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Synthesis of 4-vinyl benzyl tetra-coordinate silicate monomer

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Summary

A new 4-vinyl benzyl tetra-coordinate silicate (**VBTCS**) was synthesized from a promising highly reactive penta-coordinate potassium glycolato silicate compound through a facile and one-step reaction. FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analysis identified the structure of the 4-vinyl benzyl tetra-coordinate silicate. This new monomer was homopolymerized and copolymerized with styrene and butylmethacrylate, respectively. FT-IR, TG, DSC and GPC characterized polymers.

Introduction

Organic silicon feedstock almost comes from silica (SiO_2) of carbon-thermal reduction steps that are energy-intensive and equipment-intensive. Up to now, a challenge encountered in silicon chemistry is to use silica and other cheap materials as resources for directly making chemicals and polymers. Several groups had striven to explore the possibility of transferring silica directly into organic silicon chemicals. In 1931, Rosenheim et al. firstly reported synthesis of the hexa-coordinate silicon compound, tris (catecholato) silicate, by the reaction of silica, sand or even quartz with catechol (1,2-dihydroxobenzene) in basic media[1]. Unfortunately, the tris (catecholato) silicate is quite stable and inactive, so it was not applied widely. Until 1980s, Corriu's group found that it could be modified effectively by reactions with expensive strong nucleophilic reagents [2-4]. However, penta-coordinate compounds that were prepared by Laine et al. are so reactive that they exist stably only under a purified nitrogen atmosphere [5]. Furthermore, as promising starting materials, they are used for synthesis of semi-conductors, ceramics, organic-inorganic hybrid materials and inorganic polymers by a series of simple reactions [6-10].

Organic silicon polymers play an important role in the industry for their excellent properties. It is attractive for organic silicon industry to obtain the cheap and accessible functional silicon monomer. In 1992, Laine et al. reported that they used the penta-coordinate potassium glycolato silicate as a starting material reacting with the dried gas of hydrogen chloride to synthesize the symmetrical dihydroxyl tetra-coordinate silicon (a) [10]. In 1998, Laine et al. conceived the preparation of ethylene-containing tetra-coordinate silicates, but the details were not claimed in their report [11]. Recently, by replacing the dried gas of hydrogen chloride with 2-chloroethanol and epichlorohydrin, respectively, Song et al. obtained dihydroxyl tetra-coordinate silicon (b) and epoxy hydroxyl tetra-coordinate silicon (c) (scheme I)[12-14].

In this report, we prepare a new 4-vinyl benzyl tetra-coordinate silicate compound (**VBTCS**) containing the styrene group (reaction (1)). Compared with penta-coordinate silicates, these tetra-coordinate silicates are relatively stable and can be further transferred to organic polymers. Being of hydroxyl and 4-vinyl benzyl, the **VBTCS** is desirable for synthesizing carbon backbone polymers for grafting and cross-linking. Noticeably, in this report, self cross-linking effect is found as a prominent property of the **VBTCS** which may be applied for solvent-resistant self cross-linking coating resin.

