

Polymerization of 3-Glycidyloxypropyltrimethoxysilane with Different Catalysts

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ABSTRACT: Polymerization reactions of 3-glycidyloxypropyltrimethoxysilane (GPTS) were carried out by different catalysts, potassium hydroxide, potassium *tert*-butoxide, and tetraphenylporphyrin aluminum chloride (TPP–AlCl), and tetrafluorophthalate zirconium isopropoxide complex. Polymer samples obtained from the ring-opening polymerization of GPTS were characterized by

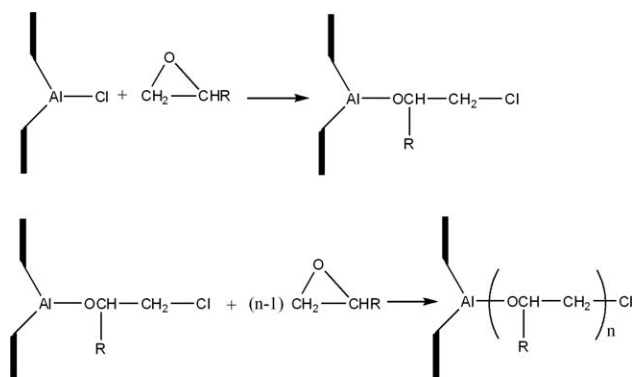
Fourier transform infrared spectroscopy, NMR spectroscopy, electrospray ionization mass spectroscopy, and gel permeation chromatography. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3527–3534, 2012

Key words: NMR; polymer synthesis and characterization; ring-opening polymerization

INTRODUCTION

Numerous interests have been devoted to the ring-opening polymerization of epoxide monomers to form polymeric and oligomeric polyether polyols, which are used for the production of detergents, nonionic surfactants, washing agents, and polyurethane production process.^{1,2}

Particularly, propylene oxide (PO) and styrene oxide of cyclic ethers have been polymerized either by cationic catalysts or anionic catalysts, and also, more selective catalyst systems and their products have been elucidated by different spectroscopic techniques.^{3–8} Inoue⁷ and Chisholm et al.⁸ suggested that the polymerization of PO initiated with porphyrin aluminum chloro complex proceeded as follows, with the alkoxide complex as the growing species:



3-Glycidyloxypropyltrimethoxysilane (GPTS) is one of the most commonly used precursors for the

preparation of inorganic–organic hybrid polymers, which are used, for example, for hard coatings of organic polymers, contact lens materials in the optical industry, electronics, membranes, sensors, nanoimprinting, wave guides, and biology.^{9–12}

So far, a lack of knowledge has existed concerning the effect of different catalysts on the epoxide ring opening and polymerization degree of GPTS in polymerization reactions.

It is interesting to see whether the side silyl group of oxirane will affect the regioselectivity and stereoselectivity of polymerization when compared with the methyl group in PO.

The first purpose of this study was to synthesize and characterize polymers of GPTS prepared with different catalysts. The second purpose was to prepare and use a new catalyst in the ring-opening polymerization of GPTS.

EXPERIMENTAL

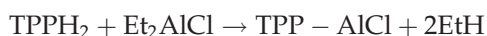
All syntheses and solvent manipulations were carried out under a nitrogen atmosphere with standard Schlenk-line and dry-box techniques. Solvents were dried in the standard procedures. 5,10,15,20-Tetra-phenylporphyrin (Acros, Ohio, USA), diethyl aluminum chloride (Et₂AlCl; 1.0M solution in hexane, Aldrich), GPTS (97%, Alfa Aesar), potassium hydroxide reagent (American Chemical Society (ACS) reagent), assay 85% minimum, GFS Chemicals), potassium *tert*-butoxide (97%, Alfa Aesar), zirconium(IV) isopropoxide isopropyl alcohol complex (99.9%, Aldrich), and tetrafluorophthalic acid (TFPA; 98%, Alfa Aesar) were used as received.

¹H-NMR, ¹³C{¹H}-NMR, and ²⁹Si-NMR experiments were carried out with a Bruker DPX-400,

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Ohio, USA (5-mm quaternary nuclei probe) and a Bruker Avance DRX-500 (5-mm broad band probe) spectrometers, respectively. The DPX-400 NMR operated at a proton Larmor frequency of 400 MHz and a carbon frequency of 100 MHz. The GPTS polymers were analyzed by a Bruker time-of-flight mass spectrometer (MicroTOF) [electrospray ionization (ESI)] mass spectrometry (MS) instrument. Samples were prepared in methanol solvent and infused into the electrospray source at a rate of 5–10 mL/min. Gel permeation chromatography (GPC) analysis was performed at 30°C on a Shimadzu Prominence GPC system equipped with a RID-10A refractive-index detector, an LC-20AD solvent-delivery unit, a CTO-10AS column oven, and a set of two columns, PSS SDV 5- μ L 1000 Å and PSS SDV 5- μ L 50 Å. Tetrahydrofuran (THF; high performance liquid chromatography (HPLC) grade) was used as the mobile phase at 1.0 mL/min. The sample concentration was 2 mg/1 mL, and the injection volume was 10 μ L. The calibration curve was made with seven polystyrene standards covering the molecular weight range from 162 to 34,300 Da. The glass-transition temperature (T_g) values of the GPTS polymers were determined with a PerkinElmer DSC 4000. The cooling rate was 5°C/min.

