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Ring opening reactions of glycidyl methacrylate copolymers to introduce bulky organosilicon side chain substituents

Kazem D. Safa, Mohammad H. Nasirtabrizi

Faculty of Chemistry, Tabriz University, 51664 Tabriz, Iran

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Summary

Glycidyl methacrylate (GMA) random copolymers with methyl acrylate (MA), ethyl acrylate (EA), n-butyl acrylate (BA), methyl methacrylate (MMA), ethyl methacrylate (EMA) and n-butyl methacrylate (BMA) were synthesized by solution free radical polymerizations, at 70 ± 1°C using α, α'-azobis(isobutyronitrile) as an initiator to give the copolymers I – VI in good yields. The copolymer compositions were obtained using related ^{1}H NMR spectra and the polydispersity indices of the copolymers determined using gel permeation chromatography (GPC). Tris(trimethylsilyl)methyl (Tsi=trisyl) groups were then covalently attached to the obtained copolymers as side chains by ring opening reaction between excess of TsiLi and expoxide groups of GMA units to give the copolymers I_{Tsi} – VI_{Tsi} in good yields. In the coupling reaction, the TsiLi reacted selectively with the epoxy groups of the backbone polymer rather than with the carbonyl groups of the backbone. This method of preparing functionalized silanes is limited by the readiness with which TsiLi abstracts a proton, if one is available, rather than attacks at carbon. In addition in the reaction with epoxides, the product alkoxide can transfer a silyl group from carbon to oxygen or ring opening polymerization. However these were shown not to occur at the conditions of interest here. The epoxy group possesses a higher reactivity for the TsiLi than the ester and chloromethyl groups. The ring opening reaction between the epoxy group and the TsiLi is simple and fast. All the resulted polymers were characterized by FT-IR and ^{1}H NMR spectroscopic techniques. The glass transition temperature (Tg) of all copolymers was determined by differential scanning calorimetry (DSC) apparatus. All the polymers containing trisyl groups showed a high glass transition temperature in comparison with unmodified copolymers (I – VI). Attaching the tris(trimethylsilyl)methyl group to macromolecular chain should lead to important modifications of polymer properties such as gas permeability and perm selectivity parameters.

Introduction

In recent years, polymers based on 2,3-Epoxypropyl methacrylate (glycidyl methacrylate) have received increasing attention. The interest in these polymers is largely due to the ability of pendent epoxide groups to enter into a large number of chemical reactions, thus offering the opportunity for chemical modification of the parent polymer for various applications. For instance, copolymers based on glycidyl methacrylate have been used for binding enzymes and other biologically active species [1], and in electronic applications as negative electron-beam resists [2]. The high reactivity of the epoxide group is primarily due to the considerable strain in the three-membered ring. The copolymers of glycidyl methacrylate can be prepared by a variety of methods. Generally, a free radical initiator is needed to induce polymerization reaction. A large number of free radical initiators (i.e.organic peroxides or azo-catalysts) are known in the literature. The polymerization is preferably carried out in solution using a solvent in which the glycidyl methacrylate polymer is soluble. It is confirmed that GMA undergoes radical polymerization exclusively on its methacrylic double bond, the oxirane function remaining unaffected [3,4]. In recent years, incorporation of various organosilyl groups with different steric hindrance into polymer structures has been utilized to modify the polymer properties such as thermal stability, weather resistance, mechanical, thermal and surface properties [5-8]. For example it is known that the polymers containing trimethylsilyl derivatives have excellent gas permeability [9]. The preparation of polymers containing very bulky organosilyl groups with studying of their properties is a novel research field. The tris(trimethylsilyl)methyl group, {$(Me_3Si)_3C$-} denoted in this paper by trisyl or Tsi in which three organosilyl substituents are bound to the central carbon atom has been used to synthesize highly sterically hindered compounds of a range of elements, many of which possesses unique structures due to their steric bulk and thus a stabilizing effect, allowed for a deeper knowledge of new processes and new stable structures in the field of organomethallic chemistry [10, 11]. The much greater steric protection exerted by trisyl and related substituents,compared to that of other groups sufficiently limits reactivity of organomethallic and organosilicon systems.There are few studies about the attaching trisyl group to polymers. For the first time, Kowalewska et al [12] described synthesis trisyl-modified macromolecular systems: polysiloxanes and polystyrene-co-chloromethylenestyrene. Recently, we report the synthesis and properties of polymers modified with trisyl groups [13-17]. In this work we report the synthesis, characterization and thermal behaviour of methacrylic and acrylic copolymers of GMA without and within very bulky trisyl groups. Attaching the tris(trimethylsilyl)methyl group to macromolecular chain should lead to important modifications of polymer properties such as potential membrane materials in separation processes [12, 18].