Experimental

Materials

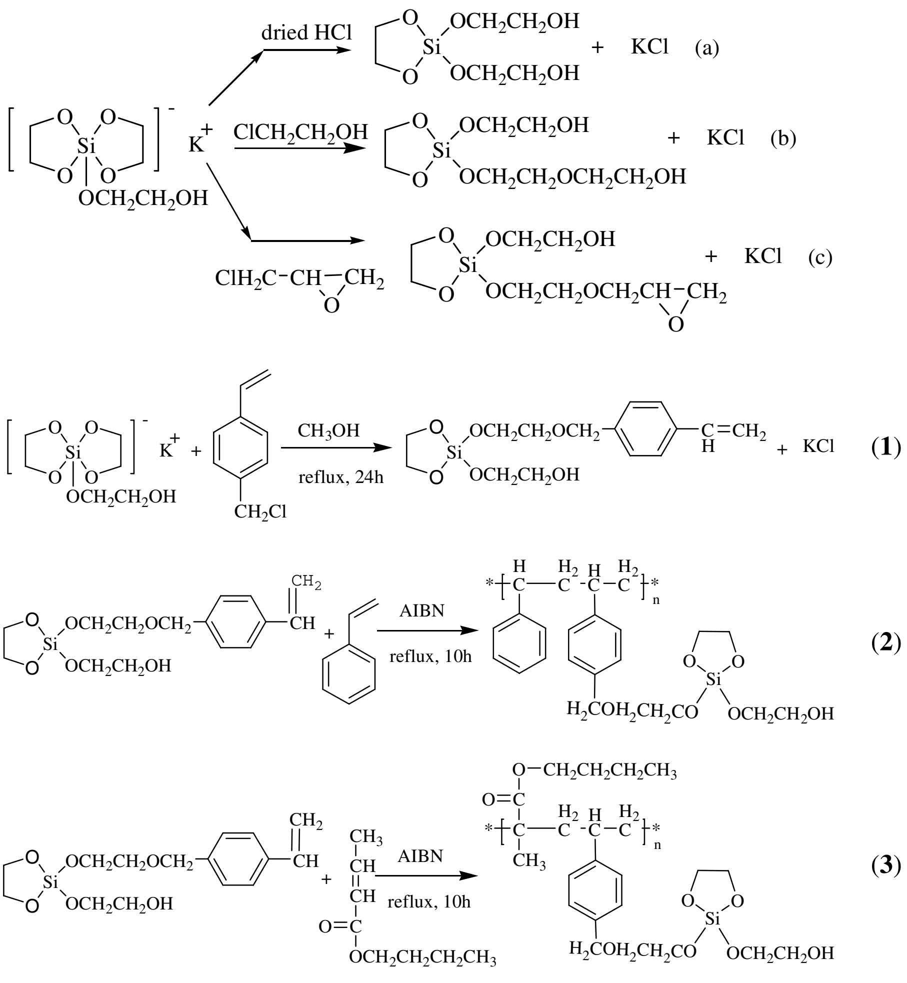
Methanol was purchased from Hangzhou Chemical Reagent Co. Ltd of China. Acetonitrile was obtained from Shanghai Tingxing Chemical Reagent Factory. Benzene came from Shanghai Lingfeng Chemical Reagent Co. Ltd. Fumed silica is the Cas-O-Sil M-5 product of Cabot Corporation. Potassium hydroxide was purchased from Shanghai Chemical Reagent Co. Ltd. All above reagents are of analytical grade. 4-chloromethyl styrene (95%, Wujin Linchuan Chemical Co, Ltd., Jiangsu), styrene and butyl methacrylate (99%, Shanghai Chemical Reagent Co. Ltd.) contain 20–40ppm tert-butylcatechol which should be removed before use and kept at -18°C. Methanol and benzene were dehydrated by 4 A molecular sieves in advance. The purity of nitrogen is above 99.9%. Penta-coordinate potassium silicate was synthesized according to the literature [5].

Measurements and instrumentations

The liquid NMR spectra were recorded on a 500MHZ Bruker spectrometer and CD_3SOCD_3 was used as solvent. IR spectra were analysed using a Nexus 870 Fourier-transform infrared spectrophotometer. Elemental analysis of the **VBTCS** was preformed on a CHN-O-Rapid elemental analyzer (Germany). Analysis of the Si content was completed by weight analysis. Thermal data were obtained by using PerkinElmer Thermal Analysis in N_2 atmosphere. Gel Permeation Chromatograph (RAX, Agilent 1100) was applied to determine molecular weight ($\overline{M_w}$ and $\overline{M_n}$) of polymers with DMF as solvent.

Synthesis of monomer

Penta-coordinate potassium glycolato silicate (7.45 g, 30mmol) was dissolved in 60mL methanol, 4-chloromethyl styrene (8.24g, 54mmol), and tri-ethylamine (0.3g) used as catalyst were added in a 100-mL dried round bottom flask. The reaction mixture was refluxed with magnetically stirring under N_2 atmosphere for 24 h. During the reaction, there was the white crystal deposition. The resulting mixture was filtered to separate the white crystal potassium chloride. The methanol was removed from the filtrate under reduced pressure and residue was washed with benzene (20mL×3), and then extracted by a mixed solvent of benzene and methanol (4:1, v/v). The upper extraction liquid was distilled off solvent under reduced pressure, and then dried under vacuum at 333K for 1 h, and the **VBTCS**, light yellow clear oil, was obtained (82.5%).



Scheme I

Synthesis of polymer and copolymers

According to Table 1 listed, the **VBTCS** was firstly homopolymerized, and then copolymerized with styrene (**St**) and butyl methacrylate (**BMA**), respectively (reaction (2), (3)). The amount of monomers **VBTCS**, St, BMA and 2,2’-azobisisobutyronitrile (AIBN) as an initiator were dissolved into 40mL methanol (as solvent), and 25% solution were placed into a 100mL three-necked round bottom flask provided with a magnetic stirrer, argon inlet, reflux condenser, the temperature of the system was raised to the boiled point of methanol. After 1h, 75% solution was added through the dropping funnel into the system in 3 h. Then the temperature of the system was kept at the boiled point for 6 h. The polymers were isolated from their solutions through precipitation in 200mL ethyl acetate. The isolated polymers were washed with ether (20mL×3) and were dried in vacuo at 50°C for 8h. Conversions of polymers were showed in Table 1.

