Synthesis and Characterization of New Polymer Systems Containing 4-Silylmethylstyrene Units

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A series of terpolymers containing silyl pendant groups were prepared by free radical cross-linking copolymerization. Et_3Si and HMe_2Si were covalently linked with 4-vinylbenzyl and abbreviated as TESiMSt and DMSiMSt, respectively. Et_3Si was covalently linked with 2-hydroxyethyl methacrylate (HEMA). The silyl-linked HEMA are abbreviated as TESiEMA. Free radical terpolymerization of the methacrylic acid (MAA) with different molar ratios of organosilyl monomers was carried out at 60-70 °C. The compositions of the polymers were determined by FT-IR spectroscopy and ^{1}H-NMR. The glass transition temperature (Tg) of the polymers was determined calorimetrically. The study of DSC curves showed that incorporation of monomers with cyclic units in polymer chains increases the rigidity of terpolymers and the Tg value is subsequently increased.

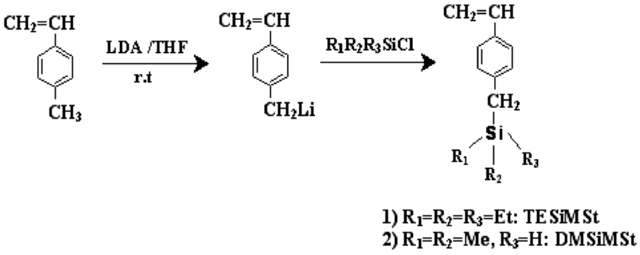
Keywords: Terpolymer; Glass transition temperature; Silyl group; Modified polymer.

INTRODUCTION

Polymers containing organosilyl groups are an interesting research field in polymer and silicon chemistry. Attaching the organosilyl groups to macromolecular chains should lead to important modifications of polymer properties such as gas permeability and permselectivity parameters, mechanical, thermal and surface properties, as well as photochemical reactivity.[1-9] These polymers usually show high oxygen permeability and a reasonably high permselectivity of oxygen against nitrogen. The permeability behavior was attributed to a high affinity of oxygen molecules to Si atoms and the relatively large free volumes between the polymers, resulting from the restricted mobility of the side chains in the repeat units.[10] Nagasaki et al. reported that the oxygen permeability coefficient (PO_2) of the organosilicone-containing polymer membranes increased with the Si content.[11-13] The increased oxygen permeability was attributed to the empty d-orbital of the Si atom, which interacts with the oxygen molecule. They found that the mobility of the side chains also strongly influenced the gas permeability of the polymer membranes because the restricted movements in the side chains increased the free volume. In 1986, Nagasaki et al. also found that lithium diisopropylamide (LDA) induced a metalation reaction of 4-methylstyrene without any side reaction such as polymerization or an addition reaction at the vinyl group of 4-methylstyrene to form 4-vinylbenzylllithum.[14] By using this reaction system, we were able to synthesize a variety of novel monomers.

The ultimate purpose of this research was to investigate a gas-permeable and enzyme-immobilizable polymeric material that can be utilized as the oxygen electrode membranes in biosensors. In this study, the organosilicon-containing styrene was chosen as a comonomer for the preparation of terpolymers. The silyl derivatives of methylstyrenes were synthesized in good yield by dropping silyl chloride derivatives, triethylsilyl chloride and dimethylsilyl chloride into the 4-vinylbenzyllithium system (Scheme I). The methacryloyloxyethyl ester of Et_3Si (TESiEMA) was prepared as a polymerizable silyl monomer.

Scheme I Synthesis of silyl derivatives of 4-vinylbenzyl



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Free radical terpolymerization of the resulting silyl monomers with methacrylic acid (MAA) in the various ratios produced silyl pendant polymers. The -COOH groups in the polymers can be employed for immobilization of enzymes *via* covalent bonding when necessary.

EXPERIMENTAL

Synthesis of monomers and copolymerization were carried out under dry argon to exclude oxygen and moisture from the reaction systems.