Experimental

Reaction involving lithium, organolithium reagents and polymerization were carried out under dry argon to exclude oxygen and moisture from the reaction systems. Synthesis of a 3, 3, 3-tris (trimethylsilyl) propane- 1- ol and TsiLi have been described in [17].

Materials

Chloroform (Merck) and diethylether (Merck) were dried by standard methods. THF (Merck) was refluxed over sodium and distilled prior to use. Me_3SiCl (Merck), MeI (Merck), Li (Merck) and ethylene oxide (Fluka) were used as received. Glycidyl methacrylate (Merck), methyl acrylate (Merck), ethyl acrylate (Merck), n-butyl acrylate (Merck), methyl methacrylate (Merck), ethyl methacrylate (Merck) and n-butyl methacrylate (Merck) were distilled to remove inhibitors before use. Initiator of α, α'-azobis(isobutyronitrile) (Merck) was purified by crystallization from methanol.

Instruments

Infrared spectra were recorded with a 4600 Unicam FT –IR spectrometer as KBr pellets. ^{1}H NMR spectra were run on a Brucker 400 MHz spectrometer at room temperature using $CDCl_3$ as a solvent. The molecular weights (M_w and M_n) were determined using a Waters 501 gel permeation chromatograph fitted with 10^2 and 10^3 nm Waters styragel columns. THF was used as an elution solvent at a flow rate of 1ml/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 midpoints of the heat flow changes.

Copolymerization of glycidyl methacrylate (GMA) with different monomers (I-VI): general procedure

Poly (GMA-*co*-MA) (I), Poly (GMA-*co*-EA) (II), Poly (GMA-*co*-BA) (III), Poly (GMA-*co*-MMA) (IV), Poly (GMA-*co*-EMA) (V), Poly (GMA-*co*-BMA) (VI) were synthesized as follows. In a pyrex polymerization tube, a mixture of 2.84 g (20 mmol) of (GMA), 0.065 g (0.4 mmol) of AIBN were dissolved in 15 ml of tetrahydrofuran. Then 1.72 g (20 mmol) of MA or 2 g (20 mmol) of EA or 2.56 g (20 mmol) of BA or 2 g (20 mmol) of MMA or 2.28 g (20 mmol) of EMA or 2.84 g (20 mmol) of BMA was added to the tube and the mixture was flushed with argon for 20 min. Each tube was sealed under vacuum and immersed in a thermostated water bath maintained at 70±1°C and shaken by a shaker machine for about 24h. The viscous solution was poured from the ampoule into 150 ml of cooled methanol. The precipitate was collected and washed with methanol for several times and dried under vacuum at room temperature for 24 h (Scheme1).The yield of copolymers is presented in Table 1.

Synthesis of the modified copolymers (I_{Tsi}-VI_{Tsi}) by the coupling reaction between the epoxy groups of (I- VI) with TsiLi

The six polymers containing Tsi groups (I_{Tsi}-VI_{Tsi}) were, separately, prepared from the reaction between the polymers with excess TsiLi. A solution of TsiLi (20 mmol) in THF (30 ml) was prepared in a 100 ml of two – necked flask equipped with a dropping funnel, argon atmosphere and magnetic stirring. 0.5 g of each copolymer (I-VI) with (2.21, 2.23, 2.29, 2.10, 2.02 and 1.68 mmol of epoxide-cotaining monomer unit respectively) was dissolved in 30 ml THF and transferred into dropping funnel under argon. Then, each solution of 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 1h 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 24h. The polymer was reprecipiated by pouring again its THF solution into methanol, and finally it was vacuum – dried overnight. The yield of modified copolymers is given in Table 2.

