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Modification of Styrene Polymer with Organosilicon Groups

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ABSTRACT: *The homopolymer of 4-chloromethylstyrene (P1) and its copolymers with styrene (in various mole ratios) were synthesized by bulk and solution free radical polymerizations, respectively, at $70 \pm 1^\circ C$ using α,α'-azobis(isobutyronitrile) as an initiator. Lithiation of these soluble polymers in THF at $-78^\circ C$ was done and reacted with electrophiles such as tert-BuMe$_2$Si, Et$_3$Si, and Me$_3$SiCH$_2$ in the presence of 4,4′-di-tert-butylbiphenyl (DTBB) as a catalyst to produce modified polystyrene. In the other way, trimethylsilylmethyl lithium substitute as a nucleophile was covalently linked to the homopolymer and copolymer. The polymers were characterized by IR, ^{1}H NMR, ^{13}C NMR, differential scanning calorimetry (DSC), and gel permeation chromatography. DSC showed that incorporation of silyl substitute in the side chains of homopolymer and copolymers increases the rigidity of the polymers and, subsequently, their glass transition temperature.* Heteroatom Chem 18:414–420, 2007; DOI 10.1002/hc.20314

INTRODUCTION

Polystyrene (PS) is one of the most important polymers of today [1]. Its popularity stems from the fact that it possesses many good properties, such as good process ability, rigidity, transparency, low-water absorbability, and that it can be produced at low casts [2]. However, it also has some disadvantages. In order to overcome these disadvantages, some works were done (for example, comonomers, chain transfer agent, or cross-linking agents were added to styrene polymer before it is polymerized) [3]. Sometimes, saturated monomers were used for reinforcement [4].

Chain transfer agents are used to regulate the molecular weight, but they are rarely used in bulk processes [5]. T-Dodecyl mercaptane is often used as a chain transfer agent. To cross-link the styrene polymer, divinylbenzene works very well, although other cross-linking agents can also be used. Highly cross-linked polymers can only be produced batchwise in bulk [6].

To improve the impact strength, polybutadiene is generally added to polystyrene, in the amount of 5–10% [1]. In order to improve the thermal properties of polystyrene, poly-2,6-dimethyl-1,4-phenyleneoxide (PPE) is added to the polymer. PPE is a polymer with a glass transition temperature of 220°C, and this polymer is miscible with polystyrene. The addition of PPE to PS results in a polymer blend with a higher glass transition temperature than PS [7].

These copolymers found interesting application. For example, copolymers with methacrylates are used in manufacture of recording tapes and toners for photocopies. Other important work in this area is attaching suitable groups as a side chain. In this work, we synthesized silyl derivative of polystyrene.

Attaching silyl groups to polymer chain is an interesting research field in polymer and silicon chemistry. In this way some important polymer

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properties, such as permeability and gas permeability parameters, and mechanical, thermal, and surface properties are modified. For example, various organosilyl groups were bounded to a number of polymers and their properties were studied [8–12]. 4-Chloromethylstyrene (CMS), also called *p*-vinyl benzyl chloride (VBC), is a monomer that can be reacted with a series of reagents to produce polymer with functional groups [13,14]. This monomer can polymerize or copolymerize before or after the functional groups reaction with benzyl chloride. The mobility of benzyl chloride bonds in poly(4-chloromethylstyren) (PMS) and related copolymers allows their reaction with various nucleophilic reagents. Also functionalized PCMS and related copolymers have been widely used in different processes such as bactericide polymers [15], photosensitizers [16], solar energy storage [17], photoresist [18], nonlinear optics [19], and prodrugs in biochemical application [20].

