The reactions of tris(trimethylsilyl)methyl lithium with some epoxides

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Tris(trimethylsilyl)methane, $[(Me_3Si)_3CH]$ (**1**),could be metallated by use of methyllithium in tetrahydrofuran.Tris(trimethylsilyl)methyl lithium (TsiLi)(**2**) reacts with ethylene oxide and poly (GMA-*co*-EHMA) with the formation of a carbon–carbon bond. This method of preparing functionalised silanes is limited by the readiness with which TsiLi abstracts a proton, if one is available, rather than attack at carbon. In addition in the reaction with epoxides, the product alkoxide can transfer a silyl group from carbon to oxygen (**5,6**), however this was shown not to occur under the conditions of interest here. $[TSiCH_2CH_2OH]$ (**7**) was halogenated (**8,9**) and estrificated (**10-I**), (**I** = 1–8) successively to the esteric and alkyl halide compounds.

Keywords: trisyl, esterification, ethylene oxide, ring opening, glycidyl methacrylate.

The tris(trimethylsilyl)methyl group, ${(Me_3Si)_3 C-}$, denoted here by trisyl or Tsi, has been shown over the years to affect the properties of a number of organometallic systems.[1,2] Extensive studies in this area led to the characterisation of novel stable compounds and new reaction mechanisms, but there are few studies about attaching the trisyl group to a carbon atom.[3] In our previous work we have described synthesis of trisylmethyl benzene (TsiMB) as a model compound for evidence of attaching the trisyl ligand to benzylic carbon. We described the preparation of 4-trisylmethyl styrene (TsiMs) and its reactions with various chemical reagents for the synthesis of some new organosilicon compounds.[4] Then we reported the synthesis and characterisation of polymers of CMS without and within very bulky trisyl groups.[5-7] We report here some reactions of TsiLi with other carbon electrophiles. Tris(trimethylsilyl)methyl lithium(TsiLi) is readily available from the reaction of trisyl with methyl lithium in tetrahydrofuran (THF). We describe first the synthesis of 3, 3, 3- tris(trimethylsilyl)propane-1-o1 (**7**) as a model compound for evidence of attaching the trisyl ligand to ethylene oxide which gave the alcohol (**7**), this could be esterified and halogenated successively to the corresponding esteric and alkyl halide compounds. Then we report the synthesis and properties of poly(glycidylmethacrylate-co-2-ethylhexylmethacrylate) modified with trisyl groups. Tris(trimethylsilyl)methyl groups are attached to the polymers by the ring opening reaction of the epoxy groups and TsiLi. Attaching the tris(trimethylsilyl) methyl group and its derivatives to a macromolecular chain should lead to important modifications of polymer properties.[8,9]

Results and discussion

Almost all the reactions in solution for ethylene oxide involve opening of the epoxide ring and the addition of a molecule of reagent; if the reagent is an anion, the reaction is completed by the solvent. The high reactivity of the epoxide group in ethylene oxide is due to the considerable strain in the three-membered ring.

Synthesis of $TsiCH_2CH_2OH$ (**7**): Tris(trimethylsilyl)methyl lithium reacts with ethylene oxide in the good yield to give $TsiCH_2CH_2OH$ at 0 °C in THF. Note that these ring opening reactions generate alkoxide group which can potentially react with silicon atoms of trisyl groups, to give the alcohol (**6**), which has one fewer silyl groups. But the silicon transfer takes *ca* 30 min at room temperature. However, this was shown not to occur at the conditions of interest here. Stilbene oxide was inert towards TsiLi; and both propylene oxide and cyclohexene oxide protonated TsiLi (¹H NMR observations)[3] (Fig.1b)

Halogenation of $TsiCH_2CH_2OH$: An alternative to the direct trisyl-polymer linkage is the incorporation of a spacer group between the trisyl group and polymer chain. Consequently the conversion of hydroxy-groups into halo-groups could attract considerable attention in polymer and silicon chemistry. Therefore, $TsiCH_2CH_2Cl$ (**8**) and $TsiCH_2CH_2Br$ (**9**) (Fig.1c) are amenable to further transformations, such as substitution and elimination, because bromide and chloride are a good leaving groups and the chemistry of the resulted products is being explored.

Esterification of $TsiCH_2CH_2OH$: The search for performant esterification processes is extremely active, testified by the several hundreds of articles, reviews, patents reported each year.[12] The ¹H NMR spectrum of the reaction of TsiLi with acyl chloride in THF clearly showed three separate but equally intense signals from trimethylsilyl groups (**3**) which suggested that the silyl enol ether had been produced[3] (Fig.1a). Therefore we became interested in esterification reaction with our alcohol. The reaction between acyl halides and alcohols is the best general method for the preparation of esters. A base (for example, triethylamine) is added to combine with the HX which is formed during the reaction (Fig.1c).

