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Synthesis and Properties of Novel Functionally Substituted Carbosilane Polymers

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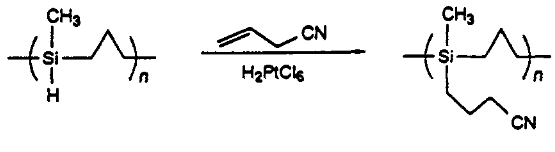
ABSTRACT: Poly[1-(3′-cyanopropyl)-1-methyl-1-silabutane], poly[1-methyl-1-[3′-(glycidyloxy)propyl]-1-silabutane], poly[1-methyl-1-[3′-(triethoxysilyl)propyl]-1-silabutane], poly[1-methyl-1-(4′,7′,10′-trioxaundecanyl)-1-silabutane], poly[1-methyl-1-(4′,7′,10′,13′-tetraoxatetradecanyl)-1-silabutane], poly[1-methyl-1-[3′-(phenyloxy)propyl]-1-silabutane], and poly[1-methyl-1-[3′-(pentafluorophenyl)propyl]-1-silabutane] have been prepared by the platinum-catalyzed hydrosilation graft reactions between poly(1-methyl-1-silabutane) and the appropriate functional alkene. These polymers have been characterized by ^{1}H, ^{13}C, ^{19}F (where appropriate), and ^{29}Si NMR as well as by FT-IR and UV spectroscopy. The molecular weight distributions of these polymers have been determined by gel permeation chromatography (GPC), their thermal stabilities by thermogravimetric analysis (TGA), and their glass transition temperatures (T_g's) by differential scanning calorimetry.

While there has been considerable work over the last 50 years on silicone polymers,[1,2] there has been much less work on carbosilane polymers. The observation of Yajima that thermal decomposition of poly(methylsilylenemethylene) $[CH_3SiHCH_2]_n$ results in loss of methane and hydrogen and formation of β-silicon carbide[3,4] has stimulated considerable interest in polycarbosilanes.[5]

This paper reports the preparation of saturated carbosilane polymers which have functionally substituted pendant alkyl chains. These have been prepared by the chemical modification, by platinum-catalyzed hydrosilation graft reactions between functional alkenes and the reactive Si–H bonds, of the saturated carbosilane polymer, poly(1-methyl-1-silabutane).[6] There is considerable interest in the chemical modification of intact polymers since this method often permits the synthesis of polymers which cannot be prepared directly.[7,8]



Background

Numerous types of silicone polymers with functionally substituted pendant alkyl chains have been prepared. The synthesis, chemical properties, and significant applications of these have been reviewed.[9-12] Some of these have properties which combine the intrinsic properties of poly(dimethylsilicones) such as low surface tension, high thermal stability, and low glass transition temperature with properties which are associated with the pendant functional chain. For example, poly[methyl-(3,3,3-trifluoropropyl)siloxane] combines thermal stability and low glass transition temperature with lubricating properties and lack of swelling in hydrocarbon solvents characteristic of perfluoroalkyl polymers.[13,14] Poly[1-(3′-cyanopropyl)-1-methylsiloxane] compounds find utility as thermally stable polar liquid phases for gas–liquid chromatography, while similar chemically bonded siloxane polymers are used in high-pressure liquid chromatography.[13] Poly(3′-aminopropyl)methylsiloxane, poly[3′-(acryloxy)propyl]-methylsiloxane, poly(3′-mercaptopropyl)methylsiloxane, poly(3′-cyanopropyl)methylsiloxane, poly[3′-(glycidyloxy)propyl]methylsiloxane are among the silicone polymers with pendant functionally substituted alkyl groups which are commercially available.[11]

Closely related to these are siloxane graft copolymers. These polymeric systems have a siloxane backbone in which some or all of the silyl centers carry functional substituted oligomeric side chains. Important examples of this type of polymer are polysiloxanes substituted with hydrophilic nonionic oligo(oxyethylene) pendant groups. These find commercial application as surfactants[16] and are of scientific interest due to their ability to complex lithium cations to form solvent-free polymer electrolytes which have reasonable ionic conductivities.[17-20] These have been prepared by the platinum-catalyzed hydrosi-

