 5 describes various grades of HQ-PDMS synthesized by using different levels of DMMH-co, octadecene and Al-HQ. Theoretical %HQ present in each sample was calculated as shown in the table 5. Octadecene was used to solubilize the HQ chromophore in toluene.

Table 5: *Various grades of HQ-PDMS containing different % loading of hydroxyanthraquinone*

Exp. code	DMMH-co (%)	Octadecene (%)	HQ (%)	Experimental (%HQ)
AM-87	61	33	5	3
AM-68	48	25	26	17 %
AM-75	48	26	26	20 %

In the next section photoprotection efficacy of HQ-PDMS was evaluated using the procedure described in section 2.4.3 and 2.4.4. The test sample, HQ-PDMS (~ 0.2 mg/cm^2) was applied on a polymethylmethaacrylate (PMMA) plate. The intensity of simulated solar atlas sun lamp was adjusted to 550 W/m^2. The transmitted energy/spectrum was recorded through the HQ-PDMS film present on the PMMA. Note:

the mixture of 2-allyloxy-1-hydroxyanthraquinones (Al-HQ, 17%) and DMMH-co was used as the control test sample.

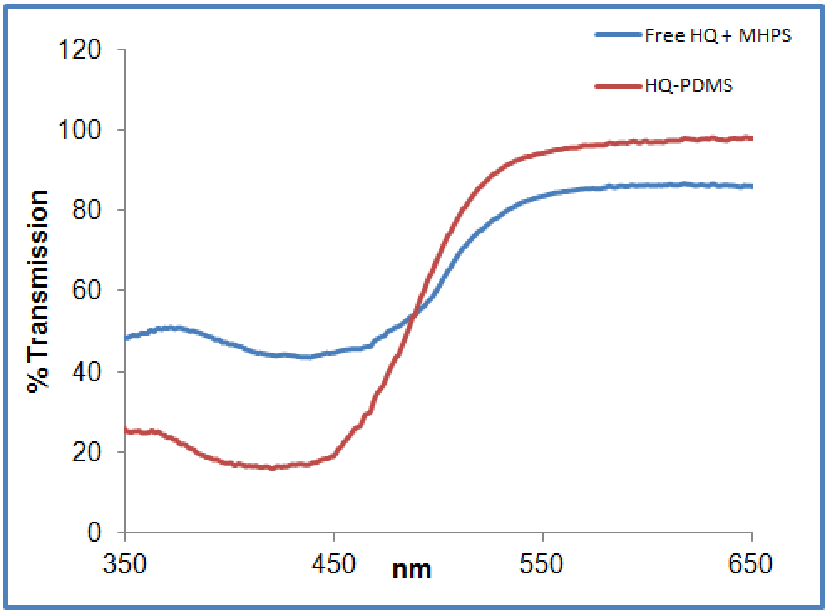


Figure 21*:* *Broad spectrum in-vitro UV-Visible absorbing efficacy of HQ-PDMS & Control (Free Al-HQ + DMMH-co)*

As seen in figure 21, ~15% transmittance was obtained through test sample HQ-PDMS v/s control which showed ~ 45% transmittance at λ_{max} 420 nm. Hence HQ-PDMS showed superior photoprotection efficacy than the control. This was presumably to be due to superior molecular solubilization of hydroxyanthraquinone chromophore in HQ-PDMS v/s control. This could have led to uniform distribution of UV absorbing chromophores on the substrate surface; resulting into the superior photoprotection efficacy.

Similarly, photostability of HQ-PDMS was evaluated using the procedure described in section 2.4.3 and 2.4.4. Once again test sample, HQ-PDMS (~ 0.2 mg/cm^2) was applied on a polymethylmethaacrylate (PMMA) plate. The intensity of simulated solar atlas sun lamp was adjusted to 550 W/m^2. The transmitted energy/spectrum was recorded through the HQ-PDMS film present on the PMMA. Same test sample, HQ-PDMS on PMMA plate was exposed to solar simulated sun light for 30, 60, 90, 120, 150 and 180 minutes, followed by measurement of respective transmitted energy / spectrum. Figure

22 shows transmittance spectra obtained before and after exposure to solar simulated sun radiations.