Results and discussion

The monomer of GMA was copolymerized with other co-monomers at 70 ± 1°C in tetrahydrofuran solvent using AIBN as the free radical initiator.

Characterization of copolymers I – VI

Solubility

The resulted copolymers I – VI were soluble in toluene, xylene, dioxane, butanone and insoluble in n-hexane, octane and hydroxyl- group- containing solvents such as methanol, ethanol or water.

Molecular weights

The number and weight average molecular weights of synthesized copolymers (I – VI) were determined by gel permeation chromatography (GPC) and are presented in Table 1. A typically GPC chromatogram of the polymer v is shown in Fig.1a. Single (monomodal) and rather symmetrical curves show that the polymers are not contaminated by homopolymers. The values of M_w/M_n in GMA copolymerization is known to depend on chain termination in the same way as in homopolymerization [3]. After standing for a long period of time even at room temperature, all of GMA polymers (I-VI) changed to be insoluble in organic solvents, probably due to intermolecular crosslinking between epoxy units. Therefore, GMA polymer reactions should be carried out immediately after polymerization.

Infrared, ^1H NMR spectra and glass transition temperature

The asymmetrical and symmetrical stretching due to the methyl and methylene groups are observed at 2995, 2948 and 2892 cm^{-1}. The band at 1732 cm^{-1} is attributed to the ester carbonyl stretching of GMA and comonomer units. The asymmetrical and symmetrical bending vibrations of methyl groups are seen at 1453 and 1380 cm^{-1}, respectively. 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}.A typically FT-IR spectrum of the copolymer I is shown in (Fig.2a).

The ^1H NMR spectra of the copolymers (I – VI) show two signals at 4.33 and 3.75 ppm due to the splitting of methylene protons in the CH_2O- group attached to the carbonyl group of the GMA unit by the methyne proton of the epoxy group. The peak at 3.4 ppm is due to the methyne proton of epoxy group. The methylene protons of the epoxy group show signals at 2.50 and 2.88 ppm. The resonance signal at 4 ppm was attributed to two methylene protons of $–COOCH_2$ in copolymers II, III, V and VI and three methyl protons of $–COOCH_3$ in copolymers I, IV appeared at 3.59 ppm. The broad signal at 0.9-2.6 ppm was due to the methylene groups of backbone and other alkyl groups. 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 polymerization. A typically H NMR spectrum of the copolymer II is given in (Fig.3a).

The glass transition temperature (Tg) of the copolymers (I – VI) were determined by DSC and the data are given in (Table 1) [15,20] .Also T_g of homopolymer of GMA and T_g of homopolymer of second monomer (For comparison) are given in Table 1. The higher Tg value of the copolymers III - VI than Tg value of the copolymers I - III is due to the α-methyl groups, which facilitate chain entanglement.The presence of $-CH_3$ groups in III-VI, comes in the way of free rotation around C-C bond of the chain backbone and, hence, hinders the chain mobility, resulting in an increase in their Tg values.

Copolymer composition

We have used ^{1}H NMR to determine copolymer compositions. The assignment of the resonance peaks in the ^{1}H NMR spectra lead to the accurate evaluation of the content of each kind of monomeric unit incorporated into the copolymer chains [3]. Thus, the mole fraction of GMA in the copolymers chain were calculated from measuring the integrated peak area of the three resonances of epoxide protons of the GMA unit and methoxyl or methylenoxyl protons of other monomer units. The following expression is used to determine the composition of copolymer (IV). Let m_1 be the mole fraction of GMA and $1 - m_1$ is that of MMA monomer. The proton resonances of the methoxyl group in MMA at 3.59 ppm and those of the epoxide group in GMA at 3.27, 2.88 and 2.70 ppm are clearly resolved. The GMA contains 3 epoxide protons and MMA contain 3 methoxyl protons:

$$A = \frac{\text{Integrated peak area of } 2.7-3.27}{\text{Integrated peak area of } 3.59}$$

$$A = \frac{3m_1}{3(1-m_1)} \qquad (1)$$

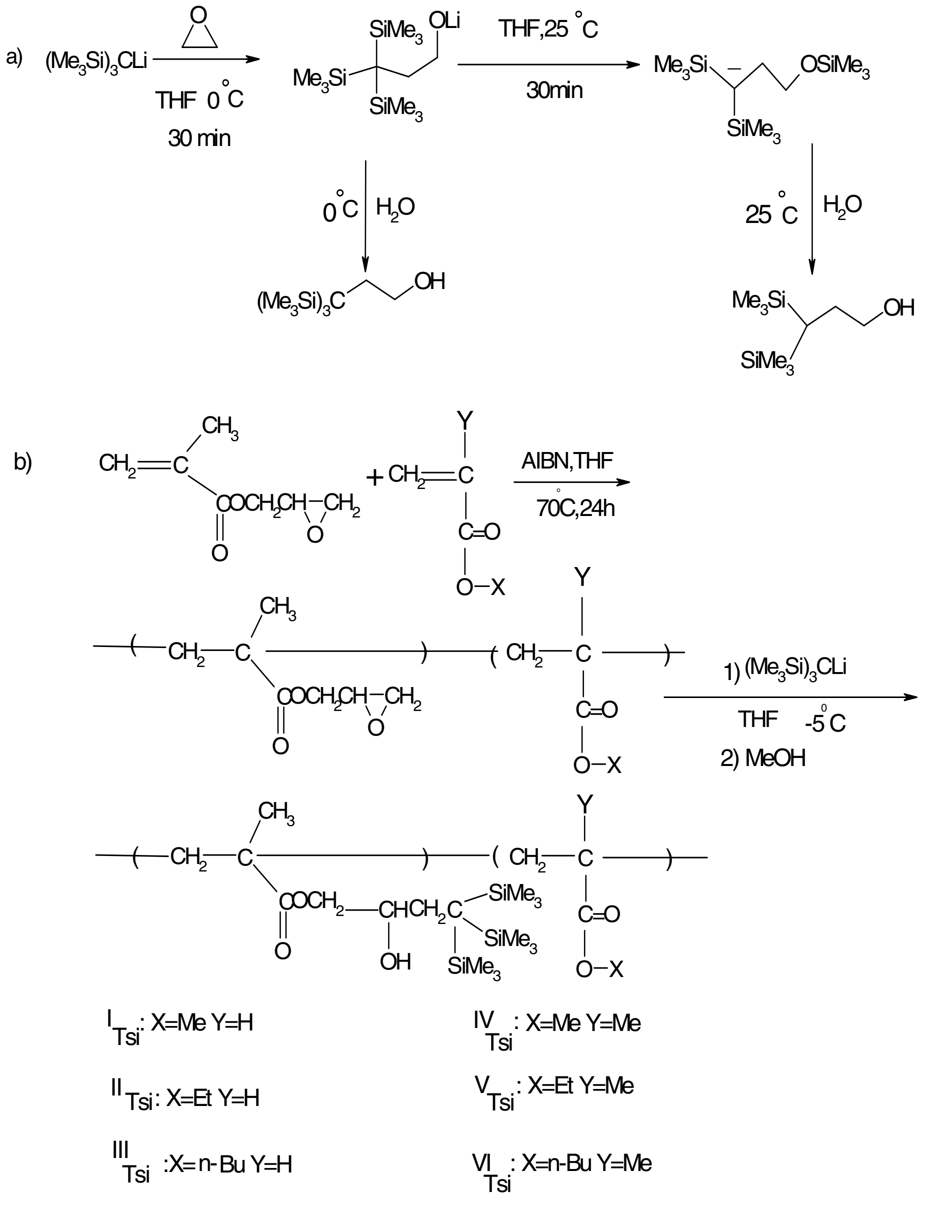
This on simplification gives:

$$m_1 = \frac{A}{1+A} \qquad (2)$$

Therefore, the mole fraction of GMA in copolymer (IV) was determined from Eq (2). A similar method was used to calculate of the mole compositions of the other copolymers. Table 1 gives the values of the corresponding mole fractions of GMA and related comonomer in the copolymers.

