Synthesis of UV-Curable Difunctional Silane Monomer Based on 3-Methacryloxy Propyl Trimethoxysilane (3-MPTS) and its UV-Curing Characteristics and Thermal Stability

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ABSTRACT: In the present investigation, silicon containing UV-curable difunctional monomer was synthesized by reacting 3-methacryloxy propyl trimethoxysilane (3-MPTS) with acrylic acid using anhydrous ether as a solvent under inert atmosphere. The synthesized acryloxymethacryloxy silane monomer was characterized by FTIR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. The silane monomer along with 4 wt % photoinitiator (Darocure 1173) was cured under UV-light for different exposure time. The curing characteristic of the monomer was investigated using FTIR spectroscopy. The conversion of the double bond due to curing has been evaluated from the peak intensity of the C=C double bond (at 1636 cm^{-1}) in the FTIR spectrum considering the peak intensity at 1720 cm^{-1} due to C=O as internal standard. The maximum double bond conversion is observed to be 72%. The optimum cure time for the silane monomer has been estimated to be 7.8 sec. The UV-cured sample decomposes at 440°C. The char residue is 35% at 700°C. The synthesized UV-curable silane monomer may be useful for UV-coating formulations, for fabrication of 3D-objects by lithographic technique and as a precursor for organic–inorganic hybrid materials. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2352–2358, 2010

Key words: UV-curable; difunctional silane monomer; double bond conversion; FTIR

INTRODUCTION

The field of research on UV-curable polymers has attracted much attention for their commercial applications. The technique of polymer coating by radiation (UV/EB) curing has been recognized as an innovative technology since this technique combines number of advantages such as low energy consumption, less environmental pollution (solvent free formulations) and very rapid curing at ambient temperatures.[1–4] Conventional heat and/or air drying techniques evaporate solvents during the curing process. Hence the initial lay down of coatings may be reduced to ∼ 50%, and it also causes emission of pollutants. However, UV-radiation cures instantly. Moreover, cured coating film thickness remains unchanged since no volatiles evaporate. The film surface properties are also better leading to high quality end products. Hence, UV-coating is successful particularly for protective and decorative surface coatings[2,4–7] and optical fiber coatings.[5,8] Besides coating applications, UV-curable polymers have potential applications in photolithography and microelectronics to produce high resolution relief images.[1,2,6] However, this is not possible by thermal curing polymeric systems. So the field of research on UV-curable polymers is able to create lots of interest both academically and commercially.

UV-curable coating formulations generally consist of three major components: (i) mono or difunctional monomers (called reactive diluents), (ii) unsaturated oligomers, and (iii) photoinitiators. Sometimes nonreactive additives such as adhesion promoters, wetting agents, pigments etc. are also added into the UV-formulations to achieve the specific application requirements.[1–5] The photoinitiator under irradiation absorbs UV-light and is converted into reactive species such as free radicals and radical ions, or long-lived intermediates such as acids or bases. These species initiate the photochemically driven polymerization and curing. The curing is normally completed in a few seconds at room temperature. Unsaturated oligomers[9–12] like acrylated epoxides, acrylated polyurethanes, unsaturated polyesters, and acrylated polyesters or polyethers are commonly used for radiation (UV/EB) curable coatings. The role of difunctional (or multifunctional) reactive diluents is very crucial to control the viscosity of the formulation, the time of crosslinking as well as crosslinking density of the final coating film. Hence many UV-curable di- or multifunctional (crosslinking) agents have been reported in the literature,[12,13] which include hexanediol diacrylate (HDDA),

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tripropyleneglycol diacrylate (TPGDA), trimethylol-propane triacrylate (TMPTA), diglycidyl methacrylate derivative of bisphenol-A (bis-GMA) etc.