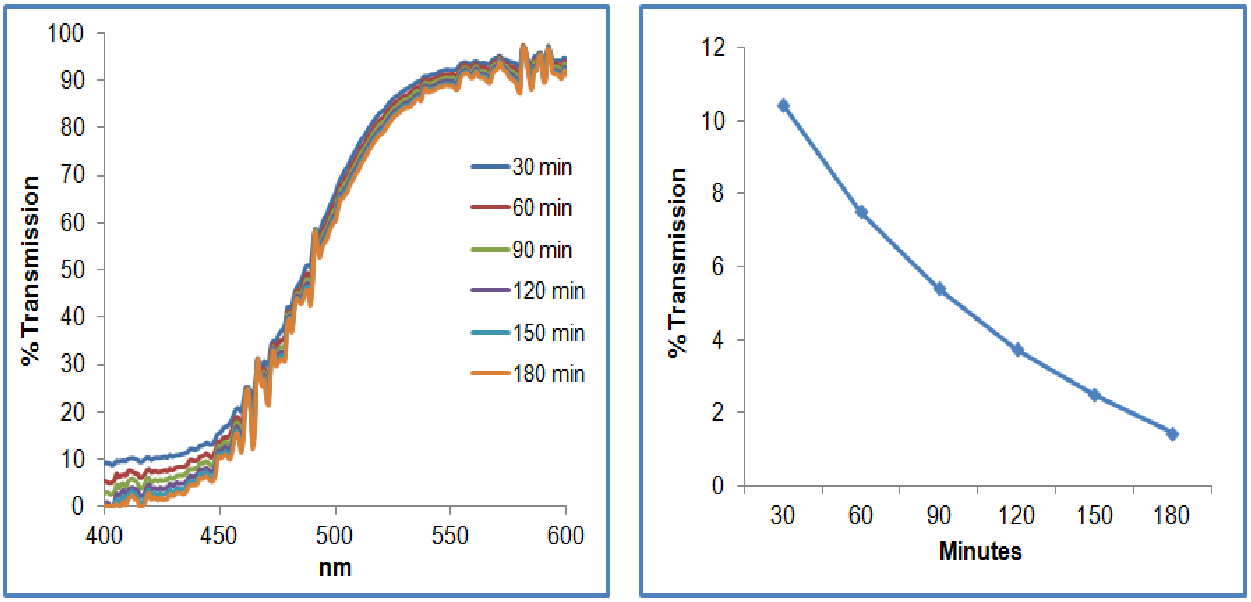


Figure 22*: Broad spectrum in-vitro transmittance i.e. UV-Visible protection efficacy of HQ-PDMS & Control-1*

Interestingly, we observed directional decrease in the transmittance with the extent of solar simulated sun exposure.. This behavior showed progressive photoprotection obtained due to HQ-PDMS probably due to UV triggered film formation, followed by reorganization of chromophores onto the surface. Recent literature [49] also showed this kind of behavior in other chromophore. The mode of action of progressive protection is not yet understood.

3.4 Photochemical Properties of 1,2-di-hydroxyanthraquinone derivatives

1,2-hydroxyanthraquinone shows photostability mainly due to its unique hydrogen bonded planar structure which undergoes excited state intramolecular proton transfer (ESIPT) [50] and emits excited energy through a dual fluorescence phenomenon [51]. The molecule in the first excited state S_1 (N*) undergoes an intramolecular proton transfer (ESIPT) to create another species in its first excited singlet state S1 (T*). This excited proton–transferred species loses its energy by a non-radiative decay process as thermal energy to S_0 (T). The fundamental form of the absorber S_0 (N) is regenerated by a reverse proton transfer mechanism [52,53,54]. Hence photo-stable HQ-PDMS or HQ-Gel was synthesized by maintaining unique hydrogen bonded planar structure present on the hydroxyanthraquinone structure.

In this section, we studied photochemical properties of 2-allyloxy-1-hydroxyanthraquinone (Al-HQ) alone and in the presence of parent pre-polymer DMMH-Co. The test solutions of Al-HQ having concentrations ranging from 2.79 – 279 ppm (i.e. 10 - 1000 μM) were prepared, followed by measurement of fluorescence spectrum. The detailed procedure is described in the section 2.4.5. Figure 23 shows fluorescence spectrum obtained from test solutions of Al-HQ alone and in the presence of parent pre-polymer DMMH-Co. Similarly, test solutions of Al-HQ having concentrations ranging from 2.79 – 279 ppm (i.e. 10 - 1000 μM) were prepared in the presence of parent pre-polymer DMMH-Co having concentrations ranging from 13.61 - 1362 ppm; followed by measurement of fluorescence spectrum. Figure 23 shows fluorescence spectrum obtained from test solutions of Al-HQ in the presence of parent pre-polymer DMMH-Co.

