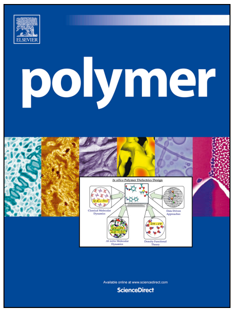


Novel multifunctional hybrid diallyl ether monomer via azide alkyne click reaction as crosslinking agent in protective coatings

Kesavarao Sykam, Shailaja Donempudi

PII: S0032-3861(15)00168-8

DOI: 10.1016/j.polymer.2015.02.017

Reference: JPOL 17630

To appear in: *Polymer*

Received Date: 9 October 2014

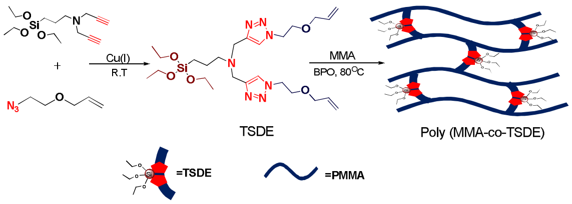
Revised Date: 14 January 2015

Accepted Date: 11 February 2015

Please cite this article as: Sykam K, Donempudi S, Novel multifunctional hybrid diallyl ether monomer via azide alkyne click reaction as crosslinking agent in protective coatings, Polymer (2015), doi: 10.1016/j.polymer.2015.02.017.

Graphical Abstract

Schematic representation



Novel multifunctional hybrid diallyl ether monomer via azide alkyne click reaction as crosslinking agent in protective coatings

Kesavarao Sykam, Shailaja Donempudi*

Polymers & Functional Materials Division, Indian Institute of Chemical Technology, Hyderabad 500007, India.

*Corresponding author: Email: sdonempudi@iict.res.in

Abstract: Functionalized hybrid monomers with crosslinking ability can provide advantages over the other monomers due to the flexibility of using it with any vinylic family of monomers. Azide alkyne click reaction is a convenient way of introducing triazole moieties into a molecule and opens up the possibility to add more functionality by suitable design of azide and alkyne compounds. In the present study, we report synthesis and use of new azide click linker containing allyl ether functionality, (3-(2-azidoethoxy) prop-1-ene)as a first example in the click reaction with a siloxane functionalized dialkyne to make a novel triazole, siloxane functionalized diallyl ether (TSDE) monomer. Chemical structure of the as synthesized TSDE, azide click linker and other compounds were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and ESI-MS techniques. Hybrid coatings of TSDE with methyl methacrylate (MMA) were evaluated for chemical structure, morphology, wettability, tensile and thermal properties by FTIR, XRD, SEM, UTM, WCA, DSC &TGA. Experimental results from EPS and fog tests indicate significant enhancements in the anticorrosion and antibacterial performance of the as synthesized new Poly (MMA-co-TSDE) hybrid coatings in comparison to PMMA.

Keywords: click chemistry, crosslinking, hybrid coatings

Introduction

The ubiquitous demand for multifunctional, high performance coatings are best met by organic inorganic hybrids that can offer synergistic benefits of both. Hybrid properties in a coating are generally obtained by sol gel method which allows incorporation of organic polymers into an inorganic network. Incorporation of siloxane network into such compounds will play a vital role in enhancing protection to metal substrates by improving barrier properties of coatings and decreasing the scope of permeability of aggressive species (O_2, H^+) to the substrate. In general, such hybrid films are known to present hydrophobic character up to 90° WCA for a well crosslinked (Si-O-Si) film forming a compact network. However, these films may suffer from hydrolysis (Si-OH) when exposed to air or aqueous medium causing reduction in the WCA[1]. Moreover, incorporation of higher concentrations of siloxane in the films makes them brittle and tends to develop cracks, thereby compromising corrosion resistance[2]. It is also known from literature that materials consisting of hetero atoms like N, O, S, P and aromatic nucleus provide better corrosion resistant properties to coatings[3].Crosslinking of coating resins is of immense practical importance as it enhances the performance of the coating. Therefore, design of a new hybrid monomer with crosslinking ability that can insert siloxane groups in to the network of the polymer by covalent bonding with the monomers and can offer flexibility for use with any chosen monomers in low volumes and provide significant enhancement in the performance of protective coatings. Key element in designing new functional polymer materials is the accessibility of starting material and ease of functionalization which can be achieved by adopting synthetic organic chemistry concepts[4].Among them, copper catalysed azide alkyne "click" reaction[5] (CuAAC) is widely used for synthesizing 1,2,3-triazole based compounds which are extensively used as functional materials in the field of corrosion resistant coatings [6,10,11],anti-fouling coatings [7], biodegradable [8], antimicrobial[10,11]and biomedical applications.[9]

In the present study, we report the use of this click reaction to synthesize a unique hybrid diallyl ether monomer functionalized with triazole and inorganic siloxane groups designated as TSDE, a first example of hybrid crosslinkable monomer. We also report synthesis of allyl ether containing azide[12]and used it as a click linker for the first time. The diallyl ether monomer (TSDE) is shown in Fig. 1 with both triazole nucleus and siloxane moiety in a single structure. Here the molecule was designed to incorporate both organic (triazole) and inorganic (siloxane) groups in the monomer such that combined benefits of improving adhesion to the substrate and enhancing hydrophobicity on surface respectively could be achieved when used in protective coatings applications. Literature reveals that admixtures of allyl containing compounds with vinyl monomers present promising applications due to improved physical and electric properties.[13]Crosslinked alkyl acrylates with allyl ethers of pentaeryhtritol, sucrose, and trimethylolpropane are reported to be safe for use in cosmetics.[14]Allyl ether maleate functional hyperbranched ester resins were synthesized by Johansonn et al. to study their curing performance and film properties.[15]Cross-linking of dendrimers with allyl ether end-groups using the ring-closing metathesis to develop new dendrimer architectures[16]and found that in the presence of a catalyst analogous hyperbranched systems can be polyallylated to give nearly complete cross-linking[17]. The difference in reactivity between allyl acrylate and diallyl ether was reported by Busfield et al stating that in case of allyl acrylates, products were formed by H-abstraction as well as addition of both allyl and acryloyl double bonds whereas for allyl ethers it was H-abstractionalone[18]. However, it was reported that at lower compositions of < 10 mol %, these diallyl compounds show similar reactivity to that of methyl methacrylate homopoymer. The crosslinking efficiency of the as synthesized hybrid TSDE was investigated by copolymerizing with MMA and their performance as hybrid coatings was evaluated by subjecting them to anticorrosion and antibacterial study in comparison to the unmodified PMMA coatings. Crosslinking ability of TSDE with vinylic monomers and choice of its content in the resin opens up an alternative and easy method of making hybrid resins useful in high performance protective coatings.

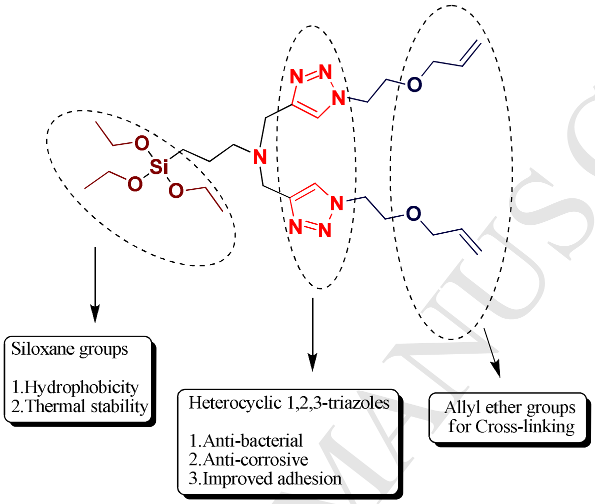


Fig.1 Multifunctionality in hybrid TSDE structure

Experimental section

Materials

Sodium azide (99% extra pure), calcium hydride (93%), allyl bromide (99% stabilized), propargyl bromide (80 Wt% solution in toluene) and tetrahydrofuran (99.5% extra dry over molecular sieves stabilized), were purchased from Acros organics, Belgeum. Sodium hydride (57-63% oil dispersion powder) and (3-Aminopropyl) triethoxysilane (98%) were purchased from Alfa Aesar, Massachusetts, USA. Copper(I)iodide 98%, 2-chloro ethanol 98% were purchased from Avra Chemicals, Hyderabad, India. Dry n-pentane, dichloromethane and diethyl ether were purchased from Finar chemicals Ltd, Mumbai, India. Methyl methacrylate and benzoyl peroxide were purchased from Aldrich chemicals. Benzoyl peroxide was recrystallized before use and remaining all above chemicals were used without further purification.

