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Microwave assisted synthesis of high molecular weight polyvinylsilazane via RAFT process

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ABSTRACT

The microwave-assisted synthesis of high molecular weight polyvinylsilazane (H-PVSZ) leads to a narrow molecular weight distribution at accelerated polymerization rates under controlled/living polymerization, while retaining the excellent controllability offered by reversible addition fragmentation chain transfer (RAFT) polymerization in a thermal reaction process. Under microwave irradiation, higher molecular weight H-PVSZ (6250 vs. 4370) was obtained with higher conversion (86.7 vs. 30.1%) than under conventional heating through a simple 3 h reaction of vinylcyclicsilazane with a molecular weight of 314 in the presence of dithiocarbamate derivatives (RAFT agent) and 2,2′-azobis-isobutyronitrile (AIBN, thermal initiator). H-PVSZ with a well-controlled high molecular weight is useful for synthesizing inorganic–organic diblock copolymer polyvinylsilazane-*block*-polystyrene (PVSZ-*b*-PS) with a higher molecular weight and lower polydispersity than by conventional heating of the PVSZ-derived product.

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1. Introduction

Preceramic polymers, such as polycarbosilane and polysilazane, are useful precursors for silicon carbide (SiC) and silicon nitride (Si_3N_4) ceramic materials [1]. These polymers enable a near-net shape manufacturing process for applications in a range of technologies, such as high temperature structural coatings, bulk ceramics, and MEMS devices [2–4]. Since the pioneering work of Verbeek and Winter [5] and Yajima et al. [6] in the 1970s, many studies have focused on the ability of various preceramic polymers to form amorphous, non-glassy Si-based ceramics. These ceramics have high resistance to chemical degradation [4], creep [7,8], oxidation [9], thermal shock, decomposition and softening [10], which are quite attractive in many structural ceramic and electronic applications [11]. In accordance with the expansion of their applications, the molecular weight of the preceramic polymers is a critical factor for achieving a near-net shape process by precisely controlling the wide range of inorganic polymer viscosities for adopting plastic processes at low temperatures, as well as for producing high density ceramics with a high ceramic yield. However, there has been little work on the synthetic routes to produce high molecular weight preceramic polymers, with the exception of the synthesis of high molecular weight polycarbosilane as an SiC ceramic precursor. However, a high temperature autoclave decomposition process at 400 °C could not be used to improve the molecular weight of alternative inorganic polymers. Recently, we reported an effective approach for enhancing the molecular weight of polyvinylsilazane (PVSZ) by reversible addition fragmentation chain transfer (RAFT) polymerization as a radical polymerization process [12]. However, the controlled molecular weight of the polymer structures involved a long reaction time (3 days), which is typical for RAFT chemistry. Microwave-irradiation has long been used to accelerate the reaction kinetics of conventional free-radical organic polymerization due to the rapid volume heating capability, resulting in much higher product yield [13]. This paper reports a facile microwave-assisted route for the rapid synthesis of high molecular weight PVSZ (H-PVSZ) with a narrow distribution at the accelerated kinetics of living radical polymerization, while retaining the excellent controllability offered by RAFT polymerization in the thermal reaction process. This is the first example of microwaves having such a dramatic effect on improving inorganic polymers. Furthermore, the enhanced H-PVSZ with a well-controlled high molecular weight was used to synthesize the inorganic-organic diblock copolymer polyvinylsilazane-*block*-polystyrene (PVSZ-*b*-PS).

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Table 1
Molecular weight of the enhanced H-PVSZ obtained by conventional heating and microwave processes in a toluene solvent and an AIBN initiator at 120 °C.

