



# Synthesis and characterization of three novel alkoxy-silanes and their uses in the acrylate functionalized alkyds through free radical copolymerization



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## ABSTRACT

Three novel allyl-containing alkoxy-silanes, allyl 3-(trimethoxysilyl) propyl ether (ATSE), allyl 3-(trimethoxysilyl) propyl thioether (ATST) and 4-(trimethoxysilyl) propoxy-4-methacryloxydiphenyl sulfone (TSMS) were prepared by the condensation reaction of allyl alcohol with chloropropyl-trimethoxysilane (CPTS), allyl chloride with (3-mercaptopropyl)-trimethoxysilane (MPTS) and methacrylic acid with bis (4-hydroxyphenyl) sulfone and also with CPTS, respectively. Also acrylic groups were hybrid with alkyds via free radical chemistry. The alkyd comprised soybean oil, glycerol and phthalic anhydride. To closely model acrylated-alkyds, a mixture of acrylic monomers were copolymerized with the alkyd including: methyl methacrylate (MMA), butyl acrylate (BA), methacrylic acid (MAA), and alkoxy-silanes ATSE, ATST and/or MPTS.

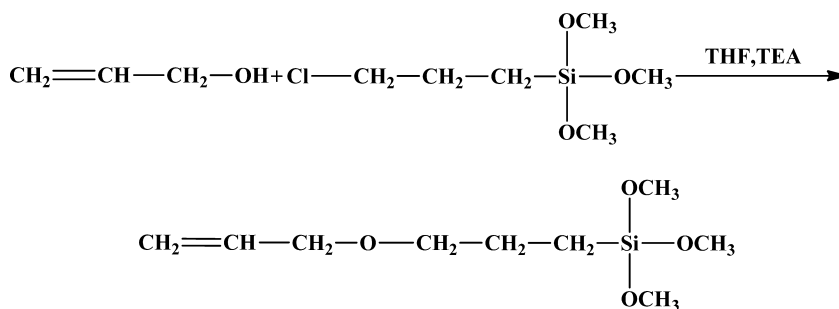
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## 1. Introduction

Alkyds are a special class of polyesters that are derived from bio-based materials, such as linseed oil and soybean oil, polyols, and dibasic acids [1,2]. The monobasic acids that are found in drying oils contain long hydrocarbon chains which contribute to the hydrophobicity of the alkyd. The need to chemically modify alkyds has grown due to the hydrolytic instability of alkyds in aqueous dispersions. Several approaches have been used over the years to modify alkyds with hydrophilic groups that increase the stability in water. One approach to improve hydrolytic stability of alkyds has been to produce alkyds with higher acid values (around 50 mg of KOH/g of sample) by adding free carboxylic acid groups to increase the compatibility with water [3]. Monoglyceride reaction with carboxylic acid groups is one approach, while reacting a completed alkyd with maleic anhydride is another approach for achieving modified alkyds of this type [3–5] (monoglycerides are typically formed by transesterification of a polyol and a (semi)drying oil). Other approaches include acrylating the alkyd with different acrylic groups through mini-emulsion techniques and free radical chemistry reactions between completed alkyds and acrylic monomer

mixtures [3–15]. This provides a hybrid material with water compatibility and the attributes of both the acrylic and the alkyd components. Over the years commercialized acrylated-alkyd systems have incorporated co-monomer acrylic systems to achieve final performance properties [15]. Different acrylic monomers provide certain properties for final product performance. The acrylic monomers that were used for the acrylic co-monomer phase of the acrylic-alkyd hybrid synthesized materials were selected based on their wide use in commercially available materials. MMA provides exterior durability, hardness, and water resistance [6]. BA adds flexibility and exterior durability [6]. MAA affords compatibility with water as well as flexibility and solvent resistance [6]. Alkoxy-silane monomers afford an additional crosslinking mechanism for the acrylic phase of the acrylated-alkyd material. Several studies have been conducted on grafting mechanisms of these two materials in hybrid mini-emulsions. Much work was done in this area by researchers to understand the grafting efficiency, effect of monomer conversion, level of alkyd in the mini-emulsion, and crosslinking levels [5,11–13]. Another study reported a new type of acrylated-alkyd prepared grafting acrylic copolymers via radical polymerization to the unsaturated sites located in the backbone and the fatty acid chains [10]. Blending emulsified alkyds with acrylic co-monomer emulsions is another approach that has been used [6]. Characterization of resulting structures from in situ formation has been a challenge due to the complexity of the chemical make-up.