Measurements

The FT-IR spectra of synthesized molecules and polymers were recorded on Thermo Nicolet Nexus 670 spectrometer. ^{1}H NMR and ^{13}C NMR of the synthesized samples were done with BRUKER-300 MHz spectroscopy by taking $CDCl_3$ as solvent and tetramethylsilane (TMS) as reference at room temperature. The Electro spray Ionization – Mass Spectroscopy (ESI-MS) analysis was done on Waters Micromass Quattro micro, API instrument. The morphology of hybrid free films was characterized by Scanning Electron Microscopy (SEM) using JEOL JSM-6550F. The Thermo Gravimetric Analysis (TGA) was conducted for synthesized cross-linker based PMMA films with temperature ramp rate at 10^{o}C per minute under continuous Nitrogen atmosphere by TGA Q500 Universal TA instrument (UK) and Differential Scanning Calorimetry(DSC) was carried out with DSC Q100 Universal TA instrument (UK). Tensile properties of the films (5x1 cm2) with a thickness of 100 microns were tested on a Universal Testing Machine (EPS) of TSDE loaded PMMA coated mild steel panels with 2×2 cm2 were subjected to test the corrosion resistance by Tafel method in 3.5% NaCl solution with IM6ex (ZAHNER Elektrik, Germany). The contact angle studies of coating free films were carried out with KRUSS contact angle measuring system G10, Germany. The gel content, crosslink density, $\nu_{c,s}$ and the average molecular weight between cross-links, M_c , for the free films of Poly (MMA-co-TSDE) (TSDE = 2.5%, 5%, 7.5% and 10%) were determined by soaking a sample of 0.1g in chloroform for 2 days. The swollen polymer was separated from the dissolved portion by filtration and then dried. From the weights of both swollen and dry gel, weight fraction of the non-dissolved part i.e., gel content; $\nu_{c,s}$ and M_c were calculated based on Flory's equation 1 [19]

$$M_c = \frac{\rho}{\nu_{c,s}}$$

$$\nu_{c,s} = -\{\ln(1-V_r) + V_r + \chi V_r^2\}/V_1(V_r^{\frac{1}{3}} - \frac{2}{\phi}V_r) \quad \text{…..(2)}$$

Here, ρ is the density of the polymer (PMMA=1.18 g/cm^3 @ 25 °C), V_r in eq (2) is the volume fraction of polymer in the swollen gel, and χ is the polymer-solvent interaction parameter (0.345; calculated from solubility parameter values[20]. V_1 is the molar volume of the solvent (80.7cm/mol), and □ is the number of functional groups on a crosslinked point(4). Solvent swelling data can give absolute values for crosslink density. However, this calculation stands only as an approximation as it assumes that the polymerization goes to completion, which is not always the case.

Synthetic procedures

Synthesis of (N-(prop-2-ynyl)-N-(3-(triethoxysilyl) propyl) prop-2-yn-1-amine) (Compound-1)

APTES (13.28g, 60 mmol) was dissolved in 200ml of dry THF in a round bottom flask. To this calcium hydride (12.6g, 300mmol, 5 eq.) and of propargyl bromide (15.70g, 120mmol, 2 eq.) were added. The mixture was stirred for 12 hours at room temperature under nitrogen atmosphere. To the resulting mixture, 200 ml of dry n-pentane solvent was added. The residual calcium hydride was then removed by vacuum filtration and the n-pentane solvent was removed under vacuum to get the final product as viscous orange coloured liquid (85% yield). The schematic representation of the reaction was shown in Scheme 1.

IR (neat, cm^{-1}): 3300 (≡C-H Str), 1108-1080 (Si-O Str); ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.61(t, 2H), 1.23(t, 9H), 1.59(q, 2H), 2.21(t, 2H), 2.53(t, 2H), 3.44(d, 4H), 3.82(q, 6H); ^{13}C NMR (75 MHz, $CDCl_3$):δ (ppm) 7.83, 18.27, 20.79, 42.07, 55.87, 58.32, 72.73, 78.91; ESI-MS m/z calculated for $C_{15}H_{27}NSiO_3$ is 297, found (M+H) peak 298.

Synthesis of 2-azido ethanol (Compound 2)

In a round bottom flask, 2-chloro ethanol (10g, 0.124mol, 1 eq.) and sodium azide (20.153g, 0.31, 2.5 eq.) were dissolved in 100ml of deionised water. The reaction mixture was refluxed for 24 hours with continuous stirring. To the resulting mixture, 25 g of sodium sulphate was added and stirred for another 20 minutes. The mixture was filtered and the product in the filtrate was extracted using dichloromethane (3×50 ml). After evaporating the solvent the product 2-azidoethanol was obtained as a colourless liquid with 90 % yield. (Scheme 1)

IR (neat, cm-1): 3382(O-H Str), 2937,2881(C-H Str), 2100(N_3Str); 1H NMR (300 MHz, CDCl3): δ (ppm) 3.2 (s, 1H), 3.44 (t, 2H), 3.77 (t, 2H); ^{13}C NMR (75 MHz, $CDCl_3$):δ (ppm) 52.92, 60.74 ; ESI-MS m/z calculated for $C_2H_5ON_3$ is 87.08 found (M+H) peak 88.

Synthesis of 3-(2-azidoethoxy) prop-1-ene (Compound-3)

2-azidoethanol (7.5g, 0.08mol, 1eq) in 10 ml dry THF was added to the solution of the Sodium hydride (4.17g, 0.17mol, 2 eq.) in 35ml of dry THF at 0^{o}C. After the complete addition, 50 ml of diethyl ether solvent was added. The reaction mixture was stirred for 30 minutes under nitrogen atmosphere. To the reaction mixture, allyl bromide (12.5g, 0.1 mol, 1.2 eq.) was added drop wise and the stirred for overnight at room temperature. The reaction mixture was cooled to 0^{o}C and 50 ml deionised water was added to quench the reaction. The diethyl ether layer was separated and the aqueous layer was washed with 25ml diethyl ether for three times. The combined diethyl ether layers were dried over sodium sulphate. After filtration, the final product was obtained by removing the solvent under reduced pressure. The product was acquired as a pale yellow viscous liquid with 80 % of yield. (Scheme 1)

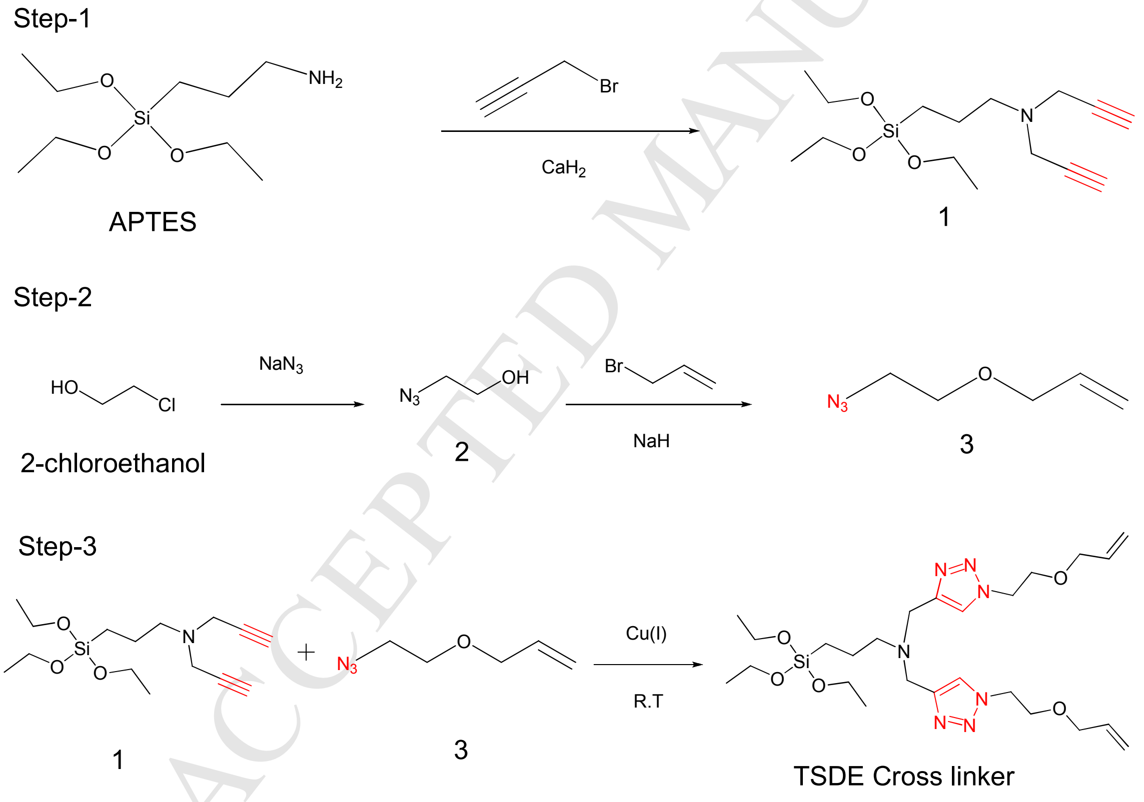
IR (neat, cm^{-1}): 3050(=C-H Str), 1630(C=C Str), 2100(N_3 Str) ;^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.39(t, 2H), 3.62(t, 2H), 4.04(d, 2H), 5.2(d, 1H), 5.32(d, 1H), 5.91(m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 50.4, 68.5, 72.3, 134, 117.02; ESI-MS m/z calculated for $C_5H_9ON_3$ is 127, found (M+H) 128.