Synthesis of copolymer (I): Polymers of glycidyl methacrylate have received significant attention due to the pendent epoxide groups which enter into a large number of chemical reactions,[10] thus offering the opportunity for chemical modification of the parent polymers for various uses. The monomer of GMA was copolymerised with 2-ethyl hexyl methacrylate (EHMA) at 70 ± 1°C in THF solvent using AIBN as the free radical initiator (Fig.1d). The number and weight average molecular weights of synthesised copolymer was determined by gel permeation chromatography (GPC). After standing for a long period of time, even at room temperature, all of GMA polymers changed to be insoluble in organic solvents, probably due to intermolecular cross linking between epoxy units. Therefore (GMA) polymer reactions should be carried out immediately after polymerisation. We have used ¹H NMR to determine copolymer compositions. Gel permeation chromatography (GPC) was used to determine the number and weight-average molecular weights of copolymer soluble in THF and the results are listed in Table 1. The assignment of the resonance peaks in the ¹H NMR spectrum leads to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains.[11] Thus, the mole fractions of GMA in the copolymer chains were calculated from measuring the integrated peak area of the three resonances of epoxide protons of the GMA unit and methylenoxyl protons of EHMA units. Let m_1 be the mole fraction of GMA and $1-m_1$ is that of EHMA monomer. The proton resonances of the methylenoxyl group in EHMA and GMA at 3.7–4.2 ppm and those of the epoxide group in GMA at 3.27, 2.88 and 2.70

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ppm are clearly resolved. The GMA contains three epoxide protons and EHMA contain two methenoxyl protons:

$$A = \frac{\text{Integrated peak area of } 2.7\text{--}3.27}{\text{Integrated peak area of } 3.7\text{--}4.2} \quad (1)$$

$$A = \frac{3\,m_1}{2(1\text{-}m_1) + 2\,m_1}$$

This on simplification gives:

$$m_1 = \frac{2A}{3} \quad (2)$$

Therefore, the mole fraction of GMA in copolymer was determined from Eqn (2). Table 1 gives the mole fractions of GMA and comonomer in the copolymer.

The FT–IR spectrum of copolymer(**I**) are shown in Fig. 2. The shoulder at 1732 cm^{-1} is attributed to the ester carbonyl stretching of GMA and EHMA units. The symmetrical stretching of the epoxy group is observed at 1273 cm^{-1}. Another band seen at 907 cm^{-1} is due to the asymmetric stretching of the epoxy group. The C–O stretching is observed at 1161 cm^{-1}. The ^{1}H NMR spectrum of the copolymer (Fig. 3a) shows two signals at 4.33 and 3.75 ppm due to the splitting of methylene protons in the –CH$_2$O group attached to the carbonyl group of the GMA unit by the methyne proton of
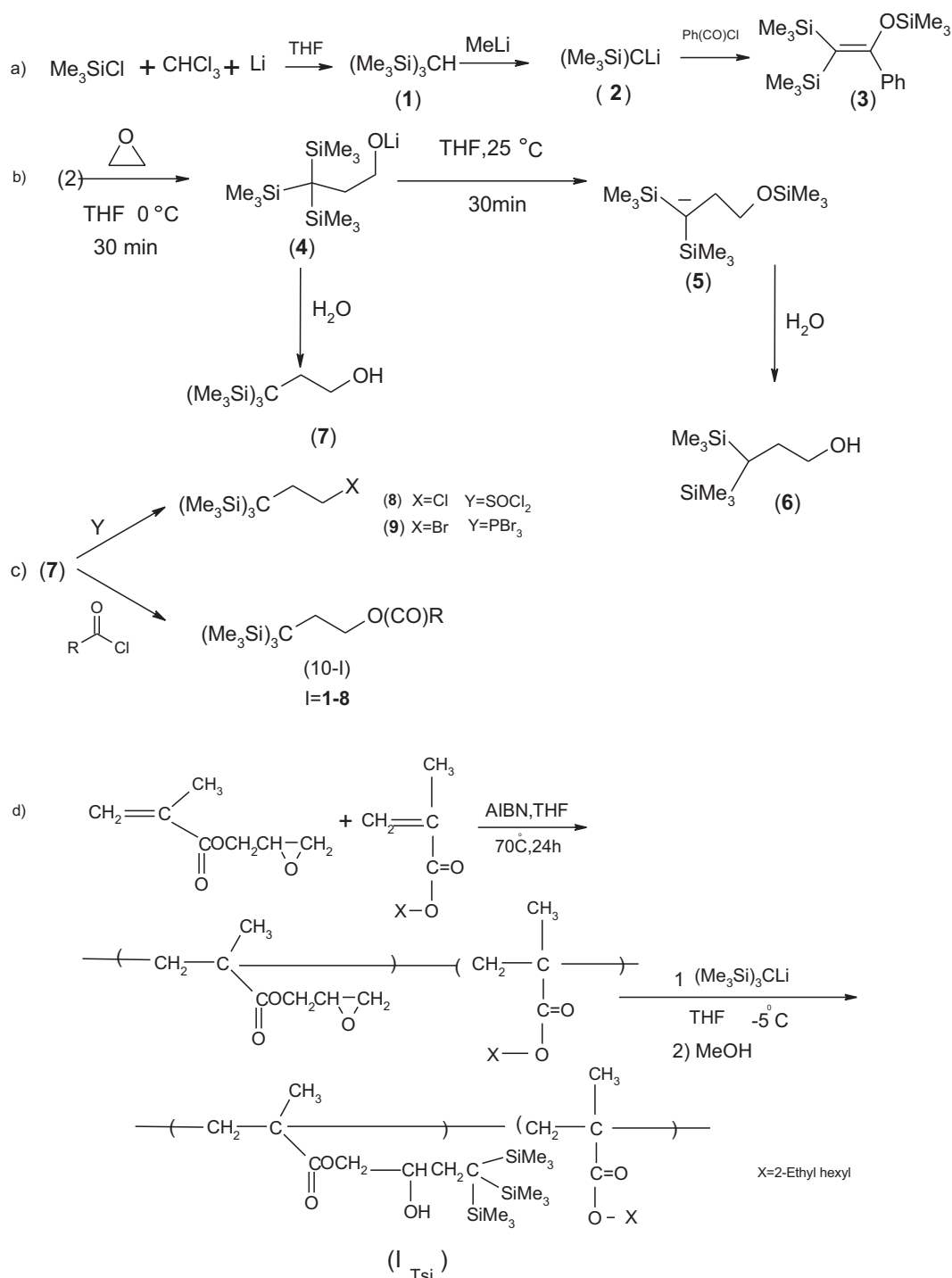
Fig.1 Synthetic routes for preparation of: (a) tris (trimethylsilyl)methane(**1**), trisyllithium(**2**) and silyl enol ether(**3**); (b) 3, 3- bis (trimethylsilyl)propane-1-ol(**6**) 3, 3, 3-tris(trimethylsilyl)propane-1-ol(**7**); (c) halogenated (**8,9**) and esteric derivatives(**10-I**) of (**7**); (d) synthesis of copolymer and substitution of trisyl groups at copolymers **I-VI**