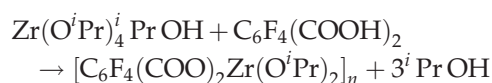
Preparation of the tetraphenylporphyrin aluminum chloride (TPP–AlCl) complex



where TPPH₂ is tetraphenylporphyrin. TPP–AlCl was prepared according to the literature.^{13,14} A solution of Et₂AlCl (1.0M solution in hexane, 1.8 mL, 1.8 mmol) was added to a solution of TPPH₂ (1.0 g, 1.6 mmol) in 30 mL of dichloromethane. The addition was done slowly at room temperature (RT). The resulting solution was left stirring for 3 h, after which the volatile fractions were removed *in vacuo* to give a purple powder.

¹³C{¹H}-NMR (CDCl₃, δ , ppm): 120.73, 126.95, 128.06, 132.39, 134.23, 141.14, 148.51 (for aromatic carbons).

Preparation of [C₆F₄(COO)₂Zr(O^{*i*}Pr)₂]_{*n*}



TTPA (0.01 mol, 2.43 g) was added to 0.01 mol (3.88 g) of zirconium(IV) isopropoxide isopropyl alcohol complex in 30 mL of isopropoxide (or THF). The reaction mixture was stirred for 4 h at RT. Then, the solvent and liberated isopropoxide were removed from the white solid product under low pressure by a vacuum pump. The product was washed again with solvent isopropoxide (or THF) and dried *in vacuo*.

TABLE I
Conversion of the Monomer (GPTS) to Polymers (with KOH Catalyst)

Time (h)	Temperature	Conversion (%)
48	RT	35
60	RT	50
24	40°C, with stirring	95
24	75°C, with stirring	100

MS [ESI, weight-average molecular weight (M_w) = 1864.98 for C₅₉H₆₄F₁₆O₂₅Zr₄Na⁺ = MNa⁺]: 1864.7 (MNa⁺). ¹H-NMR (25°C, CDCl₃, ppm, δ): 1.23 [doublet (*d*), gem-dimethyl (gem-Me₂) of O^{*i*}Pr], 4.05 (septet (septet), CH of O^{*i*}Pr). ¹³C-NMR (dimethyl sulfoxide, ppm): 163.10 (COO), 143.51 (*d*, coupling constant between carbon and fluorine (¹J_{CF}) = 241.5 Hz, CF, C3, C6 of C₆F₄), 139.67 (*d*, ¹J_{CF} = 254.6 Hz, CF, C4, C5 of C₆F₄), 122.26 (C1, C2 of C₆F₄), 72.52 (OCH), 25.76, 25.51 (gem-Me₂ of O^{*i*}Pr). Fourier transform infrared (FTIR) spectroscopy (KBr, cm⁻¹): 1600 (strong, asymmetric vibration (ν_{as}) CO₂), 1522, 1478, 1430 (strong, symmetric vibration (ν_{s}) CO₂), 1348, 1282, 1130 (terminal O^{*i*}Pr), 1086, 965, 846, 813, 791, 756.

Polymerization of GPTS with KOH

The catalyst (25 mg, KOH) was placed in a vial, and 1.2 mL of GPTS was added under nitrogen in a dry box. The mixture was stirred at various temperatures and times, as indicated in Table I. The conversion of monomer to polymer was followed by ¹H-NMR spectroscopy. The following data belong to the stirring at 40°C for 24 h.

¹H-NMR (CDCl₃, ppm, δ): 4.28 (CH, broad (br)), 3.71–3.17 (CH, CH₃O, CH₂, 2CH₂O, br), 1.74 (CH₂, br, CH₂CH₂CH₂), 0.76–0.70 (CH₂–Si, br). ¹³C-NMR [carbon distortionless enhancement by polarization transfer (¹³C-DEPT), C₆D₆, ppm, δ): for the CH region: 78.77–78.64 (CH, dyad, isotactic (*i*)/syndiotactic (*s*)), 71.75 (CH, singlet), 70.94–70.82 (CH, dyad, *i/s*), 58.65, 58.49, 58.40 (CH); for the CH₂ region: 74.54–74.49–74.44 (CH₂, triad, *i/is-si/s*), 73.75 (CH₂, singlet, *i*); other signals: 73.44, 73.23, 72.92 (CH₂, OCH₂CH₂), 72.81, 72.46 (CH₂, singlet, ring-CH₂–O–), 49.95, 49.87 (CH₃O), 23.94, 23.15 (CH₂, CH₂–CH₂–CH₂), 7.39, 6.32, 5.43 (CH₂–Si; Fig. 1). ²⁹Si-NMR (C₆D₆, ppm, δ): –42.0 (T° , standard, GPTS, monomer), –44.1 (trifunctional silan with no condensation (T°), polymer 1, 60%), –44.9 (T° , polymer 2, 40%).

Polymerization of GPTS with *t*-BuOK

The catalyst (30 mg, potassium *tert*-butoxide (*t*-BuOK)) was placed in a vial, and 1.2 mL of GPTS



Figure 1 ^{13}C -DEPT spectrum of polymers of GPTS obtained from polymerization with KOH at 40°C . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

was added under nitrogen in a dry box. The mixture was stirred at two different temperatures for 24 h. The conversion of monomer (GPTS) to polymers was 60% for stirring at RT and 100% for stirring at 75°C . The following data belong to the stirring at 75°C for 24 h.