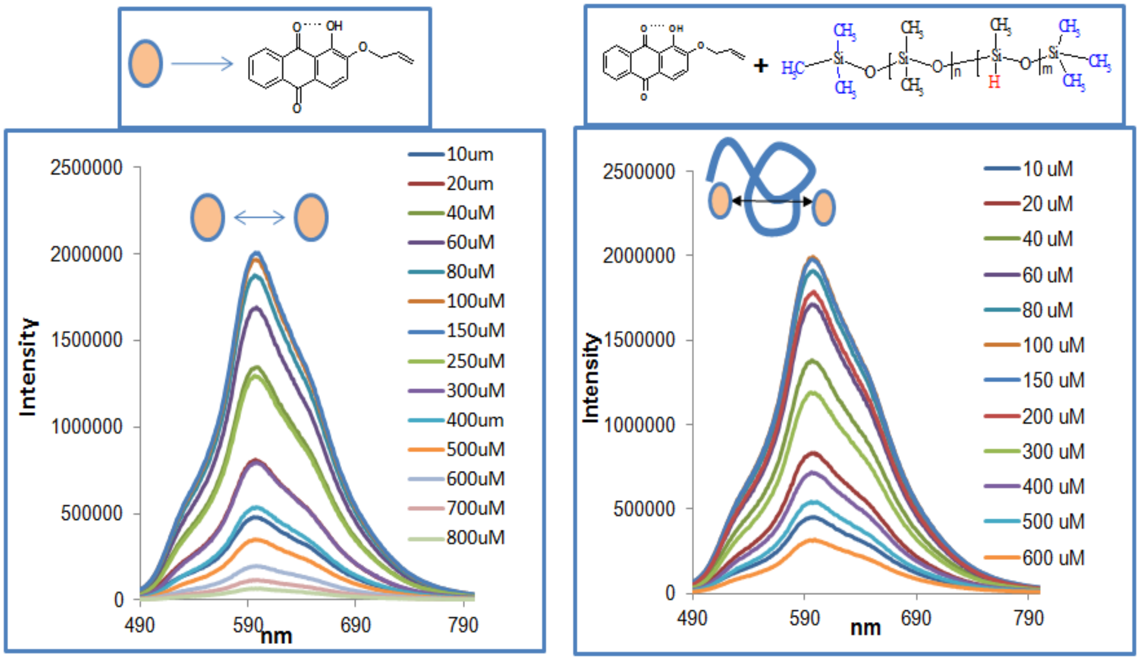
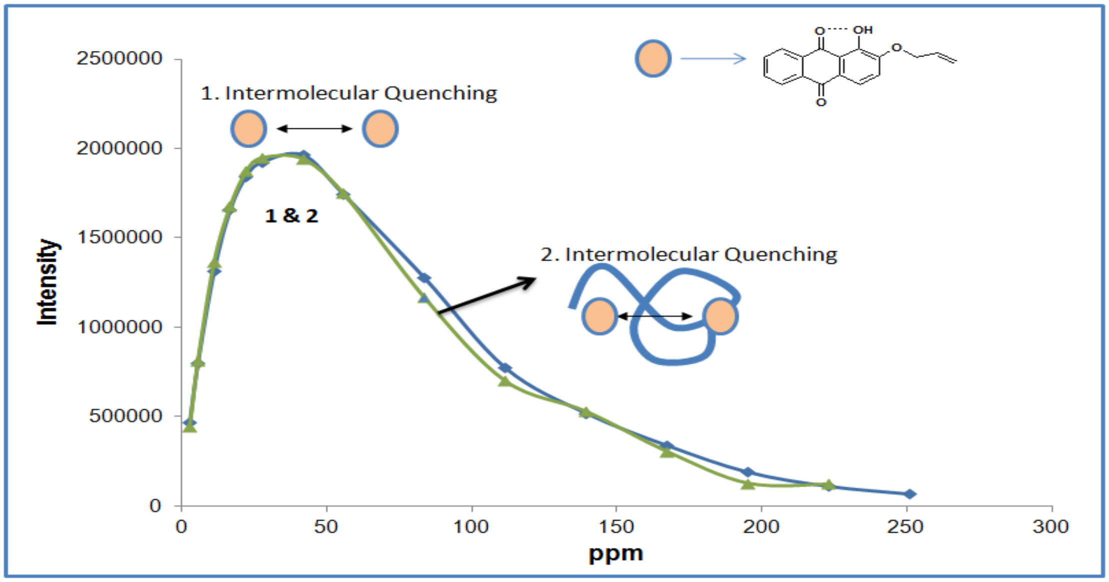


Figure 23: *Fluorescence Quenching of Al-HQ and physical mixture (Al-HQ in presence of DMMH-co)*

As seen in the figure 24, the fluorescence intensity at Emλ_{max} = 600 nm was plotted against concentrations of Al-HQ alone (figure 24, line 1) and in the presence of parent pre-polymer DMMH-Co (figure 24, line 2). As expected fluorescence intensity due to Al-HQ increased with the concentration up to 150 μM followed by significant drop with further increase in the concentration. This was possibly to be due to self quenching of excited hydroxyanthraquinone at 150 μM concentration. The kinetics of self was remain unaffected parent pre-polymer DMMH-Co.



.

Figure 24: *Fluorescence Quenching of Al-HQ and physical mixture (Al-HQ and DMMH-co)*

In this section, we studied photochemical properties of HQ-PDMS. The test solutions of HQ-PDMS having concentrations ranging from 16.4 – 981 ppm were prepared, followed by measurement of fluorescence spectrum. *Note that the effective concentrations of hydroxyanthraquinone present in these test solutions were ranging from 2.79 – 279 ppm; same as used in figure 23.* Figure 25 shows fluorescence spectrum obtained from test solutions of HQ-PDMS compared with Al-HQ at same range of concentrations. As seen in the figure 26, the fluorescence intensity at Emλ_{max} = 600 nm was plotted against effective concentrations HQ. As expected, in the case of HQ-PDMS fluorescence intensity increased with the effective concentration of HQ, up to 150 μM followed by significant drop with the further increase in the concentration. This was again possibly to be due to self quenching of excited hydroxyanthraquinone above 150 μM concentration.

