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SYNTHESIS AND CHARACTERIZATION OF DIAMINECARBOSILAZANE-CONTAINING POLYMERS

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ABSTRACT

A series of diaminecarbosilazane-containing polymers of the general formula [-SiPh$_2$-NH-R-NH-]$_n$, (R is 1,2-ethane, 1,3-propane, 1,4-butane, 1,6-hexamethylene and 1,4-phenylene) has been prepared by polycondensation of dichlorodiphenylsilane with the corresponding aliphatic and aromatic diamines in the presence of a weak base. These carbosilazane polymers were characterized by elemental analysis, thermogravimetric analysis (TGA), infrared (FT-IR), ^{1}H NMR and electronic (UV-vis) spectroscopy. The average molecular weight and n value of these polymers were found to range from 6000 to 9500 and 20 to 37, respectively.

Key Words: Carbosilazane; Silylamine; Organosilicon polymer; Thermogravimetric analysis

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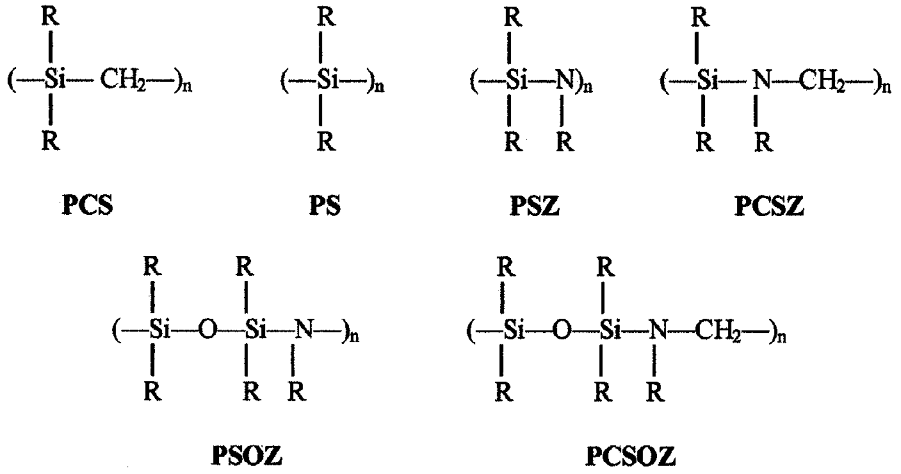
INTRODUCTION

Research on organosilicon polymers possessing Si-C, Si-N and Si-Si bonds in their backbone has steadily grown in recent years.[1–6] These include polycarbosilane (PCS), polysilane (PS), polysilazane (PSZ), polycarbosilazane (PCSZ), polysiloxazane (PSOZ), and polycarbosiloxazane (PCSOZ), Sch. 1.[7–9]

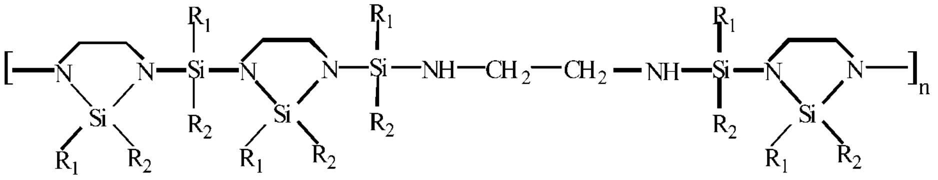
These silicon-containing polymers have been reported to exhibit interesting electronic, thermal, and mechanical properties. Their applications as precursors for non-oxide ceramics (silicon carbide, silicon nitride and silicon carbonitride), protective coatings and semi-conducting electronic devices have been reported.[2,10]

Polycarbosilazane (PCSZ) is an important class of organosilicon polymers containing Si-N-C or C-Si-N in their backbone structure. Various synthetic strategies have been developed for the preparation of PCSZ polymers including ring opening, polycondensation and thermal rearrangement methods.[7,8] Few studies have addressed polycarbosilazane containing diamine units in their backbone.[2,11] The synthesis of ethylene-bridged PCSZ has been described in the literature many years ago.[2] Recently, Mariam and coworkers showed that the structure of ethylene-bridged PCSZ is composed of cyclic and linear segments, Sch. 2.[12]

In this paper, we report a high yield, one-pot synthesis of a new series of polymeric diaminecarbosilazane of the general formula $[\text{-SiPh}_2\text{-HN-R-NH-}]_n$, where Ph is phenyl and R is 1,2-ethane, 1,3-propane, 1,4-butane, 1,6-hexamethylene and 1,4-phenylene.