Synthesis of copolymers containing trisyl substituents (I_{Tsi} – VI_{Tsi})

We have modified well-known polymers by incorporation of very bulky $(Me_3Si)_3C$ groups (Scheme1). The trisyl groups were attached to the obtained copolymers as side chains by ring opening reaction between excess of TsiLi and expoxide groups of GMA units to give the copolymers I_{Tsi} – VI_{Tsi} in good yields. For the purpose of modifying polymers a starting material must fulfil two basic requirements, it must be sufficiently reactive to effect substitution on a polymer chain and it must be isolable in a good yield by a simple procedure. Tris(trimethylsilyl)methane readily undergoes metallation when treated with methyllithium in a mixture of tetrahydrofuran and diethyl ether and the tris(trimethylsilyl)methyllithium produced is markably stable in tetrahydrofuran. The ease of formation and the stability of the organolithium compound maybe associated with stabilization of the carbanion $(Me_3Si)_3$ C^- by delocalization of the lone pair of electrons in to the d-orbitals of silicon atom.



Scheme1. Synthetic routes for preparation of: (a) 3, 3, 3- tris(trimethylsilyl)propane-1-ol (b) substitution of trisyl groups at copolymers I-VI

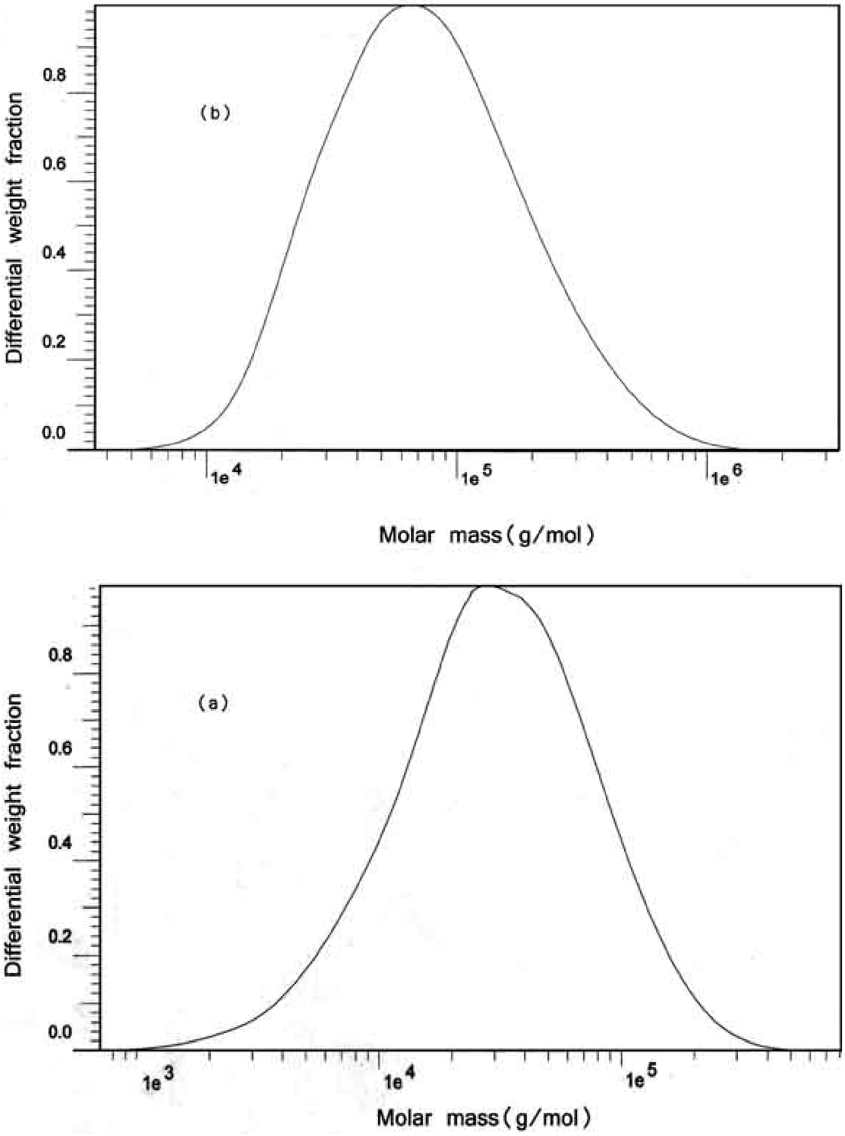


Fig.1. GPC chromatograms of polymer **V** (a) and of the corresponding modified polymer $\mathbf{V_{Tsi}}$ (b) obtained from SEC of polymers.