However as seen in figure 26, line 3, in the case of HQ-PDMS, fluorescence intensity obtained at 150 μM concentration was almost 50% less than what was observed with free Al-HQ (figure 26, line 1) and in the presence of parent pre-polymer DMMH-Co (figure 26, line 2).

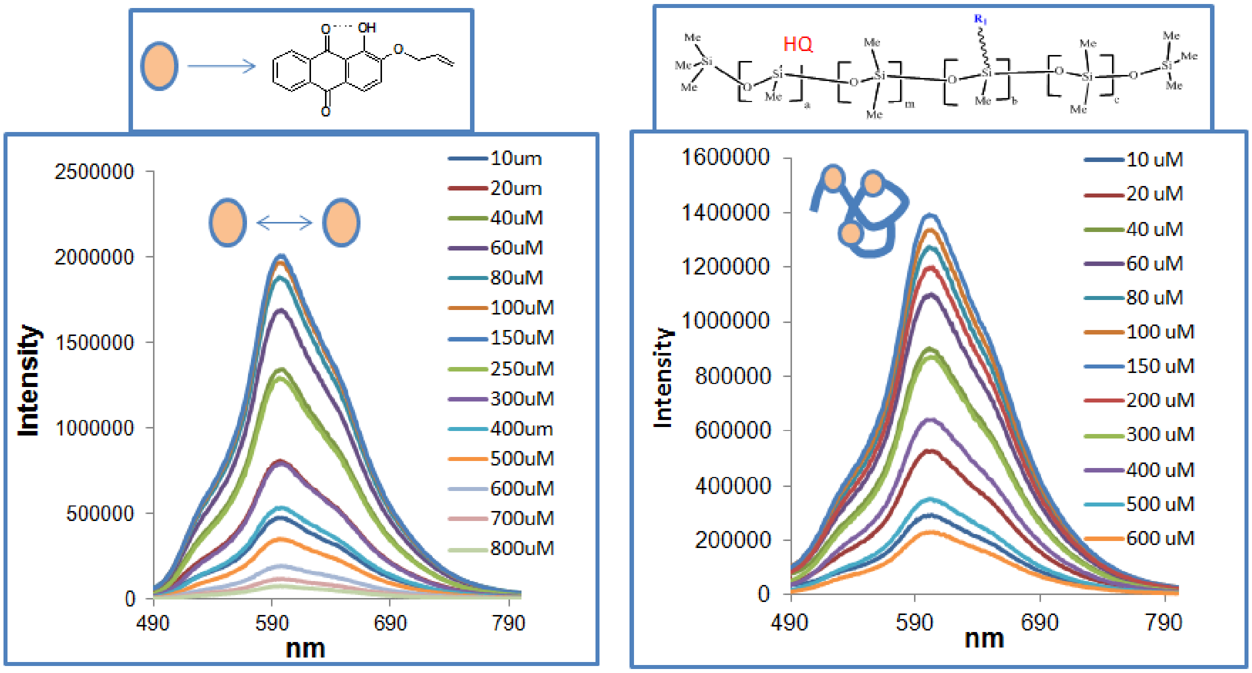


Figure 25: *Fluorescence Quenching of Al-HQ and HQ-PDMS*

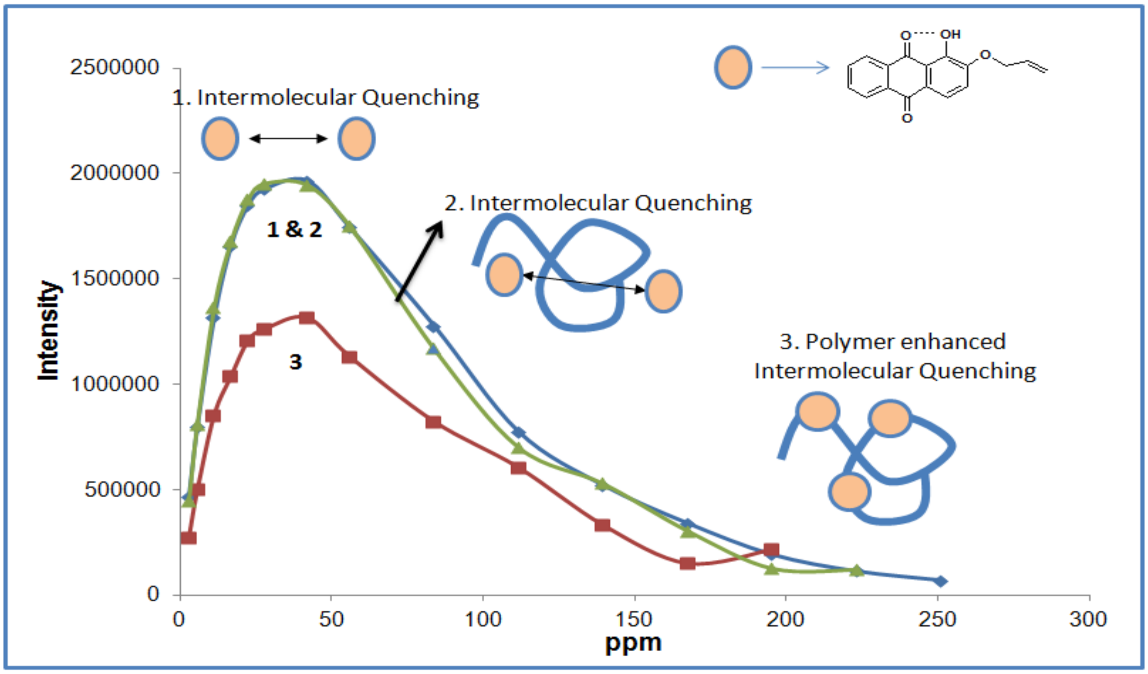


Figure 26: *Comparison between free Al-HQ, HQ-PDMS, free Al-HQ + octadecene + DMMH-co*

We observed enhanced fluorescence quenching or self quenching between the photoexcited chromophores, when they are covalently attached to the flexible polymer backbone such as polysiloxanes. However various parameters such as (a) effect of chromophores attached to the polymer backbone, (b) molecular weight of the parent polymer; (c) type of chromophores could play significant role in the quenching kinetics. Also interaction between donor (e.g. photodegradable molecules) and acceptor (e.g. quencher or photostabilizing molecules) can be enhanced using this model polymer system.

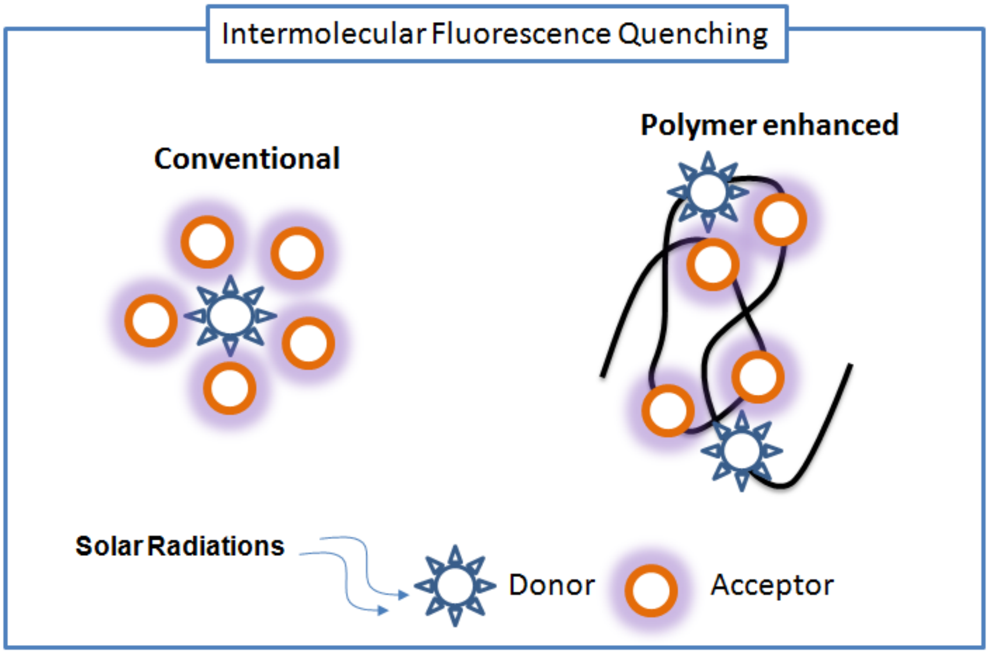


Figure 27*:* figure showing donor - acceptor interactions can be possible on a polymeric backbone.