Silicon based UV-curable monomers as well as coating formulations are widely used as pressure sensitive adhesives and weather resistant coatings. The presence of silicon offers important properties as low surface energy, nonpolarity, chemical inertness and long term weather resistance of the coatings.[14–18] Modified polysiloxane, silicon-acrylic resins synthesized by the copolymerization of acrylate monomers and a silicon monomer, and silicon containing multi-functional methacrylates. have been used in UV-coating formulations.[14–18] Silicon containing monofunctional monomers, particularly, 3-methacryloxy propyl trimethoxysilane (3-MPTS) and 3-(trimethoxysilyl)-propanethiol (TSPT) are often used in the formulations for UV-coating applications.[16] We also used 3-MPTS for functionalization of carbon nanotubes.[19] However, in the present investigation, a bifunctional UV-curable silane monomer was synthesized using 3-MPTS for the purpose that the synthesized bifunctional monomer will act as reactive diluent as well as crosslinker in the process of UV-formulations. The synthesized acryloxymethacryloxy propyl silane monomer was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. For the development of UV-curable polymers for any application (UV-coating or lithography), it is first essential to understand the curing behavior of such monomers/polymers. Hence we also report the study of the UV-curing characteristics of the silane monomer using FTIR spectroscopy. The double bond conversion due to curing has been quantitatively estimated from the peak intensity of the double bond in FTIR spectrum. Thermal stability of the cured film of the bifunctional monomer is also reported here.
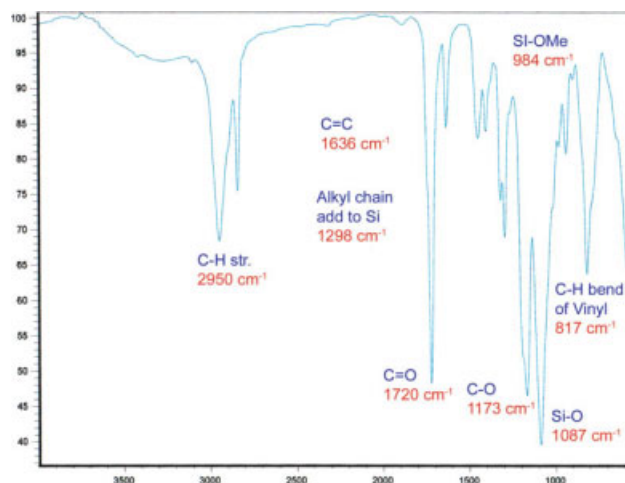
EXPERIMENTAL

Chemicals

Acrylic acid (99%, Aldrich), 3-methacryloxy propyl-trimethoxysilane(3-MPTS) (98%, Aldrich) and diethyl
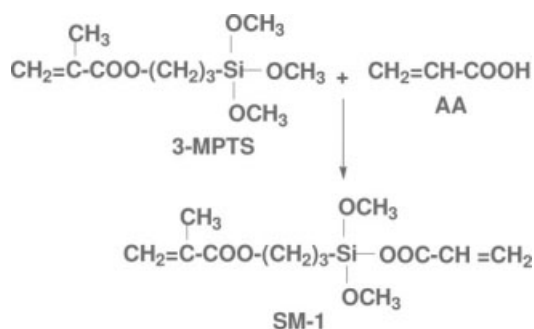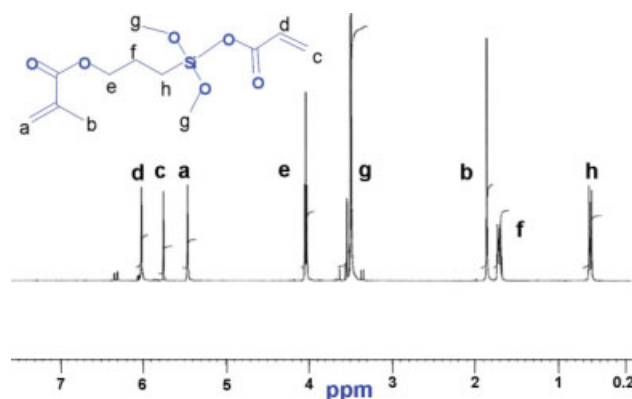
Scheme 1 Synthesis of difunctional silane monomer.

Figure 1 FTIR spectrum of silane monomer (SM-1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ether (Aldrich) were used as received to synthesize the UV-curable silane monomer. The photoinitiator, Darocure1173 (2-hydroxy-2-methyl-1-phenyl-1-propanone) (Ciba Speciality Chemicals) was used as received.

Synthesis of difunctional silane monomer

A UV-curable silane monomer (SM-1) was synthesized by reacting 0.142 mol of 3-methacryloxy propyltrimethoxysilane (3-MPTS) with 0.125 mol of acrylic acid (in mole ratio 1.13 : 1) in anhydrous ether. The reaction was carried out under moisture free condition using dry nitrogen atmosphere in dark at room temperature for 3 h. The product was dried by rotary vacuum evaporation at 50°C. Thus the byproduct, methanol and solvent, diethyl ether are removed during 2.5 hrs. Then the sample was further purified by passing it through silica gel column kept in a globe box having dry nitrogen