^1H -NMR (CDCl_3 , ppm, δ): 4.28 (CH, br), 3.74–3.2 (CH, CH_3O , CH_2 , $2\text{CH}_2\text{O}$, broad (brs)), 1.75 (CH_2 , br, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.72–0.70 (CH_2 -Si, br). ^{13}C -NMR

(C_6D_6 , ppm, δ): for the CH region: 79.19–79.06 (CH, dyad, s/i), 78.81–78.68 (CH, dyad, s/i), 71.77–71.69 (CH, dyad, s/i), 70.96–70.86 (CH, dyad, i/s), 58.66, 58.51, 58.42 (CH); for the CH_2 region: 74.54 (CH_2 , broad singlet), 73.78 (CH_2 , singlet), 72.00–71.94 (CH_2 , dyad, s/i); other signals: 73.47, 73.27, 72.98 (CH_2 , OCH_2CH_2), 72.86, 72.49 (CH_2 , ring- CH_2 -O-), 49.99, 49.89, 49.72 (CH_3O), 23.96, 23.11 (CH_2 , CH_2 - CH_2 - CH_2), 7.51–7.33, 6.39, 5.49 (CH_2 -Si; Fig. 2). ^{29}Si -NMR (C_6D_6 , ppm, δ): -42.05 (T° , standard, GPTS, monomer), -44.15 (T° , polymer 1, ca., 55%), -44.9 (T° , polymer 2, ca., 45%).

Polymerization of GPTS with TPP-AlCl

The catalyst (100 mg, TPP-AlCl) was placed in a vial, and 1.2 mL of GPTS was added under nitrogen in a dry box. The mixture was stirred at RT for 60 h.

MicroTOF MS, m/z : 1912.8 ($\text{C}_{72}\text{H}_{160}\text{NaO}_{40}\text{Si}_8$), 1676.7 ($\text{C}_{63}\text{H}_{140}\text{NaO}_{35}\text{Si}_7$), 1439.6 ($\text{C}_{54}\text{H}_{120}\text{NaO}_{30}\text{Si}_6$), 1203.5 ($\text{C}_{45}\text{H}_{100}\text{NaO}_{25}\text{Si}_5$), 967.4 ($\text{C}_{36}\text{H}_{80}\text{NaO}_{20}\text{Si}_4$), 731.3 ($\text{C}_{27}\text{H}_{60}\text{NaO}_{15}\text{Si}_3$). ^1H -NMR (C_6D_6 , ppm, δ): 4.17 (CH, br), 3.8–3.3 (CH_3O , CH_2 , CH_2O , brs), 3.22 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 1.67 (CH_2 , br, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.65 (CH_2 -Si, br; Fig. 3). ^{13}C -NMR (C_6D_6 , ppm, δ): for the CH region: 79.13–78.98 (CH, dyad, s/i), 78.89–78.74 (CH, dyad, s/i), 71.81 (CH, singlet), 71.04 (CH, dyad, i/s), 58.70, 58.47 (CH, singlet); for the CH_2 region: 74.64–74.58 (CH_2 , dyad, i/s), 73.80 (CH_2 , singlet); other signals: 73.57, 73.34 (CH_2 , singlet, from O- CH_2 - CH_2 -), 72.86, 72.55 (CH_2 , singlet, from ring- CH_2 -O), 50.08, 49.98 (CH_3O), 24.0, 23.18 (CH_2 from $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.48, 6.46, 5.55 (CH_2 -Si). ^{29}Si -NMR (C_6D_6 , ppm, δ): -42.05 (T° , standard, GPTS, monomer), -44.1 (T° , polymer 1, higher intensity, 82%), -46 (T° , polymer 2, small intensity, 18%).

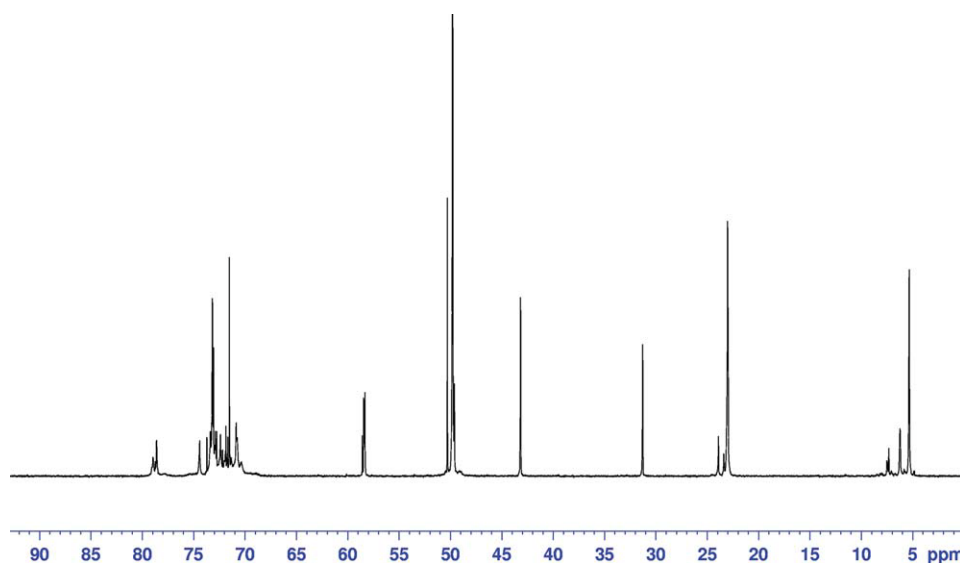


Figure 2 ^{13}C -NMR spectrum of polymers of GPTS obtained from polymerization with potassium tert-butoxide (KO^tBu) at RT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