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Scheme 1. Synthesis of ATSE.

In this paper, a co-monomer system consisting of MMA, BA, MAA and alkoxy silanes ATSE, ATST and/or MPTS was used for the acrylic phase with a medium-oil soybean based alkyd.

## 2. Experimental

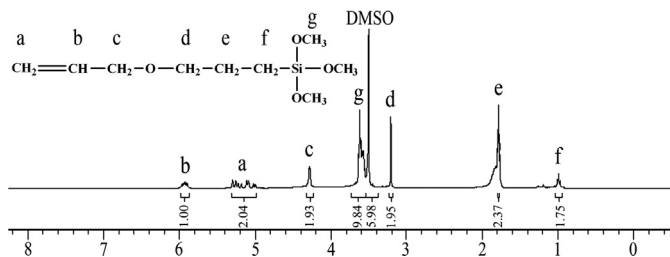
### 2.1. Materials

The monomers (MMA and BA, Merck Chemicals Co., Darmstadt, Germany) were freed from the inhibitor by shaking with 10% aqueous NaOH, washing with water and drying over  $\text{Na}_2\text{SO}_4$ . They were then distilled under reduced pressure before use and stored at  $-15^\circ\text{C}$  to avoid thermal polymerization. The MAA (Merck) was distilled directly under vacuum and stored at  $0^\circ\text{C}$ . The initiator 2,2-azobisisobutyronitrile (AIBN) (Merck); phthalic anhydride (PA), lithium hydroxide monohydrate and xylene were supplied by Merck, Hohenbrunn, Germany, and were used as received. Soybean oil was supplied from (Indiamart, New Delhi, India). Glycerol, bis (4-hydroxyphenyl) sulfone, triethylamine (TEA), allyl alcohol, tetrahydrofuran (THF), allyl chloride, MPTS and CPTS were supplied by Merck, Hohenbrunn, Germany, and were used as received.

Fourier-transform infrared (FT-IR) spectroscopy analysis was performed with a Nicolet Impact 400D Model spectrophotometer (Nicolet Impact, Madison, USA) using KBr pellets. The spectra were obtained over the wave-number range  $4000\text{--}400\text{ cm}^{-1}$  at a resolution of  $2\text{ cm}^{-1}$  using an MCT detector with co-addition of 64 scans. NMR Spectra were recorded on a Bruker AV600 NMR Spectrometer ( $^1\text{H}$ , 600 MHz,  $^{13}\text{C}$ , 150 MHz). Chemical shifts were reported in ppm and referenced to residual solvent resonances ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or an internal standard. DSC thermograms were taken on a Mettler TA 4000 Model apparatus at a heating rate of  $10^\circ\text{C}/\text{min}$ . TGA measurements of copolymers were carried out by a Dupont TGA 951 under nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ .

### 2.2. Synthesis of allyl 3-(trimethoxysilyl) propyl ether (ATSE)

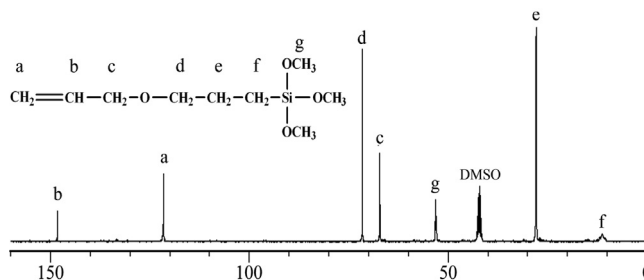
In a 100 mL three-necked round bottom flask which was dried, purged with nitrogen, equipped with a reflux condenser, a dropping funnel and nitrogen inlet, 0.726 g (12.5 mmol) allyl alcohol, 25 mL tetrahydrofuran (THF) and 1 mL triethylamine (TEA) were taken. To this, 2.485 g (12.5 mmol) CPTS was added drop-wise maintaining temperature at  $60^\circ\text{C}$  under argon atmosphere. After complete addition, the reaction mixture was maintained at  $60^\circ\text{C}$  for 6 h and then 1 h under stirring at room temperature. Use of TEA promotes the desirable condensation between allyl alcohol  $-\text{H}$  and CPTS  $-\text{Cl}$  and avoids the self-condensation of silicone intermediates. The viscous crude product was recovered after removing the solvent using an evaporator and the residue was finally dried in a vacuum at  $25^\circ\text{C}$ . The final product was viscous pale yellow oil. Yield = 85%. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 2980 (CH), 1089 (Si-OCH<sub>3</sub>), 1193 (C-O-C), 1512 (C=C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, ppm): 5–6 ( $\text{CH}_2=\text{CH}$ ), 5.026 ( $\text{CH}_2=\text{CH}-\text{CH}_2$ ), 4.278 (O-CH<sub>2</sub>), 1.773 ( $-\text{O}-\text{CH}_2-\text{CH}_2$ ), 1.0

Fig. 1.  $^1\text{H}$  NMR spectrum of ATSE.

( $\text{CH}_2-\text{CH}_2$ ), 3.50 (OCH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz,  $\delta$  ppm): 110–140 ( $\text{CH}_2=\text{CH}-$ ), 62.82 ( $\text{CH}_2=\text{CH}-\text{CH}_2$ ), 62.86 (O-CH<sub>2</sub>), 26.0 ( $-\text{O}-\text{CH}_2-\text{CH}_2$ ), 6.50 ( $\text{CH}_2-\text{CH}_2$ ), 47.07 (OCH<sub>3</sub>). Elemental analysis calculated for  $\text{C}_9\text{H}_{20}\text{O}_4\text{Si}$  (%): C 49, H 9.07, found: C 48.80, H 8.80. The reaction path is given in Scheme 1 and the  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra are given as Figs. 1 and 2, respectively.

### 2.3. Synthesis of allyl 3-(trimethoxysilyl) propyl thioether (ATST)

In a 100 mL three-necked round bottom flask which was dried, purged with nitrogen, equipped with a reflux condenser, a dropping funnel and nitrogen inlet, 2.454 g (12.5 mmol) MPTS, 25 mL tetrahydrofuran (THF) and 1 mL triethylamine (TEA) were taken. To this, 0.956 g (12.5 mmol) allyl chloride was added drop-wise maintaining temperature at  $60^\circ\text{C}$  under argon atmosphere. After complete addition, the reaction mixture was maintained at  $60^\circ\text{C}$  for 6 h and then 1 h under stirring at room temperature. Use of TEA promotes the desirable condensation between allyl chloride  $-\text{Cl}$  and MPTS  $-\text{H}$  and avoids the self-condensation of silicone intermediates. The viscous crude product was recovered after removing the solvent using an evaporator and the residue was finally dried in a vacuum at  $25^\circ\text{C}$ . The final product was viscous brown oil with yield = 83%. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 2944 (CH), 1086 (Si-OCH<sub>3</sub>), 1192 (C-O-C), 1510 (C=C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, ppm): 6–7 ( $\text{CH}_2=\text{CH}-$ ), 3.0 ( $\text{CH}_2=\text{CH}-\text{CH}_2$ ), 2.60 (S-CH<sub>2</sub>), 1.50 ( $-\text{S}-\text{CH}_2-\text{CH}_2$ ), 0.59 ( $\text{CH}_2-\text{CH}_2$ ), 3.0 (OCH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz,  $\delta$  ppm): 110–150 ( $\text{CH}_2=\text{CH}-$ ), 40.60 ( $\text{CH}_2=\text{CH}-\text{CH}_2$ ), 45.60 (S-CH<sub>2</sub>), 26.70

Fig. 2.  $^{13}\text{C}$  NMR spectrum of ATSE.

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