Table 1 Composition, molecular weights and Tg of polymer

| Polymer	mol/ % GM	mol/ % EHMA	$M_w/10^3$	$M_n/10^3$	M_w/M_n	$T_g/°C$
I	48	52	138.38	46.52	2.97	25
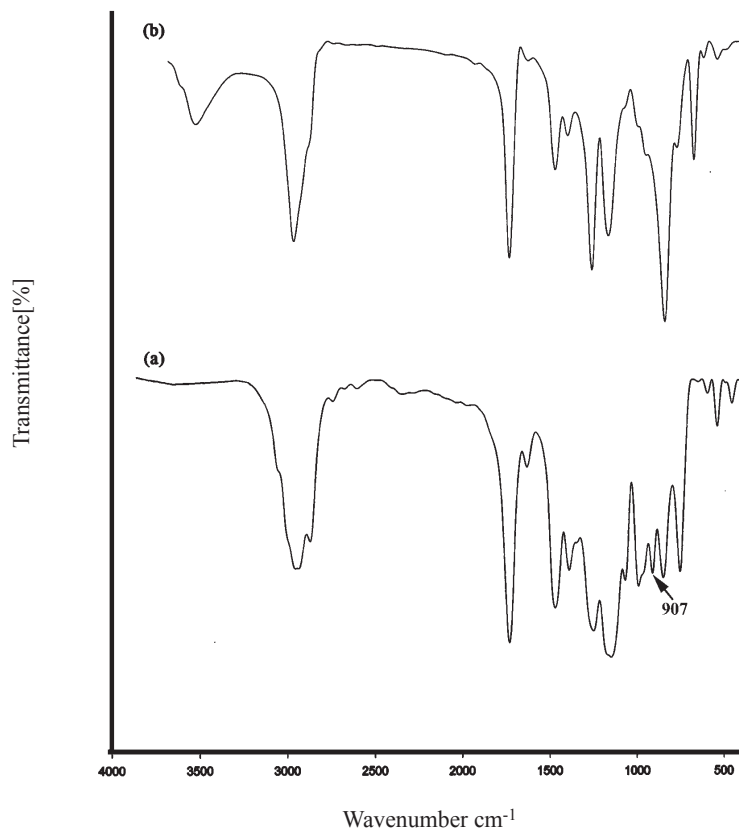
Fig.2 Infrared spectra of copolymers (a) **I** and (b) **I$_{Tsi}$**. The epoxy groups, 907 cm⁻¹, which are well defined in the unmodified (**I**) (a) modified with trisyl groups in **I$_{Tsi}$** (b).