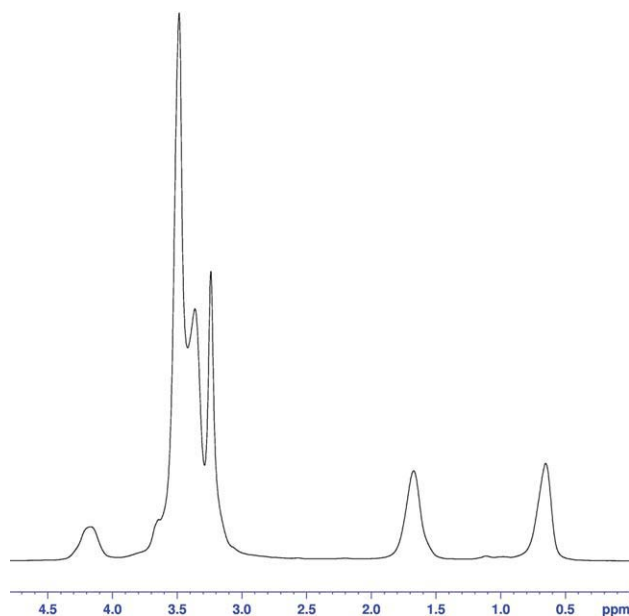


Figure 3 ^1H -NMR spectrum of polymers of GPTS obtained from polymerization with TPP-AlCl at RT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymerization of GPTS with $\text{C}_6\text{F}_4(\text{COO})_2\text{Zr}(\text{O}^i\text{Pr})_2$

The catalyst [80 mg, $\text{C}_6\text{F}_4(\text{COO})_2\text{Zr}(\text{O}^i\text{Pr})_2$] was placed in a vial, and 1.5 mL of GPTS was added under nitrogen in a dry box. The mixture was stirred at two different temperatures, 60 and 75°C, for 48 h.

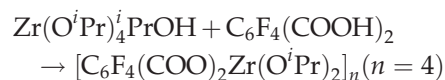
^{13}C -NMR data for polymers prepared at 60°C (C_6D_6 , ppm, δ): for the CH region: 80.95 (CH, singlet, i), 71.02 (CH, singlet, i), 58.44 (CH, singlet); for the CH_2 region: 74.56, 73.54 (CH_2 , singlet, i); other signals: 73.32 (CH_2 from $\text{O}-\text{CH}_2-\text{CH}_2-$), 72.52 (CH_2 , from ring- CH_2-O), 50.00 (CH_3O), 23.23 (CH_2 , from $\text{CH}_2\text{CH}_2\text{CH}_2$), 6.39 (CH_2-Si).

Data for polymers prepared at 75°C. MicroTOF MS, m/z : 1675.7 ($\text{C}_{63}\text{H}_{140}\text{NaO}_{35}\text{Si}_7$), 1441.6 ($\text{C}_{54}\text{H}_{120}\text{NaO}_{30}\text{Si}_6$), 1203.5 ($\text{C}_{45}\text{H}_{100}\text{NaO}_{25}\text{Si}_5$), 967.4 ($\text{C}_{36}\text{H}_{80}\text{NaO}_{20}\text{Si}_4$), 731.3 ($\text{C}_{27}\text{H}_{60}\text{NaO}_{15}\text{Si}_3$). ^1H -NMR (CDCl_3 , ppm, δ): 4.17 (CH, br), 3.51–3.23 (CH_3O , CH_2 , $2\text{CH}_2\text{O}$, bars), 1.67 (CH_2 , br, $\text{CH}_2\text{CH}_2\text{CH}_2$), 0.66 (CH_2-Si , br). ^{13}C -NMR (C_6D_6 , ppm, δ): for the CH region: 80.93 (CH, singlet, i), 71.80 (CH, singlet, i), 71.01 (CH, singlet, i), 58.42 (CH); for the CH_2 region: 74.59–74.54 (CH_2 , dyad, i/s), 73.79 (CH_2 , singlet, i); other signals: 73.53, 73.38, 73.31 (CH_2 , from $\text{O}-\text{CH}_2-\text{CH}_2-$), 72.52, 72.84 (CH_2 , from ring- CH_2-O), 49.99 (CH_3O), 23.24 (CH_2 , from $\text{CH}_2\text{CH}_2\text{CH}_2$), 7.44, 6.38 (CH_2-Si ; the monomer GPTS peaks also appeared in the ^{13}C -NMR spectrum). ^{29}Si -NMR (C_6D_6 , ppm, δ): -42.05 (T° , standard, GPTS, monomer), -44.1 (T° , polymer 1, higher intensity, 90%), -44.9 (T° , polymer 2, small intensity, 10%; Fig. 4).