Synthesis of triazole siloxane based multifunctional cross-linker (TSDE):

The above synthesized compounds 1 and 3 were taken in 1:2 ratios and dissolved in dry THF solvent. To the resulting mixture 5 mol% of Copper iodide was added portion wise. The mixture was stirred for 24 hours under nitrogen atmosphere. The reaction was monitored by using FT-IR spectroscopy. The reaction was stopped when the azide stretching peak around 2100 cm^{-1} was disappeared. Finally, the product was collected after evaporating the solvent as a viscous green liquid with nearly 100% yield. (Scheme 1)

IR (neat, cm^{-1}): 3100(Triazole C-H Str), 1630(=C-H Str), 1450(Triazole C=C Str) 1080-1103(Si-O Str); 1H NMR (300 MHz, CDCl3):δ (ppm) 0.60(t, 2H), 1.22(t, 9H), 1.67(m, 2H), 2.49(t, 2H), 3.76(m,4H), 3.80(m,10H), 3.97(d, 4H), 4.54(t, 4H), 5.19(m,2H), 5.8(m, 2H), 7.72(s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$):δ (ppm) 14.2, 18.5, 23.2, 50.02, 56.5, 57.6, 58.4, 63, 73.5, 144.8, 118.2, 124.9, 134.6; ESI-MS m/z calculated for $C_{25}H_{45}N_7SiO_5$ is 551, found (M+H) 552 .

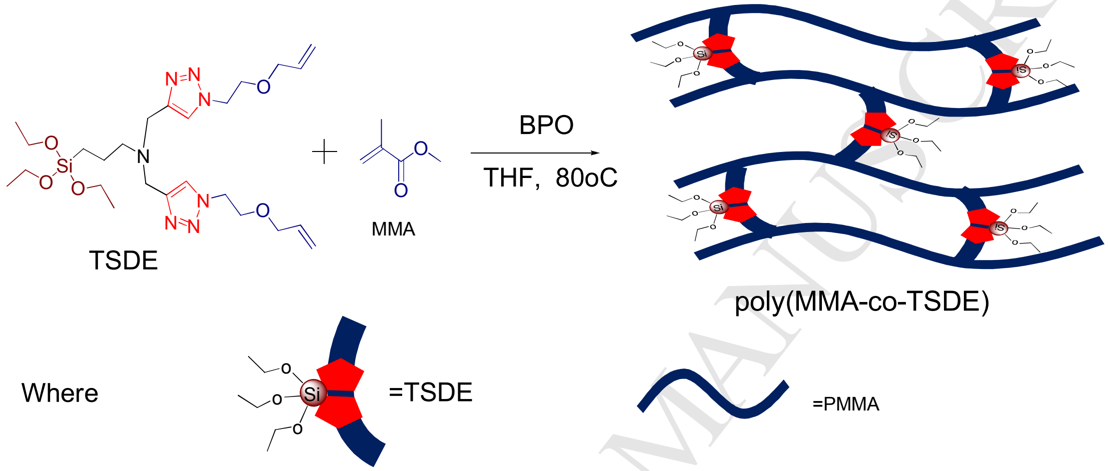
Scheme 1 Synthetic steps involved in synthesis of TSDE.



Synthesis of poly (MMA-co-TSDE)

Copolymerization of TSDE crosslinker with vinylic monomers (methyl methacrylate) was examined under free radical polymerization conditions. The monomers MMA and TSDE were copolymerized in presence of benzoyl peroxide initiator. For this initially, MMA and TSDE (0, 2.5, 5, 7.5 and 10 wt% with respect to MMA) monomers were taken in dry THF along with BPO initiator (1 wt% with respect to monomers)and the mixture was stabilized for 30 mins with agitation under nitrogen atmosphere at room temperature. The temperature was then raised to 80°C and the reaction was continued for 10-15 hours until a viscous liquid was obtained (Scheme 2).Coatings of Poly methyl methacrylate (PMMA) and TSDE crosslinked PMMA named as TSDE-2.5, TSDE-5, TSDE-7.5, TSDE-10 were prepared by manually driven applicator to test the effect of TSDE crosslinking and its content on the performance of Poly(MMA-co-TSDE) hybrid coatings in comparison to PMMA homopolymer.

Scheme 2 Synthesis of poly (MMA-co-TSDE).



Results and discussions

^{1}H NMR, ^{13}C NMR and ESI-MS analysis

The formation of chemical structures of compound-**1**, 2-azidoethanol, compound-**3** and TSDE cross-linker was confirmed by ^{1}H NMR, ^{13}C NMR and ESI-MS spectroscopic techniques. The ^{1}H NMR, ^{13}C NMR spectras of various compounds were shown in Fig. 2,3. And the ESI-MS spectra were shown in Fig. 4. The formation of compound-1 was confirmed by the occurrence of a doublet at δ 3.44 ($C\underline{H}_2$-C≡CH) and triplet at δ 2.21 (CH_2-C≡C$\underline{H}$) in ^{1}H NMR spectra; the presence of peaks at δ 42.07 ($\underline{C}H_2$-C≡CH), δ 72.73 (CH_2-C≡$\underline{C}$H) and δ78.91 (CH_2-$\underline{C}$≡CH) in ^{13}C NMR spectra corresponding to propargyl group. The formation of 2-azidoethanol was confirmed by the presence of a triplet at δ 3.44 ($C\underline{H}_2$-N_3) in ^{1}H NMR spectra and a sharp peak at δ 52.92 ($\underline{C}H_2$-N_3) in ^{13}C NMR spectra. The compound-3 was confirmed by the presence of two doublets at δ 5.2 (CH_2-CH=$C\underline{H}_2$), δ 5.32 (CH_2-CH=$C\underline{H}_2$), a multiplet at δ 5.91(CH_2-C$\underline{H}$=CH_2) and a doublet at δ 4.04 ($C\underline{H}_2$-CH=CH_2) in ^{1}H NMR spectra; the presence of δ 72.3 ($\underline{C}H_2$-CH=CH_2), δ117 (CH_2-CH=$\underline{C}H_2$) and δ134 (CH_2-$\underline{C}$H=CH_2) in ^{13}C NMR spectra corresponding to allyl group. The occurrence of click reaction between compound-**1** and **3** was confirmed by the presence of new peaks at δ 7.72 (triazole C-$\underline{H}$) in ^{1}H NMR and at δ 124.9 (triazole $\underline{C}$-H) in ^{13}C NMR spectra of TSDE cross-linker.

From ESI-MS analysis the formation of compound-**1**, 2-azidoethanol, compound-**3** and TSDE cross-linker was supported by the presence of a (M+H) peaks at m/z 298, 88, 128 and 552 respectively.

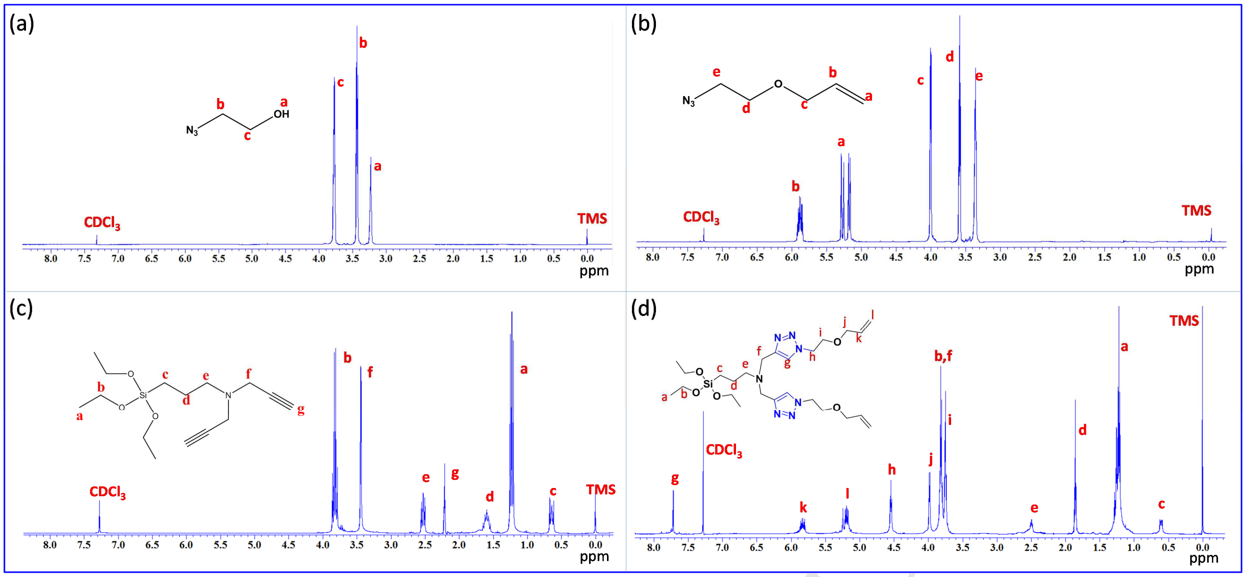


Fig. 2 ^{1}H NMR spectra of (a) 2-azido ethanol, (b) 3-(2-azidoethoxy) prop-1-ene, (c) (N-(prop-2-ynyl)-N-(3-(triethoxysilyl) propyl) prop-2-yn-1-amine), (d) TSDE.

