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Formation, Characterization, and Stability of Novel Aluminocarbosilazane Macromolecules

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ABSTRACT

A novel class of polycarbosilazane · $AlCl_3$ macromolecules (AlCSZ) with a Si/Al molar ratio of 1 : 1, 2 : 1, and 3 : 1 were prepared by a two-step reaction, formation of $H_2NCH_2CH_2NH_2 \cdot AlCl_3$ adducts followed by condensation of $H_2NCH_2CH_2NH_2$ with $(CH_3)_2SiCl_2$ in an aprotic solvent containing triethylamine base. The resulting AlCSZ materials were examined by elemental analysis, infrared spectroscopy (FT-IR), mass spectrometry (MS), and powder x-ray diffraction (XRD). The average polycarbosilazane chain–chain distances in the aluminum-free polycarbosilazane and these AlCSZ macromolecules were estimated from the XRD data and found to be 5.94, 6.75, 6.88, and 7.19 Å, respectively. This demonstrates that $AlCl_3$ is incorporated between the polycarbosilzane chains and has caused chain–chain expansion. The thermal properties of these AlCSZs were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). They are air stable white solids but decompose in water forming the corresponding dimethylsiloxane, ethylenediamine, and aluminum oxide.

Key Words: Aluminocarbosilazane; Carbosilazane; Metallopolymer; Organosilicon polymer; Macromolecular adduct.

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INTRODUCTION

There has been a growing interest in inorganic and organometallic polymers in which main group elements constitute the polymer backbone.[1–12] These materials have been shown to exhibit interesting electronic, thermal and mechanical properties not found in classical organic polymers. A variety of inorganic polymers with E—N backbone have been reported, where E is Si, P, B and S.[2,4–12] Silazane (Si—N), carbosilazane (C—Si—N, Si—N—C), phosphazane (P=N), carbophosphazane (C—P=N), borazane (B=N), sulfur nitride (S—N), oxathiazane (RS(O)=N—) and others were reported. Polysilazanes and polycarbosilazanes have received increasing attention as preceramic precursors for silicon nitride, oxynitride and carbide.[9–17] On the other hand, there has been long standing interest in inorganic polymers containing B, Al, and Si in the polymer backbone.[18–25] These materials are of great technological value. Although a variety of polyaluminoorganosiloxanes with Al—O—Si chains have been prepared and characterized, polyaluminoorganosilazane (AlSZ) and polyaluminocarbosilazane (AlCSZ) containing Al—N—Si backbones are rarely addressed in the literature.[21–24]

Recently, we have directed our research towards the synthesis and pyrolysis of metal-containing organosilazanes and carbosilazanes. This class of materials is an important single-source polymeric precursor for the synthesis of homogeneous metal-containing composite materials. In this paper, we describe a convenient method for the preparation of air-stable polycarbosilazane $\cdot$ $AlCl_3$ (AlCSZ) macromolecules with Si/Al molar ratio of 1 : 1, 2 : 1, and 3 : 1. This interest is motivated by their potential use as precursors for obtaining aluminosilicon nitrides ($AlSiN_x$), aluminosilicon oxynitrides ($SiAlO_xN_y$, sialon) and aluminosilicon carbonitrides ($AlSiCN_y$).[14,19,22,23] The two-step synthetic procedure involved the formation of $H_2NCH_2CH_2NH_2 \cdot AlCl_3$ adducts followed by condensation of the resulting adduct with $(CH_3)_2SiCl_2$ in the presence of triethylamine base. The thermal and hydrolytic stability of these materials are addressed.

EXPERIMENTAL

All preparations were carried out under nitrogen. All chemicals and solvents were reagent grade and used as received without further purification [dichlorodimethylsilane (Acros, 99%), ethylenediamine (Janssen Chimica, 99%), anhydrous $AlCl_3$ (Merck), triethylamine (Scharlau)]. Infrared spectra (FT-IR) were recorded on a Nicolet Impact 410 system as KBr pellets. Mass spectrometric studies were performed on VGA 7070. Powder x-ray diffraction (XRD) was measured on Philips PW 1729 x-ray spectrometer using Cu, $K_{\alpha 1}$ radiation ($\lambda = 1.5404\,Å$) generated at 35 kV and 40 mA and 2θ angle ranging from 5° to 100° with 0.04-degree increments. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done on a Shimadzu TGA50 and DSC50, respectively. Elemental analysis (CHN) was done at MHW Laboratories, Phoenix, Arizona, and chloride was analyzed by titration with aqueous $AgNO_3$.