Figure 2 ^{1}H-NMR spectrum of silane monomer (SM-1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
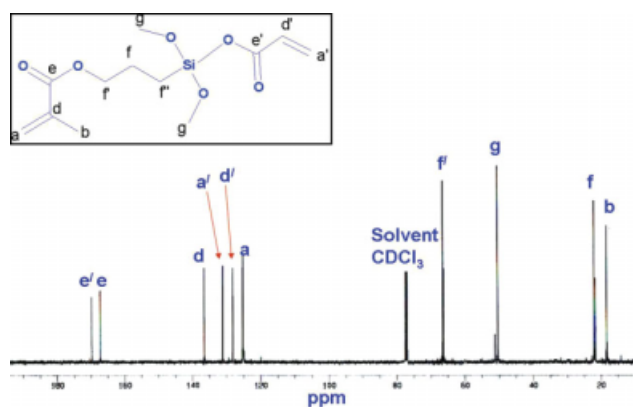
Figure 3 ^{13}C-NMR Spectrum of Silane Monomer (SM-1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

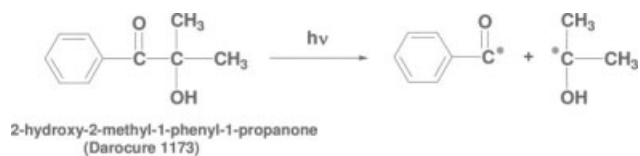**Scheme 2** Decomposition of photoinitiator upon UV-irradiation.

atmosphere. After purification and complete drying acryloxymethacryloxy silane monomer was flushed with dry nitrogen and stored in a refrigerator.

Characterization

The synthesized silane monomer was characterized by FTIR using a Magna-IR 750 (Series II, Nicolet) spectrometer. The ^{1}H-NMR and ^{13}C-NMR spectra were taken on a Varian Gemini 300MHz spectrometer in CDCl$_3$ using tetramethylsilane as an internal standard. Thermal analysis of the samples was carried out using TGA 2950 TA Instrument (USA) under N$_2$-atmosphere at a heating rate of 10°C/min.

Study of UV-curing property

The synthesized acryloxymethacryloxy silane monomer was studied for its UV-curing characteristic.

The monomer was mixed with 4 wt % photoinitiator (Darocure 1173) and then cast on a Teflon coated Al-plate. It was then exposed under UV-light (Fusion UV-curing, Fusion UV Systems, Light intensity = 8 W/cm^2) to study the UV-curing property by varying the exposure time. The curing behavior of the difunctional monomer was monitored from the peak intensity (peak area) of the double bond in the FTIR spectrum. The spectrum of the liquid difunctional silane monomer (SM-1) was recoded by spreading the liquid between two KBr dishes while the spectra of the cured samples were recorded with KBr pellets. The conversion of double bond due to curing was calculated from the peak intensity of the double bond (C=C) considering C=O peak as internal standard and using the following formula:

Percent double bond conversion (DBC) %

$$= \frac{(AR)_i - (AR)_t}{(AR)_i} \times 100$$

where, $(AR)_i$ and $(AR)_t$ are the area ratios of C=C and C=O peaks in the FTIR spectrum for uncured and sample cured for 't' time respectively.
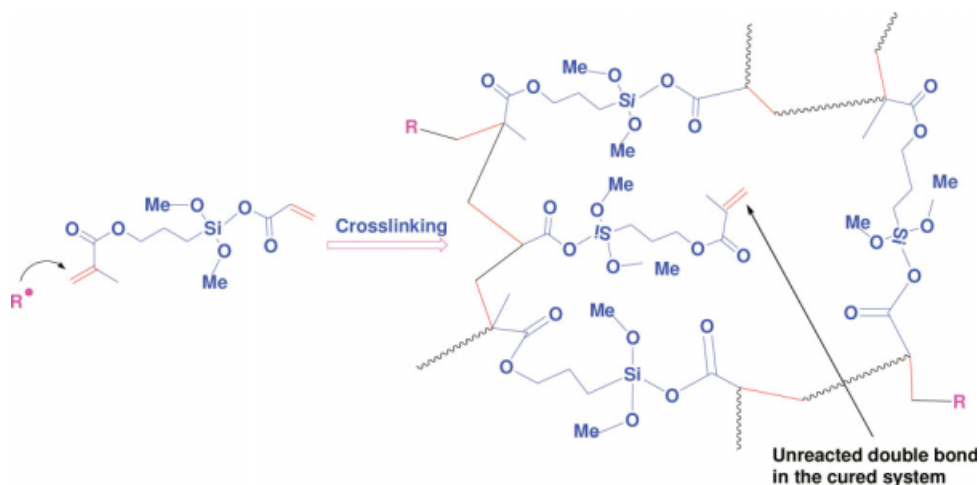
Scheme 3 Formation of three dimensional network structure of difunctional silane monomer upon UV-curing. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
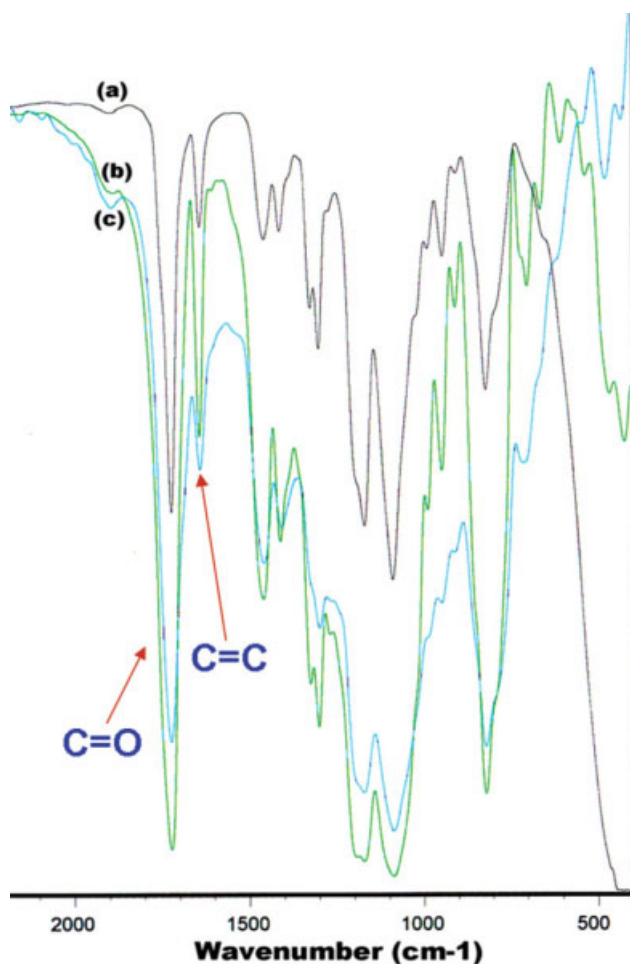
Figure 4 FTIR spectra of (a) silane monomer and samples after UV-exposure for (b) 4.2 sec and for (c) 5.4 sec. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Synthesis and characterization of acryloxy methacryloxy propyl silane monomer

Difunctional silane monomer (SM-1) was synthesized by reacting 3-methacryloxy propyltrimethoxysilane (3-MPTS) with acrylic acid in anhydrous ether (Scheme 1). The synthesized silane monomer (SM-1) was characterized by FTIR and NMR techniques.

FTIR analysis

The FTIR spectrum of SM-1 monomer is shown in Figure 1. The absorption peaks at 984 cm^{-1} and 1087 cm^{-1} are due to siloxane functionality. The vinyl protons appear at 817cm^{-1}. The peak at 2950 cm^{-1} is due to C—H stretching vibration of alkyl groups. The peak at 1636 cm^{-1} indicates the C=C bond. Stretching vibrations of C=O and C—O appear at 1720 cm^{-1} and 1173 cm^{-1} respectively. From these

two peaks it can be inferred that ester group is present in the synthesized monomers which is formed during the reaction of 3-MPTS and acrylic acid. Moreover, the absence of any remarkable OH peak in the spectrum indicates the absence of unreacted acrylic acid. It also ignores the possibility of hydrolysation reaction of Si—OMe to Si—OH.

The sharp peak at 1636 cm^{-1} indicates the C=C bond of the synthesized difunctional monomer and no unreacted materials like 3-MPTS and acrylic acid. Again, it is to mention here that usually two types of C—H bending vibrations of vinyl protons (=CH$_2$) are expected for this difunctional monomer which should appear at 817 cm^{-1} (for methacrylate) and at 812 cm^{-1} (for acrylate function). However, only a peak at 817 cm^{-1} having a shoulder at the lower side of it probably indicating the second kind of vinyl protons and no separate peaks are observed because of the molecule (SM-1) as a whole (Scheme 1). Again, no peak at 812 cm^{-1} is certainly confirming the absence of residual acrylic acid starting reactant in the synthesized product.