the epoxy group. The peak at 3.16 ppm is due to the methyne proton of epoxy group. The methylene protons of the epoxy group show signals at 2.78 and 2.51 ppm. The resonance signal at 4 ppm was attributed to two methylene protons of –COOCH$_2$ in the copolymer. No peak appears around 5.00 and 5.30 ppm which indicates the absence of the protons corresponding to the methacrylic unsaturation. The appearance of these absorption bands not only confirms the incorporation of both monomeric units in the copolymers but also shows the intactness of the epoxy group during the polymerisation. The glass transition temperature (Tg) of the copolymer was determined by DSC. The synthesised copolymer shows a single Tg showing the absence of formation of a mixture of homopolymers or the formation of a block copolymer.

Synthesis of copolymer containing trisyl substituents (**I$_{Tsi}$**):
We have modified poly (GMA-co-EHMA) by incorporation of very bulky (Me$_3$Si)$_3$C groups (Fig. 1c). Tris(trimethylsilyl) methane readily undergoes metallation when treated with methyllithium in a mixture of THF and diethyl ether, and the TsiLi produced is markably stable in THF. The ease of formation and the stability of the organolithium compound might be associated with stabilisation of the carbanion (Me$_3$Si)$_3$ C⁻ by delocalisation of the lone pair of electrons into the d-orbitals of the silicon atom.The epoxy group possesses a higher reactivity for the TsiLi than the chloromethyl groups in chloromethyl styrene polymers even though this coupling reaction is very rapid at –5 °C. It was still necessary

for a reaction time of 60 min in order to ensure a complete conversion. One of the GMA copolymers was synthesised in order to separate the GMA monomers from each other along the chain. Although GMA is randomly distributed along the chains, it can be considered that two GMA monomers are separated on average by one comonomer. Following this interpretation, it can be anticipated that modification of the copolymer with voluminous trisyl groups will lead to more complete conversion of the GMA moieties. The backbone copolymers of GMA employed in the present paper contain not only epoxy groups in GMA units, but also carbonyl groups in both comonomer and GMA units. For this reason, it was necessary to identify the positions where the coupling reaction took place. A THF solution of poly (methyl methacrylate)(MMA) was prepared by the radical homopolymerisation of MMA, which was carried out using AIBN as initiator in THF at 70 °C, for 30 h. The polymer solution was introduced into the TsiLi solution and the stirring was continued for 1 h at –5 °C. The red colour of the TsiLi remained during the whole process until a small amount of methanol was added. A mixture of poly (MMA) and TsiH were recovered (determined by NMR). This experiment excluded the possibility of a reaction between the carbonyl group and the TsiLi. Consequently, only the epoxides of GMA units have acted as coupling sites. The epoxy group possesses a higher reactivity for the Tsi⁻Li⁺ than the ester groups. Figure 2 shows the IR spectra of copolymers after modification in comparison with the spectra of the original polymer.
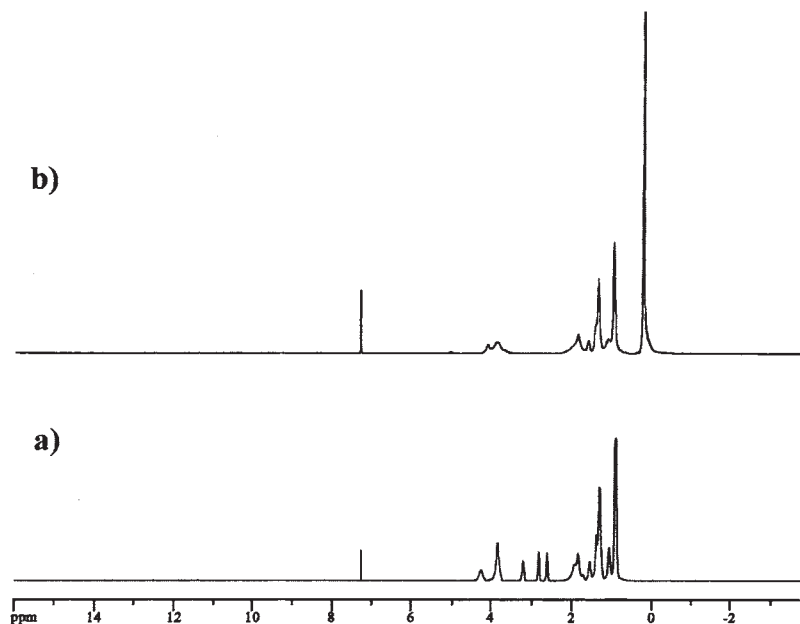
Fig.3 ¹H NMR spectra: (a) **I** and (b) **I**$_{Tsi}$ in CDCl$_3$ without tetramethylsilane (TMS). The epoxy groups (δ = 2.5–3.4 ppm), which are well defined in the unmodified copolymer (a) disappear after modification (b).