Synthesis of AlCSZ Macromolecular Adducts

$[(-SiMe_2NHCH_2CH_2NH-)-AlCl_3]_n$ (AlCSZ1)

Anhydrous $AlCl_3$ powder (13.30 g, 0.10 mole) was suspended in magnetically stirred toluene (100 mL) under nitrogen atmosphere. To this suspension, $H_2NCH_2CH_2NH_2$ (6.00 g, 0.10 mole) was added and left to equilibrate for 10–15 min. The suspension became colloidal, indicating the formations of $H_2NCH_2CH_2NH_2 \cdot AlCl_3$ adduct. To this colloidal suspension, Et_3N base (22.00 g, 0.20 mole) was added followed by $(CH_3)_2SiCl_2$ (13.60 g, 0.105 mole dissolved in 30 mL toluene). A vigorous reaction immediately started and the viscosity of the reaction mixture gradually increased. The reaction mixture was heated to reflux for 4–5 h, cooled to ambient temperature and left under nitrogen overnight. The solvent was removed under vacuum. The resulting white solid was suspended in stirring absolute methanol (excess) to dissolve the Et_3NHCl salt. The resulting insoluble white solid was filtered off, washed several times with methanol and vacuum dried at 50–60°C. Yield: 23.0 g (92%). Elemental analysis calcd. for $[(-SiMe_2NHCH_2CH_2NH-)AlCl_2OH]$: C, 20.79%; H, 5.67%; N, 12.12%; Cl, 30.68%. Found: C, 20.29%; H, 7.12%; N, 12.73%; Cl, 31.06%. Color and state: white solid mp (decomposition): 320°C.

$[2(-SiMe_2NHCH_2CH_2NH-)-AlCl_3]_n$ (AlCSZ2)

This macromolecular adduct was prepared as described above using anhydrous $AlCl_3$ (6.65 g, 0.05 mole), $H_2NCH_2CH_2NH_2$ (6.00 g, 0.10 mole), Et_3N (22.00 g, 0.20 mol), and $(CH_3)_2SiCl_2$ (13.50 g, 0.105 mole). Yield: 16.5 g (87%); Elemental analysis, calcd. for $[(-SiMe_2NHCH_2CH_2NH-)_2AlCl_3 \cdot H_2O]$: C, 25.24%; H, 6.83%; N, 14.59%; Cl, 27.70%. Found: C, 26.04%; H, 7.77%; N, 14.12%; Cl, 27.15%. Color and state: white solid mp (decomposition): 325°C.

$[3(-SiMe_2NHCH_2CH_2NH-)-AlCl_3]_n$ (AlCSZ3)

This macromolecular adduct was obtained as described above using anhydrous $AlCl_3$ (6.65 g, 0.05 mole), $H_2NCH_2CH_2NH_2$ (9.00 g, 0.15 mole), NEt_3 (33.00 g, 0.30 mole) and $(CH_3)_2SiCl_2$ (20.00 g, 0.155 mole). Yield: 20.0 g (81%). Elemental analysis calcd. for $[(-SiMe_2NHCH_2CH_2NH-)_3AlCl_3]$: C, 29.90%; H, 7.53%; N, 17.43%; Cl, 22.06%. Found: C, 27.91%; H, 7.17%; N, 17.31%; Cl, 21.76%. Color and state: white solid mp (decomposition): 330°C.

$[-SiMe_2NHCH_2CH_2NH-]_n$ (PEDCSZ)

This oligomer was prepared and characterized as described by Mariam and coworkers.[9,10] $(CH_3)_2SiCl_2$ (33.00 g, 0.255 mole) in 50 mL toluene was reacted with a mixture of $H_2NCH_2CH_2NH_2$ (15.00 g, 0.25 mole) and Et_3N (51.00 g, 0.50 mole) in 50 mL toluene under nitrogen. A white solid (Et_3NHCl salt) immediately formed. The reaction mixture was refluxed for 4–5 h. The resulting solid was filtered off. The solvent was removed under reduced pressure. The resulting viscous liquid was washed several times with ether and vacuum dried at room temperature for several hours. Yield: 17.50 g (64%). Color and state: creamy viscous solid.