Table 1. Synthesis conditions, differential scanning calorimetry and molecular weight data of polymers

Polymers	PVBTCS	P (BMA-co-VBTCS)	P (St-co-VBTCS)
VBTCS (Mmol.)	100	20	20
Styrene (Mmol.)			80
Butyl mathacrylate (Mmol.)		80	
Conversion (%)	82	73	75
$\overline{M_w}$ (10^4)		6.73	2.61
$\overline{M_n}$ (10^4)	0.262*	3.38	1.58
$\overline{M_w}/\overline{M_n}$		1.99	1.65

The weight of AIBN is equivalent to 0.5% monomers weight.

*: The figure is molecular weights of the **PVBTCS** calculated by peak value of the GPC curve.

Results and discussion

IR analysis of monomer

Shown in Fig. 1 are infrared spectra of 4-chloromethyl styrene, **VBTCS** and penta-coordinate potassium glycolato silicate. In the spectrum of **VBTCS**, there are three strong characteristic absorption bands at 3300-3400cm^{-1} (ν_{OH}), 1090 cm^{-1} ($\nu_{Si\text{-}O\text{-}C}$), and 2800-3000cm^{-1} (ν_{CH}), which are assigned to the spectra of penta-coordinate silicon complex [15]. It indicates that the glycolate silicon group is the part of **VBTCS** structure. In addition, all peculiar peaks of 4-chloromethyl styrene at 3087cm^{-1} (ν_{CH}), 1630cm^{-1} ($\nu_{C=C}$), and 1450-1600 cm^{-1} for the backbone of benzene, except 681cm^{-1} and 730cm^{-1} ($\nu_{C\text{-}Cl}$) and 1265cm^{-1} for CH_2Cl [16,17], appears in the spectra of **VBTCS**. The disappearance peaks of 681cm^{-1}, 730cm^{-1} and 1265cm^{-1}, in contrast to the spectra of 4-chloromethyl styrene, verifies that chlorine has been removed and the styrene group is incorporated into the **VBTCS** structure.

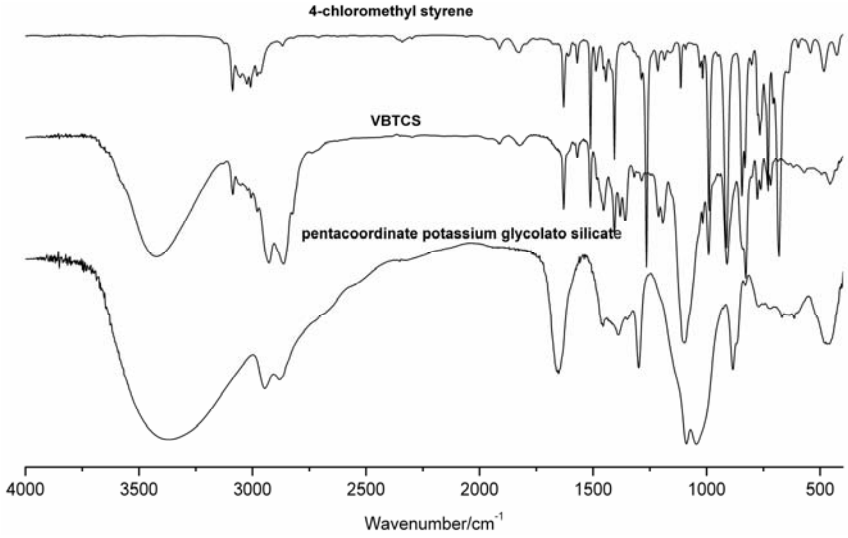
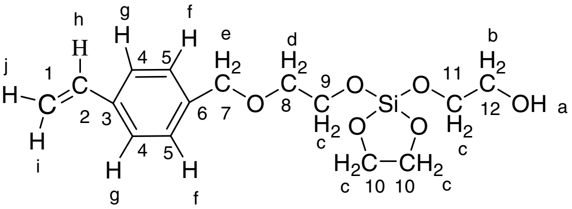


Figure 1. FTIR spectra of 4-chloromethyl styrene, **VBTCS** and penta-coordinate potassium glycolato silicate



Scheme II

Nuclear magnetic resonance analysis of monomer

^{1}H NMR (DMSO-d_6): δ7.33-7.43 (m, H-g), 7.25-7.33 (m, H-f), 6.66-6.73 (q, H-h), 5.83 (d, *J* = 7.5 Hz, H-j), 5.25 (b, *J* = 6.0 Hz , H-i), 4.64-4.66 (t, H-a), 4.46-4.55 (t, H-e), 3.50-3.53 (t, H-d), 3.38-3.47(m, H-c), 3.27-3.29 (t, H-b) (scheme II).