NMR analysis

The NMR analysis of the silane monomer further confirms the structure which is observed by the chemical shift values at desired positions. The ^{1}H-NMR spectrum of a silane monomer (SM-1) is shown in Figure 2. The peak at 1.9 ppm is due to
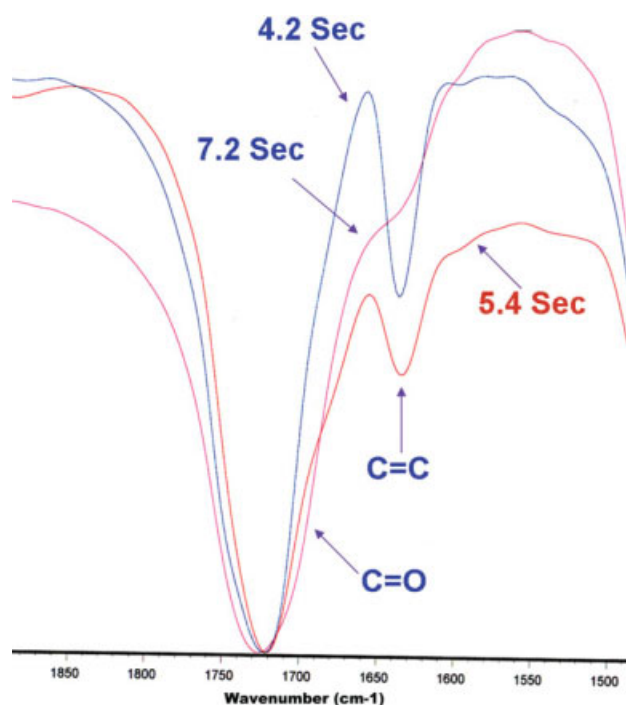
Figure 5 FTIR spectra of UV-cured samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
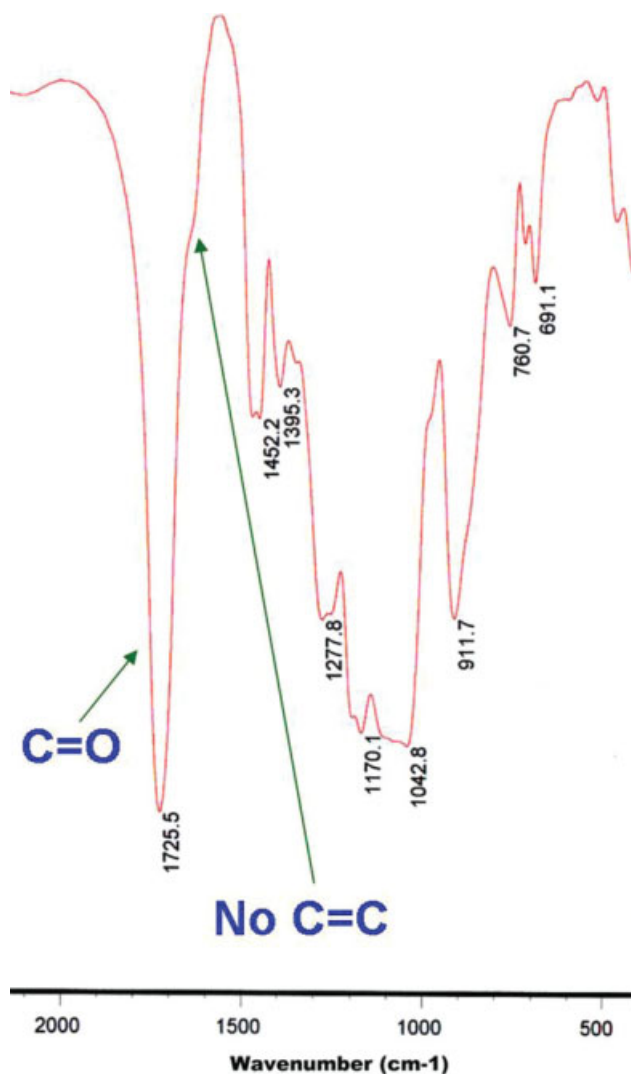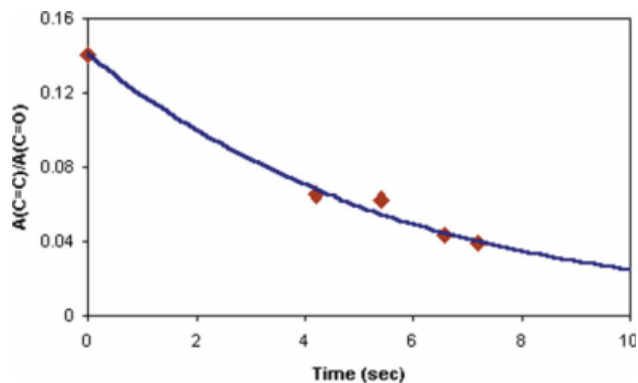
Figure 6   FTIR spectrum of cured silane monomer sample after UV exposure for 9 sec. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

