Aminopropyl-Terminated Polydimethylsiloxane과 Trichlorogermyl 곁가지 그룹을 갖는 Polyamide 블록공중합체의 합성, 구조분석 및 열적거동

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Synthesis, Structural Characterization and Thermal Behaviour of Block Copolymers of Aminopropyl-Terminated Polydimethylsiloxane and Polyamide Having Trichlorogermyl Pendant Group

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Abstract : Block copolymers of the general formula $[(-CO-R'-CO-HN-Ar-NH-CO-R'-CO)_xNH(CH_2)_3-(Me_2SiO)_y(CH_2)_3NH_2]_n$, [n=18.00 to 1175.0] where $R'=CH_2CH(CH_2GeCl_3);CH_2CHGeCl_3CH_2;$ and $Ar=-C_6H_4;-(o.CH_3C_6H_4)_2;-o.CH_3OC_6H_4)_2; -(o.CH_3C_6H_4)$ were prepared by a polycondensation reaction of polyamide containing a pendant trichlorogermyl group and terminal acid chloride $Cl(-CO-R'-CO-NH-Ar-NH-CO-R'-CO-)_xCl$ with aminopropyl-terminated polydimethylsiloxane $H_2N(CH_2)_3(Me_2SiO)_y-(CH_2)_3NH_2]$, (PDMS). These polymers were characterized by elemental analysis, T_g, FT-IR, ^{1}H-NMR, solid state ^{13}C-NMR, and molecular weight determination. The thermal stability of these copolymers was examined using thermal analysis techniques, such as TGA and DSC. Their molecular weights as determined by laser light scattering technique ranged 5.13×10^5 to 331×10^5 g/mol. These polymers display their T_g in the range of 337 to 393 ℃ with an average decomposition temperature at 582 ℃.

Keywords : synthesis, organogermanium polyamide, aminopropyl-terminated polydimethylsiloxane, block copolymer, thermal characterization.

Introduction

Polydimethylsiloxane has unique physical and chemical properties, such as higher thermal stability, oxidative stability, ultraviolet resistance, low glass transition temperature (T_g), low surface energy, water repellency, low dielectric properties, and high gas permeability.[1-3] Polydimethylsiloxane has, therefore several favorable properties in the manufacture of medical devices such as adhesives, insulators for pacemakers' leads, contact lenses and membranes for oxygenators.[2] Although polydimethylsiloxane has several favorable properties, yet it is mechanically weak, as such it poses a serious problem that must be overcome to facilitate its use in the field of medicine. Thus, in order to utilize polydimethylsiloxane without chemical cross-linking a controlled synthesis of block copolymers, containing polydimethylsiloxane as the soft block and various thermoplastics as the hard segment is necessary.[4] Ever since the description of first silicon-containing polymer[5] several kinds of organometallic block copolymers such as poly(ferrocenylsilane-*b*-dimethylsiloxane)[6] and polydimethylsiloxane-polyamide multiblock copolymers[7] have been synthesized and their properties described. The condensation polymers containing Ge in the main chain and bonded to four carbon atoms have been described.[8-10] However, block copolymers having Ge as a pendant group of the main chain have not been described so far, except poly(ferrocenylgermanes)[11] and poly(diphenylacetylenes).[12] The germanium compounds being photoreactive undergo a photoscission process that makes them attractive as photo-resists.[13]

In continuation of our previous work,[14-16] we deemed it worthwhile to synthesize these materials by copolymeri-

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zation of polyamides containing acid chloride end groups and trichlorogermyl pendant group with aminopropyl terminated polydimethylsiloxane. Since aromatic polyamides based on aromatic diamines are the oldest high-temperature materials, and offer balance between physical and chemical properties, their polymerization with soft polydimethylsiloxane block can prove to be promising by the introduction of elastomeric properties into such macromolecular materials. These copolymers, containing homobifunctional polydimethylsiloxane derivatives as one component, can be used for covalent assembly of layer by layer (LbL) films for gas separation membranes, biological material and as protective layer.[17,18] As LbL deposition is being increasingly used for various applications, the embedding of macromolecules is very promising since it could help to introduce elastomeric properties into such films. The hard-soft block copolymers are expected to exhibit optimum properties which enable them to be applicable in a number of technological fields.

Experimental

Materials. Aminopropyl-terminated polydimethylsiloxane (PDMS) $H_2N(CH_2)_3(Me_2SiO)_y(CH_2)_3NH_2$, t-glutaconic acid, itaconic acid, phenylene diamine (PDA) were purchased from Sigma Aldrich Chemie. o-Dianisidine (o.DA), o-tolidine (o.TD), 2,5-dimethyl 1-4 phenylene diamine (DMPDA) were obtained from Avocado Organics and used as purchased. Tetrahydrofuran (THF), thionyl chloride and triethylammine (TEA), purchased from Sigma Aldrich Chemie were dried and distilled prior to use as per standard methods.[19] All reactions were carried out under inert atmosphere of argon using standard glassware.