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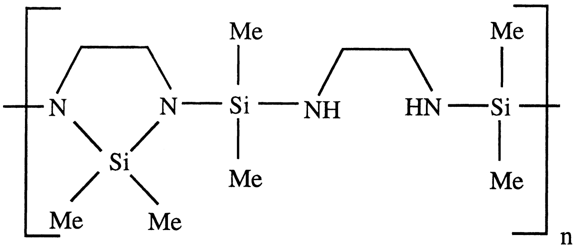
RESULTS AND DISCUSSION

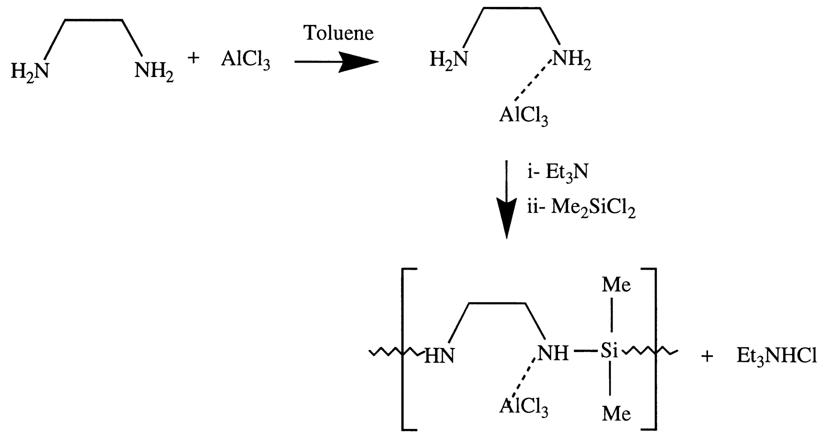
Synthesis and Structure

The condensation reaction of $H_2NCH_2CH_2NH_2$ with $(CH_3)_2SiCl_2$ in an aprotic solvent containing triethylamine under inert atmosphere to give poly-*N*,*N*′-bis(dimethylsilyl)ethylenediamine (PEDCSZ) was reported several years ago by Mariam and coworkers.[9–12] They proposed that the backbone structure is composed of cyclic and linear segments where the cyclic : linear ratio depends upon the reaction conditions.[11] The preparation of the AlCSZ macromolecules involved two main steps, formation of $H_2NCH_2CH_2NH_2 \cdot AlCl_3$ adducts in various molar ratios (Lewis base/Lewis acid = 1 : 1, 2 : 1, and 3 : 1) followed by silylation of the $H_2NCH_2CH_2NH_2$ moiety in presence of a weak base (Et_3N) as shown in Sch. 1. Anhydrous $AlCl_3$ readily form adducts with strong nitrogen bases. Given the bidentate characteristics of $H_2NCH_2CH_2NH_2$ and the various Lewis acid/base molar ratios, it difficult to describe the structure of these adducts. Furthermore, significant numbers of amino groups are expected not to interact with $AlCl_3$ Lewis acid. The interaction between $AlCl_3$ and $H_2NCH_2CH_2NH_2$ results in an increase in NH acidity of the attached amino group.[26] This is expected to facilitate the formation of Si—N bonds in the second step. During this step, $AlCl_3$ acts primarily as a template in the condensation reaction. However, in all cases the $AlCl_3$ is presumed to be uniformly distributed in the final AlCSZ products. The structure of the resulting macromolecules can be reasonably described as Lewis acid-base adducts where $AlCl_3$ is incorporated within PEDCSZ as shown in Sch. 1. Although these AlCSZs were prepared under nitrogen atmosphere in anhydrous conditions, the presence of moisture in the final products may have been introduced during the isolation step. They are air-stable white solids. The air-stability of these AlCSZs was checked over a period of three months using TGA and IR spectroscopy and found that negligible amounts of moisture was absorbed when stored in a closed container. This observation suggests that the $AlCl_3$ is entrapped within hydrophobic carbosilazane matrix. The stability of these materials is consistent with earlier reports on the stability of Si—N bond.[15,28] However, they are unstable to hydrolysis in acidic, neutral, and basic aqueous media (see stability section). All these AlCSZ adducts were obtained in high yields. They are insoluble in common organic solvents.



PEDCSZ

It is important to emphasize that the variation of carbosilazane: $AlCl_3$ (Si/Al) molar ratios yields aluminum-containing carbosilazane materials with different compositions and microstructures. Consequently, varying the carbosilazane : $AlCl_3$ molar ratios imparts



Scheme 1. Schematic representation for the formation of aluminocarbosilazane macromolecules (AlCSZ1).

different thermo-structural characteristics on these materials. In fact the carbosilazane chain–chain spacing and the thermal properties of these AlCSZ materials were found to depend upon Si/Al molar ratios (XRD and thermal analysis sections). Moreover, variation of carbosilazane : $AlCl_3$ ratio permits one to control the hydrophobic/hydrophilic properties of the AlCSZ network.