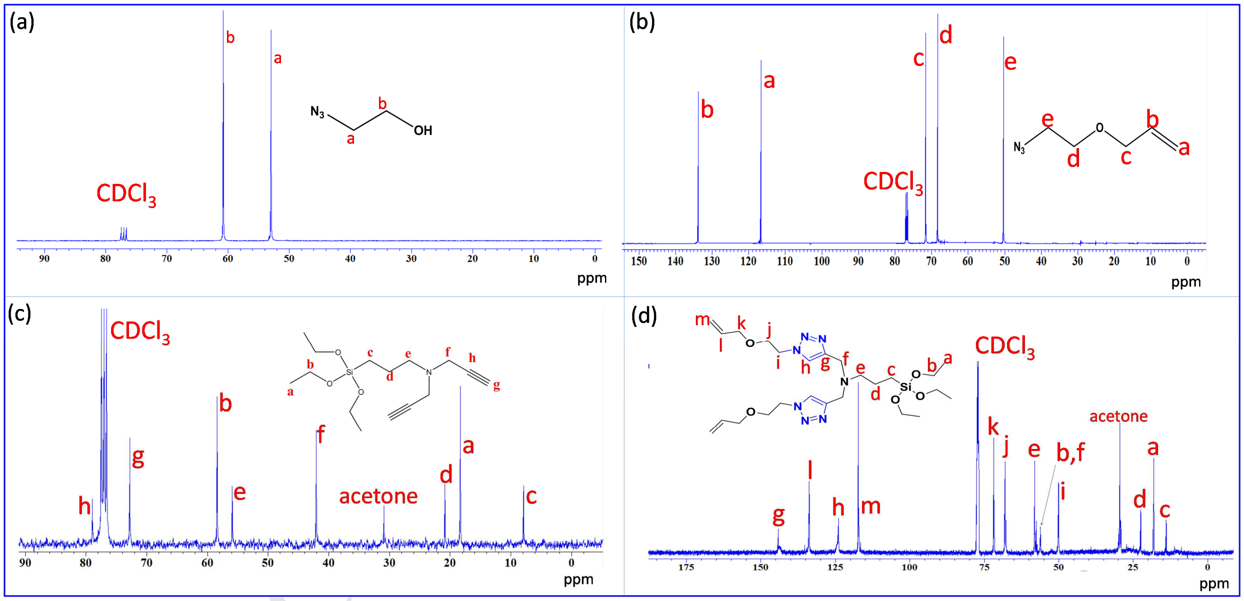


Fig. 3 ^{13}C NMR spectra of (a) 2-azido ethanol, (b) 3-(2-azidoethoxy) prop-1-ene, (c) (N-(prop-2-ynyl)-N-(3-(triethoxysilyl)propyl)prop-2-yn-1-amine), (d)TSDE.

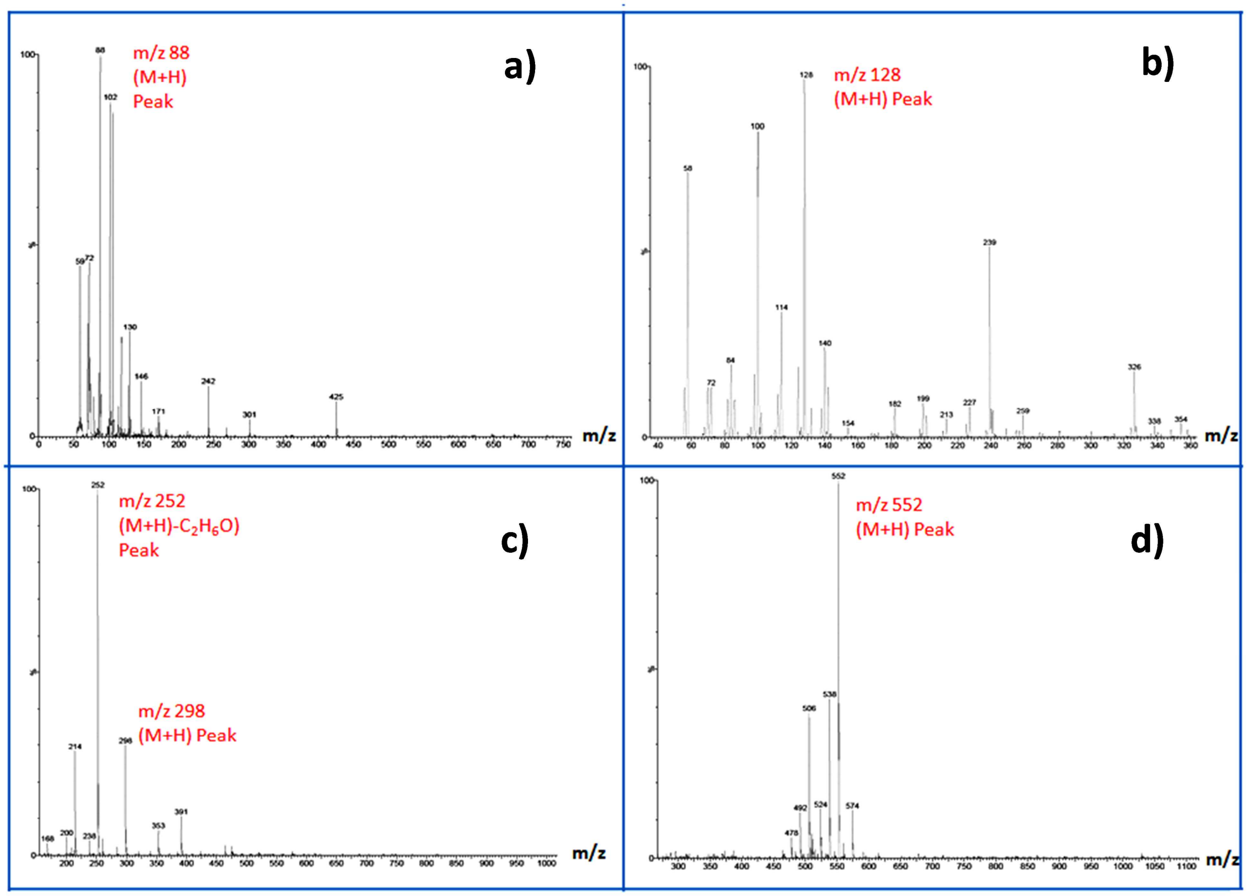


Fig. 4 ESI-MS analysis of (a) 2-azido ethanol, (b) 3-(2-azidoethoxy)prop-1-ene, (c) (N-(prop-2-ynyl)-N-(3-(triethoxysilyl)propyl)prop-2-yn-1-amine), (d) TSDE.

XRD studies

The synthesized poly (MMA-co-TSDE) free films such as PMMA,TSDE-2.5, TSDE-5, TSDE-7.5, TSDE-10were examined for the crystalline behaviour by using X-ray diffraction technique. It is observed that a broad peak present in between 10 and 20 on 2 theta-scale in all the samples (Fig.7). Initially, upon addition of 2.5% of TSDE cross-linker, the crystallinity of the sample was decreased but with increase in the TSDE percentage, the crystalline nature of the polymeric film gradually increases and which is credited to the high cross-linking ability of siloxane groups.

Morphology

The micrographs reported in (Fig.5) shows a clear difference between the crosslinked and linear PMMA films. Appearance of lighter regions representing the inorganic moieties was noticed to be proportional to the degree of crosslinking. PMMA-siloxane hybrid films made by sol gel method tend to develop cracks causing discontinuities in the film due to brittle nature of the film on crosslinking. Here, the images present a perfect hybrid film with no macroscopic phase separation. Formation of uniformly networked structure can be attributed to the covalent bonding between TSDE and MMA during polymerization.