Measurements. The FT-IR spectra were recorded on BIO-RAD, Merlin FT-IR spectrometer as neat samples in KBr cells. The ^{1}H-NMR were recorded on BRUKER-300 NMR as solution in $CDCl_3$, solid state ^{13}C-NMR spectra were obtained on Varian Infinity Plus-300 NMR. The thermogravimetric analysis (TGA) was carried on TGA-7 Perkin Elmer. The differential scanning calorimetry (DSC) measurements were performed on a DSC 404-NETZSCH instrument. Elemental analysis was carried out on Exeter Analytical 440 CHNOS elemental analyzer at Midwest Microlabs, Indiana polis, USA. GC-MS was carried on Agilent Technologies-GC 6890 N Network GC System, MS 5973 Inert Mass Selective Detector. Weight average molar mass was determined on a commercial light-scattering spectrometer (ALV/SP-150 equipped with an ALV-5000 multi-τ digital time correlator) with an Argon-ion laser (Coherent innova 90 operated at λ=488 nm with output power ≈ 400 mW) as

light source. For each sample single dilute concentrations ($\sim 1.0 \times 10^{-4}$ g/mL) were prepared in THF. All polymer solutions for LLS were filtered to remove any insoluble material, using a 0.50 μm Whatman. These measurements were carried out at 25±0.1 ℃.

Synthesis. General Procedure of Trichlorogermyl Dicarboxylic Acid : 2-(trichlorogermylmethyl)butanedioic acid **(1)** and 3-(trichlorogermyl)pentanedioic acid **(2)**, were prepared by the following general procedure adopted from ref.[20]

GeO_2 (47.5 mmol) and NaH_2PO_2 H_2O (105 mmol) were dissolved in HCl (37% 50.0 mL) distilled H_2O (15.0 mL), in a round bottom flask, fitted with magnetic stirrer and reflux condenser. The mixture was allowed to reflux for 3 hours at 105 ℃. The resulting reaction mixture was first allowed to cool to room temperature and then to -5 ℃ in an ice bath. Then unsaturated diacid (0.0475 mmol) was added to this mixture along with diethyl ether (30 mL) and stirred over night till the organic phase turned transparent. The organic layer was separated and aqueous layer was extracted twice with 20 mL ether. All organic layers were collected, dried over anhydrous $MgSO_4$ and filtered. The solvent was pulled off on rotary evaporator to give viscous oil which was crystallized in few drops of conc. HCl to yield 85% of the product as white crystalline solid.

For 2-(trichlorogermylmethyl)butanedioic acid **(1)**: melting point: 115-117 ℃; Anal. Found (Calculated) for $C_5H_7Cl_3GeO_4$: C, 19.33 (19.35); H, 2.19 (2.25)%; FT-IR (KBr) cm^{-1}: 425 w (Ge-Cl), 589 s (Ge-C), 1701 b (C=O), 3200 b (O-H); ^{1}H-NMR (300 MHz, CD_3OD, ppm): δ=1.31 (m, 1H, HCCO$_2$H), 2.52 (m, 2H, CH$_2$COOH, 3.11 (m, 2H, CH$_2$GeCl$_3$); ^{13}C-NMR (300 MHz, CD_3OD, ppm): δ=173.9, 176.0 (C=O), 36.0 (CH$_2$GeCl$_3$), 35.8 (CH), 36.5 (CH$_2$).

For 3-(trichlorogermyl)pentanedioic acid **(2)**: melting point: 159-162 ℃; Anal. Found (Calculated) for $C_5H_7Cl_3GeO_4$: C, 19.32 (19.35); H, 2.25 (2.26)%; IR (KBr) cm^{-1}: 422 w (Ge-Cl), 580 s (Ge-C), 1255(C-O), 1728 b (C=O), 3300 b(O-H); ^{1}H-NMR (300 MHz, CD_3OD, ppm): δ=1.45 (m, 1H, HCGeCl$_3$), 2.83 (m, 4H, HC-(CH$_2$CO$_2$H)$_2$); ^{13}C-NMR (300 MHz, CD_3OD): δ=172.5 (C=O), 33.6 (CH$_2$), 33.0 (CH).