One of the modifications of PCMS and related copolymers is achieved by nucleophilic substitutions of the chlorine atom, with the steric hindrance nucleophile, i.e., tris(trimethylsilyl) methyl anion [21]. Also a series of soluble polymers that have linear character metallated and reacted with some electrophilic reagents [22–24]; for example, lithiation of soluble polymer such as pol(4-chloromethylstyrene) was done and reacted with electrophiles in the presence of 4-4-di-*tert*-butylbiphenyl (DTBB) as a catalyst using or not using Barbier-type reaction conditions at –78°C, to produce polymer with a silyl group in a polymer chain [14].

In the literature, there are already examples of some interest in this area. Among those were carbosilanes with Me_3SiCH_2substituents [25], substituted poly(acetylenes) such as poly(1-trimethylsilyl-1-propyne) [26], or its alkylated analogous [27].

In this way, we first synthesized the homopolymer of 4-chloromethyl styrene and its copolymer with styrene by radical polymerization. Then some silyl groups were attached to the resulting polymers. Then these polymers with an organosilicon chain were characterized and studied for their properties.

EXPERIMENTAL

Measurements

Infrared spectra were recorded with a 4600 Unicam FT-IR spectrophotometer as KBr pells. ^{1}H NMR spectra were run on a Bruker 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 (GPC) 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 standard was employed for calibration. The glass transition temperature was determined with a Perkin-Elmer DSC differential scanning calorimeter at a heating rate of 10°C/min in air.

Materials

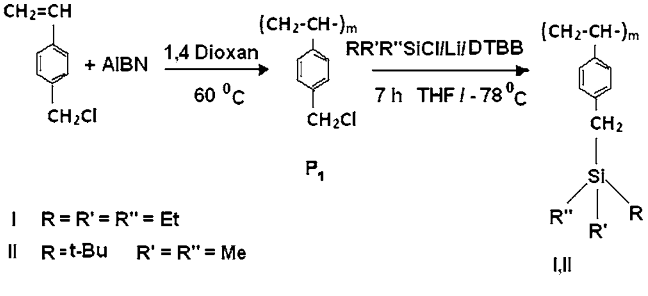
Solvents such as Dioxan (Merck) and THF (Merck) were dried by standard methods. Et_3SiCl, *t*-$BuMe_2SiCl$, Ph_3SiCl, Me_3SiCH_2Cl, and Li powder were used as received. 4-Chloromethylstyrene and styrene were distilled under reduced pressure to remove inhibitors, before use. The initiator of α,α'-azobis (isobutyronitril) (Merck) was purified by crystallization from methanol.

Homopolymerization of 4-Chloromethylstyrene

In a quickfit pyrex polymerization tube, 1% molar of 1,1′-azobis (isobutyronitrile) (AIBN) as an initiator was dissolved in 10 mmol of CMS and the solution was flushed gently with argon for about 20 min. Then the solution was shaken vigorously in a thermostatic water bath at 70 ± 1°C by a shaker machine under argon for 48 h. After this, the resulted solid was dissolved in 20 mL THF and poured into 150 mL of cooled methanol as nonsolvent. Then the obtained white precipitate was washed with methanol and dried in vacuum at room temperature to give P1 (1 g) (Scheme 1).

^{1}H NMR ($CDCl_3$, ppm): 1–1.8 (CH_2—CH), 4.5 (CH_2—Cl), 6.5–7.3 (Ar—CH_3).

FT-IR (KBr, cm^{-1}): 3050 (aromatic, C—H), 2910, 2850 (aliphatic, C—H), 1420, 1611 (aromatic, C=C).



SCHEME 1 Preparation of P1 and modified homopolymers.

Copolymerization of 4-Chloromethylstyrene with Styrene

For preparing of copolymers (P2, P3, and P4), a mixture of styrene (150 mmol) with different amounts of 4-chloromethylstyrene (30, 150, and 50 mmol) with molar ratios of 5:1, 1:1, and 3:1, respectively, was dissolved in 15 mL of dioxan and was mixed with 1,1′-azobis(isobutyronitrile) (AIBN) (1% molar) as a radical initiator, in a pyrex glass ampoule. The ampoule was degassed, sealed under vacuum, and maintained at 70 ± 1°C in a water bath, with stirring for about 72 h. Then the solutions were poured from ampoules into cooled methanol. The precipitates were collected and washed with methanol and dried under vacuum to give copolymers (P2, P3, and P4) (Scheme 2).