3.5 Synthesis & Photostability of Hydroxyanthraquinone Modified Silicone elastomer gel.

2-allyloxy-1-hydroxyanthraquinone and octadecene were reacted with DMMH-co in the presence of platinum catalyst and toluene. The reaction scheme is shown in figure 4 and synthetic procedure is shown in experimental section. The reaction was monitored by disappearance of FTIR peak due to Si-H at 2159 cm^{-1} (figure 13). After the reaction ~ 80% toluene was removed. The gel was washed with cold methanol until it was free from unreacted 2-allyloxy1-hydroxyanthraquinone*.* Finally it was swollen in D$_5$. Covalent attachment of hydroxyanthraquinone to polymer backbone was reconfirmed using NMR.

Appearance of peak at δ 0.6 indicated formation of [-Si-C$\underline{\mathbf{H}}_2$CH$_2$CH$_2$-O-hydroanthraquinone] linkage shown in figure 14-1. The UV-Visible efficacy of the hydroxyanthraquinone modified silicone elastomer gel (HQ-Gel) was determined by the amount of active hydroxyanthraquinone moiety covalently present on the polymer chain. We therefore prepared control-1 mixture containing 17% free hydroxyanthraquinone and DMMH-co. In vitro analysis showed that visible light absorbing efficacy of control mix was almost double that of HQ-gel (figure 28).