RAFT agent	Process	Time (h)	Mn	PDI	Conversion (%)
DTBA[a]	Thermal heating	36	4300	1.53	57.2
		48	8100	1.43	71.5
		60	10 503	1.35	80.4
	Microwave	1	1280	2.28	69.4
		2	4080	1.15	86.3
		3	6590	1.08	86.7
BPCD[b]	Thermal heating	48	2550	1.36	45.8
		60	8510	1.02	68.6
		72	8750	1.03	70.4
	Microwave	1	1057	1.95	69.8
		2	4045	1.13	77.3
		3	6234	1.07	81.7
HPCB[c]	Thermal heating	48	5850	1.92	28.2
		60	4370	2.16	30.1
	Microwave	1	1580	2.49	73.7
		2	4440	1.16	78.0
		3	**6250**	**1.12**	**86.7**
		4	5980	1.14	85.1

[a] 4-Diethyl thiocarbamoyl sulfanylmethyl-benzoic acid.
[b] Benzyl-1-pyrrolecarbodithioate.
[c] 4-[4-(2-Hydroxy-ethyl)-piperazine-1-carbothioylsulfanylmethyl]-benzoic acid.

2. Experimental section

All reactions were carried out in a purified argon atmosphere using standard Schlenk techniques. All glassware used was stored for several hours in a drying oven at 100 °C. Anhydrous toluene (99.99%, Aldrich Co. Ltd.) was used as-received. The styrene was purchased from Aldrich Co. Ltd. and purified by distillation over CaH_2 under a reduced pressure. 2,2′-Azobis-isobutyrylnitrile (AIBN) was obtained from ACROS Organic and used as-received. In this study, three types of RAFT agents, 4-Diethyl thiocarbamoyl sulfanylmethyl-benzoic acid (DTBA), benzyl-1-pyrrolecarbodithioate (BPCD) and 4-[4-(2-Hydroxy-ethyl)-piperazine-1-carbothioylsulfanylmethyl]-benzoic acid (HPCB), were used. The RAFT agents were synthesized as previously reported [12].

2.1. Microwave-assisted synthesis of H-PVSZ

High molecular weight H-PVSZ was prepared using an 800 psi microwave reactor (MARS-5, CEM) with a maximum power of 1200 W. The temperature was controlled using an RTP 300 probe sensor. In this process, 5 ml (16.7 mmol) vinylcyclicsilazane (KiON VL20, molecular weight 314) was added to the vessel of a microwave reactor, followed by the addition of 55 mg (0.33 mmol) of 2,2′-azo-bis (isobutyronitrile) (AIBN), 68 mg (0.21 mmol) of HPCB (47 mg and 57 mg with BPCD and DTBA, respectively, for the same number of moles) and 2 ml of toluene. The vial was then sealed, pre-stirred to dissolve the initiator before being subjected to microwave irradiation. The microwave reactions were carried out at 120 °C for the desired reaction time. The desired temperature was reached typically within 15 min and the microwave power was adjusted by tuning the cooling nitrogen flow. For comparison, high molecular weight H-PVSZ was also produced using a conventional heating process in an oil bath. Briefly, sealed vials with the desired amount of reactants and solvent were prepared in a similar manner to that used in the microwave-assisted reaction, immersed into a 120 °C oil bath and heated with constant stirring for 72 h.

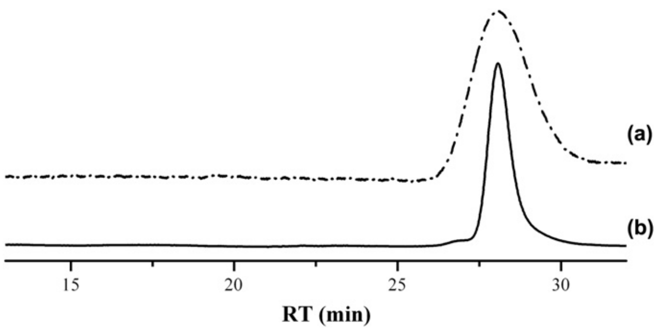


Fig. 1. GPC data of H-PVSZ obtained by (a) conventional heating for 60 h and (b) microwave process for 3 h in the presence of the HPCB agent.