^{1}H NMR ($CDCl_3$, ppm) for P2, P3, and P4: 1–1.8 (CH_2—CH), 4.5(CH_2—Cl), 6.4–7.2 (Ar—CH_3).

FT-IR (KBr, cm^{-1}): 3027 (aromatic C—H), 2925, 2850 (aliphatic C—H), 1451–1600 (aromatic C=C).

General Procedure for the Preparation of Modified Polymers (Compounds **I–VII***)*

To a dark green suspension of lithium powder (12 mmol) and DTBB as a catalyst (10% molar) in dry THF (25 mL), a solution of the copolymers (P2, P3, and P4) (1 mmol), or homopolymer (P1) (1 mmol), with related electrophiles (1.5 mmol) in THF, was slowly added from a dropping funnel under argon at –78°C. After stirring for about 7 h at the same temperature, the resulting mixture was poured into cold methanol and the resulting precipitate was filtered, and was washed several times with cold methanol to produce pure compounds. Preparation of P1, **I, II**, and **III–VII** is shown in Schemes 1 and 2, respectively.

For **I**: ^{1}H NMR ($CDCl_3$, ppm): 0.55 (CH_2—Si), 0.85 (CH_3—), 1.2–1.9 (CH_2—CH), 6.6–7.0(Ar—H), 3.0 (CH_2—Ar). FT-IR (KBr, cm^{-1}): 3016 (aromatic C—H), 2957 (aliphatic C—H), 1456 and 1610 (aromatic C=C), 1261 (C—Si).

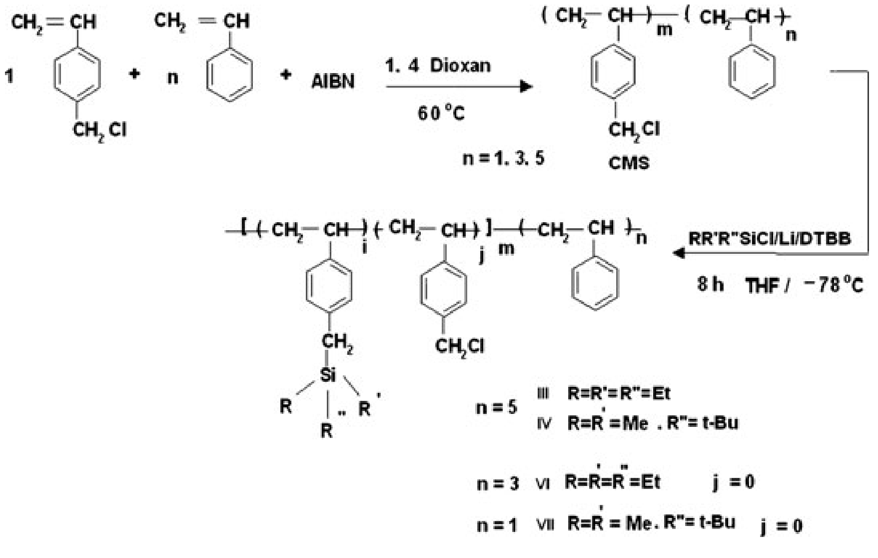
For **II**: ^{1}H NMR ($CDCl_3$, ppm): 0.09 (CH_3—Si), 0.9 (*t*-Bu), 3.0 (CH_2—Ar), 1.2–1.9 (CH_2—CH), 7.0–7.4 (Ar—H). FT-IR (KBr, cm^{-1}): 3023 (aromatic C—H), 2923 (aliphatic C—H), 443, 1611 (aromatic C=C), 1264 (C—Si).