Table 2 The results of reaction between 0.5 g of polymer with TsiLi

Modified polymer	Weight/g	Yield/ %	T_g/°C
I$_{Tsi}$	0.7	85	81

A decrease in the epoxide absorbances at 907 cm⁻¹ is clearly visible (Fig. 2b). At the same time, new absorption bands at 900 and 1250 cm⁻¹ are observed, corresponding to the (C–Si) band in trisyl groups. The large peak at 3550 cm⁻¹ is assigned to the presence of secondary hydroxyl groups on the polymer chains, which is indicative of the ring opening reaction. Figure 3b presents the ¹H NMR spectra of copolymers after modification. Addition of trisyl groups to copolymers lead to a large decrease in the intensity of the peaks of the oxirane groups. Also, a new signal related to 27 methyl protons of C[Si(CH$_3$)$_3$] appears at 0.12 ppm. The other chemical shift assignments for copolymer (I$_{Tsi}$) are the same as those observed for copolymer (**I**). It is concluded that the reaction proceeds by opening of the epoxide ring and by the formation of a new C–C linkage and a secondary hydroxyl group. Study of DSC curves clearly showed that incorporating trisyl substituents in copolymer side chains as well as hydroxyl groups increases the chain rigidity of polymer(25–81) (Tables 1 and 2).The chemical modifications of GMA copolymers have been shown to significantly alter physical properties such as glass transition temperatures (Tg).

Experimental

Reactions involving lithium, organolithium reagents and polymerisation were carried out under dry argon to exclude oxygen and moisture from the reaction systems.

Materials
Chloroform(Merck), THF (Merck), diethylether (Merck), *n*-hexane (Merck), dichloromethane (Merck) and triethylamine (Merck) were dried by standard methods. Me$_3$SiCl (Merck), MeI (Merck), Li (Merck) and ethylene oxide (Fluka) were used as received. Thionyl chloride, phosphorus tribromide and acyl chlorides (Merck)were distilled. Glycidyl methacrylate (Merck), 2-ethyl hexyl methacrylate (Merck) was distilled under reduced pressure to remove inhibitors before use. Toluene was stirred over calcium hydride for 24 h

and distilled under a dry argon atmosphere. The initiator of α, α'-azobis(isobutyronitrile) (Merck) was purified by crystallisation from methanol.

Measurements
IR spectra were recorded with a 4600 Unicam FT–IR spectro-photometer as KBr pellets. ¹H NMR and ¹³C NMR spectra were run on a Bruker 400 MHz. spectrometer at room temperature using CDCl$_3$ as solvent. Mass spectra were obtained with a Shimudzu Qp 100X spectrometer at 70eV. Elemental analyses were carried out with a Hereus CHNO-RAPID instrument. The molecular weights (Mw and Mn) were determined using a Waters 501 gel permeation chromatograph fitted with 10² and 10³ nm Waters styragel columns. THF was used as an elution solvent at a flow rate of 1 ml/min and polystyrene standards were employed for calibration. The glass transition temperature was determined with Shimadzu DSC-50 differential scanning calorimeter at a heating rate of 10 °C/min. The Tgs were taken at the midpoint of the heat flow changes.

Preparation of tris(trimethylsilyl)methyl lithium (TsiLi) (**2**): TsiLi was prepared in the usual way.[1]

Preparation of a model compound 3, 3, 3- tris(trimethylsilyl) propan-1-ol (**7**): This product was synthesised by the described method.[3]

Preparation of TsiCH$_2$CH$_2$Cl (**8**): In a dry 25 ml flask fitted with a reflux condenser and a dropping funnel and a stirrer under an argon atmosphere was placed 0.43 g (3.6 mmol) of thionyl chloride (distilled). *The reaction flask must be cooled in water bath.* A mixture of (0.5 g, 1.8 mmol) TsiCH$_2$CH$_2$OH in distilled chloroform (5 ml) was added dropwise through the funnel to the thionyl chloride during which time there was a copious evolution of sulfur dioxide and hydrogen chloride. After all the TsiCH$_2$CH$_2$OH had been added the water bath was removed and the reaction mixture was stirred for 6 h at 35 °C. Then the CHCl$_3$ was evaporated. A pure sample for elemental analysis was obtained by TLC (silicagel, 1: 8 THF-*n*-hexanes). The product was obtained as white crystals. Yield 45 %, m.p. 237–238 °C, v_{max} = 1259 cm⁻¹ (SiMe$_3$),¹H NMR 0.14 (s, 27 H, SiMe$_3$), 2.01 (t, 2H, CH$_2$), 4.14 (m, 2H, CH$_2$–Cl) ¹³C NMR (CDCl$_3$), 1.66 (SiMe$_3$), 2.6 (C–Si), 29.83 (CH$_2$), 61.69 (CH$_2$Cl), *m/e* 296 (M⁺ 50 %), 259 (25 %), 171 (60), 73 (90), (Found: C, 48.5; H, 10.7, Calc: C, 48.6; H, 10.5).