Infrared Spectroscopy

The infrared absorption spectra for the PEDCSZ and AlCSZ macromolecules were recorded in the 4000–600 cm^{-1} region as KBr pellets. Characteristic absorption IR bands and their tentative assignment are listed in Table 1. In all cases, these materials display a band at 1260 cm^{-1} region due $Si{-}CH_3$, Fig. 1. This band is strong in the case of PEDCSZ whereas it is medium-weak in all the AlCSZ macromolecules. The observed decrease in the intensity of $Si{-}CH_3$ band in the IR spectra of these AlCSZs compared to that of PEDCSZ matrix at 1260 cm^{-1} region may be explained based on two considerations, the number of vectors ($Si{-}CH_3$) giving rise to these bands and the local symmetry at silicon. The low intensity of this band in the IR spectra of AlCSZs suggests that the number of $Si{-}CH_3$ bonds in the carbosilazane backbone is less in AlCSZs than in PEDCSZ matrix. This observation demonstrates that the degree of polymerization is higher in the aluminum-free PEDCSZ matrix than in aluminum-containing AlCSZ macromolecules. This conclusion is supported by the appearance of bands at 3200 cm^{-1} region due to ν_{N-H}. Furthermore, the interaction between $AlCl_3$ and the nitrogen of the carbosilazane segment as shown in Sch. 1 may distort the local symmetry at $Si{-}CH_3$ group and hence, cause reduction in the intensity of its IR bands.

Moreover, all these AlCSZ materials exhibit a single strong band in 3200 cm^{-1} region assigned to N—H stretching mode of the ($-SiMe_2NH-$) group. The decrease in the intensity of asymmetric stretching frequency for the amino group of the $H_2NCH_2CH_2NH_2$ and the appearance of new bands at 1085–943 cm^{-1} regions due to ν_{N-Si-N} and ν_{Si-N}

Table 1. FT-IR spectral data of PEDCSZ and AlCSZ macromolecular adducts (cm^{-1}).[a]

Macromolecules	ν_{N-H}	ν_{Si-N} and ν_{N-Si-N}	ν_{Si-CH_3}
PEDCSZ	3140 (sh)	1083 (s) 1024 (vs) 945 (s)	1265 (s) 836 (s)
AlCSZ1[b]	3191 (s)	1088 (m) 1046 (vs) 1005 (s)	1180 (w) 870 (w)
AlCSZ2[b]	3195 (s)	1085 (s) 1034 (vs) 1007 (s)	1270 (m) 810 (m)
AlCSZ3[b]	3191 (s)	1085 (s) 1036 (vs) 1005 (s)	1264 (m) 820 (m)

Note: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder.

[a] Recorded as KBr pellets, important characteristic group frequencies are reported.

[b] Broad feature appeared in 3440–3500 cm^{-1} region (not shown in Table 1) are assigned to water entrapped in the crystal lattice.

indicate that the silylation occurred at nitrogen, Sch. 1. These observations indicate that silylation has occurred but not to a large extent. The ν_{N-H} band of PEDCSZ appeared as a shoulder, which indicates the formation of extensive cyclic carbosilazane, segments as proposed by Mariam and coworkers.[12] Furthermore, all the AlCSZ adducts display a broad feature in 3500 cm^{-1} region. This suggests that their crystal lattices contain trace

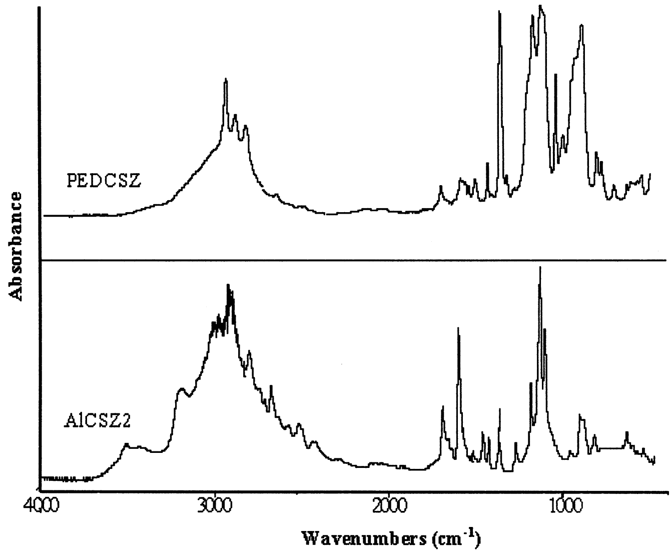


Figure 1. FT-IR Spectra of PEDCSZ and AlCSZ2 macromolecules.

amounts of water. This conclusion is in agreement with the thermal data obtained (see thermal analysis section).