Scheme 1.



where $R_1 = CH_3$; $R_2 = H$, CH_3, $-CH{=}CH_2$.

Scheme 2.

EXPERIMENTAL

Materials

1,4-phenylenediamine (PhDA, Merck, 98%) was crystallized from ethanol. All other chemicals (triethylamine (TEA, Scharlau, 99%), 1,2-ethylenediamine (EDA, Janssen Chimica, 99%), 1,3-propanediamine (PrDA, Acros, 99%), 1,4-butanediamine (BuDA, Acros, 98%) 1,6-hexamethylenediamine (HMDA, Aldrich, 98%), and dichlorodiphenylsilane (Ph_2SiCl_2, Acros, 96%)) and solvents were reagent grade and used as received without further purification.

Measurements

FT-IR spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer as thin liquid films on NaCl plates for viscous and as KBr pellets for the solid carbosilazane polymers. Thermogravimetric analysis was done on a Shimadzu TGA-50 system under nitrogen atmosphere. ^{1}H NMR spectra were recorded on Bruker WP-80 SY 80 MHz spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard. Electronic absorption was recorded on UNICAM (Helios Alpha). Elemental analysis was performed by MHW Laboratories, Phoenix, Arizona. The molecular weights were measured by vapor pressure osmometry (VPO) as described in the literature.[13]

Synthesis of Polydiaminediphenylcarbosilazane Polymer

Poly-1,2-ethylenediaminediphenylcarbosilazane (PEDACSZ)

A solution of EDA (3.64 g, 0.06 mol) and TEA (13.42 g, 0.132 mol) in 50 mL toluene was placed in a 250 mL three-neck round bottom flask fitted with a reflux condenser, a dropping funnel and a nitrogen inlet. This solution was magnetically stirred. To this solution, Ph_2SiCl_2 (15.82 g, 0.06 mol) in 50 mL toluene was then added slowly from the dropping funnel (over 20 min). The reaction mixture was refluxed for 4–5 h, then cooled to ambient temperature and allowed to stand overnight under nitrogen. The $N(C_2H_5)_3{\cdot}HCl$ salt was filtered off and the filtrate was rotaevaporated to remove the solvent and other volatile components. The remaining yellow oil was dried at 70°C under vacuum, where an off-white solid was obtained. Melting point: 95°C, M_n: 7012 (VPO, benzene, 35°C), $\lambda_{max} = 285$ nm, Yield: 14.12 g (98%).

Poly-1,3-propanediaminediphenylcarbosilazane (PPrDACSZ)

This carbosilazane polymer was prepared as described above using Ph_2SiCl_2 (15.82 g, 0.06 mol), 1,3-PrDA (4.47 g, 0.06 mol) and TEA (13.42 g, 0.132 mol). The isolated pale yellow oil became viscous and partially solidified upon drying under vacuum. Melting point: 196°C, M_n: 9524 (VPO, benzene, 35°C), $\lambda_{max} = 284$ nm, Yield: 14.50 g (95%).

Poly-1,4-butanediaminediphenylcarbosilazane (PBuDACSZ)

A similar procedure was adopted using Ph_2SiCl_2 (15.82 g, 0.06 mol), 1,4-BuDA (5.37 g, 0.06 mol) and TEA (13.42 g, 0.132 mol). Melting point: 235°C, M_n: 5879 (VPO, benzene, 35°C), $\lambda_{max} = 286$ nm, Yield: 7.50 g (93%).