Preparation of TsiCH$_2$CH$_2$Br (**9**): In a dry 25 ml flask fitted with a reflux condenser and a dropping funnel and a stirrer under an argon atmosphere was placed a mixture of TsiCH$_2$CH$_2$OH 0.5 g (1.8 mmol) in distilled toluene. Then PBr$_3$ was added dropwise through the funnel to the mixture at room temperature. The reaction flask was placed on a steam bath and heated for 2 hours until the colour of the mixture became orange. Then, the mixture was separated on a Buchner funnel and was well washed with water and ether. A pure

sample for elemental analysis was obtained by TLC (silicagel, 1: 8 THF-*n*-hexane). The product was obtained as white crystals. Yield 55 %, m.p = 248 °C, v_{max} 1259 cm^{-1} (SiMe$_3$), ^{1}H NMR 0.06–0.17 (s, 27 H, SiMe$_3$), 2.02–2.07 (t, 2H, CH$_2$), 4.16–4.2 (q, 2H, CH$_2$-Br),^{13}C NMR (CDCl$_3$), 1.63 (SiMe$_3$), 2.57 (C–Si), 30.44 (CH$_2$) 66.86 (CH$_2$–Br), *m/e* 339 (M$^+$, 20 %), 299 (40), 73 (91), 71 (30), (found: C, 42.6; H, 9.4, Calc. C, 42.4; H, 9.2).

General procedure

In a dry 25 m flask fitted with a condenser and a dropping funnel and a stirrer under an argon atmosphere was placed acetyl chloride (1 mol) and *the flask must be cooled in a mixture of salt and ice*. Then a mixture of alcohol (**7**) (1 mol) in dry and distilled chloroform was added dropwise to the acetyl chloride and then the mixture of dry and distilled triethylamine (0.3 mol) in dry and distilled chloroform was added. The mixture was stirred at room temperature. The reaction was monitored by TLC. The mixture was separated in a Buchner funnel and was washed with ice (cool water) and ether. A pure sample is obtained by TLC.

Preparation of TsiCH$_2$CH$_2$O(CO)CH$_2$Cl (**10-1**): The reaction was carried out using the above general procedure and the reaction solution was stirred for 16 h. A pure sample was obtained by TLC (silicagel, 8: 1, *n*-hexane-THF), Yield 65 %, m.p 61–62 °C, v_{max} 1751 cm^{-1} (C=O), ^{1}H NMR (CDCl$_3$), 0.14 (s, 27 H, SiMe$_3$), 1.93–1.97 (t, 2H, CH$_2$), 4.06 (s, 2H, CH$_2$–Cl), 4.3 (t, 2H, CH$_2$–O), ^{13}C NMR (CDCl$_3$), 1.58 (SiMe$_3$), 2.6 (C-Si), 28.34 (CH$_2$), 39.95 (CH$_2$–Cl), 65.56 (CH$_2$–O), 166.1 (C=O), *m/e* 354 (M$^+$), 257, 171, 97, 73 (found: C, 48.0; H, 9.2, Calc: C, 47.7; H, 9.4).

Preparation of TsiCH$_2$CH$_2$O(CO)CHCl$_2$ (**10-2**): The reaction was carried out using the general procedure and was stirred for 16 h. A pure sample was obtained by TLC (silicagle, 8: 1 *n*-hexane-THF).Yield 75 %, m.p. 63 °C, v_{max} 1751 cm^{-1} (C=O), ^{1}H NMR (CDCl$_3$), 0.14 (s, 27H, SiMe$_3$) 1.96–2.01 (t, 2H, CH$_2$), 4.42–4.46 (t, 2H, CH$_2$–O), 5.94 (s, H, CHCl$_2$).^{13}C NMR (CDCl$_3$), 1.56 (SiMe$_3$), 2.6 (C–Si), 28.06 (CH$_2$), 63.29 (CHCl$_2$), 66.9 (CH$_2$–O), 163.42 (C=O), *m/e* 387 (80), 171 (630), 73 (100) (found: C, 43.7; H, 8.4, Calc: C, 43.4; H, 8.3)