General Procedure of Synthesis Block Copolymers : 2.25 mmol of trichlorogermyldioic acid was allowed to react with freshly distilled $SOCl_2$ (0.49 mL, 6.75 mmol) in a two necked 100 mL round bottom flask, with mild heating under inert atmosphere to prepare 3-(trichlorogermyl)dioyl chloride. The oily mass obtained was vacuum dried for 12 hours. 2.20 mmol of para substituted aromatic diamine was dissolved in 40 mL dry THF in a three necked round bottom flask fitted with reflux condenser magnetic stirrer and vacuum line. 5.0 mL triethylamine (TEA) was added from a dropping funnel maintaining

the temperature at 0 ℃. A solution of trichlorogermyldioyl chloride in 10 mL dry THF was added drop by drop at 0 ℃ with constant stirring for 2 hours. 0.20 mmol aminopropyl terminated polydimethylsiloxane dissolved in 10 mL THF was then added drop wise to the reaction mixture. The temperature was slowly raised to room temperature and refluxed for 72 hours. The homogenous reaction mixture was poured into excess of methanol. The precipitated polymer was further purified by dissolving in dry THF and precipitating with methanol.

PA1: 2–(trichlorogermylmethyl)butanedioylchloride 0.780 g, (2.25 mmol), phenylene diammine, 0.238 g (2.205 mmol), aminopropyl terminated polydimethylsiloxane 5.51 g (0.20 mmol). Light brown gelatinous mass in 67.7% yield. Anal. Found (Calculated) for $(C_{758}H_{2198}N_6Si_{360}Cl_{24}Ge_4O_{368})_n$ C, 32.12 (31.92); H, 7.76 (7.71)%; FT–IR (cm^{-1}): 3107 w (N–H), 2966 s (CH$_3$), 1708 b (C=O), 1568 w (C=C aromatic) 1262 vs (Si–CH$_3$), 1038 vs (Si–O–Si), 625 m (Ge–C), 503 w (Ge–Cl); ^{1}H–NMR. (300 NMR, CDCl$_3$, ppm): δ=0.083 (C$\underline{H}_3$Si), 1.267 (C$\underline{H}_2$Si), 1.696 (CH$_2$C$\underline{H}_2$CH$_2$), 3.15 (C$\underline{H}_2$GeCl$_3$), 3.208 (C$\underline{H}_2$NH), 6.927, 7.624 (aromatic), 9.535 (N$\underline{H}$CO); Solid state ^{13}C–NMR (ppm) δ : 0.9 (Si–CH$_3$), 8.10 (CH$_2$–Ge), 22.3 (CH), 37.4 (CH$_2$), 121.7 136.3, 144.7 (aromatic), 174.0 (HNCO).

PA2: 2–(trichlorogermylmethyl)butanedioylchloride 0.780 g, (2.25 mmol), o.Tolidine 0.4680 g (2.205 mmol), aminopropyl terminated polydimethylsiloxane 5.51 g (0.20 mmol). Dark brown gelatinous mass in 63.7% yield. Anal.Found (Calculated) for $(C_{774}H_{2222}N_6Si_{360}Cl_{24}Ge_4O_{368})_n$ C, 34.87 (32.36); H, 7.97 (7.74) %; FT–IR (cm^{-1}): 3595 w (N–H), 2965 s (CH$_3$), 1770, 1707 (C=O), 1661 w (C=C aromatic), 1262 s (Si–CH$_3$), 1094 s (Si–O–Si), 625 m (Ge–C), 511 m (Ge–Cl); ^{1}H–NMR. (300 NMR, CDCl$_3$, ppm): δ=0.049 (C$\underline{H}_3$Si), 1.265 (C$\underline{H}_2$Si), 1.534 (CH$_2$C$\underline{H}_2$CH$_2$), 2.149 (CH$_3$–Ar) 3.15 (C$\underline{H}_2$GeCl$_3$), 3.470 (C$\underline{H}_2$NH), 6.718, 7.726 (aromatic), 8.50 (N$\underline{H}$CO); Solid State ^{13}C–NMR (ppm) δ: 0.9 (Si–CH$_3$), 8.6 (CH$_2$–Ge), 18.0 (CH$_3$), 36.0 (CH), 125.8, 134.7 (aromatic), 175.0 (HNCO).

PA3: 2–(trichlorogermylmethyl)butanedioyl chloride 0.780 g, (2.25mmol), o.Dianisidine 0.5386 g, (2.205 mmol); aminopropyl terminated polydimethyl siloxane, 5.51 g, (0.20 mmol). Light brown gelatinous mass in 71.3% yield. Anal. Found (Calculated) for $(C_{774}H_{2222}N_6Si_{360}Cl_{24}Ge_4O_{372})_n$ C, 32.10 (32.97); H, 7.92 (7.88)%; FT–IR (cm^{-1}): 3596 w (N–H), 2909 s (CH$_3$), 1713 (C=O), 1607 w (C=C aromatic) 1259 s (Si–CH$_3$), 1085 s (Si–O–Si), 629 m (Ge–C), 500 m (Ge–Cl); ^{1}H–NMR. (300 NMR, CDCl$_3$, ppm): δ=0.085 (C$\underline{H}_3$Si), 1.268 (C$\underline{H}_2$Si), 1.620 (CH$_2$C$\underline{H}_2$CH$_2$), 2.369 (C$\underline{H}$CONH), 3.208 (C$\underline{H}_2$NH), 3.778 (C$\underline{H}_3$OAr), 6.928, 7.346, 7.626 (aromatic), 9.535 (N$\underline{H}$CO); Solid state ^{13}C–NMR (ppm) δ: 0.2 (Si–CH$_3$), 9.3 (CH$_2$– Ge), 20.4 (CH), 36.4(CH$_2$), 55.4 (OCH$_3$), 109.9, 119.1, 148.6, 156.2 (aromatic), 180.0 (HNCO).