^{13}C NMR (DMSO-d_6): 138.4 (C-6), 136.3 (C-2), 133.8 (C-3), 127.8 (C-4), 126.0 (C-5), 114.0 (C-1), 73.3 (C-7), 71.7 (C-8), 70.3 (C-12), 62.8 (C-10), 60.3 (C-11), and 57.5 (C-9).

Elemental analysis

Elemental analysis of **VBTCS**: Calc. for: $C_{15}H_{22}O_6Si$: C, 55.26%; H, 6.78%; Si, 8.59%. Found: C, 53.79%; H, 7.08%; Si, 8.89%.

IR structure analysis of the polymers

The FT-IR spectra of the Homopolymer (**PVBTCS**) and Copolymers of Styrene and **VBTCS** (**P(St-co-VBTCS)**) and butyl methacrylate and **VBTCS** (**P(BMA-co-VBTCS)**) is shown in Fig. 2. In the IR spectrum of three polymers showed same strong characteristic absorption peaks at 3300-3400cm^{-1} (ν_{OH}), 1090 cm^{-1} ($\nu_{Si\text{-}O\text{-}C}$), and 2800-3000cm^{-1} (ν_{CH}), which are assigned to the spectra of tetra-coordinate silicon compound. The absorption peak of 1630cm^{-1} ($\nu_{C=C}$) disappearance indicated the **VBTCS** monomer can be polymerized and incorporated into copolymers.

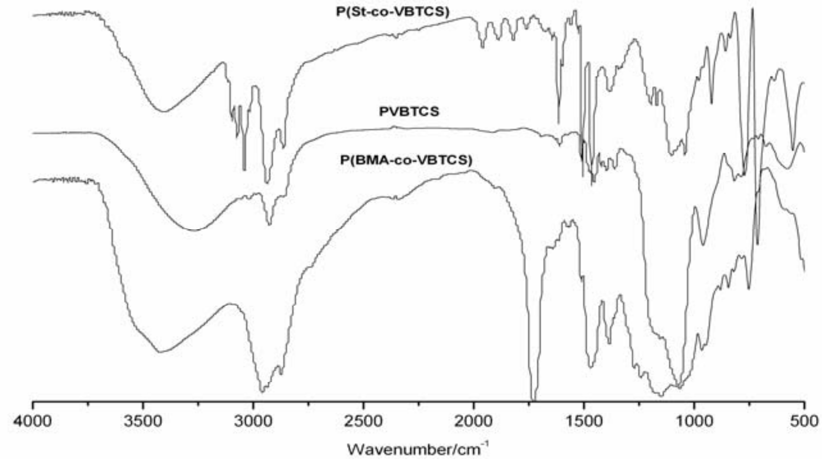


Figure 2. FT-IR spectra of P (St-co-VBTCS), PVBTCS and P (BMA-co-VBTCS)

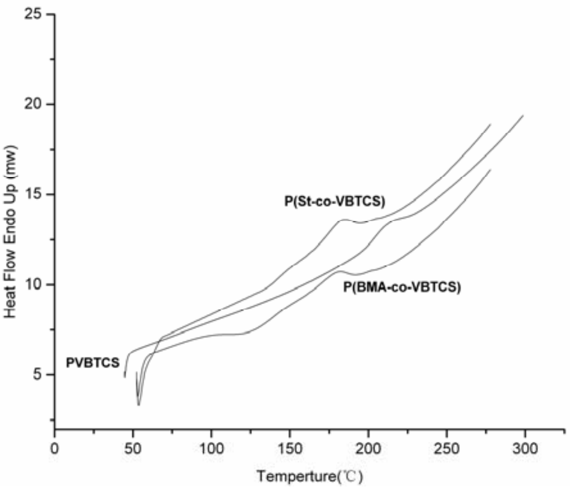


Figure 3. DSC curves of the polymers heated in nitrogen at a heating rate of 10°C/min