In previous works [13-16] we describe synthesis of trisylmethyl benzene as a model compound for evidence of attaching trisyl ligand to benzylic carbon [12]. Our next electrophile is ethylene oxide. Tris(trimethylsilyl)methyl lithium was shown to be sufficiently reactive towards ethylene oxide to give 3, 3, 3-tris (trimethylsilyl) propane- 1- ol in 90% yield at (0°C). Note that these ring opening reactions generate a alkoxide group which can potentially react with silicon atoms of trisyl groups (at 25°C), gave adifferent alcohol [19], which has one fewer silyl groups (Scheme1a.).

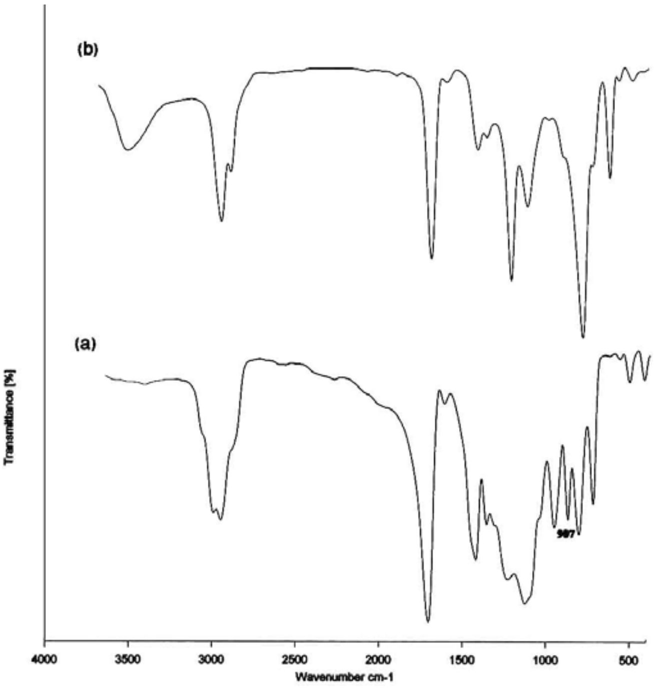


Fig.2. Infrared spectra of copolymers (a) **I** and (b) **I**$_{Tsi}$**.** The epoxy groups, 907 cm^{-1}, which are well defined in the unmodified (I) (a) modified with trisyl groups in I$_{Tsi}$ (b).

Table1. Compositions, molecular weights and (Tg) of polymers **(I-VI)**

Polymer	**I**	**II**	**III**	**IV**	**V**	**VI**
mol-% GMA	50.5	55	60	52	52	48
mol-% MA	49.5	-	-	-	-	-
mol-% EA	-	45	-	-	-	-
mol-% BA	-	-	40	-	-	-
mol-% MMA	-	-	-	48	-	-
mol-% EMA	-	-	-	-	48	-
mol-% BMA	-	-	-	-	-	52
M$_w$/10^3	42	59	73	18	44	59
M$_n$/10^3	18	26	37	11	18	24
M$_w$/ M$_n$	2.35	2.25	1.99	1.58	2.41	2.39
Yield (%)	61	71	66	75	69	73
Tg (ºC)^a	85	85	85	85	85	85
Tg (ºC)^b	-9	-22	-54	103	65	15
Tg (ºC)^c	25	50	22	100	80	60