For **III**: ^{1}H NMR ($CDCl_3$, ppm): 0.5 (CH_2—Si), 0.9 (CH_3—), 1.1–2.1 (CH_2—CH), 3.0 (CH_2—Ar), 4.5 (CH_2Cl), 6.6–7.2 (Ar—H).FT-IR (KBr, cm^{-1}): 3060 (aromatic C—H), 2848–2923 (aliphatic C—H), 1452 and 1600 (aromatic C=C), 1263 (C—Si).

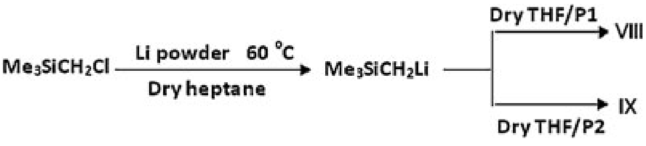
For **IV**: ^{1}H NMR ($CDCl_3$, ppm): 0.1 (CH_3—Si), 0.9 (*t*-Bu), 1.1–2.0 (CH_2—CH), 3.7 (CH_2—Ar), 4.5 (CH_2Cl), 6.6–7.2 (Ar—H). FT-IR (KBr, cm^{-1}): 3027 (aromatic C—H), 2925 (aliphatic C—H), 1494 and 1610 (aromatic C=C), 1263 (C—Si).

For **V**: ^{1}H NMR ($CDCl_3$, ppm): 0.1 (CH_3—Si), 1.0–2.3 (CH_2—CH), 3.4 (CH_2—Ar), 4.5 (CH_2Cl), 6.1–7.1 (Ar—H). FT-IR (KBr, cm^{-1}): 3025 (aromatic C—H), 2924 (aliphatic C—H), 1452 and 1601 (aromatic C=C), 1265 (C—Si).

For **VI**: ^{1}H NMR ($CDCl_3$, ppm): 0.65 (CH_2—Si), 0.98 (CH_3), 1.20–2.50 (CH_2—CH), 2.78 (Ar—CH_2), 6.60–7.26 (Ar C—H). FT-IR (KBr, cm^{-1}): 1265 and



SCHEME 2 Preparation of P2 and modified copolymers (**III**, **IV**, **VI**, and **VII**).



SCHEME 3 Preparation of trimethylsilylmethyllithium and attaching it to P1, (**VIII**), and P2, (**IX**).

823 (C—Si), 1492 and 1601 (C=C), 2923 (aliphatic C—H), 3025 (Ar C—H).

For **VII**: 0.48–0.53 ($SiCH_3$), 0.89–1.00 (t—Bu), 1.04–2.30 (CH_2—CH—), 2.79–3.02 (Ar—CH_2), 6.60–7.26 (Ar C—H). FT-IR (KBr, cm^{-1}): 1265, 825 (C—Si), 493, 1602(C=C), 2923 (aliphatic C—H), 3025 (Ar, C—H).

Organolithium Method for Preparation of Modified Polymers (Compounds **VIII–IX***)*

Trimethylsilylmethyllithium was prepared by reaction of chloromethyltrimethylsilane and lithium metal powder suspension in the dry heptane. The halide solution was added dropwise at room temperature over a 1 h period to a suspension of lithium powder in about 1.5-fold excess with stirring. The system was heated with stirring at 55–60°C for 5 h, and then lithium chloride and excess lithium were filtered on a frit, the solvent stripped off in vacuum. The solid was dissolved in THF and added dropwise from an ampoule into a flask that includes polymer solution in THF under argon. Then the mixture was refluxed over 5–6 h and poured into the cold methanol; the residue was filtered and washed with methanol (Scheme 3).

For **VIII**: ^{1}H NMR ($CDCl_3$, ppm): 0.09 (CH_3—Si), 1.2–1.9 (CH_2—CH), 2.8 (CH_2—Ar), 4.5 (CH_2Cl), 6.4–7.5 (Ar, C—H). FT-IR (KBr, cm^{-1}): 3027 (aromatic C—H), 2925 (aliphatic C—H), 1494 and 1610 (aromatic C=C), 1262 (C—Si).