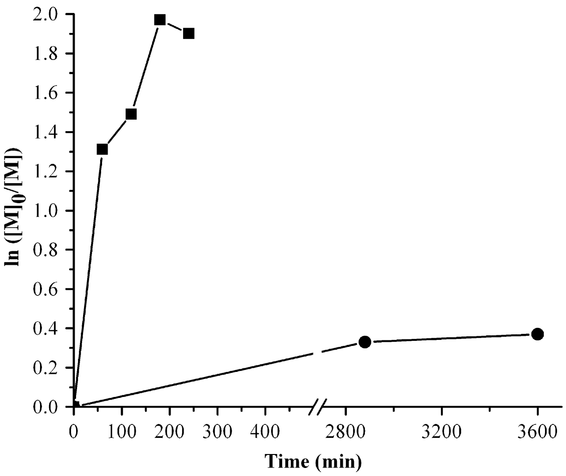


Fig. 2. Kinetic plot for RAFT polymerization of PVSZ using HPCB as RAFT agent with thermal heating (cycle) and microwave process (square).

2.2. Synthesis of polyvinylsilazane-block-polystyrene diblock copolymer

2 g H-PVSZ and 3 ml toluene were added to a Schlenk tube. A solution containing 3 g of styrene and 5 mg of AIBN was then added. After the solution was degassed with three freeze–evacuate–thaw cycles and sealed, the tube was heated to 120 °C for 4 h. The volatiles were removed under reduced pressure to give polyvinylsilazane-*block*-polystyrene [14]. The resulting polymer was diluted in THF and precipitated by adding excess *n*-hexane. The purified polyvinylsilazane-*block*-polystyrene (PVSZ-*b*-PS) was filtered and vacuum dried.

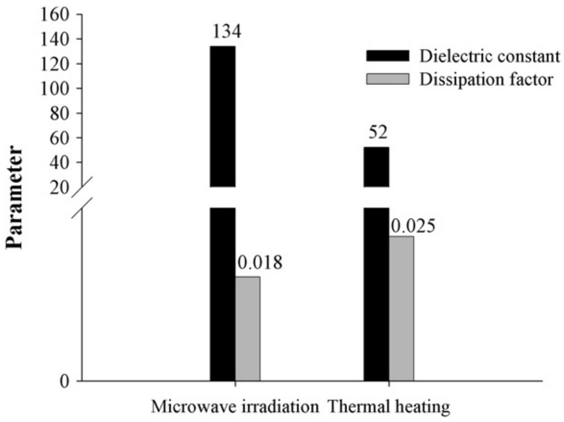
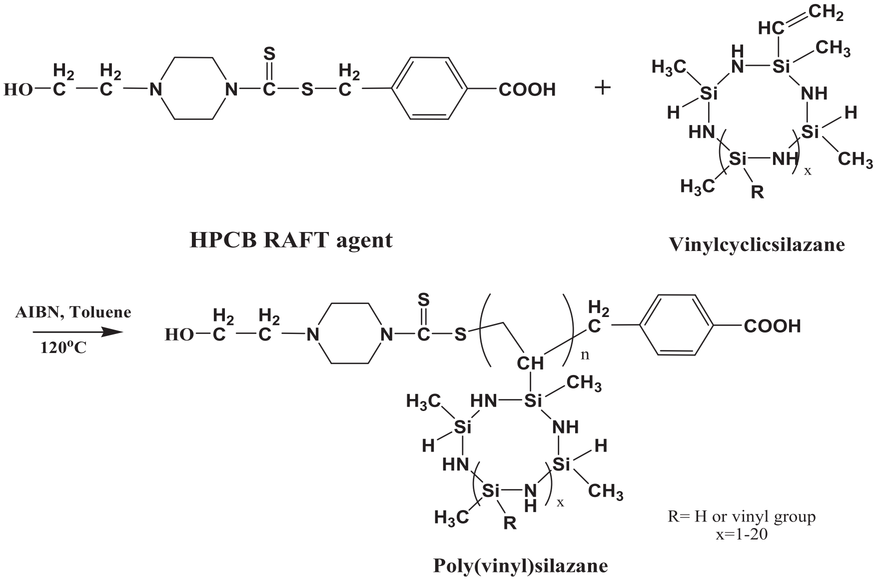


Fig. 3. Dielectric constant and dissipation factor of the H-PVSZ mixture under conventional oil bath and microwave irradiation (measured at 100 kHz) conditions.