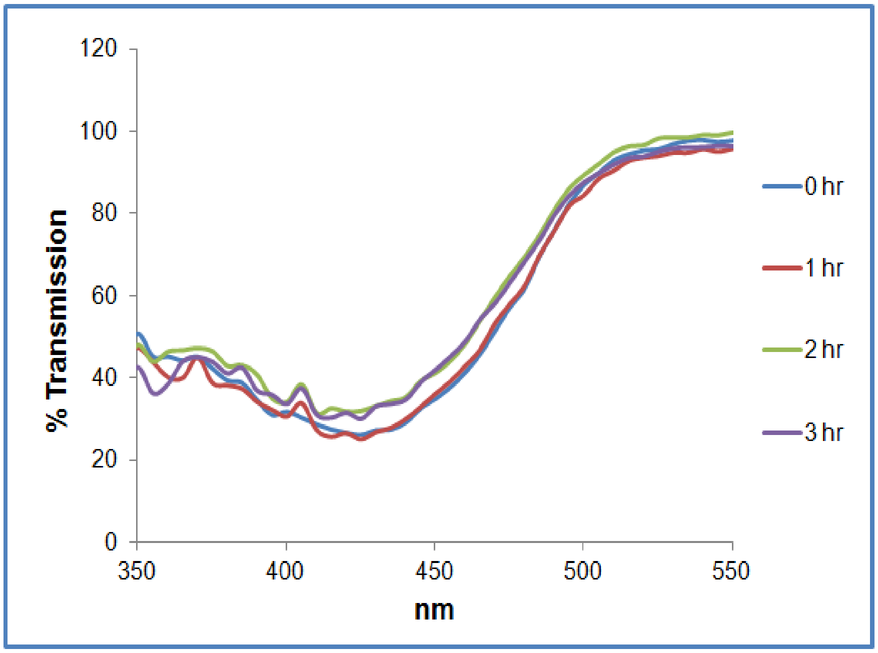


Figure 28: P*hotoprotection efficacy of hydroxyanthraquinone modified elastomer*

Conclusions

The molecular solubilization of hydroxyanthraquinone was achieved through its covalent attachment to the specialty polymers. Photostable 1-hydroxyanthraquinone-tagged poly(dimethyl siloxane) (HQ-PDMS) showed superior spreading due to uniform distribution of HQ chromophores on the substrate surface. We observed enhanced fluorescence quenching between the HQ chromophores, when tagged on the HQ-PDMS over free Al-HQ. Hence intermolecular photo-quenching processes between two chromophores (donor and/or acceptor) could be enhanced through covalent attachment to flexible polymer backbone.

References

---

1 Hayden, C.G.J.; Cross, S.E.; Anderson, C.; Saunders, N.A.; Roberts, M.S. Sunscreen Penetration of Human Skin and Related Keratinocyte Toxicity after Topical Application. *Skin Pharmacol. Physiol*. 2005, *18*, 170-174

2. Hayden, C.G. J.; Roberts, M.S.; Benson, H.A.E. Systemic absorption of sunscreen after topical application. *The Lancet*. 1997, *350*, 863-864

3. Zhang, X.M.; Nakagawa, M.; Kawai, K.; Kawai, K. Erythema-multiforme-like eruption following photoallergic contact dermatitis from oxybenzone. *Contact Dermatitis.* 1998, *38*, 43-44

4. Maeran, L.; Law, S.; Storrs, F. Contact urticaria, allergic contact dermatitis, and photoallergic contact dermatitis from oxybenzone. *American J. Contact dermatitis*. 2003, *14(1),* 33-34

5. Gustavsson , G.H.; Farbrot, A.; Larko, O. Percutaneous absorption of benzophenone-3, a common component of topical sunscreens. *Clinical and Experimental Dermatology*. 2002, *27,* 691-694

6 Schaefer, H.; Redelmeier, T.E.; Benech-Kieffer, F. The skin and its permeability. In Novel Cosmetic Delivery System, by Shlomo Magdassi & Elka Touitou eds. Chapter 2, Page 29 -30

7 Janjua, NR.; Mogensen, B.; Andersson, A-M.; Petersen, JH.; Henriksen, M.; Skakkebæk, NE.; Wulf, HC. Systemic Absorption of the Sunscreens Benzophenone-3, Octyl-Methoxycinnamate, and 3-(4-Methyl-Benzylidene) Camphor After Whole-Body Topical Application and Reproductive Hormone Levels in Humans *Journal of Investigative Dermatology*, 2004, *123*, 57–61

8. Jiang R.; Roberts, M.S.; Collins, D.; Benson, H.A. Absorption of sunscreens across human skin: an evaluation of commercial products for children and adults. *J. Clin. pharmacol*. 1999, *48(4)*, 635-637