PA4: 3–(trichlorogermyl)pentanedioyl chloride 0.780 g (2.25 mmol), phenylene diamine 0.238 g (2.205 mmol), aminopropyl terminated polydimethylsiloxane 5.51 g (0.20 mmol). Light brown gummy mass in 62.3% yield. Anal. Found (Calculated) for $(C_{758}H_{2206}N_6Si_{360}Cl_{24}Ge_4O_{368})_n$ C, 33.57 (31.92); H, 7.91 (7.74)%; FT–IR (cm^{-1}): 3595 w (N–H), 2963 s (CH$_3$), 1774 (C=O), 1665 w (C=C aromatic), 1260 s (Si–CH$_3$), 627 w (Ge–C), 500 w (Ge–Cl); ^{1}H–NMR. (300 NMR, CDCl$_3$, ppm): δ=0.085 (C$\underline{H}_3$Si), 1.267 (C$\underline{H}_2$Si), 1.599 (CH$_2$C$\underline{H}_2$CH$_2$) 2.286 (HC–C$\underline{H}_2$CONH), 3.286 (C$\underline{H}_2$NH), 7.626 (aromatic), 8.188 (N$\underline{H}$CO); Solid state ^{13}C–NMR (ppm): δ =1.2 (Si–CH$_3$), 26.4 (CH–Ge), 35.0 (CH$_2$), 122.4, 135.6, 145.2, (aromatic), 172.1 (HNCO).

PA5: 3–(trichlorogermyl)pentanedioyl chloride 0.780 g (2.25 mmol) o–Tolidine (0.238 g 2.205 mmol), aminopropyl terminated polydimethylsiloxane 5.51 g (0.20 mmol). Light brown gelatinous mass in 67.1% yield. Anal. Found (Calculated) for $(C_{774}H_{2222}N_6Si_{360}Cl_{24}Ge_4O_{372})_n$ C, 33.83 (32.61); H, 7.92 (7.80)%; FT–IR (cm^{-1}): 3643, 3277 w (N–H), 2963 s (CH$_3$), 1760 s (C=O), 1443 w (C=C aromatic) 1260 s (Si–CH$_3$), 1092 s (Si–O–Si), 626 m (Ge–C), 500 m (Ge–Cl); ^{1}H–NMR. (300 NMR, CDCl$_3$, ppm): δ=0.05 (C$\underline{H}_3$-Si), 1.26 (C$\underline{H}_2$Si) 1.57 (CH$_2$C$\underline{H}_2$CH$_2$) 1.84 (H$\underline{C}$GeCl$_3$), 2.20 (C$\underline{H}_2$CO), 2.82 (C$\underline{H}_2$NH), 6.928, 7.346, 7.625 (aromatic) 8.189 (NHCO); Solid state ^{13}C–NMR (ppm): δ=0.9 (Si–CH$_3$), 17.0 (CH$_3$), 26.6 (CH–Ge), 35.0 (CH), 125.8, 134.2 (aromatic), 171.1 (HNCO).

PA6: 3–(trichlorogermyl)pentanedioyl chloride 0.780 g (2.25 mmol) ; o.Dianisidine 0.5386 g, (2.205 mmol); aminopropyl terminated polydimethylsiloxane, 5.51 g, (0.20 mmol). Light brown gummy mass in 67.7% yield. Anal. Found (Calculated) for $(C_{774}H_{2222}N_6Si_{360}Cl_{24}Ge_4O_{368})_n$ C, 33.70 (32.35); H, 7.82 (7.74)% ; FT–IR (cm^{-1}): 3765 w (N–H), 2963 s (CH$_3$), 1601 (C=O), 1443, 1411 w (C=C aromatic) 1260 s (Si–CH$_3$), 1093 s (Si–O–Si), 627 m (Ge–C), 500 w (Ge–Cl); ^{1}H–NMR (300 NMR, CDCl$_3$, ppm): δ=0.061 (C$\underline{H}_3$-Si), 1.241 (C$\underline{H}_2$Si), 1.548 (CH$_2$C$\underline{H}_2$CH$_2$) 1.950 (H$\underline{C}$GeCl$_3$), 2.096 (C$\underline{H}_2$CO), 2.163 (C$\underline{H}_2$NH), 3.462 (C$\underline{H}_3$OAr), 6.899, 7.183, 7.316, 7.597, (aromatic), 8.110 (N$\underline{H}$CO).