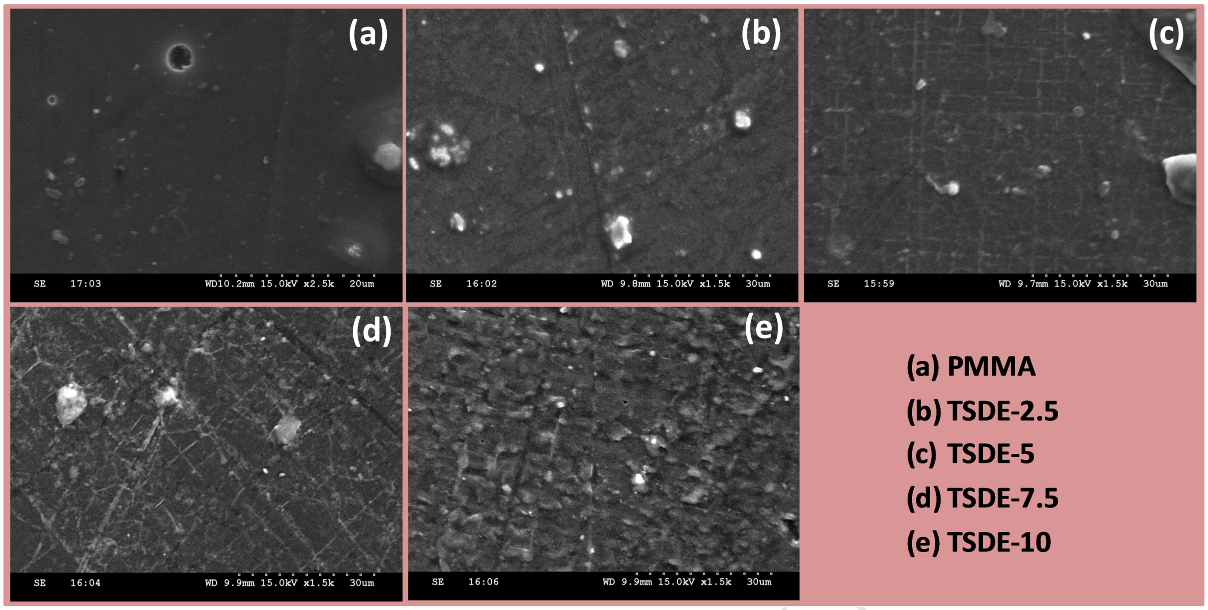


Fig.5 SEM images of PMMA and Poly (MMA-co-TSDE) free films.

Thermal analysis

The thermal stability of the synthesized poly (MMA-co-TSDE) free films along with pure PMMA was evaluated using Thermo gravimetric analysis studies. (Fig.6). The onset decomposition temperature (T_{ON}), maximum degradation temperature (T_d max), 10%, 30%, 50% weight loss temperatures and percentage of weight remained at 400^oC of all the samples were tabulated in the (Table 1). The thermal stability of the polymeric films gradually increases with the loading of TSDE cross-linker percentage. For instance, the maximum decomposition temperature and the percent weight remaining at 400^oC for PMMA, TSDE-2.5, TSDE-5, TSDE-7.5, TSDE-10 are 373^oC, 391^oC, 412^oC, 414^oC and 416^oC; 2.9, 15.1, 41.5, 44.9 and 45.9 respectively. It is known from the literature that the PMMA shows three step thermal degradation [21]. From DTG analysis, it is observed that all the polymeric samples are showing a three step degradation profile. However, the maximum decomposition temperature (T_d max) is increased with the loading of TSDE cross-linker. For instance the T_d max of PMMA, TSDE-2.5, TSDE-5, TSDE-7.5, TSDE-10are 373.85, 391.03, 412.39, 414.75 and 416.74 respectively. A similar type of result is obtained from DSC analysis (Fig.7). The glass transition temperature (T_g) of the polymeric films was improved with the loading of TSDE cross-linker. For instance the T_g of PMMA, TSDE-2.5, TSDE-5, TSDE-7.5, TSDE-10 are 80.04^oC, 88.14^oC, 92.29^oC, 94.21^oC and 94.32^oC respectively. The overall improvement in the thermal stability and glass transition temperature of the polymeric films is credited to the presence of highly thermally stable 1,2,3-triazole and siloxane units on TSDE cross-linker.

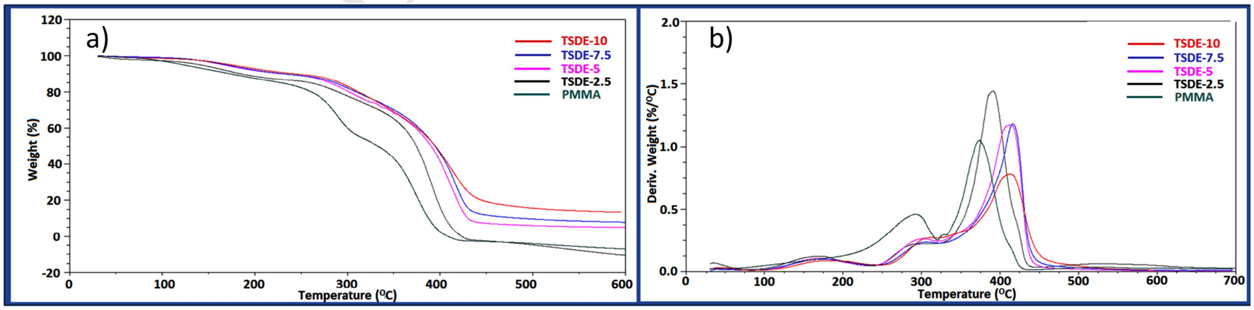


Fig.6 (a) TGA and (b) DTG profiles of PMMA and Poly (MMA-co-TSDE) films

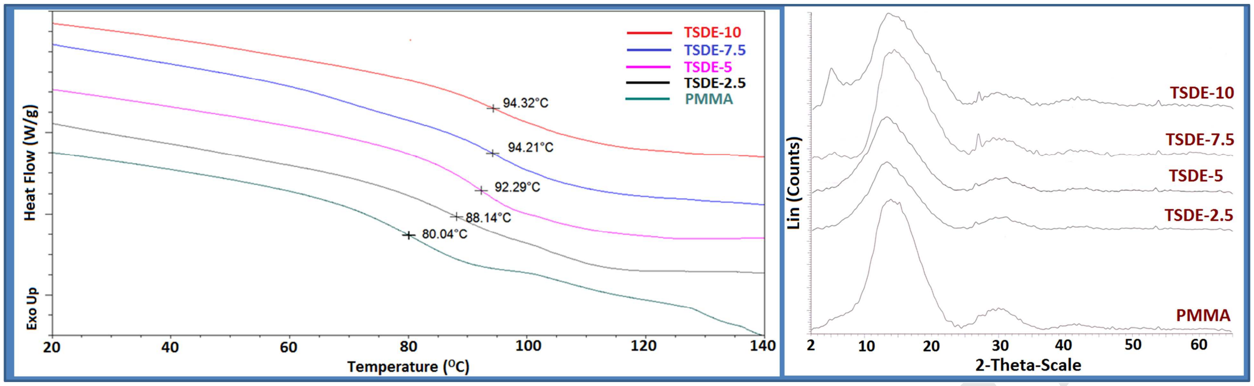


Fig. 7.DSC scans and XRD patterns of PMMA and Poly (MMA-co-TSDE) films.

Table 1 Thermal stability and glass transition temperatures of PMMA and Poly (MMA-co-TSDE) free films.

Sample code	**T_{ON} (°C)**	**$T_d$max(°C)**	**T_d 10%(°C)**	**T_d 50%(°C)**	**%Weight remains at 400 °C**	**Tg (°C)**
PMMA	288.07	373.85	165.62	333.45	2.912	80.04
TSDE-2.5	290.90	391.03	178.63	374.64	15.05	88.14
TSDE-5	299.26	412.39	219.70	390.02	41.53	92.29
TSDE-7.5	302.37	414.75	225.91	394.37	45.93	94.21
TSDE-10	309.79	416.74	233.07	394.51	45.89	94.32

Crosslink density

Table 2 summarizes the cross linking characteristics of Poly (MMA-co-TSDE) samples by swelling method.The results display gel content enhancement leading to increased crosslink densities and lower number of monomer units between the cross links with higher TSDE contents and a more significant change was noticed for TSDE-10 sample. Because, the 10% TSDE loaded PMMA would be less capable of swelling to the same magnitude as others due to the drastic decrease in the number of elastically active chains comparatively. Generally, increasing degree of crosslinking is always associated with a decrease in M_c leading to lower chain flexibility that results in enhanced glass transition temperatures [22]. The results of Tg from DSC measurements as expected are also in support of the observation.

Table 2 Characteristics of Poly (MMA-co-TSDE) samples from the swelling data using Flory's equation.

Sample Code	**Weight of swollen gel (W_2)g**	**Weight of dry gel (W_1)g**	**Gel content W_2/W_1x100 (Wt %)**	**Equilibrium swelling $S=(W_2-W_1/W_1)$**	**V_r $1/(1+S)^3$**	**(g/mol)**	**M_c (mol/cm^3)**
TSDE-2.5	0.067	0.015	15	3.47	0.01	$9.31\text{x}10^{-7}$	1.27×10^{6}
TSDE-5.	0.083	0.026	26	2.19	0.03	$6.23\text{x}10^{-6}$	1.89×10^{5}
TSDE-7.5	0.095	0.032	32	1.97	0.04	$1.04\text{x}10^{-5}$	1.13×10^{5}
TSDE-10	0.119	0.060	60	0.98	0.13	$3.74\text{x}10^{-3}$	3.15×10^{2}

Tensile properties

The tensile strength and elongation at break values for PMMA and TSDE cross linked PMMA samples are presented in Table 3 and represented in Fig. 10. It is a well-known feature that average molar mass between cross links, M_c, affects the tensile properties of the films. Therefore, as M_c decreases, crosslink densities of the polymer increase resulting in higher tensile strength due to greater maximum stress values and lower elongation at break.

Table 3. Tensile properties of PMMA and Poly(MMA-co-TSDE) free films.