9. Felix, T.; Hall, B.J.; Brodbelt, J.S. Determination of Benzophenone-3 and metabolites in water and human urine by solid phase microextraction and quadrupol ion trap GC-MS. *Anal. Chim Acta*. 1998, *371(2-3)*, 195-203

---

10. Kadry, A.M.; Okereke, C.S.; Abdel-Rahman, M.S.; Friedman, M.A.; Davis, R.A. Pharmacokinetics of Benzophenone 3 after oral exposure in male rat. *J. Appl. Toxicol*. 1995, *15*, 97-102

11. Hany, J.; Nagel, R.; Nachweis, von. Detection of UV screen in brest milk *Deutsche Lebensmittel-Rudschau*, 1995, *91*, 341-345

12 Kerr, A.; Niklasson, B.; Dawe, R.S.; Escoffier, A-M.; Krasteva, M.; Sanderson, B.; Ferguson, J. A double-blind, randomized assessment of the irritant potential of sunscreen chemical dilutions used in photopatch testing. *Contact Dermatitis,* 2009, *60(4)*, 203-209

13 Madan, V.; Beck, M.H. ontact allergy to octocrylene in sunscreen with recurrence from passive transfer of a cosmetic. *Contact Dermatitis*, 2005, *53(4)*, 241-242

14 Carrotte-Lefebvre, I.; Bonnevalle, A.; Segard, M.; Delaporte, E.; Thomas, P. Contact allergy to octocrylene. *Contact Dermatitis,* 2003, *48(1)*, 46-47

15 Karlsson, I.; Vanden, B.K.; Mårtensson, J.; Goossens, A.; Börje, A. Clinical and experimental studies of octocrylene's allergenic potency. *Contact dermatitis*, 2011, *64(6)*, 343-52

16 Marzulli, F.N.; Green, S.; Maibach, H.I. Hair dye toxicity--a review *J. Environmental Pathology and Toxicology*, 1978, *1(4)*, 509-30

17 Kumar, P.A S; Talari, K.; Dutta, T.K. Super vasomol hair dye poisoning *Toxicology International*, 2012, *19(1)*, 77-8

18 Sosted, H.; Johansen, J.D.; Andersen, K.E.; Menne, T. Severe allergic hair dye reactions in 8 children. *Contact Dermatitis*, 2006, *54(2)*, 87-91

19 Tsomi, V.; Kalopissis, G. Cutaneous penetration of some hairdyes in the hairless rat. *Toxicological European Research,* 1982, *4(3)*, 119-27

20 Yuin-Chew, C.; See-Ket, N.; Chee-Leok, G. Positive patch-test reactions to para-phenylenediamine, their clinical relevance and the concept of clinical tolerance Contact Dermatitis, 2001, *45(4)*, 217-220

21 Darbre, P.D.; Harvey, P.W. Paraben esters: review of recent studies of endocrine toxicity, absorption, esterase and human exposure, and discussion of potential human health risks. *J. Applied Toxicology*, 2008, *28(5)*, 561-578

22 El, H.S.; Muret, P.; Berard, M.; Makki, S.; Humbert, P. Assessment of principal parabens used in cosmetics after their passage through human epidermis–dermis layers (*ex-vivo* study). *Experimental Dermatology; 2007, 16(10)*, 830-836

23 Darbre, P.D. Environmental oestrogens, cosmetics and breast cancer. *Best Practice & Research Clinical Endocrinology & Metabolism, 2006, 20(1)*, 121-43

24 Pedersen, S.; Marra, F.; Nicoli, S.; Santi, P. In vitro skin permeation and retention of parabens from cosmetic formulations . *Int. J. Cosmet. Sci*. 2007, *29(5)*, 361-7

25 Caon, T.; Costa, A.C.O.; Augusto, L.M.; Amadeu, M.G.; Simoes, C.M.O. Evaluation of the transdermal permeation of different paraben combinations through a pig ear skin model. *Int. J Pharmaceutics, 2010, 391(1-2)*, 1-6

26 Bos, J.D.; Meinardi, M.M.;. The 500 Dalton rule for the skin penetration of chemical compounds and drugs. *Exp Dermatol*. 2000, *9(3)*, 165-9.

27 Holger, I.L.; Herrwerth, S.; Hartung, C. *Personal Care,* 2007, *May*, 11

28 Vaidya A,A.; Ghosh, N.G.; Balu, K. A silicone compound Pat. Appl.
WO 2011045149A1 2011 (Unilever)

29 Vaidya A,A.; Ghosh, N.G. A silicone compound and photoprotective personal care compositions comprising the same Pat. Appl. WO2012143242 (Unilever)

30 Marquais-Bienewald, S.; Wallquist, O.; Cremer, C.; Fröhling, B.; Möck, A. Polymeric hair dyes US 20090255063 A1 2009 (Ciba)

31 De Boni, M.; Laguitton, B.; Jean-Daniel, D. Leave-in hair dyeing process
using a composition comprising a colored polymer and an active cosmetic agent,
WO 2008032003 2008 (L'Oreal)