Poly-1,6-hexamethylenediaminediphenylcarbosilazane (PHMDACSZ)

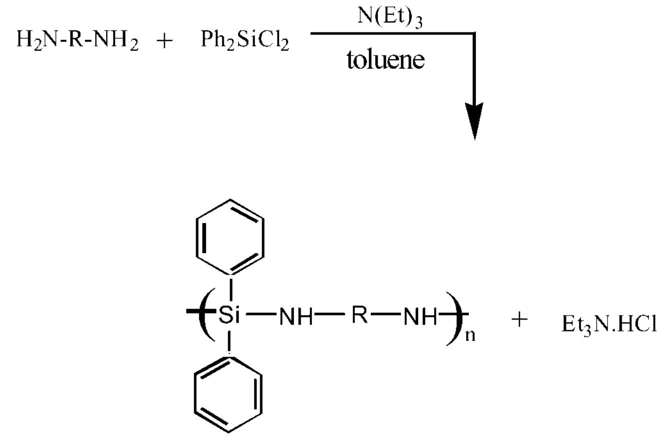
This polymer was analogously prepared using was Ph_2SiCl_2 (15.82 g, 0.06 mol), 1,6-HMDA (7.11 g, 0.06 mol) and TEA (13.42 g, 0.132 mol). Melting point: 194°C, M_n: 7751 (VPO, benzene, 35°C), $\lambda_{max} = 285$ nm, Yield: 11.42 g (64%).

Poly-1,4-phenylenediaminediphenylcarbosilazane (PPhDACSZ)

This carbosilazane polymer was prepared as shown above using Ph_2SiCl_2 (15.82 g, 0.06 mol), 1,4-PhDA (6.59 g, 0.06 mol) and TEA (13.42 g, 0.132 mol). Melting point: 97°C, M_n: 5857 (VPO, benzene, 35°C), $\lambda_{max} = 285$ nm, 327 (shoulder), Yield: 6.50 g (75%).

RESULTS AND DISCUSSION

This series of carbosilazane polymers were synthesized by condensing dichlorodiphenylsilane with the corresponding aliphatic and aromatic diamines in the presence of a weak base under nitrogen atmosphere, Sch. 3.



R= 1,2-(CH_2)$_2$-, 1,3-(CH_2)$_3$-, 1,4-(CH_2)$_4$-, 1,6-(CH_2)$_6$-, and 1,4-(C_6H_4)-.

Scheme 3.

No attempt was made to control polymer chain growth, termination or branching. Removal of solvent and other volatile products by rotaevaporation resulted in the formation of carbosilazane polymers with average M_n of 6000–9500 and n ranges from 20 to 37, Table 1. The physical and elemental analysis data for the prepared carbosilazane polymer are summarized in Table 1. These polymeric materials are air stable and no physical or chemical

Table 1. Physical Properties and Elemental Analysis Found (Calculated)[a] for Aliphatic- and Aromatic-Diamine-Bridged Diphenylcarbosilazane Macromolecules

						Elemental Analysis		
PDACSZ	Yield(%)[b]	State	Color	m·p (°C)	n	C%	H%	N%
PEDACSZ	98	Solid	Off-White	95	29	69.73	6.47	7.57
						(69.95)	(6.71)	(11.65)
PPrDACSZ	95	Viscous[c]	Pale-Yellow	196	37	66.46	6.89	6.31
						(70.81)	(7.13)	(11.01)
PBuDACSZ	93	Viscous[c]	Off-White	235	22	67.03	6.83	6.16
						(71.59)	(7.51)	(10.43)
PHMDACSZ	64	Viscous[c]	Off-White	194	26	67.36	7.76	6.87
						(72.92)	(8.16)	(9.45)
PPhDACSZ	75	Solid	Brown	97	20	73.66	5.96	8.56
						(74.96)	(5.60)	(9.71)

[a] Calculated for the corresponding monomers.

[b] The % yield was calculated based on the diamine.

[c] The viscous liquid is partially solidified upon drying under vacuum.

changes were observed upon storage for a period of six months. They swell forming colloidal solution in benzene and toluene.

Elemental analysis of all the prepared PDACSZ showed that the experimental C% and N% are smaller than those calculated for the proposed structure. Such deviation has been reported in silicon-based materials.[14,15] These discrepancies may be attributed to the fact that the monomeric formula does not truly represent the actual structures. Generally, organosilicon polymers show high tendency to form cyclic and acyclic segments within the structure.[7,12] The cyclic/acyclic ratio depends upon preparation conditions.