Mass Spectrometry

The PEDCSZ and all the AlCSZ adducts were examined by mass spectrometry. All fragments with relative intensity >3% and their tentative assignments are given in Table 2. Fragments at 30 ($CH_2{=}NH_2$), 44 ($CH_3CH{=}NH_2$), 58 (Me_2Si), 86 ($Me_2SiN{=}CH_2$), and 101 ($HSiMe_2N{=}CHCH_3$) were observed in the mass spectra of PEDCSZ and all AlCSZ materials. In all the cases, the base peak appeared at 86 mass units. Close examination of these MS data indicates that the fragmentation pattern of PEDCSZ is similar to those of AlCSZs. This observation suggests that the fragmentation processes is similar in PEDCSZ and all AlCSZs. This indicates that $AlCl_3$ has a small influence on the fragmentation of the PEDCSZ matrix. It is important to note that a number of fragments corresponding to high m/z values appeared at 149, 157, 172, 198, and 207 mass units, (Table 2). This clearly suggests that these materials are macromolecules.

Powder X-Ray Diffraction

The powder x-ray diffraction (XRD) was performed on PEDCSZ and all the AlCSZ adducts, (Fig. 2). The XRD profile of PEDCSZ consists of a superposition of sharp peaks (crystalline reflections) on two broad diffraction features at $2\theta = 14.9^\circ$ and 28.5° and a small broad peak at 2θ range of 8°. This shows that PEDCSZ is predominantly amorphous in nature. The average chain–chain spacing was estimated from Braggs Law ($n\lambda = 2d\sin\theta$) using the θ value of the main broad peak ($2\theta = 14.9^\circ$) and found to be 5.94 Å.[27] The XRD patterns of the AlCSZ macromolecules are composed of two sets, broad peaks for the PEDCSZ phase and a set of sharp peaks that can be indexed for polycrystalline phase of $AlCl_3$. This demonstrates that AlCSZ macromolecules are phase mixtures of PEDCSZ matrix and $AlCl_3$. However, the small peak at $2\theta = 8^\circ$ did not appear in the XRD profiles of AlCSZ macromolecules. Furthermore, the positions of the broad peaks are shifted to lower 2θ values. The first broad peak shifts from 14.9° in PEDCSZ to 12.3°, 12.9°, and 13.1° in AlCSZ1, AlCSZ2 and AlCSZ3, respectively. This demonstrates that inter-chain distance has increased from 5.94 Å in PEDCSZ to 7.19 Å, 6.88 Å, and 6.75 Å in AlCSZ1, AlCSZ2, and AlCSZ3 macromolecules, respectively. These increases in the inter–chain distances demonstrate that the $AlCl_3$ is incorporated between the PEDCSZ chains. Moreover, the expanded inter-chain distances gradually decrease as $AlCl_3$ content decrease. Furthermore, it is obvious that the amorphous phase is more pronounced in AlCSZ3 compared with that in the other two AlCSZs. This is consistent with the fact that AlCSZ3 contains less $AlCl_3$ than in AlCSZ2 and AlCSZ1. Comparison between the XRD patterns of AlCSZs shows that the XRD profiles of AlCSZ2 and AlCSZ3 are similar and that of AlCSZ1 contains additional sharp diffraction peaks, (Fig. 2). This indicates that AlCSZ2 and AlCSZ3 have similar structures but different from that of AlCSZ1. This difference in the XRD patterns is also supported by the thermal and elemental analysis data obtained on these materials.

Table 2. Mass spectral data of PEDCSZ and AlCSZ macromolecular adducts; m/z (% relative intensities) and assignments.