32 Marquais-Bienewald et al. : US 2009/0255063 A1, 2009

33 Vaidya, A.A.; Chavan, M.; Gadgil, V. A sunscreen composition Indian Pat. Appl
514/MUM/2006 2006 (Unilever)

34 Vaidya, A.A.; Chavan, M A sunscreen composition Indian Pat. Appl.
2084/MUM/2006 2006 (Unilever)

35 Liang, J.; Chen, Y.; Barnes, K.; Wu, R.; Worley, S. D.; Huang, T.- S. N-halamine quat/siloxane copolymer for use in biocidal coating *Biomaterial,* 2006, *27(11)*, 2495-2501

36 Kenawy, el-R.; Worley, S.D.; Broughton, R.The Chemistry and Applications of Antimicrobial Polymers: A State-of-the-Art Review. *Biomacromolecules*, 8(5), 2007, 1359

37 Kratzer, C.; Tobudic, S.; Macfelda, K.; Graninger, W.; Georgopoulos, A. In Vivo

Activity of a Novel Polymeric Guanidine in Experimental Skin Infection with Methicillin-Resistant *Staphylococcus aureus*. *Antimicrobial Agents and Chemotherapy*, 2007, *51(9)*, 3437–3439

38 Kedik, S.A.; Bocharova, O.A.; An, Ha-Kam; Panov, A.V.; Sedishev, I. P.; Zhavoronok, E.S.; Timofeeva, G. I.; Suslov, V.V.; Beksaev, S.G. Structure and molecular-weight characteristics of oligo(hexamethyleneguanidine) hydrochlorides Pharmaceutical *Chemistry Journal*, 2011, *44(10)*, 568-573

39 Tabellout, M.; Rogalskiy, S.; Bardeau, J-F.; Tarasyuk, O.; Fatyeyeva, K. Novel antimicrobial composition, use and preparation thereof. Eur. Pat. Appl. EP 2386589 A1 (Centre National de la Recherche Scientifique)

40 Nyzhnyk, J.V.; Baranova, G.I.; Marievskyi, V.F.; Fedorova, L.M.; Nadtoka, O.M.; Nyzhnyk, T.J. Method for producing polyguanidines with high biological activity for antiseptics and cosmetics. PCT Int. Appl. WO 2008039162 A1 2008 (Board of Supervisors of Louisiana State University and Agricultural and Mechanical College)

41 Sajomsang, W.; Gonil, P.; Saesoo, S.; Ovatlarnporn, C. Antifungal property of quaternized chitosan and its derivatives. *Int. J. Biological Macromolecules*, 2012, *50(1)*, 263-269

42 Daly, W.H.; Manuszak-Guerrini, M.A. Biocidal chitosan derivatives US 6306835 2001 (Board of Supervisors of Louisiana State University and Agricultural and Mechanical College)

43 J. Liang et al. : Biomaterials 27 (2006) 2495–2501

44 Hoon-Je Cho et al : Macromolecules 2003, 36, 6704-6710

45 Valery Shibaev*, Alexey Bobrovsky, Natalia Boiko : J. Mater. Chem., 2011, 21, 1094–1101

46 Y. Zhao, Shuying Bai, Karen Asatryan and Tigran Galstian: Adv. Funct. Mater. 2003, 13, No. 10, October

47 International SPF Test Method, COLIPA, 2006

48 The analytical chemistry of silicones by A. Lee Smith (section 3.2)

49 Adaya Gallardo et al: Photochem. Photobiol. Sci., 2010, 9, 530–534

50 Shin-ichi Nagaoka , Umpei Nagashima, Chemical Physics, 1996, 206, 353

51 Sasirekha, V. M. Umadevi b, V. Ramakrishnan, Spectrochimica Acta, 2008, Part A 69, 148.

---

52 Weller, A. Naturwissenshaften 1955,42, 175

53 Mosquera, M.; Penedo, J.C.; Rodrı´guez, M.C.R.; Rodrı´guez- Prieto, F. J. Phys. Chem., 1996, 100, 5398.

54 (a) Woessner, G.; Goeller, G.; Kollat, P.; Stezowski, J.J.; Hauser, M.; Klein, U.K.A.; Kramer, H. E. A. J. Phys. Chem., 1984, 88, 5544.

(b) W. Klo¨ pffer, Adv. Photochem., 1977, 10, 311.

(c) Ghiggino, K. P.; Scully, A.. D. Leaver, I. H. J. Phys., 1986, 90, 5089.

(d) Otterstedt, J. E. A J. Chem. Phys., 1973, 58, 5716.

(e) Keck, J. Roessler, M.; Schroeder, C.; Stueber, G.J.; Waiblinger, F.; Stein, M.; LeGourrie´rec, D.; Kramer, H.E.A.; Hoier, H.; Henkel, S.; Fischer, P.; Port, H.; Hirsch, T.; Rytz, G.; Hayoz, P. J. Phys. Chem. B, 1998, 102, 6975