Materials

The methacryloyloxyethyl ester of Et_3Si (TESiEMA) was prepared by the method described in the literature.[9] The solvents and reagents were purchased from Merck and Fluka Co. THF was dried by the standard method and Et_3SiCl, $(CH_3)_2HSiCl$ and 4-methylstyrene used as received. Initiator of azobisisobutyronitrile (AIBN) was purified by crystallization from methanol.

Measurements

^1H-NMR spectra were recorded on a Bruker 400 AC spectrometer in $CDCl_3$. The IR spectra were recorded on a Shimadzu FT IR-408 spectrophotometer. The DSC curves were obtained on a TGA/SDTA 851 calorimeter at heating and cooling rates of 10 °C/min in air.

Molecular weight of the polymers was determined in formic acid by a cryometric method using a Knauer cryoscopic unit analysis instrument. Polyethylene glycols (with molecular weights 4000, 10000 and 15000) were used to calibrate the instrument.

Synthesis of 4-triethylsilylmethylstyrene: (TESiMSt)

To a stirred THF solution (15.8 mL) of diisopropylamine (2.02 g, 20 mmol), a cyclohexane solution (3 mL) of n-butyllithium (0.65 g, 10 mmol) was added in a 100 mL round-bottomed flask equipped with a three-way stop-cock and an isobaric-type dropping funnel. After stirring for a few minutes to complete the formation of lithium diisopropylamide, 4-methylstyrene (1.18 g, 10 mmol) was added by syringe. The color of the mixture turned yellow immediately. Then a THF solution (11 mL) of triethylsilyl chloride (1.7 g, 11 mmol) was dropped from the isobaric-type dropping funnel into the mixture for 3 h at 20 °C. After the reaction, low boiling materials were evaporated and the residue was chromatographed over silica gel by hexane to yield (70%) of TESiMSt. IR (neat, cm^{-1}): 3026, 2958, 1610, 1450, 1257, 887. ^1H-NMR ($CDCl_3$, ppm) δ 0.57 (q, 7.9 Hz, 6H, $SiCH_2$-CH_3), 0.92 (t, 7.9 Hz, 9H, $SiCH_2$-CH_3), 2.14 (s, 2H, Ar-CH_2), 5.23 (d, 6 Hz, 1H, CH=CH_2), 5.73 (d, 12 Hz, 1H, CH=CH_2), 6.71 (q, 12 Hz, 1H, CH=CH_2), 7.02 (d, 7.9 Hz, 2H, Ar), 7.31 (d, 7.9 Hz, 2H, Ar).

Synthesis of 4-dimethylsilylmethylstyrene: (DMSiMSt)

After preparation of 4-vinylbenzyllithium (10 mmol) in THF solution (10 mL), a solution of an excess amount of dimethylsilyl chloride (36 mmol) in THF (15 mL) was dropped from the isobaric-type dropping funnel into the mixture for 3 h at 0 °C. After the reaction, low boiling materials were evaporated and the residue was chromatographed over silica gel by hexane to yield (90%) of DMSiMSt. IR (neat, cm^{-1}): 3020, 2960, 2115, 1605, 1430, 1254, 897. ^1H-NMR ($CDCl_3$, ppm) δ 0.15 (d, 6H, $SiCH_3$), 1.6 (s, 3H, Ar-CH_2), 4.1 (m, 1H, SiH), 5.12 (d, 6 Hz, 1H, CH=CH_2), 5.67 (d, 12 Hz, 1H, CH=CH_2), 6.67 (q, 12 Hz, 1H, CH=CH_2), 7.16 (d, 7.6 Hz, 2H, ArH), 7.28 (d, 7.6 Hz, 2H, ArH).