Scheme 1. Synthetic route for enhanced H-PVSZ in the presence of 4-[4-(2-hydroxy-ethyl)-piperazine-1-carbothioylsulfanylmethyl]-benzoic acid (HPCB) as a RAFT agent.

2.3. Characterization

The ^{1}H nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ using a Bruker DMX600 spectrometer at 600.05 MHz with a 7788 Hz spectral width, a relaxation delay of 1.0 s, and a pulse width of 30°. The thermal properties of the polymer samples were measured by thermogravimetric analysis (TGA, TA Instrument 2050) using a platinum crucible up to 1000 °C in an argon atmosphere at a flow and heating rate of 70 ml min^{-1} and 5 °C min^{-1}, respectively. The molecular weight distribution of the synthesized polymers was examined by gel permeation chromatography (GPC, Waters 2850) using a Waters 515 HPLC isocratic pump equipped with a Waters 2414 Refractive Index detector and Waters Styragel columns (7.8 × 300, HR 1, 2, 3, 4, 5E). Tetrahydrofuran (THF) (flow rate of 1.0 ml/min) was used as the solvent and polystyrene (Shodex standard) was used as the standard for universal calibration. The IR spectra were obtained on an FT-IR spectrometer (Mattson Genesis II) using the KBr pellet technique. To measure the dielectric constant, H-PVSZ thin films were deposited on Copper clad laminate (CCL) and copper/Si substrates using pulsed laser deposition technique with a pulsed KrF excimer laser (248 nm, Lamda Physik COMPexPro 201). The dielectric constant was measured by dielectric analysis (DEA, HP Analyzer 4194A) at 100 kHz, which was obtained using the following equation: $\varepsilon = (C \times d)/\varepsilon_0$ where ε_0 is the matrix dielectric constant (8.85×10^{-14} F cm^{-1}), C is the capacitance density of the dielectric

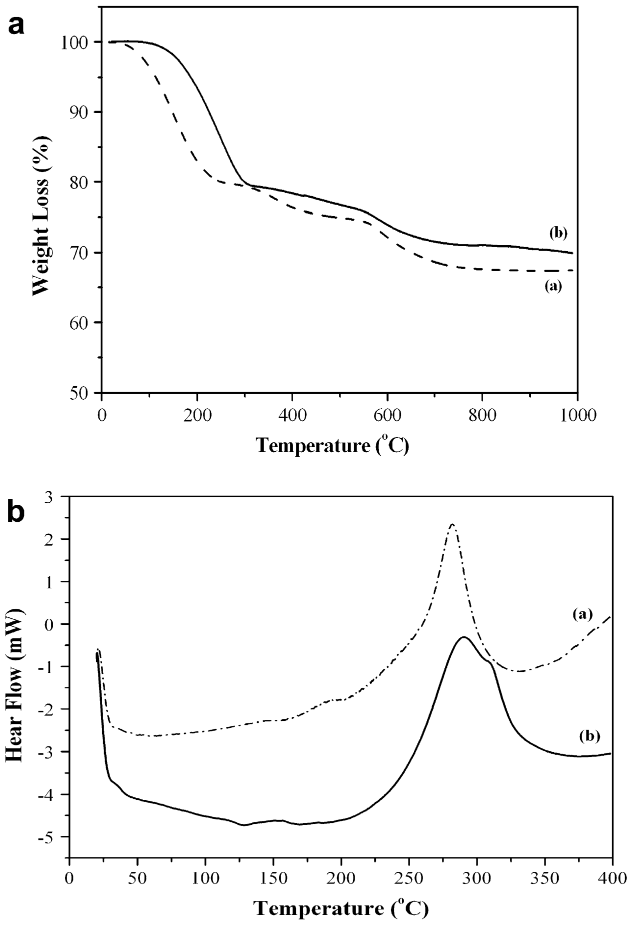


Fig. 4. TGA and DSC thermogram of H-PVSZ obtained by (a) conventional heating for 60 h and (b) microwave process for 3 h in the presence of the HPCB agent.