Thermal analysis of polymers

From differential scanning calorimetry (DSC) measurements, the glass-transition temperatures were obtained as midpoints of the glass-transition region. DSC curves and glass-transition and the decomposition temperatures of the polymers are shown in Fig. 3 and listed in Table 2, respectively. As shown in Table 2, the T_g of **P(St-co-VBTCS)** and **P(BMA-co-VBTCS)** are higher than that of pure PS and PBMA. This might be attributable to two effects. One is the bulky substituent group; copolymers bearing bulky side groups generally have a higher glass transition temperature, because for such a chain, the moving segment needs a larger energy. The other is self cross-linking of copolymerization monomer **VBTCS** between chains, which could be occurred; cross-linking restricts small segment movement and improves glass transition temperature (Details of self cross-linking effect of polymers are discussed in Potential application section). These effects are easily seen by reference to the results [18]. It is also the effect of self cross-linking that result in no glass-transition temperature for **PVBTCS** and no melting point for **PVBTCS**, **P(St-co-VBTCS)** and **P(BMA-co-VBTCS)**.

Table 2. Differential scanning calorimetry and thermogravimetric analysis data of polymers

Polymers	T_g (°C)	T_d (°C)
PVBTCS		200.5
P(BMA-co-VBTCS)	107	174
P (St-co-VBTCS)	131	181

Molecular weights of the polymers

The molecular weights of the polymers were measured by GPC with DMF as the solvent. The weight average and number average molecular weights and the polydispersity indexes of polymer samples are listed in Table 1. The weight average and number average molecular weights of the PVBTCS are both near to the value of 2620, which is the molecular weight of peak value of the GPC curve, and the degree of polymerization is approximately equal to 8. This could be explained that the monomer VBTCS is easy to be polymerized, but the polymeric chain could not be grown longer because of the steric hindrance effect of the bulky substituent group of VBTCS preventing polymeric chain from increasing longer. The polydispersity indexes of **P(St-co-VBTCS)** and **P(BMA-co-VBTCS)** are 1.65 and 1.99, respectively.

Solubility of polymers

As solubility is one of the important requirements for polymers, the solubilities of the polymers in various organic solvents were tested. The solubility of the resulting polymers is summarized in Table 3.

Table 3. Solubility data of the resulting polymers

Solvent	PVBTCS	P(BMA-co-VBTCS)	P(St-co-VBTCS)
DMF	+ +	+ +	+ +
Methanol	+ +	+ +	+ +
THF	+	+	+
DMSO	+	+	+
Toluene	+	+	+
Acetone	±	±	±
Acetonitrile	±	±	±
n-Hexane	–	±	±
Ether	–	±	±
Chloroform	–	–	–

+ +, Soluble at room temperature; +, soluble by heating; ±, swelling or party soluble at room temperature; –, insoluble

Potential applications

Self cross-linking effect is a prominent property for homopolymer **PVBTCS** and copolymers of **P(St-co-VBTCS)** and **P(BMA-co-VBTCS)**. Three polymers can not be soluble again when they are dried in vacuo at 70°C for 8h or placed in room temperature for one week. It is worth notice that the **PVBTCS**, which is placed in room temperature for one week, can be hardly swollen, but **P(St-co-VBTCS)** and **P(BMA-co-VBTCS)** can be easily swollen. The effect might be due to difference of cross-linking density. Definite mechanism of self cross-linking is awaited to further research. Nevertheless **VBTCS** with the property of self cross-linking may be copolymerized with monomer containing vinyl group to be used as self cross-linking coating resin, which is of ability of solvent-resistant.

Monomer (**VBTCS**) both has a hydroxyl and vinyl group, it is suitable for grafting and cross-linking. Especially it may be as an effective compatibilizing additive for interpenetrating polymer networks (IPNs) formation based on cross-linked polyurethane and linear polystyrene or poly (butyl mathacrylate) to modify IPNs microphase separation, viscoelastic and thermomechanical properties.

Investigation on the mechanism of self cross-linking and applications of the novel monomer (**VBTCS**) is underway.

Conclusions

A novel 4-vinyl benzyl tetra-coordinate silicate is prepared via simple process. NMR, FT-IR and elemental analysis confirmed the structure of the novel monomer. Compared with the penta-coordinate silicates that exist only under dried N_2 atmosphere, the monomer **VBTCS** is relatively stable and is able to homopolymerize and copolymerize. With self cross-linking effect, hydroxyl and vinyl group, the **VBTCS** has highly promising to be extended for practical.

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