Sample code	Max. stress (N/mm^2)	Elongation at break (%)
PMMA	16.19	5.06
TSDE-2.5	17.06	3.81
TSDE-5	18.96	3.36
TSDE-7.5	20.52	3.12
TSDE-10	24.32	3.00

Water contact angle results

The as prepared polymer hybrids were coated onto glass substrates for water contact angle measurements. Drop shape analyses of the obtained TSDE incorporated hybrid reveal an outstanding hydrophobic property with increase in the amount to cross linker. It is inferred that the silica backbone of the cross-linker forms a network making highly dense siloxane linkages leading to an enhancement in hydrophobicity. It is observed that pristine PMMA had a contact angle of $62^{o}\pm2^{o}$and following the addition of TSDE the angle boosted to $101^{o}\pm2^{o}$for TSDE-10. The water contact angles of TSDE-2.5, TSDE-5, TSDE-7.5are 73^{o},86^{o} and $91^{o}\pm2^{o}$respectively (Fig. 8).

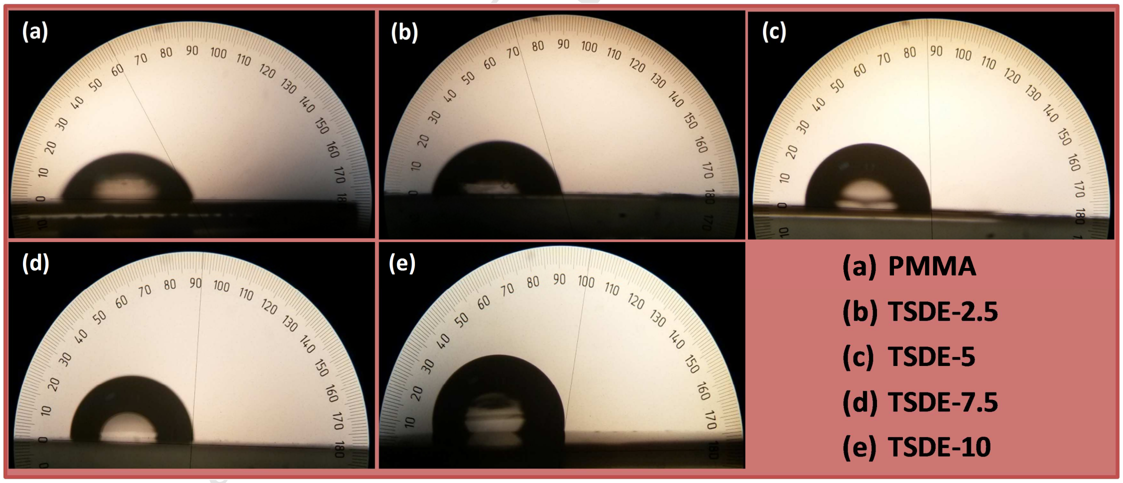


Fig. 8 Water contact angle results for plain PMMA and Poly (MMA-co-TSDE) free films.

Electrochemical Polarization Studies (EPS) and Fog tests

The corrosion of metal substrates is a major problem observed all over the world and most of the available coating formulations suffer from leaching of oxygen, moisture and ions. Incorporation of inorganic moieties and heterocyclic groups into the coating formulations is a dependable choice to address this problem. In the present work, all the synthesized polymeric films are tested for the anticorrosive properties by potentiodynamic polarization studies and salt spray fog tests [23].

Corrosion protection of metal by application of the as synthesized PMMA and the Poly (MMA-co-TSDE) coatings has been evaluated by Tafel method.The values of E_{corr}, I_{corr}, polarization resistance (Ω), and corrosion rate (mm/year) are given in Table 4. A typical Tafel plot is shown in Fig. 9.Poly (MMA-co-TSDE) films reduced the corrosion currents drastically indicating improvement in corrosion resistance in comparison to PMMA. TSDE-10 displayed better corrosion resistance with least corrosion current (I_{corr}) value and a significant shift of the corrosion potential (E_{corr}) to positive value. A gradual decrease in corrosion rate was noticed with increase in the degree of TSDE crosslinking of PMMA indicating its better corrosion resistance behaviour comparatively. Thus, it is understood that coatings with TSDE provide enhanced corrosion protection and the results comply very well with the findings from salt spray fog tests. These results support the hydrophobic nature of TSDE that repels moisture/corrosive media from being absorbed on the surface, preventing the underlying metal from corrosion attack as also evidenced by the contact angle (wettability) measurements.

The corrosion test for the coatings was performed through fog test. (Fig. 9). Each coating was cast on a thoroughly cleaned mild steel panel (3×5 cm) with acetone, ethanol and de ionized water so as to remove trace impurities, surface oils, and dust particulates. The coatings were spin coated onto these panels with a thickness around 100 microns and left for drying at room temperature for 24 hours. Following this the dried panels were placed in a salt spray chamber. The fog of 5% NaCl solution was continuously sprayed on the coated panels for about 250 hours. The coatings were monitored at regular intervals to estimate the corrosion rate. It was observed that with increase in percentage of TSDE in the coating there was a substantial increase in corrosion resistance. TSDE-10comparatively was found to give maximum corrosion resistance up to 250 hours salt spray while PMMA had shown 90% corrosion within 120 hours. This clearly indicates that the performance of the cross-linked coatings was proportional to the crosslinked percentage of TSDE. Thus, the presence of triazole and siloxane functionalities in TSDE in the coating has fulfilled their role by offering improved adhesion to the metal substrate [24] and protective barrier properties [25] at the film surface simultaneously.

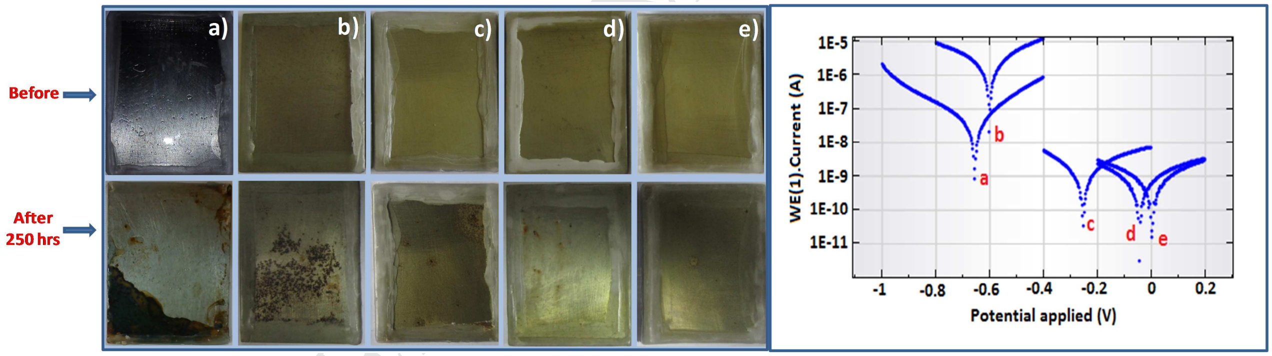


Fig. 9 Fog test results and Polarization curves on Tafel plot for PMMA and Poly (MMA-co-TSDE) coatings on mild steel panels. **a)** PMMA, **b)** TSDE-2.5 **c)** TSDE-5 **d)** TSDE-7.5 **e)** TSDE-10.

Table 4. Corrosion parameters obtained from Electrochemical Impedance Spectroscopy studies for PMMA and TSDE crosslinked PMMA films coated on mild steel.

Sample code	E_{corr} (mV)	I_{corr} (A)	Polarization resistance(Ω)	Corrosion rate (mm/year).
PMMA	-601.820	2.29 µA	27.6690 kΩ	2.6677×10^{-2}
TSDE-2.5	-656.650	44.29 nA	1.07840 MΩ	5.1473×10^{-4}
TSDE-5	-254.290	1.11 nA	42.5920 MΩ	1.2907×10^{-5}
TSDE-7.5	-46.2340	0.50 nA	98.7670 MΩ	5.8682×10^{-6}
TSDE-10	1.65500	0.24 nA	97.3630 MΩ	2.7996×10^{-6}

Antibacterial results

The antibacterial activities were measured based on the formation of inhibition zone loss of bacterial growth beneath and surroundings of the films placed on Luria Bertani agar medium. The colonies of various bacteria were grown on CzapekDox medium. (Fig.10). The CzapekDox plates consist of bacterial cultures, and the embedded films were incubated for 4−5 days at ambient temperatures of 28 ± 4 °C; loss of bacterial moss surrounds beneath the film was monitored. In the present work, *Staphylococcus aureus* and *Klebsiella pneumonia* were used as gram positive and gram negative bacterial stains. The embedded TSDE loaded PMMA polymeric films were showing excellent resistance towards the bacteria compared to the pristine PMMA. This resistance towards various bacteria can be attributed mostly to the presence of 1,2,3-triazole units in the crosslinked polymer in comparison to the similar effect contributed by the presence of catalytic amounts of Cu (1.6wt%) with respect to TSDE that may be considered almost negligible.