Preparation of TsiCH$_2$CH$_2$O(CO)CCl$_3$ (**10-3**): The reaction was carried out using the general procedure and was stirred for 7 h. A pure sample was obtained by TLC (silicagel, 40:1 *n*-hexane-THF). Yield 85 %, m.p. 89.2 °C, v_{max} 1768 cm^{-1}, ^{1}H NMR (CDCl$_3$), 0.14 (s, 27H, SiMe$_3$), 2.01–2.05 (t, 2H, CH$_2$), 4.5 (t, 2H, CH$_2$–O), ^{13}C NMR (CDCl$_3$), 1.57 (SiMe$_3$), 2.06 (C–Si), 27.88 (CH$_2$), 68.7 (CH$_2$–O),88.88 (CCl$_3$), 160.95 (C=O), *m/e* 422 (M$^+$-13 %), 317 (15), 171 (15), 73 (100), (found: C, 40.2; H, 7.4, Calc: C, 39.8; H, 7.3).

Preparation of TsiCH$_2$CH$_2$O(CO)Ph (**10-4**): The reaction was carried out using general procedure and was stirred for 65 hours. A pure sample was obtained by TLC (silicagle, 40:3 *n*-hexane-THF). Yield 70 %, m.p. 64–65 °C. v_{max} 1718 cm^{-1} (C=O), ^{1}H NMR (CDCl$_3$), 0.2 (s, 27H, SiMe$_3$), 2.08 (t, 2H, CH$_2$), 4.5 (t, 2H, CH$_2$–O), 7.4–8.08 (m, 5H, Ar),^{13}C NMR (CDCl$_3$),1.67 (SiMe$_3$), 2.7 (C–Si), 28.58 (CH$_2$), 64.26 (CH$_2$–O), 127.3–131.84 (Ar), 165.35 (C=O), *m/e* 3.5 (M$^+$-Me,15 %), 258 (45) 105 (100), 73 (60), (found: C, 59.7; H, 9.4, Calc: C, 59.9, H, 9.5).

Preparation of TsiCH$_2$CH$_2$O (CO)PhNO$_2$ (**10-5**): In a dry 25 ml flask fitted with a condenser and a dry funnel and a stirrer under an argon atmosphere was placed a mixture of *p*-nitro benzoyle chloride (0.33 g, 1.8 mmol) in dry distilled THF and the flask *must be cooled in a mixture of salt and ice*. Then a mixture of alcohol in dry and distilled THF was added dropwise to the *p*-nitrobenzoyle chloride. Then the mixture of dry and distilled triethylamine (0.3 mol) in dry and distilled chloroform was added. The reaction was stirred for 26 h. The mixture was separated in a Buchner funnel and was washed with ice (cool water) and ether. A pure sample was obtained by TLC (silicagel 10: 1, *n*-hexane-THF). Yield 65 %, m.p. 89–90 °C,v_{max} 1718 cm^{-1} (C=O), ^{1}H NMR (CDCl$_3$), 0.15 (s, 27H, SiMe$_3$), 2.08 (t, 2H, CH$_2$), 4.55 (t, 2H, CH$_2$–O), 8.2-8.3 (m, 4H, ph), ^{13}C NMR (CDCl$_3$), 1.67 (SiMe$_3$), 2.74 (C–Si), 28.53 (CH$_2$), 65.269 (CH$_2$–O), 122.4951–49.50 (ph), 163.457 (C=O), *m/e* 424 (M$^+$, 10 %), 410 (5), 274 (50), 73 (100), (found: C, 53.3; H, 8.5; N, 31.8, Calc: C, 53.6; H, 8.25; N, 3.2).

Preparation of TsiCH$_2$CH$_2$O (CO) CH$_2$CH$_3$ (**10-6**): The reaction was carried out using the general procedure and was stirred for 19 h. A pure sample was obtained by TLC (silicagle, 55:4, *n*-hexane-THF), Yield 85 %, m.p. 57–58 °C, v_{max} 1740 cm^{-1} (C=O), ^{1}H NMR, 0.14 (s, 27H, SiMe$_3$), 1.13 (t, 3H, CH$_3$), 1.92 (t, 2H, CH$_2$), 2.34 (q, 2H, CH$_2$–CH$_3$), 4.2 (t, 2H, CH$_2$–O), ^{13}C NMR (CDCl$_3$), 1.6 (SiMe$_3$), 2.6 (C–Si), 8.07 (CH$_3$), 26.5 (CH$_2$- CO), 28.5 (CH$_2$), 63.62 (CH$_2$-O), 173.2 (C=O), *m/e* 424 (M$^+$, 10 %), 410 (5), 171 (25), 73 (100), (found: C, 54.0; H, 10.7, Calc: C, 54.15; H, 10.9).