For **IX**: ^{1}H NMR ($CDCl_3$, ppm): 0.09 (CH_3—Si), 1.1–1.9 (CH_2—CH), 2.2 (CH_2—Ar), 4.5 (CH_2Cl), 6.6–7.2 (Ar—H). FT-IR (KBr, cm^{-1}): 3027 (aromatic C—H), 2925 (aliphatic C—H), 1494 and 1610 (aromatic C=C), 1263 (C—Si).

RESULTS AND DISCUSSION

The monomer of CMS was homopolymerized and copolymerized with styrene with ratios of [1:1], [1:3], [1:5] at 70 ± 1°C using AIBN as the radical initiator to produce P2, P3, and P4, respectively. The reaction conditions are shown in Table 1. The resulting polymers and copolymers are white solids and soluble in chloroform, dichloromethane, benzene, toluene, xylene, THF, *N*,*N*-dimethylformamid, and dimethylsulfoxide but insoluble in *n*-hexane, methanol, ethanol, and water.

Copolymers (P2, P3, and P4) and homopolymer (P1) compositions were determined using ^{1}H NMR spectroscopy. The molar compositions of P1, P2, P3, and P4 are presented in Table 2. Increasing the reaction time in homopolymerization in bulk referred to in solution causes high M_W and T_g in polymers. In copolymers of P3, P4 with ratios of [1:3] and [1:1], respectively, incorporation of the silyl group in the side chain of polymer was done better refer to copolymer with a ratio of 1:5, where the peak of CH_2Cl in ^{1}H NMR disappeared. This means that all of CH_2Cl groups were substituted by silyl groups. This can be referred to reducing hindrance in copolymers. In this case, we attached *tert*-butyldimethylsilyl and triethylsilyl groups to these copolymers with good yield. After preparation of homopolymer and copolymers, each

TABLE 1 Preparation Conditions of Homopolymer and Copolymer at 70 ± 1°C

Sample	*Monomer 1*	*Monomer 2*	*Ratio of 1*	*Ratio of 2*	*Solvent*	*Time (h)*	*T (°C)*	*Nonsolvent*
P1	CMS	–	1	–	–	72	70 ± 1°C	MeOH
P2	CMS	Styrene	1	5	Dioxan	72	70 ± 1°C	MeOH
P3	CMS	Styrene	1	3	Dioxan	72	70 ± 1°C	MeOH
P4	CMS	Styrene	1	1	Dioxan	72	70 ± 1°C	MeOH

TABLE 2 Composition and Molecular Weights of P1, P2, P3, and P4

Sample	*Mol % CMS*	*Mol % Styrene*	T_g *(°C)*	M_n	M_w	M_n/M_w
P1	100	–	80	41,059	32,441	1.26
P2	16.7	83.3	73	22,344	5,923	3.76
P3	25	75	73	26,122.25	1,6225	1.61
P4	50	50	79	35,373.8	1,6079	2.20

of them was lithiated with lithium powder in the presence of DTBB at −78°C and reacted with organosilicon electrophiles to produce modified homopolymers (Scheme 1) and modified copolymers (Scheme 2) with a silyl side chain. The triethylsilyl, *tert*-butyldimethylsilyl, trimethylsilyl methyl groups were used as a silyl side chain groups in these copolymers and homopolymer. In this way, we prepared some new silyl derivatives of polystyrene. In this case, the best result was obtained under Barbier-type conditions, performing the final hydrolysis with cold methanol. Thus, functionalized polymers **I–VII** were isolated. Either for the two-step or for the Barbier process, a chlorine–lithium exchange occurred prior to the reaction with the electrophile, so the corresponding benzylic organolithium intermediate is probably involved in the reaction.