[a] T$_g$ of homopolymer of GMA

[b] T$_g$ of homopolymer of second monomer

[c] T$_g$ of observed relating DSC curve

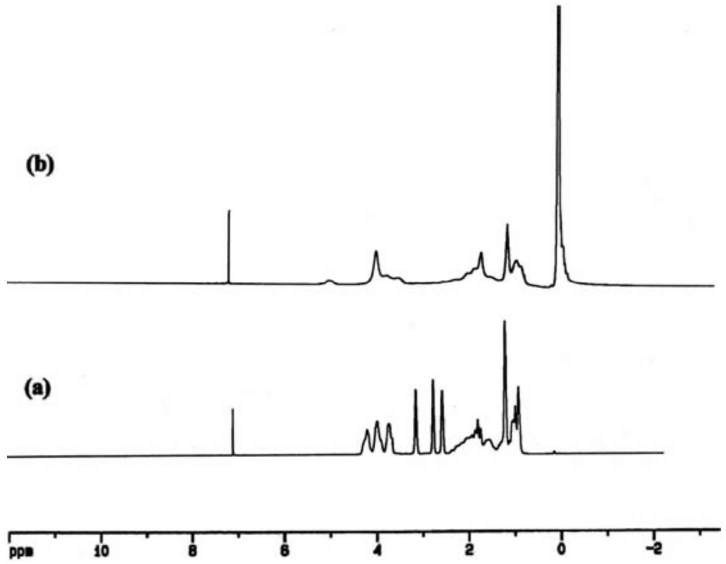


Fig.3. ^{1}H NMR spectra :(a) **II** and (b) **II$_{\mathbf{Tsi}}$** in $CDCl_3$ without tetramethylsilane. The epoxy groups ($\delta = 2.5 - 3.4\, ppm$), which are well defined in the unmodified copolymer (a) disappear after modification (**b**). Also, a new signal related to 27 methyl protons of $C\,[Si(CH_3)_3]_3$ appears at 0.12 ppm.

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 (^{1}H NMR observations) [19]. The epoxy group in polymers 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 (^{1}H NMR observations) it was still allowed to last 60 min in order to ensure a complete conversion. These ring opening reactions generate alkoxide group which can potentially react with another epoxide ring (ring opening polymerization) and silicon atoms of trisyl groups to ease cross linking, however, these were shown not to occur at the conditions of interest here. After the workup the modified polymers are quite stable. In this process the alkoxy groups are converted to hydroxyl groups.One of the main problems found in polymer functionalization with large groups is the neighboring effect, which limits the conversion and rate of modification through steric hindrance, promoted by the already grafted moieties [21]. GMA copolymers were synthesized in order to separate the GMA monomers from each other along the chain. 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 [14]. The high reactivity of the epoxide group in GMA copolymers is primarily due to the considerable strain in the three-membered ring. The reactivity of the ring is also affected by its position, by the presence of other polar groups and bulky substituents in the molecule, by the type of solvent used for preparation, and by temperature. The solvent chosen for the attachment of the trisyl groups via ring-opening of the epoxide groups was THF. This was selected because of good compatibility with GMA copolymers and high solubility of the TsiLi in this solvent and to avoid side-reactions such as hydrolytic opening of the epoxide groups.

Coupling Position

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. The reaction of TsiLi with esters give the aldehyde and vinyl ether [22]. For this reason, it was necessary to identify the positions where the coupling reaction took place. A THF solution of poly (MMA) was prepared by the radical homopolymerization 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 Tsi^-Li^+ solution and the stirring was continued for 1 h at –5°C. The red color of the Tsi^-Li^+ 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 Tsi^-Li^+. Consequently, only the epoxide of GMA units has acted as coupling sites. The epoxy group possesses a higher reactivity for the Tsi^-Li^+ than the ester groups in polymers.

Characterization of copolymers I_{Tsi} - VI_{Tsi}

The yields of modified polymers are low because some of unmodified polymer have been cross linked during time (probably due to intermolecular cross linking between epoxy units) and therefore did not participate in the reaction (Table 2).