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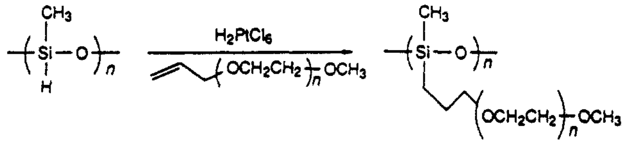
lation reaction between the reactive Si–H bonds of poly(methylsiloxane) and the terminal carbon–carbon double bonds of oligo(ethylene glycol) allyl methyl ethers.[1,16,21-23]



Experimental Section

^{1}H and ^{13}C NMR spectra were run on a Bruker AM-250 spectrometer operating in the Fourier transform (FT) mode. ^{29}Si NMR spectra were recorded on a Bruker 270-SY spectrometer. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{29}Si NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (INVGATE) with a pulse delay of 15–20 s.[24] ^{13}C and ^{29}Si NMR spectra were obtained in a 15% solution of chloroform-*d*. ^{1}H NMR spectra were obtained in a 5% solution of chloroform-*d*. Chloroform was utilized as an internal standard for ^{1}H and ^{13}C NMR spectra. ^{29}Si NMR spectra were internally referenced to TMS. IR spectra were recorded on an IBM FT-IR/30S, DTGS/CSI spectrometer. These spectra were taken of neat films on sodium chloride plates. UV spectra were recorded on a Shimadzu UV-260 spectrometer. Spectral quality ethyl ether was used to prepare solutions for UV spectra.

The molecular weight distribution of these polymers were determined by gel permeation chromatography on a Waters system. This is comprised of a U6K injector, a 510 HPLC solvent delivery system, an R401 differential refractometer, and a Maxima 820 control system. A Waters 7.8 mm × 30 cm Ultrastyragel linear column packed with <10-mm particles of mixed pore size cross-linked styrene–divinylbenzene copolymer was utilized for analysis. The column was maintained at room temperature. The eluting solvent was HPLC grade THF at a flow rate 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards, 612 000, 114 200, 47 500, 18 700, 5120, and 2200, whose M_w/M_n values are <1.09.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TGS-2 instrument with a nitrogen flow rate of 40 mL/min. The temperature program for this analysis was 50 °C for 2 min. The temperature was then increased at a rate of 4 °C/min to 750 °C. The glass transition temperatures (T_g) of these polymers were determined by differential scanning calorimetry (DSC) on a Perkin-Elmer DSC-7 instrument. The melting points of indium (156 °C) and spectral grade *n*-hexane (−95 °C) were utilized to calibrate the DSC. The temperature scans were begun at −100 °C for 5 min. The temperature was then increased at a rate of 20 °C/min to 150 °C.

Tetrahydrofuran was distilled immediately prior to use from a deep blue solution of sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) was distilled from calcium hydride and was stored over activated 4-Å molecular sieves. Platinum–divinyltetramethyldisiloxane complex in xylene was obtained from (Huls) (Pt complex). All glassware was dried overnight in an oven at 120 °C. All reactions were conducted under an atmosphere of argon.

Poly(1-methyl-1-silabutane), M_w/M_n = 19400/10300, T_g = −89 °C, was prepared by anionic ring-opening polymerization of 1-methyl-1-silacyclobutane following a literature procedure.[6]