RESULTS AND DISCUSSION

Reaction of $\text{Zr}(\text{O}^i\text{Pr})_4$

$^i\text{PrOH}$ with tetrafluorophthalic acid in a 1 : 1 molar ratio in isopropoxide (or THF) at RT gave the product of $\text{C}_6\text{F}_4(\text{COO})_2\text{Zr}(\text{O}^i\text{Pr})_2$ in accordance with the following reaction:



The tetramer structure was deduced from MS measurement of the complex. In the FTIR spectrum of the tetrafluorophthalate-Zr(IV) complex, the bands indicated presence of both bridging bidentate and chelating carboxylic groups. The FTIR spectrum of free TFPA exhibited intense bands at 1732–1720, 1636, and 1424 cm^{-1} , which corresponded to asymmetrical and symmetrical stretching vibrations of the carboxyl groups. After coordination of tetrafluorophthalate to zirconium isopropoxide, the bands at high wave numbers shifted to low wave numbers to 1600, 1522, 1478, and 1430 cm^{-1} . The carboxyl bands appeared at 1600 cm^{-1} for $\nu\text{COO}_{\text{asym}}$ and 1430 cm^{-1} for $\nu\text{COO}_{\text{sym}}$. The frequency difference of 170 cm^{-1} indicated the presence of chelate bond formation. The absorption at 1130 cm^{-1} was attributed to the terminal isopropoxyl groups.¹⁵ All of these values were consistent with those detected in a number of carboxylate-zirconium(IV) derivatives.^{15,16} The ^1H -NMR spectra of the tetrafluorophthalate-zirconium complex $\text{C}_6\text{F}_4(\text{COO})_2\text{Zr}(\text{O}^i\text{Pr})_2$ showed the expected peaks and peak multiplicities. Its ^1H -NMR spectrum showed doublets at 1.23 ppm due to gem- Me_2 protons and a septet at 4.05 ppm for the CH proton of isopropoxyl groups. The ^{13}C -NMR spectrum of the complex showed shifts for the carboxylate carbon and C1–C2 resonances compared with that of the free tetrafluorophthalic acid molecule. The single resonance at $\delta = 163.10$ ppm was attributed to the $\text{COO}-$ groups in the complex.¹⁷ The signals of C1–

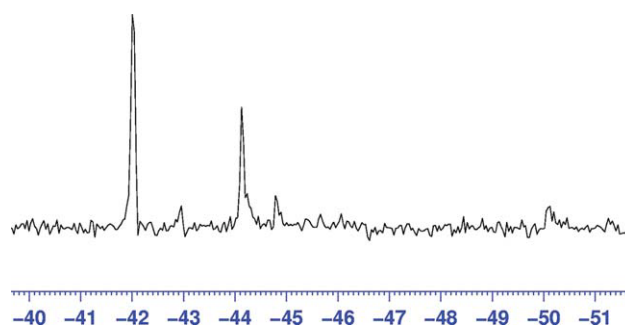


Figure 4 ^{29}Si -NMR spectrum of polymers of GPTS obtained from polymerization with $\text{C}_6\text{F}_4(\text{COO})_2\text{Zr}(\text{O}^i\text{Pr})_2$ at 75°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

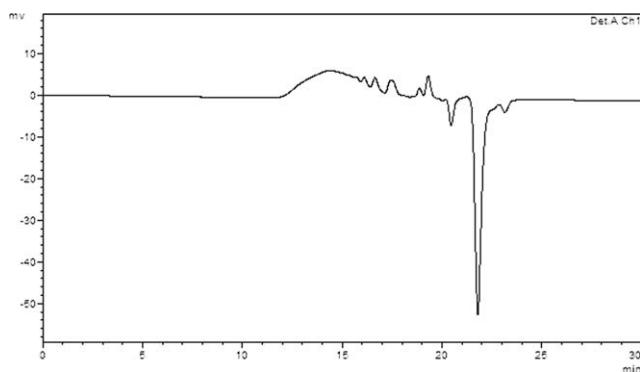


Figure 5 Gel permeation chromatograms of GPTS polymers prepared at 40°C with KOH.

C2 shifted to higher values, to 122.26 from 118.27 ppm (for TFPA). This was attributed to the influence of the deprotonated carboxyl groups in the zirconium complex. In the zirconium complex, the $^1J_{C-F}$ coupling constants for carbons 3–6 and 4–5 were 241.5 and 254.6 Hz. The chemical shifts and coupling constants were in agreement with reported values.¹⁷

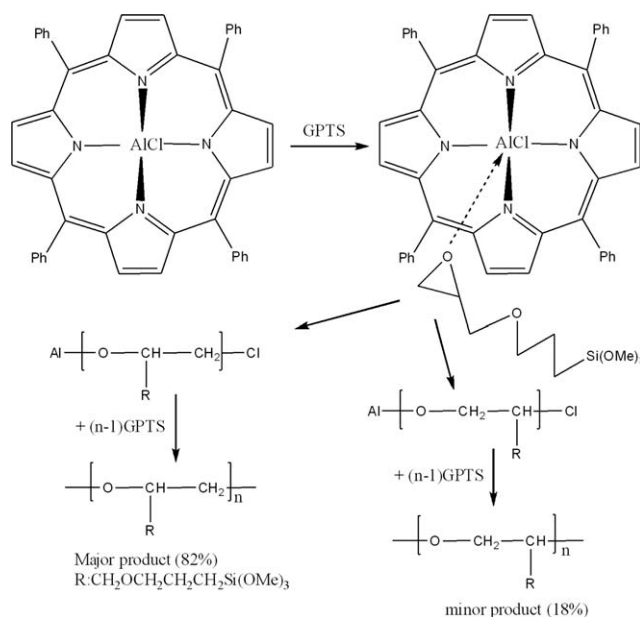
Polymer samples obtained from the ring-opening polymerization of GPTS were characterized by 1H -NMR, ^{13}C -NMR, ^{29}Si -NMR, FTIR spectroscopy, ESI MS, and GPC (Fig. 5). ^{13}C -DEPT, $^{13}C\{^1H\}$ -NMR, and 1H -NMR spectra were obtained at a ^{13}C frequency of 100 MHz and a 1H frequency of 400 MHz. The 1H -NMR assignments of pure GPTS were as follows:

$$\left[\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{fCH}_2 - \text{cCH} - \text{dCH}_2 - \text{O} - \text{cCH}_2 - \text{bCH}_2 - \text{aCH}_2 - \text{Si}(\text{O}^g\text{CH}_3)_3 \end{array} \right]_n$$
 $^a\text{CH}_2$, 0.71; $^b\text{CH}_2$, 1.74; $^c\text{CH}_2$, 3.39; $^d\text{CH}_2$, 3.20 and 3.52; ^eCH , 2.96; $^f\text{CH}_2$, 2.34 and 2.50; and $^g\text{CH}_3$, 3.50 ppm. The 1H -NMR spectrum showed that the main change occurred at the CH and CH_2 protons of the epoxy ring when GPTS was polymerized. The CH and CH_2 protons shifted to higher values, 3.8–4.25 ppm, from 2.34–2.96 ppm. These values were consistent with those in the literature.¹⁸ The 1H -NMR spectrum of GPTS polymers gave peaks at 0.65 ppm ($^a\text{CH}_2$), 1.67 ppm ($^b\text{CH}_2$), 3.22 ppm ($^c\text{CH}_2$), 3.3–3.8 ppm ($^d\text{CH}_2$, $^f\text{CH}_2$, and $^g\text{CH}_3$), and 4.17 ppm (^eCH ; as shown in Fig. 3). The ^{13}C -NMR spectrum of pure GPTS showed six resonances, which were attributed to the six carbon atoms as follows:^{19,20} a, 5.43; b, 23.11; f, 43.24; g, 49.87; e, 50.39; d, 71.58; and c, 73.18 ppm.

The CH, CH_2 , and OCH_3 carbons of the GPTS polymers were easily determined from the ^{13}C -DEPT spectra. ^{13}C -DEPT-135 gave all CH and CH_3 in a phase (peaks up) opposite to CH_2 (peaks down). The ^{13}C -NMR spectra for the characterization of GPTS polymers were more specific than the 1H -NMR spectra. The ^{13}C -NMR spectrum of the polymers included more peaks compared to that of pure

GPTS. The ^{13}C -NMR data of the GPTS polymers were given in the Experimental section. For example, as shown from the ^{13}C -NMR data of GPTS polymers prepared with TPP-AlCl, both regioisomers were formed because of the two directions of the ring opening of epoxide, but the major regioisomer $-(\text{OCHRCH}_2)_n-$ [where R is $\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$] predominated by about 4 : 1. The two methine signals in the ^{13}C -NMR spectrum, at approximately 71.81 and 71.04 ppm, corresponded to the major regioisomeric polymer. The methine signals at 79.13–78.98 and 78.74–78.89 ppm corresponded to the minor regioisomeric polymer. The methine carbon resonances at 79–78 ppm region appeared as two signals readily assignable to the dyads (i and s). This was attributed to different stereosequences due to its asymmetric methine carbon. The peaks at 7.48, 6.46, and 5.55 ppm (from CH_2 -Si) in the ^{13}C -NMR spectrum also indicated that different regiosequences existed. These data suggest that, first, GPTS attacked the Al center, and then, the nucleophile Cl^- ion attacked both the CHR and CH_2 carbon atoms in GPTS, as shown in Scheme 1.

The side silyl group of GPTS had more of a stereoselective effect on the stereosequences compared to the methyl group of PO.^{7,21} The CH peak at 58.50 ppm may have belonged to the small irregularity in regiosequences. When the tetrafluorophthalate-Zr catalyst was used instead of the TPP-AlCl catalyst, the maximum recovery rate of the polymer and the maximum polymerization velocity of GPTS occurred at 75°C. The conversion of monomer GPTS to polymer was followed by NMR spectroscopy. The recovery rate of the polymers of GPTS at RT according to



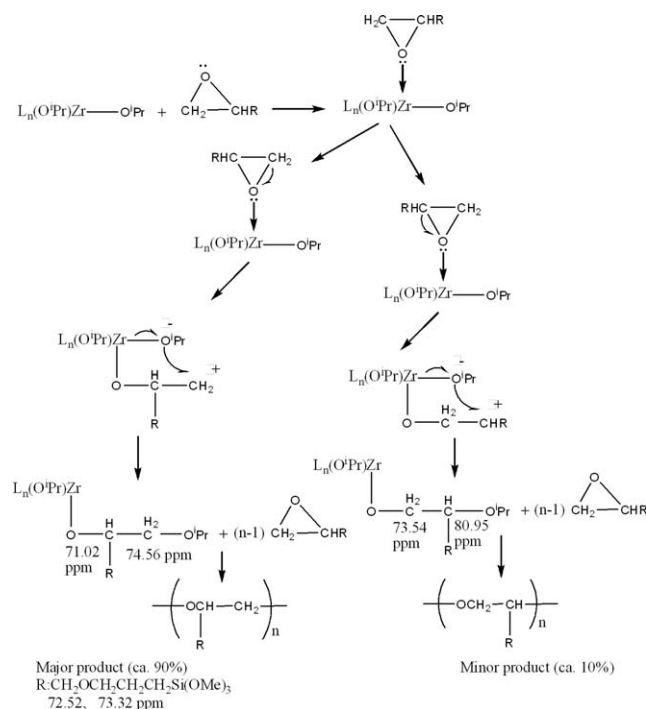
Scheme 1 Attacking of GPTS to the Al center of the TPP-AlCl catalyst.