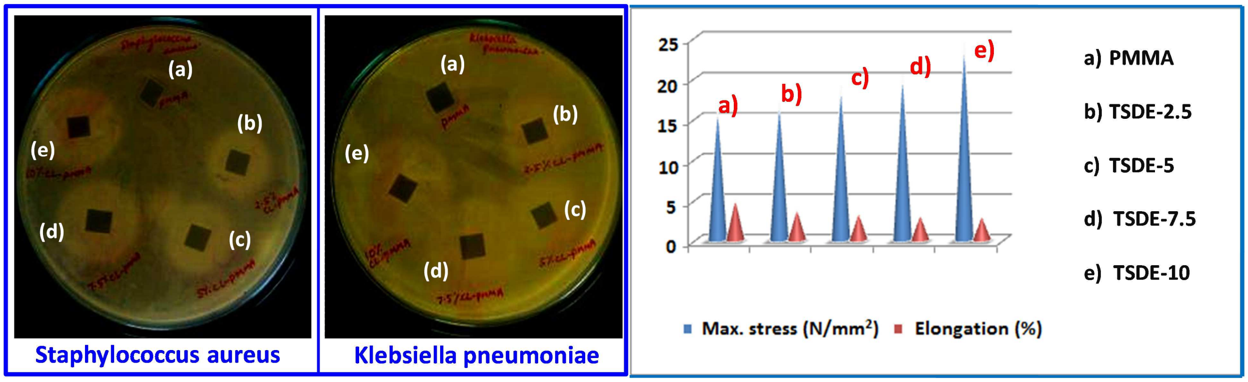


Fig. 10 Antibacterial activity and Tensile properties of PMMA and Poly (MMA-co-TSDE) free films.

Conclusions

In summary, we have reported the use of azide alkyne "click" reaction to make a multifunctional hybrid diallyl ether crosslinker compound (TSDE) with siloxane and triazole functionalities in a single structure. The as synthesized new azide click linker opens up the possibility to design a wide class of azides with other functionalities that can be used to react with the terminal dialkynes on the sol gel synthesized siloxane compound resulting in a multifunctional hybrid crosslinker. This new method opens up the scope for synthesis of such class of monomers with appropriately functionalized azide click linkers that can be useful in making variety of hybrid coatings. A comparative study of the properties like thermal, wettability, corrosion and bacterial resistance of Poly (MMA-co-TSDE) versus PMMA homopolymer have proved the enhanced performance of the hybrid coatings with a low ≤ 10% TSDE. Hence, the role of TSDE crosslinker in the coating has successfully proved the advantages of such designed monomers with hybrid functionalities that help form homogeneous and compact films useful in the field of protective coatings.

Acknowledgements

Mr. Kesavarao Sykam would like to express his gratitude to University Grants Commission (UGC) for the fellowship and the authors thank CSIR-XII Five year plan programme INTELCOAT-0114 for financial support.

References

1. Sandra Raquel Kunsta, Gustavo Aalberto Ludwiga, Henrique Ribeiro Piaggio Cardosoa, Joseane Andrade Santanab, Victor Hugo VitorinoSarmentob, Célia de FragaMalfattia. Hybrid Films with (Trimethoxysilylpropyl) Methacrylate (TMSM),Poly (Methyl methacrylate) PMMA and Tetraethoxysilane (TEOS) Applied on Tinplate. *Materials Research.* **2014**; 17(Suppl. 1): 75-81.

2. Sandra Raquel Kunst1, Henrique Ribeiro Piaggio Cardoso, CláudiaTrindade Oliveira, CíceroInácio da Silva Filho, Victor Hugo Vitorino Sarmento, Tiago Lemos Menezes, Iduvirges Lourdes Müller, Célia de Fraga Malfatti. Influence of Tetraethoxysilane Addition in Siloxane-Poly(Methyl Methacrylate) Hybrid Films Applied on Galvanized Steel.*Int. J. Electrochem. Sci.,* 8 (**2013**) 11984 – 12004.

3. A. Chetouani, K. Medjahed, K.E. Sid-Lakhdar, B. Hammouti, M. Benkaddour, A. Mansri b. Poly(4-vinylpyridine-poly (3-oxide-ethylene) tosyle) as an inhibitor for iron in sulphuric acid at 80° C. *Corrosion science* **2004**, 46.10, 2421-2430.

4. Hawker, Craig J, Karen L. Wooley. The convergence of synthetic organic and polymer chemistries.*Science* **2005**, 309, 1200-1205.

5. Qian Wang, Timothy R. Chan, Robert Hilgraf, Valery V. Fokin, K. Barry Sharpless, M. G. Finn. Bioconjugation by copper (I)-catalyzedazide-alkyne [3+ 2] cycloaddition. *Journal of the American Chemical Society* **2003**, 125.11, 3192-3193.

6.Wolfgang H. Binder,Robert Sachsenhofer. 'Click'chemistry in polymer and materials science. *Macromolecular Rapid Communications***2007**, 28.1, 15-54.

7.Markus A. Trojer, AlirezaMovahedi, Hans Blanck, Magnus Nydén1. Imidazole and triazole coordination chemistry for antifouling coatings.*Journal of Chemistry***2013**.

8. Bruno G. De Geest, Wim Van Camp, Filip E. Du Prez, Stefaan C. De Smedt, Jo Demeester,Wim E. Hennink. Degradable multilayer films and hollow capsules via a 'click'strategy.*Macromolecular rapid communications***2008**, 29.12-13, 1111-1118.

9. SravendraRana, Sun Young Lee, Jae Whan Cho. Synthesis and characterization of biocompatible poly (ethylene glycol)-functionalized polyurethane using click chemistry. *Polymer bulletin* **2010**, 64.4, 401-411.

10. SasidharKantheti, Sarath P. S., Ramanuj Narayan, K. V. S. N. Raju. Synthesis and characterization of triazole rich polyether polyols using click chemistry for highly branched polyurethanes. *Reactive and Functional Polymers***2013**, 73.12, 1597-1605.

11. KanthetiSasidhar, Ramanuj Narayan, K. V. S. N. Raju. Development of moisture cure polyurethane–urea coatings using 1, 2, 3-triazole core hyperbranched polyesters.*Journal of Coatings Technology and Research***2013**, 10.5, 609-619.

12. Gareev, G. A. et al. Allyl acetate as a new reagent for the synthesis of allyl ethers. *ZhurnalOrganicheskoiKhimii*, 1980,16(7),1546-8.

13.Yumagulova, R. Kh, Yu N. Biglova, S. I. Kuznetsov, I. A. Ionova, S. V. Kolesov, and Yu B. Monakov. Fullerene C60 in copolymerization of allyl chloride with methyl methacrylate. *Polymer Science Series A* 50, **2008**, 260-264.

14.Final Safety Assessment report on Crosslinked Alkyl Acrylates as Used in Cosmetics, Cosmetic ingredient review, November 17, 2011,1101 17th Street, NW, Suite 412 ◇ Washington, DC 20036-4702,cirinfo@cir-safety.org

15.Mats Johansson, Eva Malmströmand AndersHult. *Journal of Polymer Science Part A: Polymer Chemistry.* 15 March **1993**,619–624.

16.N. Gabriel Lemcoff, Tighe A. Spurlin, Andrew A.Gewirth, Steven C. Zimmerman, James B. Beil,Stephanie L. Elmer, and H. George Vandeveer.Organic Nanoparticles Whose Size and Rigidity Are Finely Tuned byCross-Linking the End Groups of Dendrimers.*J. Am. Chem. Soc.***2004**, 126, 11420-11421.

17. Steven C. Zimmerman, Jordan R. Quinn, EwelinaBurakowska and Rainer Haag.Cross-Linked Glycerol Dendrimers and Hyperbranched Polymers asIonophoric, Organic Nanoparticles Soluble in Water and OrganicSolvents.*Angew.Chem.***2007**, 119, 8312 –8315.

18.W. Ken Busfield, Ian D. Jenkins, San H. Thang, EzioRizzardo and David H. Solomon.Initiation mechanisms in radical polymerization: reaction of t-butoxy radicals with allyl acrylate and with diallyl ether. *J. Chem. Soc., Perkin Trans. 1*, **1988**, 485-490.

19. Flory P J. *J. Chem. Phys*, **1950,** 18, 108.

20. Koubunshi Data Handbook”, *Society of Polymer Science* ,Japan, Edit BaifukanCo.,Ltd., **1986**.

21. Gałka P, Kowalonek J., &Kaczmarek, H. Thermogravimetric analysis of thermal stability of poly (methyl methacrylate) films modified with photoinitiators. *Journal of Thermal Analysis and Calorimetry*, **2014**, *115*(2), 1387-1394.

22. Venkata M. Nivasu, Thimma T. Reddy, Shekharam Tammishetti. In situ polymerizable polyethyleneglycol containing polyesterpolyol acrylates for tissue sealant applications. *Biomaterials* 25 (**2004**) 3283–3291.

23. S. Devikala P. Kamaraj M. Arthanareeswari. Preparation, Characterization and Anticorrosive Properties of a Novel Pmma/ Zro2 Composite., *Indian Journal of Applied Research*, **2014**, 4,1-3.