PA7: 3–(trichlorogermyl)pentanedioyl chloride 0.780 g (2.25 mmol.), 2,5–dimethyl phenylene diamine, 0.2998 g, (2.205 mmol); aminopropyl terminated polydimethyl siloxane, 5.51 g, (0.20 mmol.). Dark brown gummy mass in 62.7%. Anal. Found (Calculated) for $(C_{762}H_{2214}N_6Si_{360}Cl_{24}Ge_4O_{368})_n$ C, 33.02 (32.02); H, 7.89 (7.75)% ; FT–IR (cm^{-1}): 3269 w (N–H); 2962 s (CH$_3$), 1660 w (C=O), 1645 w (C=C aro–

matic),1261 s (Si—CH$_3$), 1092,1017 s (Si—O—Si), 700 m (Ge—C),498 w (Ge—Cl). ^{1}H—NMR (300 NMR, CDCl$_3$ ppm): δ =0.084 (C$\underline{H}_3$—Si), 1.268 (C$\underline{H}_2$Si), 1.450 (CH$_2$C$\underline{H}_2$CH$_2$) 1.621 (H$\underline{C}$GeCl$_3$), 2.151 (C$\underline{H}_2$CO), 2.285 (C$\underline{H}_2$NH), 2.373 (CH$_3$Ar), 6.929, 7.625 (aromatic), 8.101 (N$\underline{H}$CO).

Results and Discussion

Block copolymers (PA1—PA7) have been synthesized by condensation of polyamide diacid chloride containing pendant trichlorogermyl group and aminopropyl terminated polydi—methylsiloxane (PDMS) as shown in Scheme 1. Polyamide

diacid chlorides containing trichlorogermyl pendant group were synthesized by the hydrogermylation of unsaturated dibasic acids such as *trans* –glutaconic acid and itaconic acid with HGeCl$_3$ produced *in situ,* followed by chlorination with SOCl$_2$ and condensing the obtained diacid chlorides with various para substituted aromatic diamines in the presence of triethylamine. 2% less than the required stoichiometric amount of para substituted diamines were used to obtain chloro terminated polyamide. The chloro–terminated poly– amides have reactive acid chloride groups and thus were characterized by converting them into their amino–terminated derivatives. The glass transition temperature (T_g) of amino
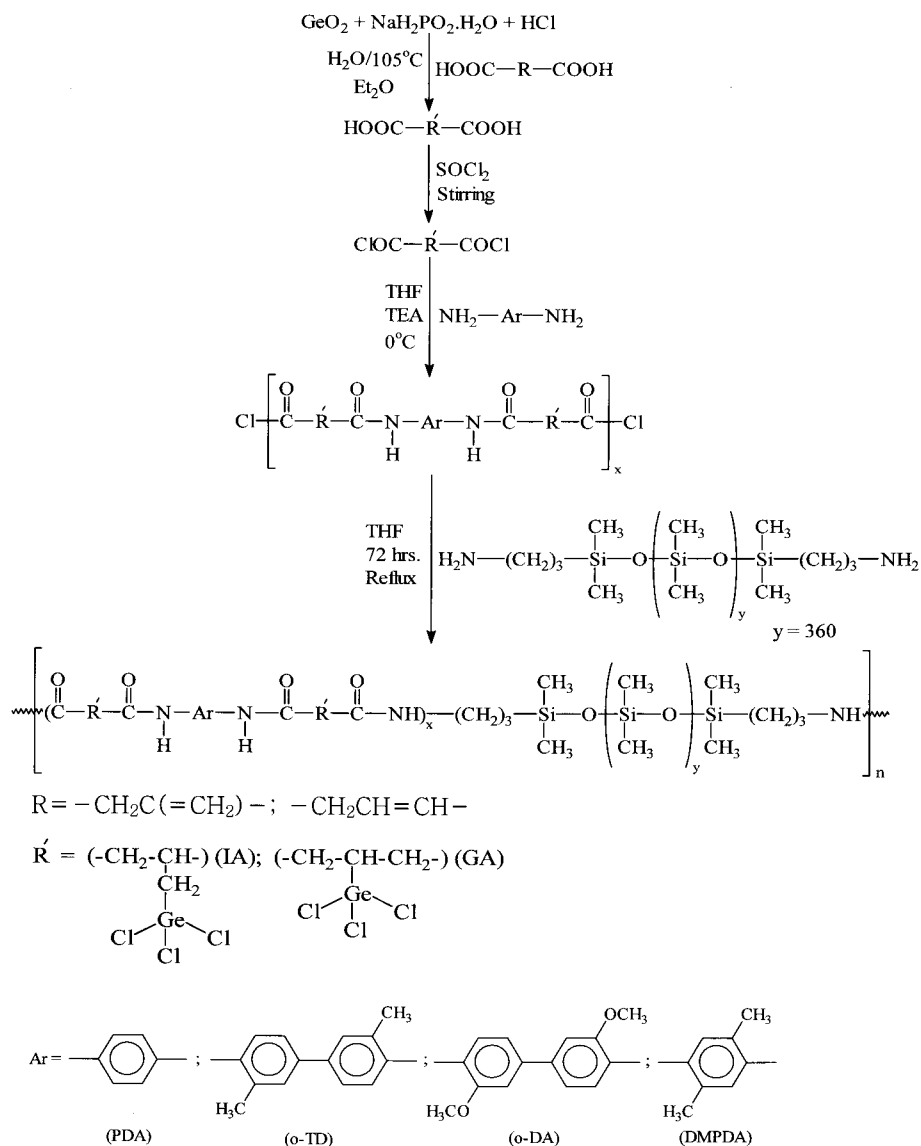
1. PDA+IA, 2. o—TD+IA, 3. o—DA+IA, 4. PDA+GA, 5. o—TD+GA, 6. o—DA+GA, 7. DMPDA+GA, 8. PDMS
PA1=1+8, PA2=2+8, PA3=3+8, PA4=4+8, PA5=5+8, PA6=6+8, PA7=7+8.