Preparation of modified polymers was done by the other method, in which chloromethyltrimethylsilane lithiated by lithium powder in heptane at 60°C then solvent evaporated, and the resultant compound was reacted with P1 and P2 to produce **VIII** and **IX** (Scheme 3). By DSC analyses, the effect of silyl groups in properties of poly(CMS) was studied. These studies showed that attaching a silyl group caused modification of polystyrene. T_g values and reaction conditions of compounds **I–VII** and **VIII–IX** are shown in Tables 3 and 4, respectively.

Replacement of chlorine atoms by Si electrophiles is determined by ^{1}H NMR, where the peak around 4.6 ppm corresponding to two methylene protons of benzyl chloride in CMS disappeared or reduced integral of peak and two new peaks appeared. In the case of homopolymer, the yield of incorporation of the silyl group is better referred to copolymer; for example, attaching triethylsilyl and *tert*-butyldimethylsilyl groups to homopolymer (P1) and copolymers (P3, P4) was done in near 100% yield, where the ^{1}H NMR peak of (CH_2-Cl) group disappeared; the ^{1}H NMR spectrum of compound **I** is shown in Fig. 1. Because in the case of homopolymer, the steric hindrance was reduced referred to copolymer; therefore, attaching the electrophiles was done better. For example, attaching the triethylsilyl or *tert*-butyldimethylsilyl groups to copolymer (P2) was done in low yield referred to homopolymer. In copolymers P3, P4 the mole percentage of chloromethystyrene is higher than that in P2; the yield is suitable. The spectrum of compound **IV** is shown in Fig. 2.

Identification of silyl derivative that was prepared from organolithium reaction was also done by a spectroscopic method; for example, a typical ^{1}H NMR spectrum of Me_3SiCH_2 derivative of P1 is shown in Fig. 3. ^{1}H NMR data of polymers are shown in Table 5.

The thermal behavior of polymer is important in relation to its properties. Differential scanning calorimetry (DSC) and thermal gravimetry (TGA) for the network polymers were evaluated. We determined glass transition temperature (T_g) of all modified polymers by the DSC analyses. T_g values of homopolymers and copolymers showed that the presence of the silyl group in the side chain increased the rigidity of polymers, and the T_g value subsequently increased. On the other hand, it appeared that in these series of polymers with increased hindrance in silyl groups, with the decrease of the chains flexibility, the T_g values increased. The T_g values in homopolymer are higher than those in

TABLE 3 Reaction Conditions and T_g Values of Modified Polymers

Modified Polymers	*Electrophiles*	*Related Polymer*	*Solvent*	*Time (h)*	*T_g (°C)*	*Reaction Conditions*
I	Triethylsilyl	P1	THF	7	98	–[a]
II	*tert*-Butyldimethylsilyl	P1	THF	7	111	–[a]
III	Triethylsilyl	P2	THF	7	104	–[a]
IV	*tert*-Butyldimethylsilyl	P2	THF	7	104	–[a]
V	Methyltrimethylsilyl	P2	THF	7	103	–[a]
VI	Triethylsilyl	P3	THF	7	105	–[a]
VII	*tert*-Butyldimethylsilyl	P4	THF	7	112	–[a]

[a]These reactions were performed under the Barbier-type condition in the presence of DTBB, and methanol was used as a nonsolvent.

TABLE 4 Reaction Conditions and T_g Values for Modified Polymers (**VIII–IX**)

Sample	*Nucleophile*	*Electrophile*	*Solvent*	*Nonsolvent*	*Time (h)*	*T_g (°C)*	*Reaction Conditions*
VIII	Me_3SiCH_2Li	P1	THF	Methanol	2	108	–[a]
IX	Me_3SiCH_2Li	P2	THF	Methanol	2	103	–[a]

[a]These reactions were performed by an organolithium reagent with electrophiles.