24.Youhong Tang, Cathy K. W. Jim, Yang Liu; Lin Ye, Anjun Qin, Jacky W. Y. Lam, Chengbi Zhao, Ben Zhong Tang. Synthesis and curing of hyperbranched poly (triazole) s with click polymerization for improved adhesion Strength. *ACS applied materials & interfaces*, **2010**, 2, 566-574.

25. P. G. Cao, J. L. Yao, J. W. Zheng, R. A. Gu, Z. Q. Tian. Comparative study of inhibition effects of benzotriazole for metals in neutral solutions as observed with surface-enhanced Raman spectroscopy. *Langmuir,* **2002**, 18, 100-104.

Highlights of the work

- A multifunctional hybrid diallyl ether monomer (TSDE) useful as crosslinking agent in polymer synthesis was synthesized using azide alkyne click chemistry as first example.
- A new allyl ether functional azide was synthesized and used as click linker for the first time.
- TDSE could be used to copolymerize with any vinylic family of monomers to make hybrid coatings with synergistic benefits from organic triazoles and inorganic siloxane functionalities.
- Siloxane groups here get incorporated into the polymer network by covalent bonding with the monomers to form a more compact film unlike the ones prepared by sol gel method.
- Copolymers of Poly (MMA-co-TSDE) result in enhanced barrier, corrosion resistance and anti-bacterial protection properties to the films in comparison to PMMA.
- This new method opens up the scope for synthesis of such class of monomers with appropriately functionalized azide click linkers that can be useful in making variety of hybrid coatings.

Supporting Information.

Novel multifunctional hybrid diallyl ether monomer via azide alkyne click reaction as crosslinking agent in protective coatings

Kesavarao Sykam, Shailaja Donempudi*

Polymers & Functional Materials Division, Indian Institute of Chemical Technology, Hyderabad 500007, India.

*Corresponding author: Email: sdonempudi@iict.res.in

FT-IR analysis

In the present work, FT-IR analysis was performed to verify the formation of various steps involved in the development of poly (MMA-co-TSDE) free films such as synthesis of (N-(prop-2-ynyl)-N-(3-(triethoxysilyl)propyl)prop-2-yn-1-amine) (compound-1), 2-azidoethanol (Compound 2), Synthesis of 3-(2-azidoethoxy)prop-1-ene (Compound-3), TSDE cross-linker and the poly (MMA-co-TSDE) polymers.(Fig.1,2)

The formation of compound-1 can be confirmed by the disappearance of broad peak of N-H str at 3400 cm^{-1} and the formation of new sharp peak at 3300 cm^{-1} (≡C-H Str). The strong peak in the range of 1108-1080cm^{-1} corresponds to Si-O stretching. The formation of 2-azidoethanol from 2-chloroethanol was confirmed by the presence of new peak at 2100 cm^{-1} corresponding to azide ($-N_3$) group. Compound-3 formation was confirmed by presence of two stretching frequencies related to the alkene functional group such as the peak at 3050 cm^{-1} (=C-H str) and the peak at 1630 cm^{-1} (C=C str). The click reaction between compound-1 and 3 for the formation of TSDE cross-linker is confirmed by the disappearance of alkyne and azide stretching frequencies around 3300 cm^{-1} and 2100 cm^{-1} respectively and the formation of new peaks related to the 1,2,3-triazole unit such as a low intense peak at 3100 cm^{-1} (triazole C-H) and a sharp peak at 1450 cm-1 (triazole C=C str). Finally, the formation of poly (MMA-co-TSDE) polymers were confirmed by the disappearance of peaks corresponding to alkene functional group at1648 cm^{-1} and the presence of stretching peaks at 1722cm^{-1} (C=O str), 1150-1250cm^{-1} (C-O-C str). 1170-1160cm^{-1}, 1085cm^{-1},970-940cm^{-1} relates to stretching frequencies of $Si-O-CH_2CH_3$ present in TSDE based PMMA.

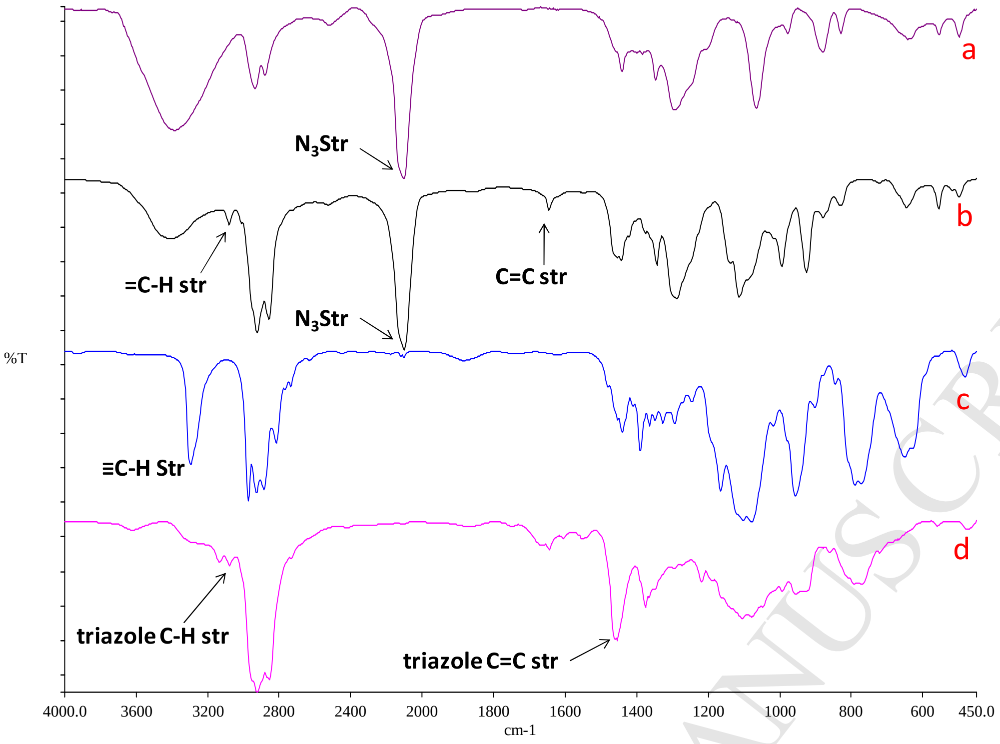


Fig. 1 FT-IR spectra of a) 2-azido ethanol b) 3-(2-azidoethoxy) prop-1-ene c) (N-(prop-2-ynyl)-N-(3-(triethoxysilyl)propyl)prop-2-yn-1-amine) d) TSDE

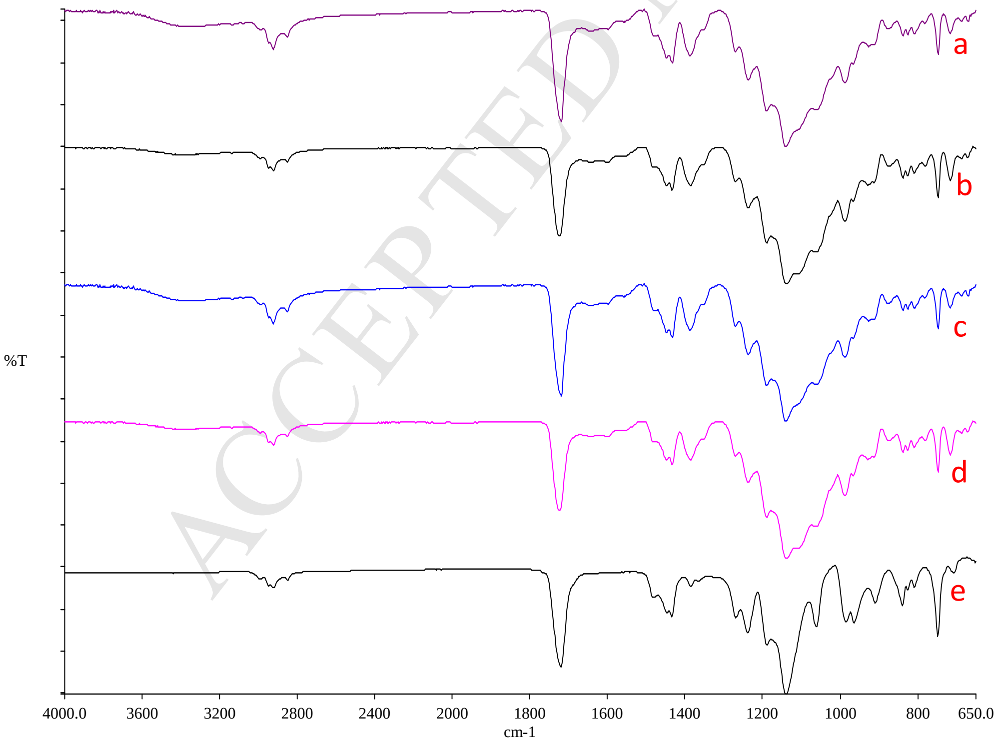


Fig. 2 FT-IR spectra of a)TSDE-10 b) TSDE-7.5 c) TSDE-5 d) TSDE-2.5 e) PMMA.