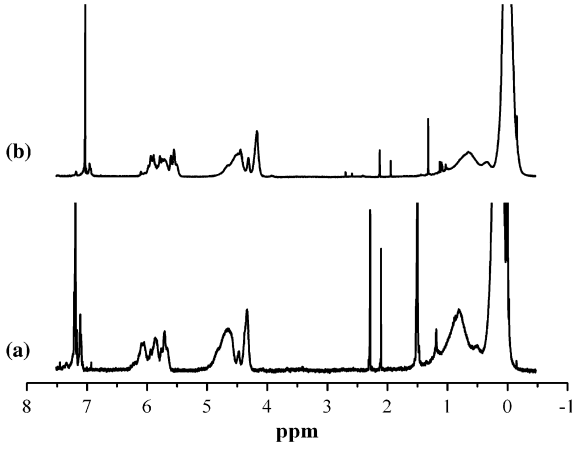


Fig. 5. ^{1}H NMR of H-PVSZ obtained using the HPCB agent by (a) thermal heating for 60 h and (b) microwave process for 3 h.

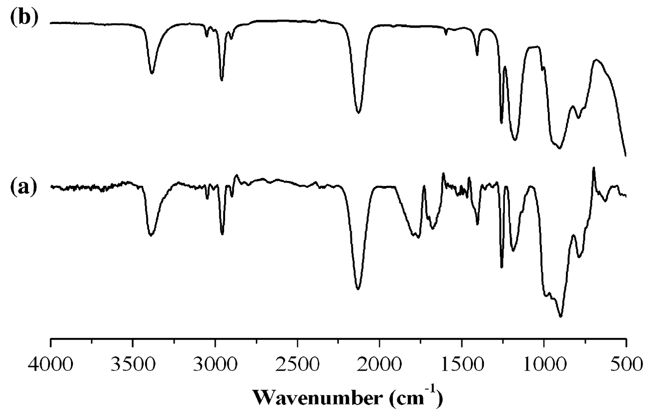


Fig. 6. FT-IR spectra of H-PVSZ obtained using the HPCB agent by (a) thermal heating for 60 h and (b) microwave process for 3 h.

between two parallel plates and *d* is the sample thickness (7.4 μm and 4.5 μm for the microwave irradiation and thermal heating sample, respectively). The degree of polymerization was calculated from the NMR spectra using the signals of the vinyl group of the polymer and monomer.

3. Results and discussion

Vinylcyclicsilazane was polymerized in the presence of AIBN as an initiator and dithiocarbamate compounds as RAFT agents under both conventional heating and microwave accelerated reactions conditions. The dithiocarbamates as RAFT agents were used preferentially because the leaving group was identical to the initiating species generated by the decomposition of the free-radical initiator, AIBN [15,16].

The effect of the chain transfer agents on the polymerization of vinylcyclicsilazane was examined using 3 types of chain transfer agents. Table 1 shows the comparative molecular weight of the various H-PVSZ products obtained under conventional heating and microwave heating conditions. First, enhanced polymerization occurred at 120 °C in toluene while there was no increase in molecular weight observed at 80 °C. The H-PVSZ products obtained transformed into a moisture sensitive pale yellow gel, which was soluble in common organic solvents, such as hexane, tetrahydrofuran, benzene and toluene.

Surprisingly, the H-PVSZ products obtained by microwave irradiation showed a significantly higher molecular weight after a reaction period of only 2–4 h, while 48–60 h was required in conventional oil bath heating. In addition, a 3 h microwave process rendered a consistently lower narrow polydispersity of 1.07–1.12, while the polydispersity after conventional heating for 60 h ranged from 1.02 to 2.16. In particular, in a conventional oil bath, the HPCB agent was less efficient in increasing the molecular weight than the other DTBA and BPCD agents, presumably due to steric hindrance, as reported elsewhere [15]. However, under microwave irradiation, the HPCB agent showed a comparable effect in obtaining the H-PVSZ product to the other RAFT agents. Interestingly, in the presence of HPCB, microwave irradiation for 3 h, the molecular weight of vinylcyclicsilazane was increased from 314 to 6250 with 87% conversion, while the conventional oil bath for 60 h produced an increase in molecular weight to 4370 with 30% conversion. Fig. 1 presents the characteristic GPC traces of the H-PVSZ obtained from the thermal heating and microwave-assisted process. Fig. 2 shows $\ln([M]_0/[M])$ as a function of time plots (where $[M]_0$ is the initial monomer concentration and $[M]$ is the monomer concentration at the corresponding time). The slope of the line of best fit suggests that the polymerization rates are higher for the microwave process than for thermal heating even with a short time reaction.