the CH_3 of CH_2=$C(CH_3)$—. Two types of vinyl =(CH_2) protons appears at 5.4 ppm and 5.7 respectively. The proton like =CH— of CH_2=$CHCO$— appears at 6.1 ppm. The peak at 1.7 ppm is due to CH_2 of propyl. The peaks of CH_2 connected to Si and —COO— appear at 0.6 and 4.1 ppm respectively. The peak due to CH_3O—Si appears at 3.5 ppm.

The ^{13}C-NMR spectrum of the silane monomer (SM-1) is shown in Figure 3. It shows peaks at 18.30 ppm for CH_3 of CH_2=$C(CH_3)CO$—, at 125 ppm for =CH_2 and 138 ppm for =$C(CH_3)$ of CH_2=$C(CH_3)CO$. Two carbons of CH_2=CH— appear at 130 and 126 ppm respectively. The peak at 167.5 ppm is appeared due to carbonyl carbon of methacryloxy. The other carbonyl carbon appears at around 170 ppm. The peak at 66.5 ppm is due to CH_2 of the alkyl chain connected to the OCO; whereas CH_2 connected to Si appears at around 6.5
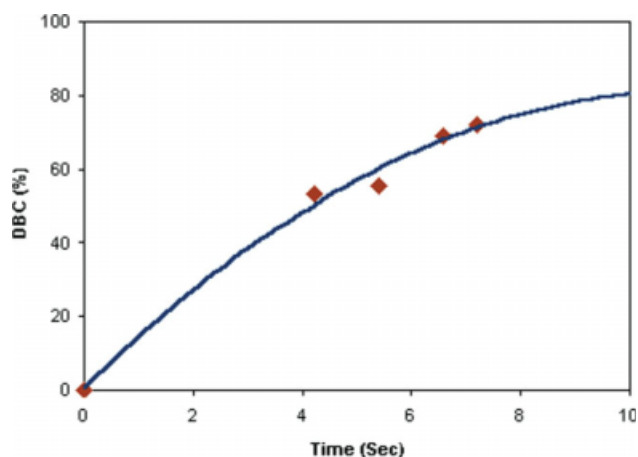
Figure 7   Reduction of FTIR double bond intensity with time of UV-exposure. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

ppm (not shown). The other CH_2 of propyl appears at 22 ppm. Methoxy carbon appears at 50 ppm.

Curing behavior of the difunctional silane monomer

The UV-curing behavior of the synthesized monomer was studied. The difunctional silane monomer was mixed well with 4 wt % of a photoinitiator (Darocure 1173) and then casted on a teflon coated Al-plate. It was then exposed under UV light to study the UV-curing property by varying the exposure time. The photoinitiator upon irradiation absorbs UV-light, decomposes and is converted into free radicals (Scheme 2). These free radicals initiate the photochemically driven polymerization of the monomer. As the UV-curable monomer contains two acryloxy groups (difunctional monomer), propagation starts from both sides of the monomer. Hence, it starts crosslinking. Finally the monomer is transformed into a cured product which is a crosslinked

Figure 8   Double bond conversion (DBC) with time of UV-exposure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
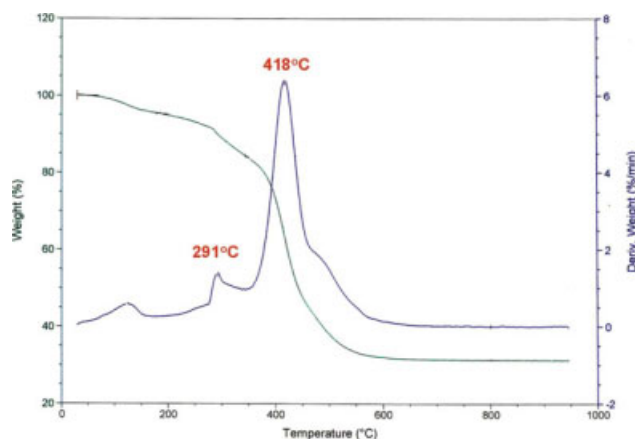
Figure 9 TGA thermogram of cured silane sample (UV exposure for 4.2 sec). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

three dimensional network structure (Scheme 3). However, extent of curing or crosslinking varies with the time of UV-exposure. The samples exposed for different time were characterized by using FTIR spectroscopy to monitor the curing behavior from the peak intensity of the double bond.