Thermal Analysis

The thermal behavior of this series of carbosilazane polymers was investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere in a temperature range of 25–500°C (heating rate: 10°C/min). The thermal data obtained for all the prepared carbosilazane polymers is summarized in Table 2. It is obvious from this data that PEDACSZ exhibit one thermal degradation step at 339°C, whereas PPrDACSZ, PBuDACSZ, PHMDACSZ, and PPhDACSZ exhibit two thermal degradation steps in the range of 95–177°C and 346–358°C, Fig. 1. In general, the first step corresponded to a smaller fraction weight loss compared to the second step. In all the cases, the residue obtained at 450°C ranged between 29–55% and PBuDACSZ gave the highest char yields.

Infrared Spectroscopy

The FT-IR spectra for this series of carbosilazane polymers were recorded in the region 4000–400 cm^{-1} as thin films on NaCl plates for the viscous and as KBr pellets for solid samples. The characteristic absorption IR bands and their tentative assignments are presented in Table 3. These assignments are based on the reported spectral data for monomeric and polymeric silazane and carbosilazane compounds.[6,7] The observation of stretching frequencies of N-H, Si-N, and Si-C are of particular importance in the identification of these products. These carbosilazane polymers exhibit a single band at 3380–3401 cm^{-1} region assigned to N-H stretching mode of silylamines. The absence of asymmetric stretching frequency for N-H bond indicates that silylation occurred at the nitrogen almost quantitatively, Fig. 2. The strong bands at 1430 cm^{-1} and 1100 cm^{-1} regions are attributed to Si-Ph.

^{1}H NMR Spectroscopy

The ^{1}H NMR spectra of this series of carbosilazane polymers were recorded in $CDCl_3$. The results are presented in Table 4. In all the cases, the

Table 2. Thermogravimetric Analysis (TGA) Data for Aliphatic- and Aromatic-Diamine-Bridged Diphenylcarbosilazane Macromolecules[a]

	Thermal Degradation Temperature °C (%wt Loss)		
PDACSZ	Step 1	Step 2	Residue (%)[b]
PEDACSZ	—	339 (71%)	29
PPrDACSZ	110 (17%)	353 (49%)	34
PBuDACSZ	95 (13%)	346 (22%)	65
PHMDACSZ	107 (19%)	358 (28%)	53
PPhDACSZ	177 (22%)	357 (38%)	40

[a] Heating rate 10°C/min; temperature recorded in the range 25–500°C.

[b] Residue% at 500°C.