TABLE II
Recovery Rate of the Polymer (GPTS) According to the Kinds of Catalyst

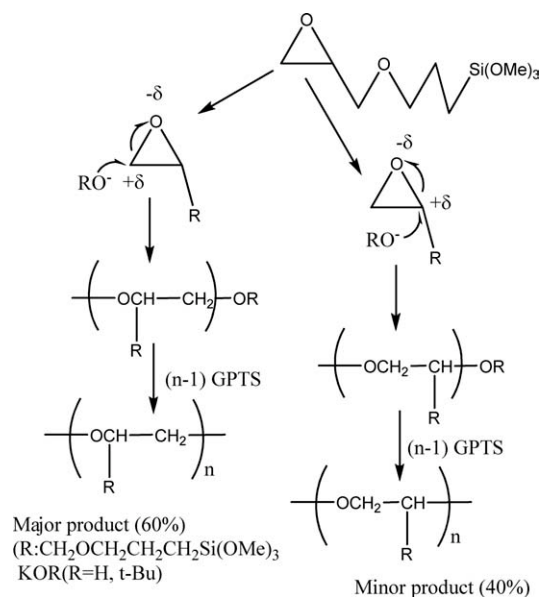
Catalyst	Time (h)	Temperature	Conversion (%)
KO ^t Bu	24	RT	60
TPP-AlCl	24	RT	50
KOH	24	RT	25
C ₆ F ₄ (COO) ₂ Zr(O ⁱ Pr) ₂	24	RT	15

the kinds of catalyst are given in Table II. The polymerization velocity of GPTS decreased in the catalyst order KO-*t*-Bu > TPP-AlCl > KOH > C₆F₄(COO)₂Zr(OⁱPr)₂. Less viscose polymers were obtained when the Zr-catalyst was used in the polymerization of GPTS.

The reaction pathway leading to polymer formation when the tetrafluorophthalate-Zr complex was used as a catalyst is shown in Scheme 2. As shown from the ¹³C-NMR data of GPTS polymers prepared with the tetrafluorophthalate-Zr complex, both regioisomers were formed, but the major regioisomer -(OCHRCH₂)_n- [where R is CH₂OC H₂CH₂CH₂Si(OMe)₃] predominated by about 9 : 1. More regioregular and stereoregular polymers were prepared at 60°C when the tetrafluorophthalate-Zr complex was used in the polymerization of GPTS. When the temperature was increased from 60 to 75°C, stereoirregularities increased somewhat. The methine and methylene signals in the ¹³C-NMR



Scheme 2 Attacking of GPTS to the Zr center of the catalyst tetrafluorophthalate-Zr complex.



Scheme 3 Attacking of RO⁻ to the CH₂/CHR carbon of GPTS.

spectrum at approximately 71.02 ppm (singlet, i) and 74.56 ppm (singlet, i) corresponded to the major regioisomeric polymer. The methine carbon resonances in the 80.95-ppm (singlet, i) region corresponded to the minor regioisomeric polymer. These data suggested that, first, GPTS attacked the Zr center, and then, the nucleophile OⁱPr⁻ ion attacked both the CHR and CH₂ carbon atoms in GPTS, as shown in Scheme 2.

The reaction pathway leading to polymer formation when KOH and KO-*t*-Bu were used as catalysts is shown in Scheme 3. The strong nucleophilic OH⁻ and *t*-BuO⁻ ions attacked both the CH₂ and CHR carbon atoms, as shown in Scheme 3 (ca. 60/40%). Although the two methine signals at 71.77–71.69 and 70.96–70.86 ppm in the ¹³C-NMR spectrum of the polymer prepared with *t*-BuO⁻ corresponded to the major regioisomeric polymer, the two methine signals at 79.19–79.06 and 78.81–78.68 ppm corresponded to the minor regioisomeric polymer (Fig. 2). When the temperature was increased from RT to 40 and 75°C, just the molecular weight of the polymer increased without a change in the regioselectivity or stereoselectivity (Table III). When the OH⁻ base was used as a catalyst at RT, the polymer gave methine signals at 78.77–78.64 ppm (CH, diad, i/s) in the ¹³C-NMR spectrum, but when temperature was increased from RT to 40 or 75°C, new methine signals appeared at 79.13–79.02 ppm with small intensity. The conversion of the monomer GPTS to polymers with KOH catalyst at different temperatures are given in Table I. Because of the better conversion ratios, the polymerization was performed at 40 and 75°C.