High dielectric materials can induce rapid volume heating effect under microwave irradiation [17,18]. Fig. 3 shows the dielectric constant of an H-PVSZ mixture obtained from the polymerization of vinylcyclicsilazane with a HPCB agent under microwave irradiation and conventional oil bath conditions. The H-PVSZ mixture treated with the microwave process showed a dielectric constant of 134, which is much higher than the 52 obtained from the H-PVSZ mixture heated in a conventional oil bath. The difference in dielectric constant is most likely due to the different concentrations of radicals and ions generated from the RAFT agent. This suggests that the H-PVSZ mixture can favorably absorb microwave energy to be heated rapidly and uniformly, compared to the conventional heating system. Moreover, the dissipation factor under microwave irradiation was 0.018 for the H-PVSZ mixture, which is lower than the 0.025 in the oil bath. This suggests that there was less heat loss during the reaction time under microwave irradiation than in the conventional heating process.

It is obvious that microwave irradiation can maintain a constant and uniform energy input for rapid RAFT polymerization kinetics due to the overall increase in both the propagation rate and addition–fragmentation rates of the degenerative chain transfer reaction. In particular, the HPCB agent, despite having a sterically hindered chemical structure, also performed rapid chain transfer due to the strong energy generated from the microwave irradiation, presumably to promote polymerization of the vinyl group, as shown in Scheme 1. In addition, it allowed excellent control over the molecular weight with a narrow distribution. This is in contrast to the conventional heating process, highlighting the potential use of this process for fabricating dense ceramic parts.

Fig. 4 shows the results of thermogravimetric analysis (TGA) of the enhanced H-PVSZ products from the HPCB agent under conventional heating for 60 h and microwave irradiation for 3 h. The H-PVSZ product synthesized by the microwave method showed a 70 wt% ceramic yield while the product produced using the conventional heating method showed a slightly lower yield of 67%. This is consistent with the DSC thermogram in that H-PVSZ with higher molecular weight by the microwave process showed an exothermic

Table 2
PVSZ-*b*-PS diblock copolymers produced by various H-PVSZ products.

Process for H-PVSZ	Time[a] (h)	$M_{n(\mathrm{PVSZ})}$ (g/mole)	$M_{n(\mathrm{PVSZ\text{-}b\text{-}PS})}$ (g/mole)	PVSZ_m-*b*-PS_n (*m:n*)	PDI	f_{PVSZ}[b]	Conversion[c] (%)
Thermal heating	60	4370	8910	15:44	1.51	0.48	58.1
Microwave irradiation	2	4440	10,130	15:54	1.24	0.42	60.1
	3	6250	13,500	21:69	1.20	0.45	71.5
	4	5980	11,640	19:53	1.23	0.50	65.3

[a] Time taken to synthesize the first block H-PVSZ using the oil bath and microwave process. The block copolymers were synthesized by adding a mixture of styrene and AIBN and heating at 120 °C for 4 h.

[b] Volume fraction of the PVSZ block, controlled by change in reaction stoichiometry.

[c] Conversion of block copolymerization.

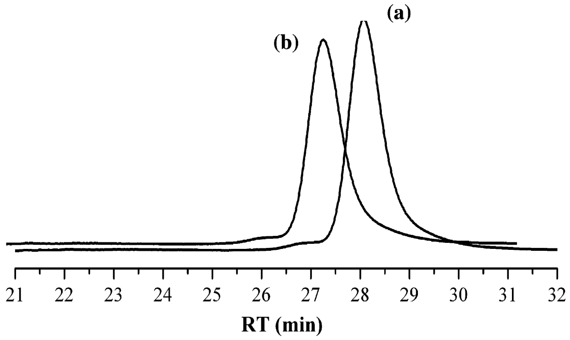


Fig. 7. GPC traces of (a) H-PVSZ obtained by microwave process ($M_n = 6250$ g/mol; PDI = 1.12), and (b) PVSZ-*b*-PS ($M_n = 13,500$ g/mol, PDI = 1.20).

peak at a slightly higher temperature of 290 °C, compared to the peak at 281 °C for the product from conventional heating.