Macromolecules	m/z (% relative intensities), assignments[a–c]
PEDCSZ	57 (85) $\mathrm{Me_2Si{-}H}$;
	73 (70) $\mathrm{Me_2SiNH}$;
	86 (100) $\mathrm{Me_2SiN{=}CH_2}$;
	97 (22) $\mathrm{MeSiN{=}CHCH{=}NH - H}$;
	101 (20) $\mathrm{Me_2SiN{=}CHCH_3 + H}$;
	111 (15) $\mathrm{Me_2SiN{=}CHCH{=}NH - 2H}$;
	149 (22) $\mathrm{H_2NCH_2CH_2NHMe_2SiNHCH_3 + 2H}$;
	205 (5) $\mathrm{D + 2H - CH_2{=}NH}$
AlCSZ1	58 (30) $\mathrm{Me_2Si}$;
	71 (17) $\mathrm{Me_2SiN - H}$;
	86 (100) $\mathrm{SiMe_2N{=}CH_2}$;
	92 (50) $\mathrm{M - HSiMe_2 + Cl}$;
	101 (17) $\mathrm{Me_2SiN{=}CHCH_3 + H}$;
	157 (5) $\mathrm{D - Me_2SiNH_2 - H}$;
	172 (3) $\mathrm{D - Me_2Si - 2H}$;
	198 (3) $\mathrm{Me_2SiN{=}CHCH{=}NSiMe_2N{=}CH_2}$
AlCSZ2	58 (95) $\mathrm{Me_2Si}$;
	72 (10) $\mathrm{Me_2SiN}$;
	86 (100) $\mathrm{Me_2SiN{=}CH_2}$;
	101 (30) $\mathrm{Me_2SiN{=}CHCH_3 + H}$;
	207 (7) $\mathrm{D - Me_2Si - 2H + Cl}$
AlCSZ3	58 (45) $\mathrm{Me_2Si}$;
	72 (7) $\mathrm{Me_2SiN}$;
	86 (100) $\mathrm{Me_2SiN{=}CH_2}$;
	101 (25) $\mathrm{Me_2SiN{=}CHCH_3 + H}$;
	149 (5) $\mathrm{H_2NCH_2CH_2NHMe_2SiNHCH_3 + 2H}$;
	207 (3) $\mathrm{D - Me_2Si - 2H + Cl}$.

[a] EI = 70 eV.

[b] M = monomer, $m/z = 116$ ($\mathrm{{-}Me_2SiNHCH_2CH_2NH{-}}$); D = Dimer, $m/z = 232$ ($\mathrm{({-}Me_2SiNHCH_2CH_2NH{-})_2}$).

[c] All macromolecules gave peaks at $m/z = 30[\mathrm{CH_2{=}NH_2}]^+$ and 44 $[\mathrm{CH_3CH{=}NH_2}]^+$.

Thermal Analysis

The thermal behavior of PEDCSZ and AlCSZ macromolecules was investigated by TGA and DSC techniques under nitrogen atmosphere in a temperature range of 25–500°C (heating rate: 20°C min^{-1}). The TGA data are summarized in Table 3. PEDCSZ exhibits a three-step degradation process at 254, 354, and 452 with a total weight loss of 100% at 500°C. It was observed that the TGA profile of PEDCSZ varies depending upon the reaction conditions where a single degradation step at 335°C was recorded in different preparations. This observation can be explained based on the ratio of cyclic to linear segments present in the backbone of the polycarbosilazane, which suggests that multi-step

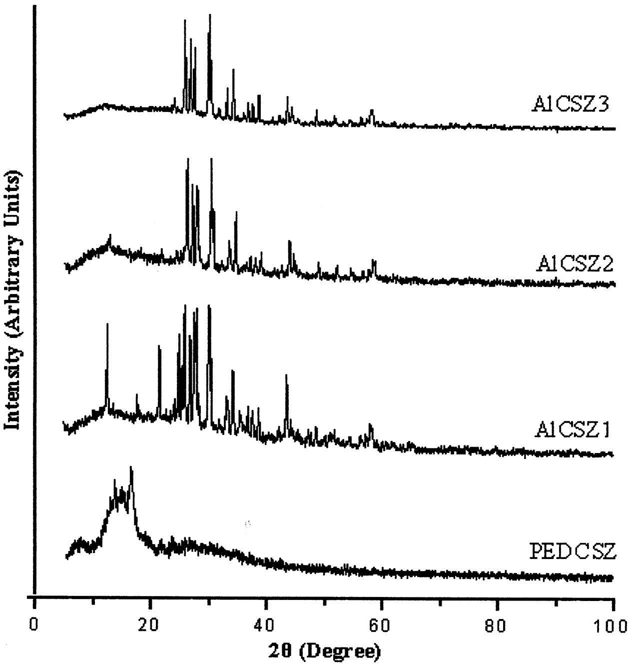


Figure 2. Powder x-ray diffraction patterns for PEDCSZ and AlCSZ macromolecules.