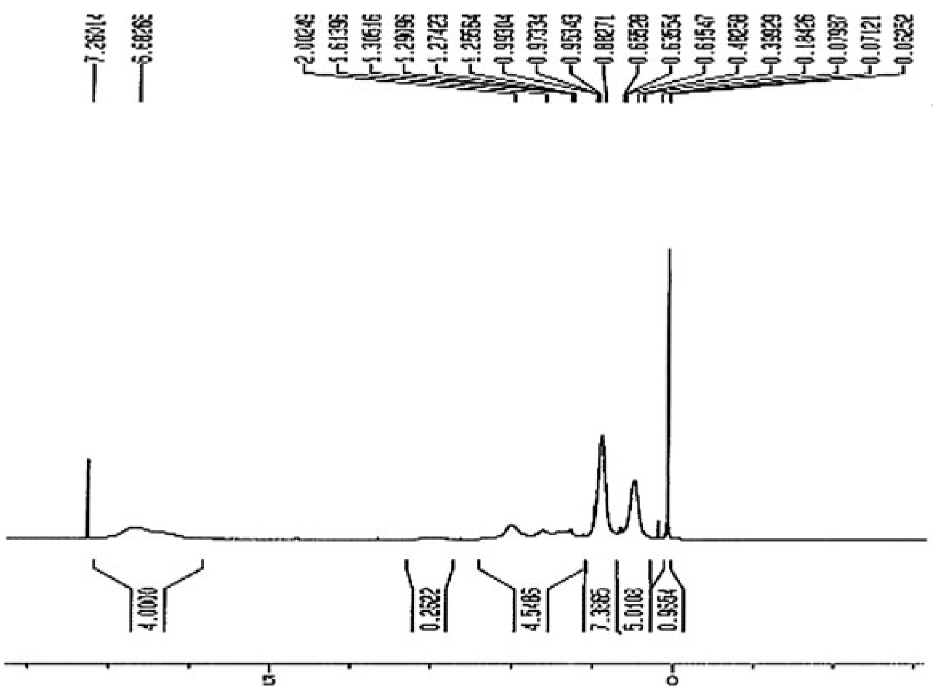


FIGURE 1 ^{1}H NMR spectrum of (P1-Et_3Si) (**I**).

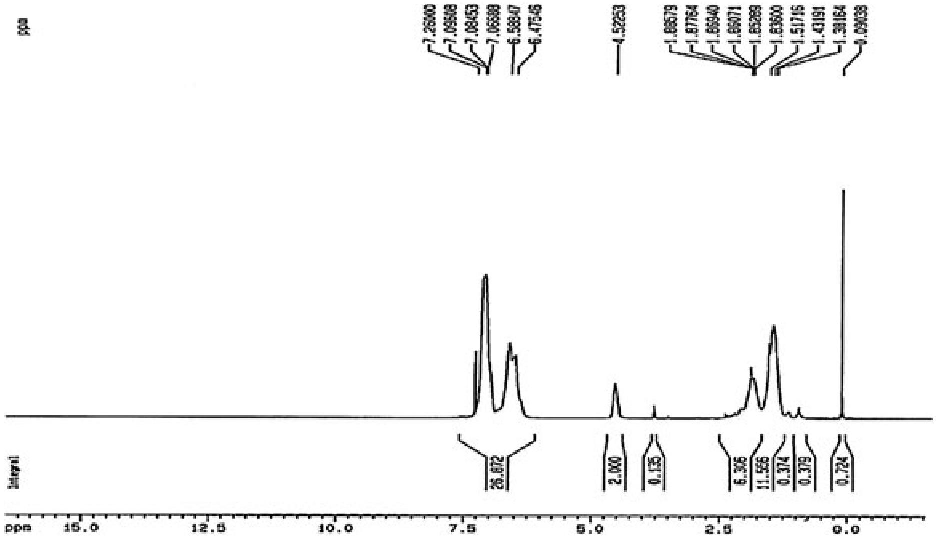


FIGURE 2 ^{1}H NMR spectrum of (P2-*t*-$BuMe_2Si$) (**IV**).