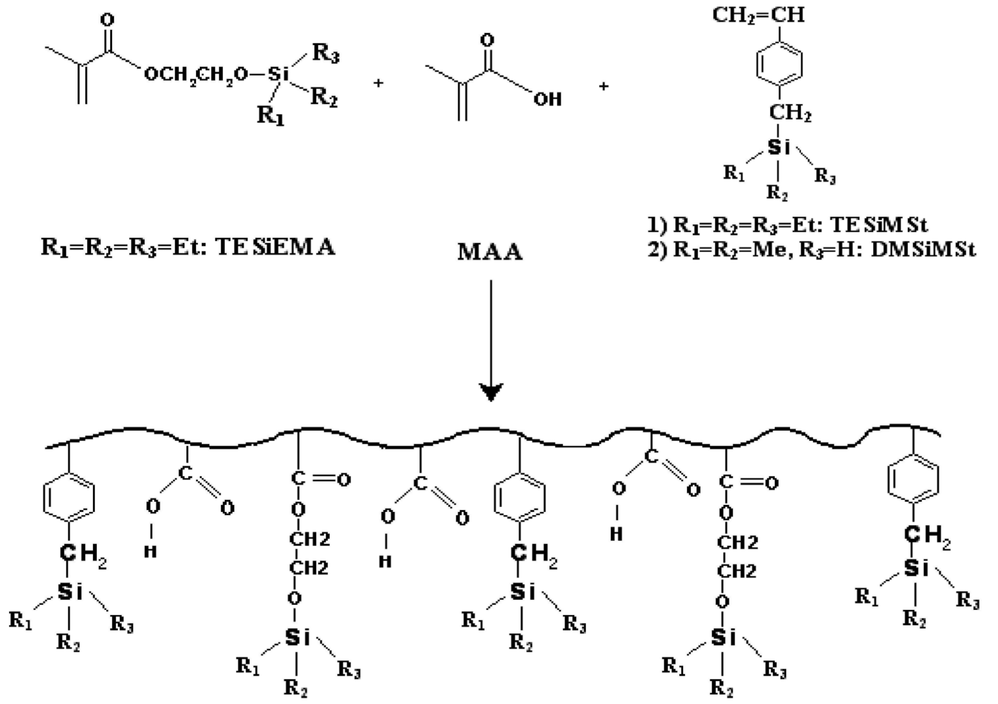
Copolymerization

Terpolymer (MAA, TESiEMA and TESiMSt) (P-1) and Terpolymer (MAA, TESiEMA and DMSiMSt) (P-2) in two different molar ratio was synthesized as in the following general method. In three pyrex glass ampoules, a mixture (MAA, TESiEMA and TESiMSt: 1:1:1), (MAA, TESiEMA and DMSiMSt: 1:1:1) and (MAA, TESiEMA and DMSiMSt: 1:2:1) by using azobisisobutyronitrile (AIBN) as initiator ([I] = 0.02 M) was dissolved in dioxane, respectively. Then the ampoules were degassed, sealed under vacuum and maintained at 70 °C in a water bath and shaken by a shaker machine for about 60 h. Then the viscous solutions were poured from the ampoules into 100 mL of cooled methanol, separately. The precipitates were collected and washed with methanol several times and dried under vacuum at room temperature to give 85% of terpolymer P-1, 91% of terpolymer P-2 and 95% of P-3. (Scheme II).

P-1: IR (neat, cm^{-1}): 3423, 2955, 2876, 1733, 1509, 1458, 1261, 830. ^1H-NMR (d-DMSO, ppm) δ 0.41-0.47 (q, 12H, $SiCH_2$), 0.88 (t, 18H, CH_3CH_2Si), 1.02-2 (br, CH_3, CH_2), 3.55-3.87 (br, 4H, -OCH_2-CH_2O-), 6.99 (br, Ar-H), 11.97 (br, 1H, -COOH).

P-2: IR (neat, cm^{-1}): 3428, 2951, 2859, 2116, 1727,

Scheme II Preparation of acrylate-styrene terpolymers containing silyl groups



1513, 1454, 1261, 888. ^{1}H-NMR (d-DMSO, ppm) δ 0.07 ($SiCH_3$), 0.47 ($SiCH_2$), 0.88 (CH_3CH_2Si), 0.91-1.9 (br, CH_3, CH_2-Ar), 3.86 (br, 4H, -OCH_2-CH_2O-), 4.76 (br, Si-H), 6.76 (br, Ar-H), 12 (br, -COOH).

P-3: IR (neat, cm^{-1}): 3443, 2958, 2735, 2114, 1731, 1455, 1261, 888. ^{1}H-NMR (d-DMSO, ppm) δ 0.047 ($SiCH_3$), 0.43 ($SiCH_2$), 0.88 (-CH_3, CH_3CH_2Si), 1.0-1.9 (br, CH_3, CH_2-Ar), 3.86 (br, 4H, -OCH_2-CH_2O-), 4.76 (br, Si-H), 6.74-7.19 (br, Ar-H), 12 (br, -COOH).