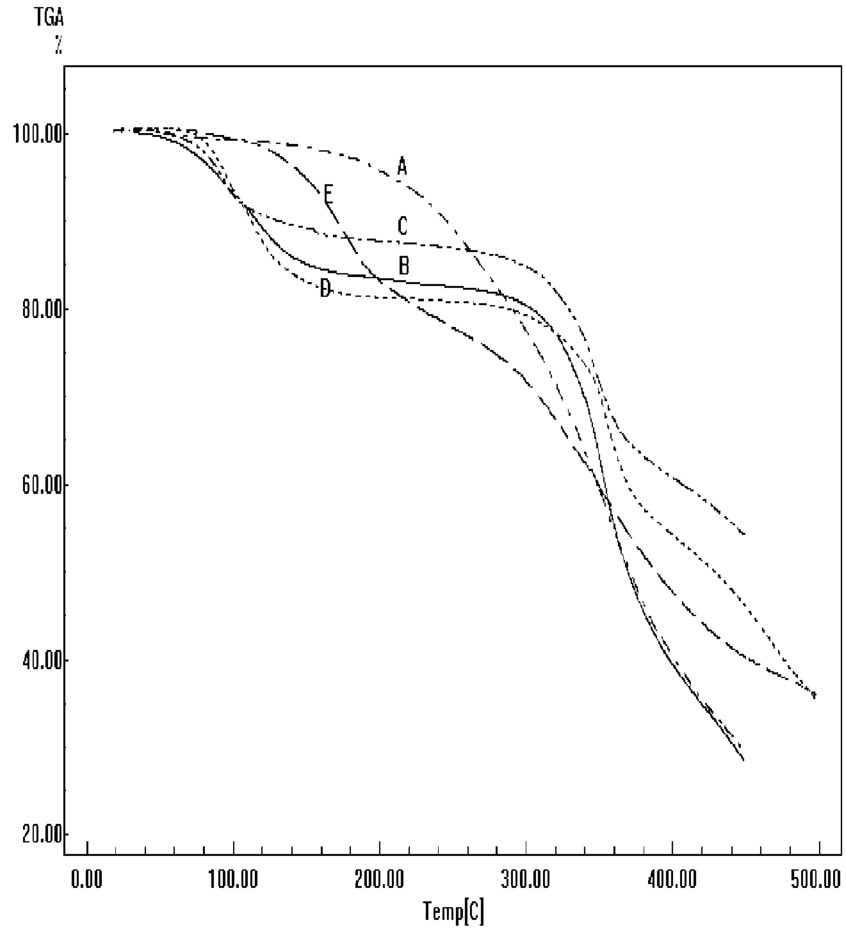


Figure 1. Thermograms of carbosilazane polymers, PEDCSZ (A), PPrDACSZ (B), PBuDACSZ (C), PHMDACSZ (D), and PPhDACSZ (E).

Table 3. FT-IR Spectral Data for Aliphatic- and Aromatic-Diamine-Bridged Diphenylcarbosilazane Macromolecules

PDACSZ	$\nu_{N\text{-}H}cm^{-1}$	$\nu_{Si\text{-}Ph}cm^{-1}$	$\nu_{C\text{-}N}cm^{-1}$	$\nu_{Si\text{-}N}cm^{-1}$	$\delta_{Si\text{-}Ph}cm^{-1}$
PEDACSZ	3382 (m)	1431 (vs) 1116 (s)	1190 (m)	1066 (s)	720 (vs) 523 (vs)
PPrDACSZ	3401 (m)	1425 (s) 1110 (vs)	1184 (m)	1061 (s)	733 (vs) 523 (vs)
PBuDACSZ	3407 (m)	1425 (vs) 1116 (vs)	1190 (m)	1079 (s)	733 (vs) 523 (vs)
PHMDACSZ	3395 (m)	1425 (s) 1116 (vs)	1190 (m)	1079 (s)	727 (vs) 523 (vs)
PPhDACSZ	3380 (m)	1425 (s) 1116 (s)	1079 (m)	1079 (s)	721 (s) 523 (s)

vs, very strong; s, strong; m, medium.

^{1}H NMR spectra displayed multiplets in the aromatic region corresponding to the ten aromatic protons of the diphenylsilyl group (-Si$\underline{Ph}_2$HN-R-NH-). Additional aromatic signal appeared at 7.53 ppm for the phenylene bridge of PPhDACSZ, Fig. 3. The peaks due to the aliphatic bridging units in PEDACSZ, PPrDACSZ, PBuDACSZ and PHMDACSZ were observed in the region between 1.26 and 1.73 ppm. The four proton of the α-C of the bridge (-SiPh$_2$HNC$\underline{H}_2$R′C$\underline{H}_2$NH-) displayed broad singlets at 1.52–1.73 ppm. This observation is more pronounced in PEDACSZ and PPrDACSZ where the aliphatic bridging units are short. This broadness in the spectra is attributed to dipolar chain-chain interactions and to the restricted mobility of the carbosilazane chain. The proton attached to the nitrogen of the silylamine group (-SiPh$_2\underline{H}$N-R-N$\underline{H}$-) gave a signal at 2.71–3.72 ppm region. This assignment was confirmed by D$_2$O exchange. Close examination of these signals in aliphatic-bridged carbosilazanes showed that the resonance shifts from 3.20 to 2.71 ppm as the bridge length increased (Table 4).

Although the ^{1}H NMR spectra of these carbosilazane polymers are in good agreement with the suggested structure, low intensity signals indicating the presence of small amounts of byproducts were observed. Partial precipitation from different solvents did not eliminate these signals. The structure of these carbosilazane polymers will be further investigated.