TABLE 5 ^{1}H NMR Data of Polymers

Polymers	δ(ppm) in CD_3Cl
I	0.55 (CH_2—Si), 0.85 (CH_3—), 1.2 –1.9 (CH_2—CH), 6.6–7 (Ar—H), 3 (CH_2—Ar).
II	0.09 (CH_3—Si), 0.9 (*t*-Bu), 3 (CH_2—Ar), 1.2–1.9 (CH_2—CH), 7–7.4 (Ar—H).
III	0.5 (CH_2—Si), 0.9 (CH_3—), 1.1–2.1 (CH_2—CH), 3 (CH_2—Ar), 4.5 (CH_2Cl), 6.6–7.2 (Ar—H).
IV	0.1 (CH_3—Si), 0.9 (*t*-Bu), 1.1–2 (CH_2—CH), 3.7 (CH_2—Ar), 4.5 (CH_2Cl), 6.6–7.2 (Ar—H).
V	0.1 (CH_3—Si), 1–2.3 (CH_2—CH), 3.4 (CH_2—Ar), 4.5 (CH_2Cl), 6.1–7.1(Ar—H).
VI	0.65 (CH_2—Si), 0.98 (CH_3), 1.20–2.50 (CH_2—CH), 2.78 (Ar—CH_2), 6.60–7.26 (Ar C—H).
VII	0.48–0.53 ($SiCH_3$), 0.89–1.00 (t—Bu), 1.04–2.30 (CH_2—CH), 2.79–3.02 (Ar—CH_2), 6.60–7.26 (Ar C—H).
VIII	0.09 (CH_3—Si), 1.2–1.9 (CH_2—CH), 2.8 (CH_2—Ar), 4.5 (CH_2Cl), 6.4–7.5 (Ar—H).
IX	0.09 (CH_3—Si), 1.1–1.9 (CH_2—CH), 2.2 (CH_2—Ar), 4.5 (CH_2Cl), 6.6–7.2 (Ar—H).

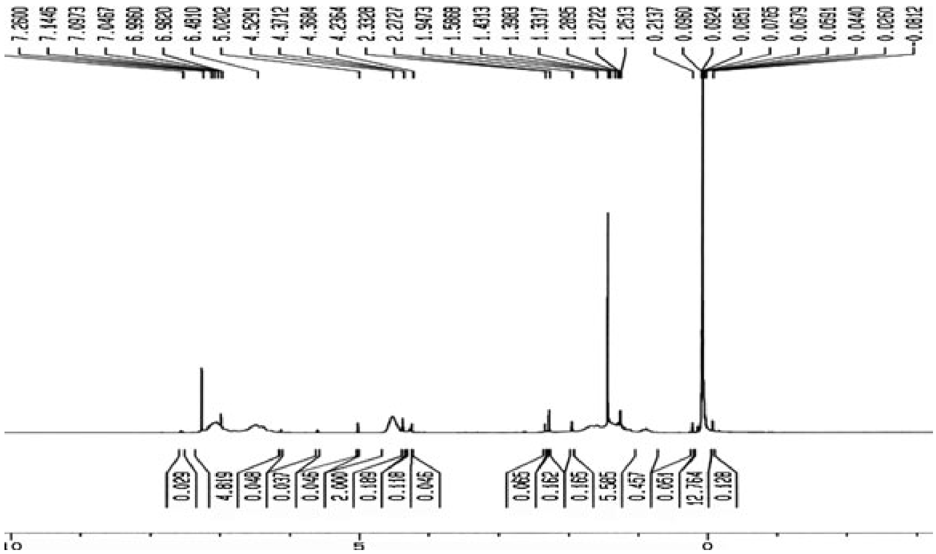


FIGURE 3 ^{1}H NMR spectrum of **VI**.

copolymer and in the bulk polymerization is more referred to in solution polymerization.

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