Thermal Behaviour

The glass transition temperature (Tg) of all polymers was determined by DSC analyses. The values are given in Table 1. Several factors affect the Tg: decreased mobility of polymer chains, increased chain rigidity, and a resulting high Tg. Materials characterized as having high Tg have high degrees of crystallinity, crosslinking, or rigid chains and yield high strength and low elongation. High elongation flexible side groups increase chain separation, and the Tg decreases. Cyclic monomers tend to exhibit high Tg values. The rigidity of polymer chains is especially high when there are cyclic structures in the main polymer chains. The study of DSC curves showed that incorporation of TESiMSt and DMSiMSt with cyclic units in polymer chains increases the rigidity of terpolymers and the Tg value is subsequently increased. But TESiEMA increases the flexibility of hard polymers and reduces its Tg. The aliphatic silyl units not only reduced internal hydrogen bonds between the polymer chains but also as a plasticizer increased the flexibility of hard polymers and reduced its Tg.

Table 1. DSC data and molar composition of terpolymers

Copolymer	Molar composition of monomers in the feed	(% mole) m	(% mole) n	(% mole) q	Mn[a]	Tg (°C)
P-1: (TESiEMA)m (ESiEMA)n (MAA)q	1:1:1	43	29.5	27.5	8500	115
P-2: (DMSiMSt)m (ESiEMA)n (MAA)q	1:1:1	57.5	16.3	26.2	11000	129
P-3: (DMSiMSt)m (ESiEMA)n (MAA)q	1:2:1	21.5	60.2	18.3	13500	100

[a] Determined by a cryometric method in formic acid.

RESULTS AND DISCUSSION

The copolymer compositions were calculated from the ^{1}H-NMR spectra data. In the past few decades, ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the determination of copolymer compositions because of its simplicity, rapidity and sensitivity.[9] The molar compositions of TESiMSt, TESiEMA and MAA in a copolymer of P-1 were calculated from the ratio integrated intensities of the peaks around δ 6.99 ppm, corresponding to four protons of phenyl in TESiMSt units and peaks around δ 3.5 ppm, which were attributed to four protons of TESiEMA units and peaks around 12 ppm, which were attributed to one proton of MAA units.

The molar compositions of TESiEMA, TESiMSt and MAA were calculated from Eqs. (1), (2) and (3) where m, n and q were the mole fractions of TESiEMA, TESiMSt and MAA, respectively.

$$\frac{\text{Area at 3.5-3.87 ppm}}{\text{Area at 6.99 ppm}} = \frac{4m}{4n} \quad (1)$$

$$\frac{\text{Area at 3.5-3.87 ppm}}{\text{Area at 12 ppm}} = \frac{4m}{q} \quad (2)$$

$$m + n + q = 1 \quad (3)$$

Similar methods were used to calculate the molar composition of copolymers P-2 and P-3. The composition of copolymers is presented in Table 1. As shown in Table 1, the low reactivity ratio of TESiMSt in copolymer (P-1), perhaps related to the steric effect of the bulky silyl group in TESiMSt, which reduces the molar composition of this monomer and molecular weight of polymers. With the reducing of the steric effect in DMSiMSt (P-2) more than in TESiMSt, the molar composition of DMSiMSt in the polymer chain and molecular weight increased.

CONCLUSION

For preparation of polymerizable monomers, it is necessary to design synthetic conditions mild enough to allow attachment without any side reaction at the vinyl group. By using a metalation reaction of 4-methylstyrene to form 4-vinylbenzylllithum, we synthesized novel silyl monomers. This type of monomer can easily be copolymerized with various vinyl monomers to improve the hydrolytic behavior by introducing hydrophilic units along the polymer chain. The terpolymeric hydrogels containing silyl pendant groups were synthesized by free radical copolymerization. Synthesis of new organosilyl polymers can produce novel polymer systems with new physical and chemical properties and new applications. The polymers with silyl groups have been used as a membrane before; therefore, we expect these polymers also possess membrane properties.

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