degradation is observed when both cyclic and linear units are present.[8,11,12] However, AlCSZ materials decompose in a one- or two-step process at 185–210°C and 319–326°C range with a total weight loss of 75–87% at 500°C, (Fig. 3). The TGA curves indicate that the thermal degradation of AlCSZ3 proceed in one step at about a 325°C region whereas, AlCSZ1 and AlCSZ2 proceed in two steps at 185–210°C and 319–326°C range. This observation suggests that, in AlCSZ1 and AlCSZ2, the presence of $AlCl_3$ has destabilized the thermal properties of carbosilazane matrix whereas, in AlCSZ3 the presence of $AlCl_3$ has caused enhancement in the thermal stability of the matrix. Examination of the inorganic residue at 500°C showed that it was aluminum oxide/hydroxide. This suggests that the degradation processes in these AlCSZs involved the elimination of the organosilicon and chloride moieties (HCl). This observation is in agreement with recent reports on the formation of chlorinated organic products during the pyrolysis of mixtures of organic materials and metal chloride salts.[29] The formation of aluminum oxide/hydroxide during the heating process can be reasonably attributed to the oxophilic nature of aluminum ion and the presence of trace amounts of moisture in the crystal lattice.

The DSC thermograms of the PEDCSZ and AlCSZ materials are depicted in Fig. 4. Each heating curve consists of three or four endothermic processes at about 150, 250, 330, and 350°C regions. All thermograms exhibit exothermic peak(s) following the main endotherm. Close inspection of the TGA and DSC curves of these materials suggest that the broad endotherms in 137–155°C range do not correspond to degradation processes and therefore they are attributed to phase transitions whereas the endothermic peaks in the 200–400 regions correspond to multi-step degradation processes. The phase transition in

Table 3. Thermogravimetric analysis data obtained for PEDCSZ and AlCSZ macromolecular adducts.[a]

Macromolecule	Degradation temperature, °C (% mass loss)[b]	Mass of moisture[b] (%)	Mass of organosilicon[c] (%)	Mass of residue[d] (%)
PEDCSZ[e]	254 (68); 354 (11); 452 (21)	—	100	0.0
AlCSZ1	210 (35.0); 319 (42.5)	7.5	77.5	15.0
AlCSZ2	185 (12.0); 326 (63.0)	5.9	75.0	19.1
AlCSZ3	325 (87.0)	<1.0	87.0	12.0

[a] TGA was recorded in room temperature −500°C range (heating rate: 20°C min^{-1}).

[b] Temperature was recorded as midpoint. Mass of moisture (%) represents mass loss below 150°C.

[c] Mass of organosilicon (%) is equal to the sum of masses lost between 150°C and 500°C.

[d] Mass of the residues (%) is reported at 500°C.

[e] TGA profile varies depending upon the reaction conditions where in some preparations a single degradation step was observed at 335°C (100%).

the aluminum-free PEDCSZ occurred at 137°C, whereas in AlCSZ3, AlCSZ2, and AlCSZ1 this phase change took place at 142, 152, and 155°C, respectively. This shows that the phase transition temperatures of these AlCSZs gradually increase as a function of increasing percentage amounts of $AlCl_3$ in the AlCSZ networks. Computation of the area under these endothermic peaks shows that the enthalpies corresponding to the phase

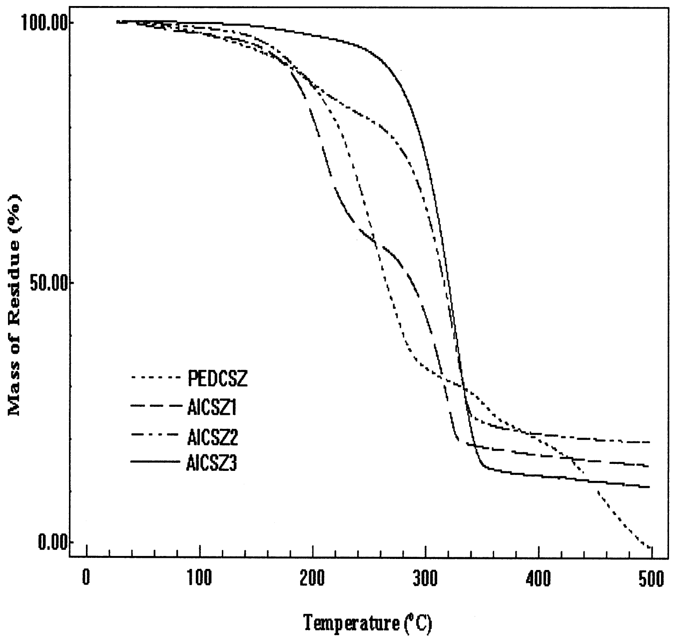


Figure 3. Thermogravimetric analysis curves for PEDCSZ and AlCSZ macromolecules.