Preparation of TsiCH$_2$CH$_2$O (CO) CH$_2$Ph (**10-7**): The reaction was carried out using the general procedure and was stirred for 15 h. A pure sample was obtained by TLC (silicagle, 20: 1-*n*-hexane-THF), Yield 55 %, m.p. viscous, v_{max} 1737 cm^{-1} (C=O), ^{1}H NMR 0.15 (s, 27H, SiMe$_3$), 1.95 (t, 2H, CH$_2$), 3.63 (s, 2H, CH$_2$–ph), 4.3 (t, 2H, CH$_2$–O), 7.25–7.36 (m,5H, Ar), ^{13}C NMR (CDCl$_3$), 1.54 (SiMe$_3$), 2.658 (C–Si), 28.49 (CH$_2$), 40.24 (CH$_2$–ph), 64.18 (CH$_2$–O), 126–133 (Ar), 170.4 (C=O), *m/e* 379 (M$^+$–Me–10), 281 (40), 259 (49), 73 (100), (found: C, 61.1; H, 9.8, Calc: C, 60.9; H, 9.9).

Preparation of TsiCH$_2$CH$_2$O (CO) CHClPh (**10-8**): The reaction was carried out using the general procedure and was stirred for 15 h. A pure sample was obtained by TLC (silicagle, 20: 1, *n*-hexane-THF), Yield 60 %, m.p. 52 °C, v_{max} 1749 cm^{-1} (C=O), ^{1}H NMR (CDCl$_3$), 0.13 (s, 27H, SiMe$_3$), 1.9 (t, 2H, CH$_2$), 4.35 (t, 2H, CH$_2$-O), 5.3 (s, H, CHPh), 7.36–7.5 (m,5H, Ar), ^{13}C NMR, (CDCl$_3$), 1.54 (SiMe$_3$), 2.65 (C–Si), 28.268 (CH$_2$), 58.053 (CH–Ph), 65.74 (CH$_2$–O), 126.9–134.8 (Ar), 167.2 (C=O), *m/e* 415 (M$^+$–Me, 5 %), 259 (16), 73 (100), (found: C, 56.0; H, 8.7, Calc: 56.0, 8.7).

Copolymerisation of glycidyl methacrylate (GMA) with 2-ethyl hexyl methacrylate (EHMA): Poly (GMA-co-EHMA) (I) was synthesised using the following general method. In a pyrex glass ampoule, a mixture of (GMA) (2.84 g, 20 mmol), AIBN (0.065 g, 0.4 mmol), EHMA (2.36 g, 20 mmol) was dissolved in THF (15 ml) then the ampoule was degassed, sealed under vacuum and maintained at 70± 1 °C in a water bath and shaken by a shaker machine for about 24 h. The viscous solution was poured from the ampoule into 150 ml of cooled methanol. The precipitate was collected and washed with methanol several times and dried under vacuum at room temperature to give 4.75 g of white copolymer (I). The yield of copolymers was 70 %. ^{1}H NMR (CDCl$_3$,ppm): 0.8(α-CH$_3$), 1.5–1.8(CH$_2$–C(CH$_3$)), 2.5–3.4 (glycidyl ring protons), 3.8–4.3 (COOCH$_2$); FT-IR (KBr,cm^{-1}): 2941, 3000 (C-H,aliphatic), 1730 (C=O), 1174 (C–O), 846–1000 (C–O, epoxide ring).

Synthesis of the modified copolymers (I_{Tsi}) by the coupling reaction between the epoxy groups of (I) with TsiLi: The coupling reaction was carried out with vigorous magnetic stirring, at –5 °C, for 1 h. A solution of TsiLi (20 mmol) in THF (30 ml) was prepared in a 100 ml two-necked flask equipped with a dropping funnel, argon atmosphere and magnetic stirring. A solution of polymer **I** (0.5 g), in THF (30 ml) was transferred into a dropping funnel under argon. Then copolymer was added dropwise with stirring to a solution of TsiLi into the flask at –5 °C. Even though this coupling reaction is very rapid, it was still allowed to last 1 h in order to ensure complete conversion. Then, the reaction was quenched by adding a small amount of methanol, and the reaction mixture was poured into methanol to precipitate the polymer. The reaction mixture was kept at 0 °C for 24 h.The polymer was reprecipitated by pouring again its THF solution into methanol, and finally it was vacuum-dried overnight. The yield of modified copolymer is given in Table 2. ^{1}H NMR (CDCl$_3$, ppm): 0.1 (SiMe$_3$), 1.2–1.8 (CH$_2$–C(CH$_3$) and CH$_2$–Tsi), 3.8–4.2 (COOCH$_2$ and OH); FT-IR (KBr, cm^{-1}): 3200–3700 (O-H), 2900–3000 (C–H,aliphatic), 1730 (C=O), 1256, 835 (C–Si), 1155 (C-O).

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