The ²⁹Si-NMR spectra of the GPTS polymers also supported the presence of major and minor

TABLE III
Data for the GPTS Polymers Obtained from GPC Measurements

Catalyst	Temperature (°C)	Time (days)	M_w	M_n	M_w/M_n
KOH	RT	1	940, 549	933, 541	1.01, 1.01
KO ^t Bu	RT	1	916, 460	861, 456	1.06, 1.01
Tetrafluorophthalate zirconium	RT	1	517	515	1.00
KOH	40	2	5685, 874, 483	3841, 851, 481	1.48, 1.03, 1.01
KO ^t Bu	40	2	2596, 950, 538	2208, 946, 528	1.18, 1.00, 1.02
Tetrafluorophthalate zirconium	75	2	1878, 778	1632, 774	1.15, 1.00

polymers in the mixture. Trisubstituted siloxane bonds were designated as T^{*n*} (*n* = 0, 1, 2, or 3), where *n* is the number of bridging Si—O—Si units. Two peaks were evident in the ²⁹Si-NMR spectra for polymers of GPTS, the major one at approximately -44 ppm (T⁰ species) and the minor one at approximately -46 ppm (T⁰ species). For example, for polymers prepared with the tetrafluorophthalate-Zr complex, ²⁹Si-NMR (C₆D₆) results were δ (ppm) = -42.05 (T⁰, standard, GPTS, monomer), -44.1 (T⁰, polymer 1, higher intensity, ca. 90%), and -44.9 (T⁰, polymer 2, small intensity, 10%; Fig. 4). All of the chemical shifts closely agreed with the values for T^{*n*} in the literature.²² The number of bridging Si—O—Si units was zero (*n* = 0) because no hydrolysis or condensation occurred among the methoxysilyl groups. There were no characteristic peaks in the ²⁹Si-NMR spectra for T¹ and T² that appeared at about -50 and -60 ppm, respectively.^{20,22}

GPC was also used to determine the molecular weight and the molecular weight distribution index of the polymers. By varying the reaction time and catalyst, we obtained polymers with different average molecular weights or number-average molecular weights (M_n 's). For polymers of GPTS prepared with KOH for 2 days of stirring at 40°C, the main peak appeared at an M_w of 5685 Da or an M_n of 3841 Da. The ratio of M_w to M_n was 1.48. There were also small peaks of average molecular weight at 874 and 483 Da (with ca. $M_w/M_n = 1.0$). These results indicated that the polymerization had a characteristic of living polymerization. When the polymerization was terminated with methanol and washed with petroleum ether, the molecular weight distribution index (M_w/M_n) decreased from 1.48 to 1.30, with the average molecular weight greater than 15,000. Data for the GPTS polymers prepared at different times and temperatures are given in Table III. As shown in Table III, the polymers prepared at RT had lower molecular weights and small molecular weight distribution indices for four catalysts. When the temperature increased to 40 or 75°C, the molecular weights and the molecular weight distribution indices of the polymer increased. The stereosequences of the GPTS polymers prepared with OH⁻ and *t*-BuO⁻ were the same at 40 and 75°C.

As shown by the GPC measurements, the polymerization was a living polymerization. However,

the mass spectra of the polymers showed that the catalysts did not remain bonded to the polymers. Because the mass measurements of the samples were taken in methanol solvent, the polymer was terminated with methanol. Therefore, the structures of polymers did not contain catalyst according to mass measurements.

The polymer structure was further verified by DSC analysis. According to the DSC test, all of the polymers showed a single T_g at approximately -48°C. T_g was taken as the midpoint of the glass transition.

FTIR studies supported the polymerization of GPTS. The monomer of GPTS showed characteristic bands at 2842–2950 cm⁻¹ (vibration of CH groups, ν_s), 1461 cm⁻¹ (CH₃, due to stretching), 12,657 cm⁻¹ (ν_s), 810–950 cm⁻¹ (ν_{as}), and 750–840 cm⁻¹ (ν_s) due to the symmetric and asymmetric vibrations of the ring stretching of the epoxy group of GPTS.^{23–25} When GPTS underwent polymerization, the peak at 1257 cm⁻¹ disappeared in the FTIR spectrum. This disappearance supported the fact that the epoxy ring of GPTS underwent a ring-opening reaction.²⁴ GPTS exhibited a strong absorption ascribed to the Si(O—C) at 1089 cm⁻¹. For polymers of GPTS, the Si(O—C) absorption appeared at 1101 cm⁻¹. These all data supported the polymerization of GPTS.

CONCLUSIONS

The four catalysts used in this study were effective for the polymerization of GPTS and had somewhat different influences on the selective synthesis of polymers. Both regioisomers were formed because of the two directions of the ring opening of epoxide. The structures of the polymers were characterized by NMR, FTIR spectroscopy, ESI MS, and GPC. The side silyl group of GPTS had a more stereoselective effect on the stereosequences compared to the methyl group of PO. Isotactic and isotactic/syntactic polymers were obtained. The polymerization velocity of GPTS decreased in the catalyst order KO-*t*-Bu > TPP-AlCl > KOH > C₆F₄(COO)₂Zr(O^{*i*}Pr)₂. When the tetrafluorophthalate-Zr complex was used as the catalyst, slow polymerization was performed, and lower molecular weight polymers were obtained. However, the tetrafluorophthalate-Zr catalyst was

more regioselective and stereoselective in the polymerization of GPTS. GPC measurements showed that the polymerization had a characteristic of living polymerization.

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