The chemical structure of both H-PVSZ products from the HPCB agent was examined by ^{1}H NMR and FT-IR (Figs. 5 and 6). In the ^{1}H NMR spectrum, the unreacted vinyl groups and Si–H groups of PVSZ were observed at $\delta = 5.79$–6.22 ppm and 4.47–4.78 ppm, respectively [14]. As shown in Fig. 5, the relative integral ratio of –CH = CH$_2$/Si–H for H-PVSZ from the microwave process was 0.61, which is lower than the 0.79 obtained from the conventional process. This is also consistent with the FT-IR spectra in Fig. 6 in that the relative intensity ratios of the unreacted vinyl group and Si–H stretching peaks at 1405 and 2100 cm^{-1}, respectively [2], were 0.63 for microwave irradiation and 0.77 for conventional heating. This confirms that the vinyl groups of vinylcyclicsilazane were consumed to increase the molecular weight of PVSZ, as proposed in Scheme 1.

It is believed that the H-PVSZ obtained from the microwave process is desirable for the synthesis of an inorganic–organic diblock copolymer due to the low polydispersity. Moreover, the living radical route can be extended readily to the production of polyvinylsilazane-*block*-polystyrene (PVSZ-*b*-PS) diblock copolymers using a RAFT agent [12]. Table 2 shows the molecular weight and polydispersity of the PVSZ-*b*-PS block copolymers synthesized using the H-PVSZ products obtained from the HPCB agent. The resulting PVSZ-*b*-PS block copolymers from the microwave irradiated H-PVSZ showed a higher molecular weight (13 500) with a narrower polydispersity (1.20), than the 8910 and 1.51 obtained for the copolymer from the conventionally heated H-PVSZ. Fig. 7 shows the characteristic GPC traces of the PVSZ-*b*-PS block copolymer and macroinitial PVSZ produced from microwave radiation. The detailed polymer chemistry with self-assembly behavior as well as pyrolytic conversion to a mesoporous ceramic phase is currently under investigation.

The microwave assisted synthesis of PVSZ-*b*-PS block copolymer reduced the total reaction time dramatically to 6–8 h (including 4 h for the thermal synthesis of organic styrene block) from the 48–72 h for the conventional synthesis of the block copolymer with a similar molecular weight [12]. It is believed that the PVSZ-*b*-PS diblock copolymer has significant potential to generate various nanostructured nonoxide ceramics in combination with the advanced chemistry and processes of organic–organic diblock copolymers.

4. Conclusion

The microwave assisted synthesis of polyvinylsilazane (H-PVSZ) with enhanced molecular weight and narrow polydispersity was carried out successfully within 3–4 h using a RAFT polymerization route, which is much shorter than the 60–72 h required in conventional heating process. The H-PVSZ obtained in the presence of the HPCB agent by microwave irradiation showed a higher conversion yield, molecular weight and polydispersity of 86.7%, 6250 and 1.12, respectively. On the other hand, the conversion yield, molecular weight and polydispersity of the H-PVSZ product by conventional oil bath heating were only 30.1%, 4370 and 2.16, respectively. This suggests that a mixture of PVSZ–HPCB produced by microwave irradiation has superior dielectric properties (134 vs. 52) to that produced by oil bath heating. Microwave irradiation generates high energy to accelerate the rates of propagation and chain transfer of the RAFT process. The resulting H-PVSZ was used successfully to synthesize polyvinylsilazane-*block*-polystyrene diblock copolymers via living radical polymerization to produce the desired block copolymers with an excellent degree of control. This is the first example of microwave radiation producing such dramatic enhancement of the inorganic polymer with rapid kinetics.

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