Electronic Absorption Spectroscopy

The electronic absorption spectra of the prepared carbosilazane polymers were recorded in toluene between 700–250 nm. They exhibit one absorption band in the UV region at 284–286 nm. This sharp band is

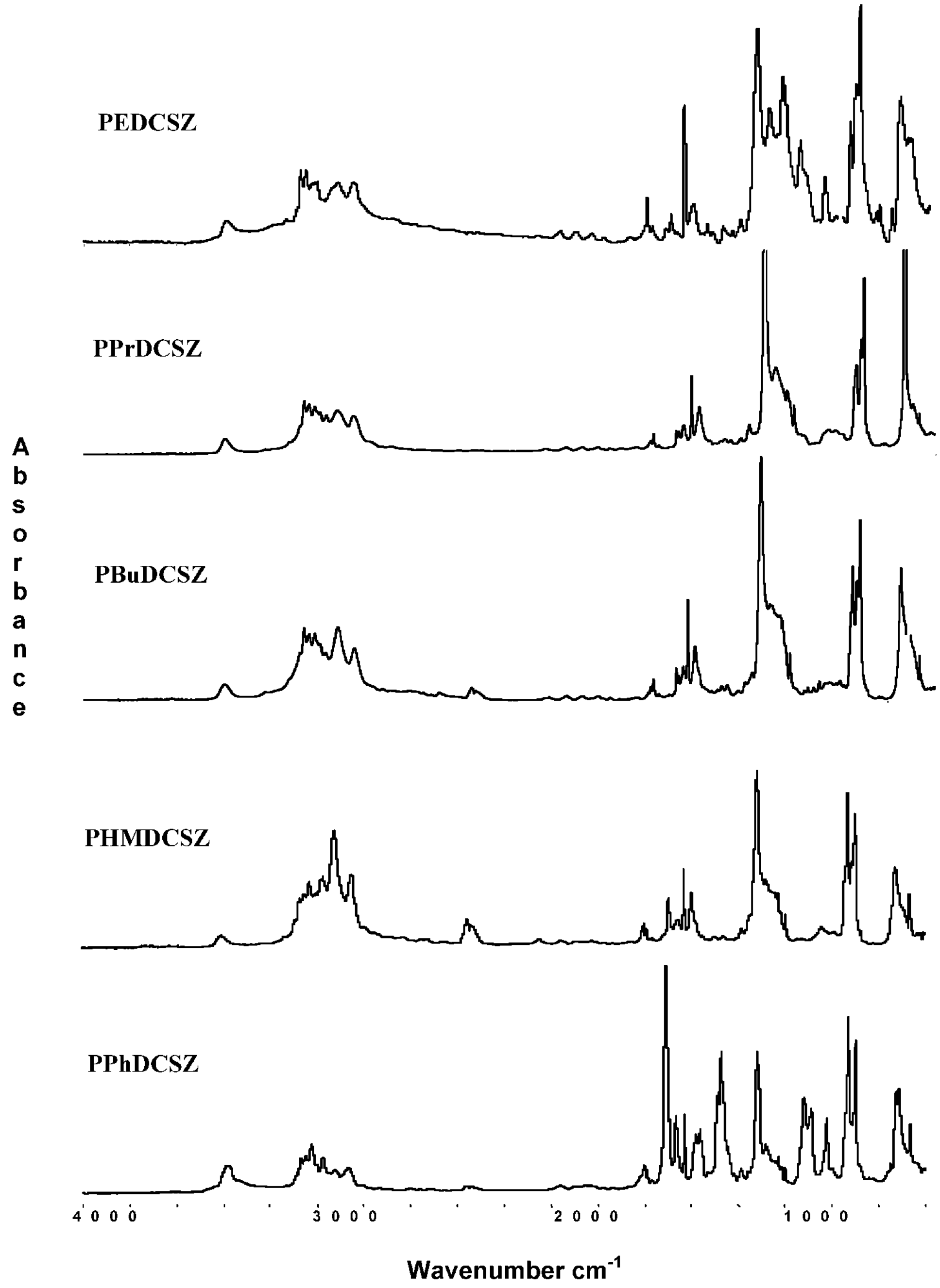


Figure 2. FT-IR Spectra of carbosilazane polymers, PEDCSZ, PPrDACSZ, PBuDACSZ, PHMDACSZ, and PPhDACSZ.