Scheme 1. Schematic representation of synthesis of block copolymers of aminopropyl—terminated polydimethylsiloxane and polyamide having trichlorogermyl pendant group.

terminated polyamides are high and fall in the range of 250 to 290 ℃ indicating their chain stiffness to result hard materials. FT−IR, ^{1}H, [13]C−NMR spectroscopy and molecular weight as determined by MALDI suggest formation of oligomeric product of composition [NH−Ar−NH−CO−R−CO−]$_n$ where n=5 to 8. PDMS was employed in copolymer formation containing hard amide segment and soft PDMS (Me₂SiO)$_{360}$ segment. Copolymerization requires prolonged heating under reflux. All these copolymers are dark brown viscous gels. They swell and then dissolve in chloroform and tetrahydrofuran on mild heating. Thus the advantage of the procedure, being used for the synthesis of these copolymers, is the solubility of the polymeric material. Structural characterization of these block copolymers was carried by FT−IR, ^{1}H and ^{13}C solid state NMR spectroscopy. All the characteristic IR absorptions of polyamide blocks have been found to occur at 3300, 1650, 1516, 625, and 500 cm^{-1} and assigned to N−H, C=O, N−H bending, Ge−C and Ge−Cl vibrations respectively.[8,21] These block copolymer exhibit strong IR absorbance at 1261 cm^{-1} and 1099−1107 cm^{-1} due to symmetrical CH₃−Si deformation modes and Si−O−Si asymmetric stretch respectively (Figure 1).[22]

[1]H−NMR spectra, of all the copolymers show one very strong peak around 0.00 ppm due to Si−CH₃ and absorptions in the region 7.23−7.99 ppm show presence of aromatic hydrogen of polyamide block. The protons attached to spacer carbons of n−propyl in the PDMS block, could also be detected in [1]H−NMR although they are of relatively low concentration.[22,23] Solid state [13]C−NMR resonances are well resolved due to the presence of all distinct carbon atoms in block copolyamides. In PA2 and PA5, signal for the methyl group present on aromatic ring of o−TD is at ca.18 ppm (Figure 2) whereas methoxy group in o.DA resonate, at 55.4 ppm due to the electron withdrawing effect of the −OCH₃ as reported in the literature.[21]

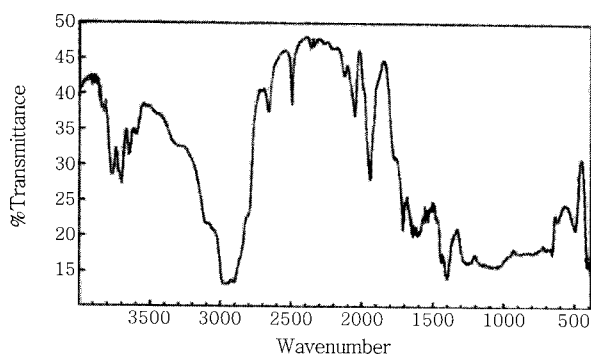The static Laser Light Scattering results are, summarized in Table 1.

The radius of gyration reflects size and this value increases with the increase in molar mass of the block copolymers as given in Table 1. The molecular weight determined through LLS was useful to calculate the degree of polymerization (n). The degree of polymerization (Table 1) varies in these polymers. It can be noted that molecular weight of PA3 is higher than the other polymers probably due to cluster formation along the individual linear chain. Cluster formation along the chains is facilitated by the presence of electron donating methoxy groups on the polyamides.