The FTIR spectra of the silane monomer as well as UV-exposed (cured) silane monomer samples for different time are shown in Figures 4 and 5. The partially cured samples exhibit similar peaks in their FTIR spectra as the uncured sample. The absorption peaks at 984 cm^{-1} and 1087 cm^{-1} are due to siloxane functionality. The peak at 2953 cm^{-1} is due to C—H stretching vibration. The stretching vibrations of C=O and C—O appear at 1720 and 1173 cm^{-1} respectively. However, the intensities of C=C bond (at 1636 cm^{-1}) and the C—H bending of vinyl proton (=CH$_2$) (at 817 cm^{-1}) are reduced with the progress of curing. Finally these peaks were disappeared (Fig. 6).

The curing behavior of the silane monomer is monitored from the peak intensity of the double bond (C=C) in the FTIR spectrum considering C=O peak as internal standard. The reduction of double bond intensity with respect to C=O peak due to UV-curing is shown in Figure 7. The conversion of double bond with time of UV-exposure is shown in Figure 8. The results of double bond conversion are: 53.5, 55.5, 69, and 72% for samples cured for 4.2, 5.4, 6.6, and 7.2 sec respectively. The maximum possible double bond conversion may be estimated/considered as 74% for sample cured for 7.8 sec (from Fig. 8). Relatively low double bond conversion values (about 60%) are often reported in photocrosslinking of multifunctional acrylates.[18] But the value depends on the multifunctional system. As the polymerization proceeds, network formation increasingly inhibits the diffusion of reactive species (chain radi-

cals, pendant acrylate groups attached to polymer network and monomers) leading to incomplete double bond conversion. The FTIR peaks of the double bond and vinyl proton were not detectable for the samples cured for 9 sec and above (Fig. 6). Thus the optimum cure time of the acyryloxymethacryloxy propyl silane monomer may be considered to be 7.8 sec (Fig. 8).

Thermal properties

The thermal stability of the cured samples has been studied using thermogravimetric analysis (TGA). The TGA thermograms are shown in Figures 9 and 10 for the samples cured for the period of 4.2 and 7.2 sec respectively. The sample cured for 9 sec exhibited almost the same thermal (TGA) behavior like the sample cured for 7.2 sec (Fig. 10). Here, both the samples start decomposing at around 240°C. However, the sample cured for 4.2 sec (partially cured sample) exhibits two-stage decomposition at 291°C and 418°C. The first decomposition is not observed for the highly cured sample (UV-exposed for 7.2 sec and above). Once the sample is fully cured whole of the polymeric system forms an three dimensional network structure and hence its decomposition is due to absolute degradation of the material as whole (at 440°C). However, for the partially cured sample the first decomposition at 291°C causes a weight loss of 11% which is due to degradation of the oligomeric materials which was yet to be a part of the total network system. The double bond conversion (DBC) is found to be 53.5% for this sample, which is much below the maximum detectable DBC for the fully cured sample (DBC = 72% for sample cured for 7.2 sec) (discussed earlier). Thus these two results support each other. Moreover, the
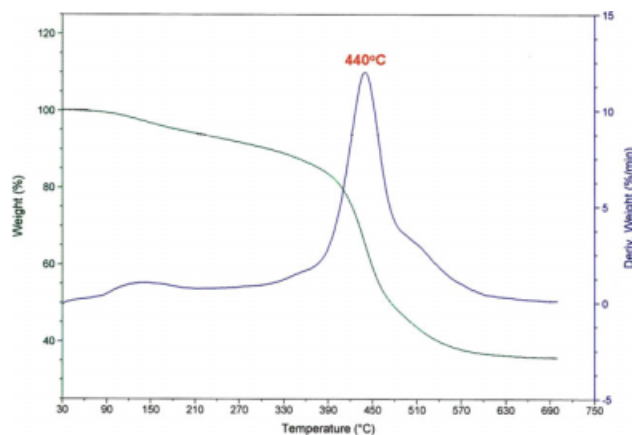
Figure 10 TGA thermogram of cured silane sample (UV exposure for 7.2 sec). [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

maximum decomposition is observed at 418°C for the sample exposed for 4.2 sec, whereas, it is 440°C for the sample exposed for 7.2 sec. The char residue for the sample cured for 4.2 sec is 31% whereas it is 36% for the sample cured for 7.2 sec at 700°C.