Table 4. ^{1}H NMR Chemical Shifts of Aliphatic- and Aromatic-Diamine-Bridged Diphenyl-Carbosilazane Macromolecules in $CDCl_3$ (δ, in ppm Relative to TMS)

PDACSZ	Si-Ph	NH	Aliphatic/Aromatic Bridge
PEDACSZ	7.15 (m, 10H)	3.20 (t, 2H)	1.71 (m, 4H)*
PPrDACSZ	7.15 (m, 10H)	3.24 (t, 2H)	1.73 (m, 4H)*; 1.30 (m, 2H)*
PBuDACSZ	7.43 (m, 8H) 6.84 (d, 2H)	2.77 (s, 2H)	1.52 (s, 4H)*; 1.26 (s, 4H)
PHMDACSZ	7.43 (m, 8H) 6.84 (d, 2H)	2.71 (s, 2H)	1.53 (s, 4H)*; 1.26 (s, 8H)
PPhDACSZ	7.34 (m, 8H) 6.56 (d, 2H)	3.72 (s, 2H)	7.53 (d, 4H)**

*Broad signal.

**Protons of the phenylene bridge.

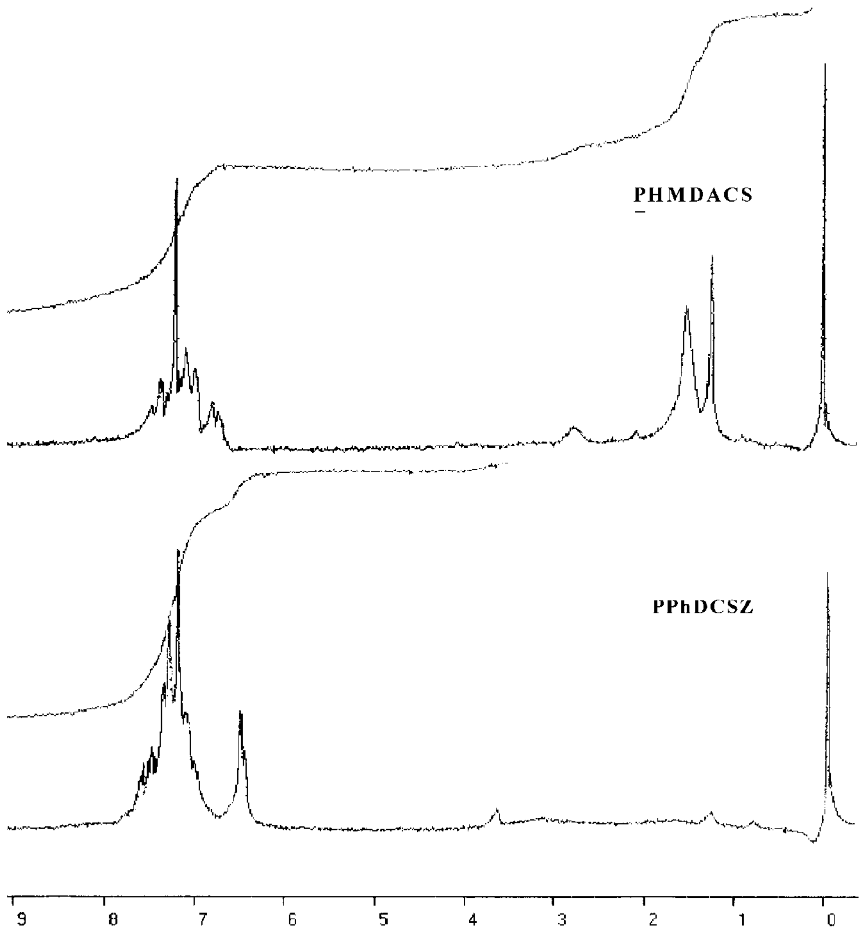


Figure 3. ^{1}H NMR Spectra of PHMDACSZ and PPhDACSZ in $CDCl_3$.

assigned to π-π* transition localized phenyl group of Si-Ph moiety.[16] However, 1,4-phenylenediamine-bridged carbosilazane polymer exhibit an additional broad band at 327 nm which is presumably due to π-π* transition at the phenylene bridge. These results indicate that the electronic absorption for carbosilazane polymers is insensitive to the carbon chain length but sensitive to the type of bridge (aliphatic/aromatic).

CONCLUSION

A series of carbosilazane polymers has been prepared by condensation method. In these polymers, the carbon chain length (spacer) has been varied systematically. This variation certainly affects chain-chain interaction, overall chain length and chain coiling properties. Furthermore, two additional structural features are obvious in these polymers, the presence of nitrogen-donor atoms and N-H moiety in the main polymer chain. These structural features make these carbosilazane polymers attractive for complexation of metal ions and for further chemical modification.

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