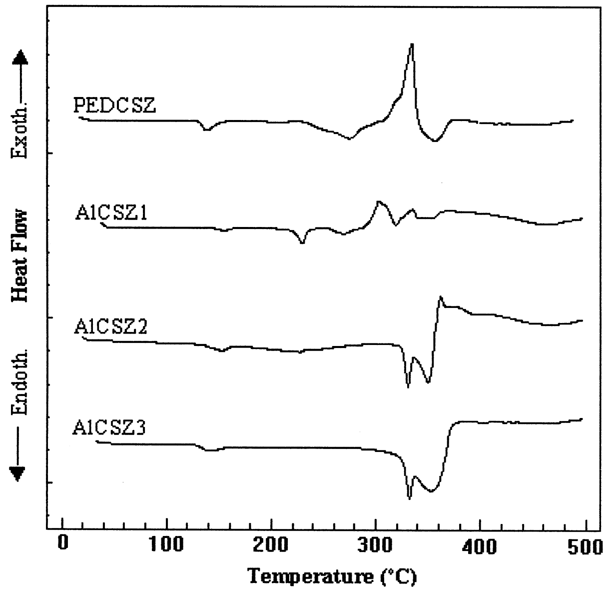
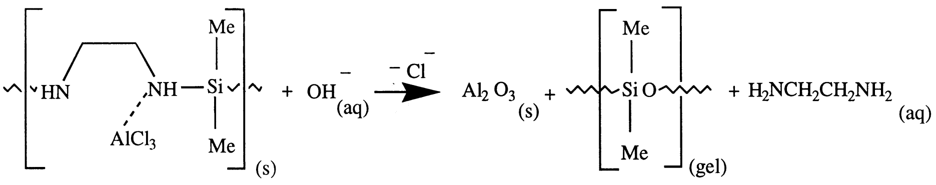


Figure 4. Differential scanning calorimetry thermograms for PEDCSZ and AlCSZ macromolecules.

transitions in PEDCSZ, AlCSZ3, AlCSZ2, and AlCSZ1 were 87, 41, 35, and 28 J g^{-1}, respectively. Furthermore, the overall enthalpies associated with the degradation endotherms were estimated from the area under the corresponding peaks and found to be 517, 443, 375, and 238 J g^{-1} for PEDCSZ, AlCSZ3, AlCSZ2, and AlCSZ1, respectively. Interestingly, the gradual decrease in the enthalpies associated with the phase transition and degradation is in agreement with the decreasing percentage amounts of carbosilazane in these materials.

Stability of AlCSZ Macromolecules

All these AlCSZ materials undergo hydrolysis when shaken with acidic, neutral, and basic aqueous solutions. It has been demonstrated that cleavage of Si—N bond involves electrophilic attack at the lone pair of the nitrogen and therefore, it is least stable in acidic media.[28] In all cases, a white gel of dimethylsiloxane (—Me_2SiO—) appeared on the



Scheme 2. Schematic representation for the degradation of aluminocarbosilazane macromolecules (AlCSZ1) in basic aqueous solution.

solution surface, Sch. 2. A white precipitate of $Al_2O_3/Al(OH)_3$ was observed when hydrolysis was performed under neutral and basic conditions. However, a soluble salt formed when the media was acidic. The presence of $H_2NCH_2CH_2NH_2$ in the solution was confirmed by complexation with $Cu^{2+}{}_{aq}$ ion.

CONCLUSION

A series of aluminum chloride-containing polycarbosilazane macromolecules has been prepared and characterized. Due to their insolubility in organic solvents, the structural details of these AlCSZ materials were not established. However, two important structural features are apparent. First, $AlCl_3$ is bound to PEDCSZ chains. Second, the presence of $AlCl_3$ in different molar ratios allows a variety of PEDCSZ chain–chain interactions and therefore, imparts different thermo-structural characteristics on the AlCSZ frameworks. More importantly is the structural versatility of this system that allows the preparation of polyelectrolyte complexes by metathesis of the chloride in the AlCSZ macromolecules with polyanions such as polyacrylate to obtain aluminocarbosilazane-polyacrylate materials. Currently, we have employed this method to prepare polysilazane-BCl_3, polycarbosilazane-BCl_3 and polyaluminosilazanes (AlSZs) adducts. This class of boron/aluminum-containing macromolecules is an important single-source polymeric precursor for the synthesis of homogeneous ternary (B—Si—N, Al—Si—N) and quaternary (B—Si—N—O, B—Si—C—N) composite materials.

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