The chain stiffness of the polymer is usually characterized by T_g. The T_g values of the block copolymers determined by DSC (Table 2, Figure 3) describe relatively much higher values in the range of 337 to 393 ℃ as compared to poly−carbonates, polythiocarbonates, polyesters and polyamides containing silicon or germanium atoms in the main chain, which have T_gs below 200 ℃.[9,24] T_gs noted for these block copolymers are also higher than the previously synthesized organometallic block copolymer of the aramid−polydimethylsiloxane type by us.[22] Presumably, this increase is due to the presence of trichlorogermyl pendant group and amide group, which limit
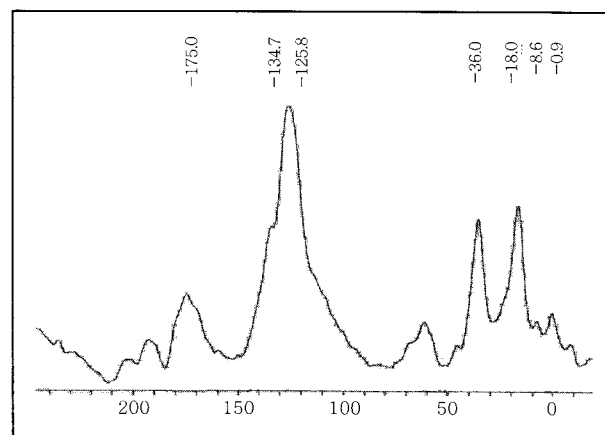

Figure 2. Representative solid state [13]C−NMR of block co−polymer PA 2.

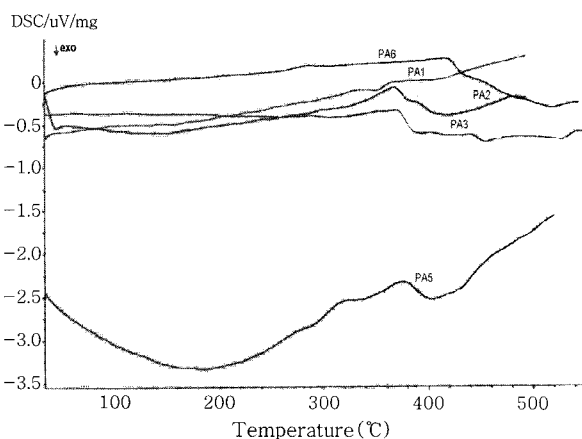Table 1. Molecular Weight and Degree of Polymerization of Block Copolymers

Polymer sample	$M_w{}^a \times 10^5$ (gmol^{-1})*	n^b	$<R_g^2>_z^{1/2} >^{c*}$
PA 1	5.13	18.00	81
PA 2	7.66	26.68	143
PA 3	331	1175.0	450
PA 4	8.82	30.95	145
PA 5	24.1	84.62	171
PA 6	−	−	−
PA 7	−	−	−

^{a}Molecular weight of block copolymer. ^{b}Degree of polymerization of block copolymers. ^{c}Radius of gyration. *The relative errors of the listed parameters are: M_w, ±5%, $<R_g^2>_z^{1/2}$ >, ±8%.

Figure 1. Representative FT−IR spectrum of block copolymer PA 3.

Table 2. Thermodynamic Parameters of Block Copolymers as Calculated from the TG Curve Using Reference[31]

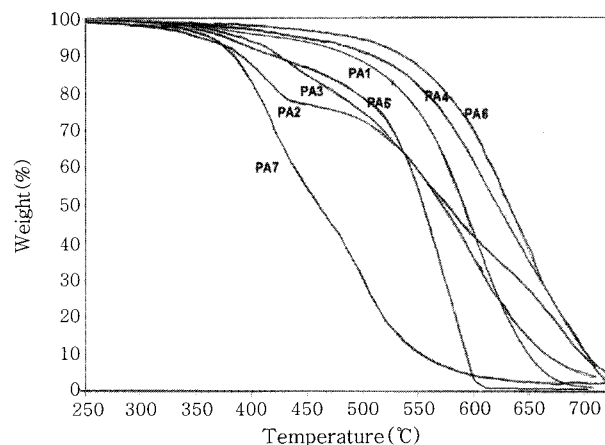| Polymer sample	T_g^a (°C)	T_d^b (°C)	Activation energy (KJ mol^{-1})	Enthalopy (KJmol^{-1})	Entropy (KJ K^{-1}mol^{-1})
PA 1	357.7	600.0	57.36	52.36	−65.38
PA 2	374.3	622.4	32.93	27.94	−169.2
PA 3	379.4	597.5	38.99	34.00	−142.9
PA 4	363.9	610.9	69.59	64.23	−19.4
PA 5	393.3	552.0	43.47	38.69	−116.0
PA 6	373.3	634.2	40.97	36.90	−96.12
PA 7	350.0	458.0	68.23	62.75	−45.83

^{a}Measured from DSC under nitrogen at heating rate of 10 °C/min. ^{b}Decomposition temperature, measured from TGA under nitrogen at heating rate of 10 °C/min.