Solubility

The copolymers I_{Tsi} - VI_{Tsi} were soluble in the same solvents that copolymers I – VI are dissolved.

Infrared, ^1H NMR spectra and glass transition temperature

A typically FT-IR spectrum of the copolymer I_{Tsi} is shown in (Fig.3b). (Fig.3) shows the IR spectra of copolymers after modification in comparison with the spectra of the original polymer (I, I_{TSi}). A decrease in the epoxide absorbances at 907 cm^{-1} is clearly visible. At the same time, new absorption bands at 900 and 1250 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.

(Fig.4b) presents the ^1H NMR spectrum of the copolymer (II) after modification (II_{TSi}). The present analysis will focus only on the GMA hydrogens next to the oxirane group. Addition of trisyl to copolymers leads to a large decrease in the intensity of the peaks oxirane groups. Also, a new signal related to 27 methyl protons of $C[Si(CH_3)_3]_3$ appears at 0.12 ppm. The other chemical shift assignments for copolymers I_{Tsi} – VI_{Tsi} are the same observed chemical shifts for copolymers I – VI. 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 groups.

The GPC peaks corresponding to unmodified polymers disappeared completely and a new single peak due to formation of the modified polymers emerged (Fig.2b). Study of these DSC curves clearly showed that incorporating of trisyl substituent in copolymer side chains as well as hydroxyl groups (leading to intermolecular hydrogen bonding) increases the chain rigidity of polymer(Table 1 and 2). The introduction of trisyl groups is believed to strongly alter the shape of the polymer chain and to cause less entanglements of the polymer backbone due to steric hindrance.The chemical modifications of GMA copolymers have been shown to significantly alter physical properties such as glass transition temperatures (Tg). Consequently, the incorporation of the tris(trimethylsilyl)methyl group into polymer structure creates macromolecules of novel architecture with potential use as membranes for fluid separation.

Table 2. The results of reaction between 0.5g of each polymer **(I-VI)** with TsiLi

Modified polymer	Weight (g)	Yield (%)	T_g (ºC)
$\mathbf{I}_{\mathbf{Tsi}}$	0.65	64	163
$\mathbf{II}_{\mathbf{Tsi}}$	0.63	64	140
$\mathbf{III}_{\mathbf{Tsi}}$	0.64	64	129
$\mathbf{IV}_{\mathbf{Tsi}}$	0.70	70	150
$\mathbf{V}_{\mathbf{Tsi}}$	0.67	69	150
$\mathbf{VI}_{\mathbf{Tsi}}$	0.68	76.5	125

Conclusions

We have detailed the preparation and characterization of novel GMA copolymers bearing trisyl groups of side chain substituents. The work described in this paper deals with the nucleophilic ring-opening of epoxides by the Tsi^-Li^+. The copolymers of GMA with different methacrylic and acrylic monomers were synthesized by free radical solution polymerization and the copolymer composition calculated by corresponding ^1H NMR analysis. Then the very bulky trisyl groups were covalently linked to the obtained copolymers in high yields bearing opening reaction of the pendant oxirane moiety with the Tsi groups. The results indicate that, in the presence of both an epoxy and carbonyl groups, the TsiLi as a nucleophilic reagent selectively reacts with the former but not with the latter. Compared to the previous coupling methods for the preparation of modified copolymers of chloromethyl styrene, the present method is simple, the coupling reaction is fast and pure copolymers are produced. The epoxy group possesses a higher reactivity for the TsiLi than the ester and chloromethyl groups. No other side reactions were observed during the modification process. Comparison of the ^1H NMR and IR spectra of copolymers before and after modification showed disappearance of the peaks assigned to the epoxy ring and appearance of a new peaks characteristic of trisyl moieties, proving thus the modification of GMA copolymers. Additionally the DSC scans show that the presence of bulky Tsi groups lead to an increase in the glass transition temperature (Tg). Because entering the trisyl groups in polymer side chain, decrease the free volume between polymer chains. The presence of the trisyl groups into polymer structures increases the rigidity of macromolecules and creates the modified polymers with novel properties and applications. For example modified polymer can be used as separation membranes.

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