CONCLUSION

A UV-curable acryloxymethacryloxy silane monomer was synthesized by reacting 3-methacryloxy propyl trimethoxy silane (3-MPTS) with acrylic acid under dry nitrogen atmosphere. It was characterized by FTIR and NMR spectroscopy. The UV-curing behavior of the silane monomer was studied using 4 wt % photoinitiator (Darocure 1173) under UV light by varying the exposure time. The curing behavior is monitored from the peak intensity of the double bond in the FTIR spectra of the UV-cured samples. The intensities of the C—H bending of vinyl proton ($=CH_2$) at 817 cm^{-1} and the C=C double bond at 1636 cm^{-1} in the FTIR spectra were reduced with the progress of curing. The optimum conversion of the double bond due to curing was estimated from the peak intensity of the double bond considering the peak intensity at 1720 cm^{-1} due to C=O as internal standard which is determined as 72% for the sample cured for 7.2 sec. The minimum time required for optimum curing of the silane monomer is estimated to be 7.8 Sec. The UV-cured sample starts decomposing at 250°C, having maximum decomposition at 440°C. The char residue is 36% at 700°C. The synthesized UV-curable silane monomer may be potentially useful for coating applications and for fabrication of 3D-objects by lithographic technique. Moreover, such acryloxymethacryloxy silane monomer may find its application for making organic–inorganic hybrids, since polymerization of silicon containing acrylates/ methacrylates is one of the methods for preparing such hybrid materials. The use of the acryloxymethacryloxy silane mono-

mer for UV-coating application will be presented in the subsequent communication.

References

1. Allen, N. S. Photopolymerization and Photoimaging Science and Technology, 1st ed.; Elsevier Applied Science: NY, 1989.
2. Fouassier, J. P.; Rabek, J. F., Eds. Radiation Curing in Polymer Science and Technology; Elsevier Appl Science: London, 1993; Vol. III.
3. Roffey, C. C. Photopolymerization of Surface Coatings; Wiley Interscience: Chichester, UK, 1982.
4. Bassi, L. G.; Lamberti, F. J Radn Curing 1987, 14, 18.
5. Masson, F.; Decker, C.; Andrieu, X. Prog Org Coat 2004, 49, 1.
6. Bag, D. S.; Dubey, R.; Lal, D.; Bhasker Rao, K. U. In Proceedings of the Polymer-2006: Frontiers in Polymer Science and Technology; Mondal, B. M., Nandi, A. K., Eds.; IACS: Kolkata, February 10–12, 2006; 55.
7. Yoshida, K.; Kakuchi, T. Prog Org Coat 2005, 52, 165.
8. Ryczkowski, J.; Rayss, J. Vibra Spectro 2000, 22, 95.
9. Inan, T. Y.; Ekinci, E.; Yildiz, E.; Kuyulu, A.; Gungor, A. Macromol Chem Phys 2001, 202, 532.
10. Liu, H.; Yu, L.; Chen, M.; Huang, Z. Mat Res Bull 2003, 38, 1607.
11. Decker, C.; Moussa, K. Euro Polym J 1991, 27, 881.
12. Randell, D. R. Radiation Curing of Polymers; RSC: London, UK, 1987.
13. Stickler, M.; Panke, D.; Hamielec, A. E. J Polym Sci Polym Chem Edn 1984, 22, 2243.
14. Eckberg, R. P.; Riding, K. D.; John, M. Adhesive Age 1989, 4, 24.
15. Tan, B.; Pan, H.; Irshad, H.; Chen, X. J Appl Polym Sci 2002, 86, 2135.
16. Priola, A.; Gozzelino, G.; Ferrero, F. Intl J Adhesn Adhes 1990, 10, 77.
17. Park, H.-S.; Yang, I.-M.; Wu, J.-P.; Kim, M.-S.; Hahm, H.-S.; Kim, S.-K.; Rhee, H.-W. J Appl Polym Sci 2001, 81, 1614.
18. Chung, C. M.; Kim, M. S.; Roh, Y. S.; Kim, J. G. J Mat Sci Lett 2002, 21, 1093.
19. Bag, D. S.; Dubey, R.; Zhang, N.; Xie, J.; Varadan, V. K.; Lal, D.; Mathur, G. N. Smart Mater Struct 2004, 13, 1263.