Figure 3. DSC curves of block copolymers, PA1, PA2, PA3, PA5 and PA6.

Figure 4. TGA curves of block copolymers, PA1−PA7 in flowing nitrogen atmosphere of 20 mL/minute and heating rate of 10 °C/min.

the chain movement due to interchain hydrogen bond formation between hydrogen and chlorine and hydrogen and oxygen.[10,25] The analogous behaviour of PA2, PA5 and PA6 maybe attributed to the use of o.TD and o.DA which have methyl and methoxy groups at 2 and 2' position at both the aromatic rings respectively, restricting chain movement and consequently causing rigidity in structure.[26,27]

The mobility of chain plays an important role in degradation of polymer. The TGA suggest loss of volatile residue at high temperature. Depolymerization of polydimethylsiloxane begins near 400 °C[28] whereas aromatic polyamides, because of intermolecular bonding and chain stiffness, possess high thermal stability.[29-31] The thermal degradation behavior of the block copolymers was measured by TGA, in 20 mL/min flowing nitrogen atmosphere (Figure 4). It has been found that copolymers PA1−PA7 depolymerize intensively in the range of 380 to 700 °C, in nitrogen atmosphere (Figure 4). The loss of weight ranges from 2.99% to 48.77% up to a temperature of 700 °C. These values are comparable to our previous preparation of aramid−polydimethylsiloxane block copolymers.[14] The pyrolysis of copolymers under vacuum,

convert them into various volatiles and decomposition products, mainly oligomeric cyclic products obtained from the degradation of copolymers as evolved gas of general formula $[(CH_3)_2SiO]_n$ where n=3−7.[32] All the oligomeric cyclic products have been identified by GC−MS at m/e ratio of $207(M-15)^+$, $281(M-15)^+$, $355(M-15)^+$, $446(M-15)^+$, $503(M-15)^+$ for hexamethylcyclotrisiloxane (D_3), octamethylcyclotetrasiloxane(D_4), decamethylcyclopentasiloxane (D_5), dodecamethylcyclohexasiloxane (D_6) and tetradecamethylcycloheptasiloxane (D_7) respectively. The fragments of polyamide block also appeared at m/e 210, 192, and 143, for $(C_7H_7N)_2$, $CHGeCl_3$, and $GeCl_2$ respectively. In all the copolymers a small weight loss occurs prior to the onset of the main decomposition process (Figure 4). This pattern of thermal depolymerization of block copolymer is similar to the thermal decomposition of polydimethylsiloxanes which is the main component of the copolymer as reported earlier.[33] It can be seen that values of activation energy for the thermal depolymerization are low and independent of the molecular weight indicating similar depolymerization mechanism of all the investigated copolymers. The thermal depolymerization of the basic siloxane framework of the block copolymer starts at ca. 400 °C in N_2 atmosphere and is mainly confined to the rupture of siloxane bond rather than Si−C bond. Although aromatic polyamides used as hard segment in these copolymers have activation energy range from 131~222.58 KJmol^{-1} [34] yet their contribution is less as being small component of the block copolymers. Further d−orbital of silicon facilitates depolymerization by expanding its valence shell. Activation energy of the block copolymers calculated from TG isotherm using Horowitz method,[35] shows variation according to the type, degree of polymerization, molecular orientation of the diamine and diacid chloride used in pre−

paring polyamides. The activation energies of copolymers PA2, PA3, PA5, and PA6 are comparable and fall in the range of 32.93 to 40.97 KJmol^{-1}. This similarity might be due to the presence of methyl and methoxy substitution on the two aromatic rings, imparting chain rigidity to the amide block. Owing to the presence of polar amide linkage, and GeCl$_3$ group in the amide block, the copolymers absorb around 5– 9% moisture by weight when soaked in water at room temperature for 48 hours, thus causing them to swell. These hard–soft polymers are expected to exhibit optimum properties which enable them to be applicable in number of technological fields such as LbL deposition of films for gas separation membranes, protective layers and also in biological application.

Conclusions

A solution phase one pot polycondensation method was employed for the synthesis of block copolymers [AB]$_x$ type, containing aminopropyl–terminated polydimethylsiloxane and polyamides with trichlorogermyl pendant group. These block copolymers were characterized by physical properties, elemental analysis, FT–IR, ^{1}H–NMR, solid state ^{13}C–NMR spectral analyses thermogravimetry and LLS molecular weight determination. Glass transition temperature (T_g) of these block co–polymers fall in the range of 337.1 ℃ to 393.3 ℃ indicating their high thermal stability. Hydrogen bonding and interchain linkage give them increased activation energy and high stability. Due to the presence of polar site the copolymers absorb 5–9% moisture when soaked in water for 48 hours at room temperature. These properties make them suitable for possible industrial application as gas separation membranes, protective layers etc.

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