Poly[1-(3′-cyanopropyl)-1-methyl-1-silabutane] (I). A 100-mL three-necked round-bottom flask was equipped with a Teflon-covered magnetic stirring bar and an efficient reflux condenser. Poly(1-methyl-1-silabutane) (0.5 g, 5.8 mmol), allyl cyanide (Alrich) (0.78, 11.6 mmol), 110 mg of Pt complex, and 20 mL of toluene were placed in the flask. The mixture was refluxed with stirring for 1 h. The color of the mixture changed to black. The solvent was removed by evaporation under reduced pressure. After workup, the residue was dissolved in a minimum amount of THF and I was precipitated from pentane. The process was repeated twice. I was dried under vacuum. A sticky material, M_w/M_n = 28100/15400; T_g = −53 °C, 1.05 g, 90% yield, was obtained: TGA, onset 410 °C, 50% dec 500 °C, residue 29%; ^{1}H NMR δ −0.045 (s, 3 H), 0.61 (m, 6 H), 1.26 (m, 2 H), 1.62 (m, 2 H), 2.33 (m, 2 H); ^{13}C NMR δ −5.26, 13.57, 18.29, 18.56, 20.70, 20.96, 119.83; ^{29}Si NMR δ 1.74; IR ν 2916, 2876, 2799, 2245, 1451, 1340, 1253, 1217, 1174, 1144, 1079, 1045, 1024, 993, 907, 858, 793 cm^{-1}. Elemental Anal. Calcd $C_8H_{15}NSi$: C, 62.72; H, 9.87. Found: C, 60.66; H, 9.72.

Poly[1-methyl-1-[3′-(pentafluorophenyl)propyl]-1-silabutane] (II). The reaction of poly(1-methyl-1-silabutane) (0.5 g, 5.8 mmol), allylpentafluorobenzene (2.40 g, 11.6 mmol), 110 mg of Pt complex, and 20 mL of toluene was carried out as above. After workup, the residue was dissolved in a minimum amount of THF and II was precipitated from pentane. The process was repeated twice. II was dried under vacuum. A sticky material, M_w/M_n = 30500/15000, T_g = −39.0 °C, 1.56 g, 91% yield, was obtained: TGA, onset 350 °C, 50% dec 475 °C, residue 18%; ^{1}H NMR δ −0.11 (s, 3 H), 0.50 (m, 6 H), 1.24 (m, 2 H), 1.53 (m, 2 H), 2.67 (t, 2 H, J = 7.3 Hz); ^{13}C NMR δ −5.43, 13.80, 18.33, 18.58, 24.09, 26.07, 115.30 (t, J = 18.83 Hz), 137.38 (d, t, J = 250.54, 16.11 Hz), 139.40 (d, m, J = 251.08 Hz), 145.04 (d, m, J = 244.48 Hz); ^{19}F NMR δ −113.54, −104.03, −99.20; ^{29}Si NMR δ 1.66; IR ν 2917, 2877, 2798, 1656, 1522, 1503, 1460, 1452, 1415, 1347, 1312, 1299, 1254, 1217, 1175, 1121, 1083, 1047, 1012, 972, 963, 944, 909, 802, 706 cm^{-1}; UV λ_{max} nm (ϵ) 215 (1878), 256 (528). Elemental Anal. Calcd $C_{13}H_{15}F_5Si$: C, 53.06; H, 5.24. Found: C, 51.49, H, 5.13.

Poly[1-methyl-1-(3′-phenoxypropyl)-1-silabutane] (III). The reaction of poly(1-methyl-1-silabutane) (0.5 g, 5.8 mmol), allyl phenyl ether (Aldrich) (1.55 g, 11.6 mmol), 110 mg of Pt complex, and 20 mL of THF was carried out as above. After workup, the residue was dissolved in a minimum amount of THF and III was precipitated from methanol. The process was repeated twice. III was dried under vacuum. A sticky material, M_w/M_n = 56200/20900, T_g = −29.0 °C, 1.15 g, 90% yield, was obtained: TGA, onset 315 °C, 50% dec 500 °C, residue 9%; ^{1}H NMR δ −0.037 (s, 3 H), 0.58 (m 6 H), 1.33 (m, 2 H), 1.75 (m , 2 H), 3.86 (t, 2 H, J = 6.6 Hz), 6.93 (m, 3 H), 7.25 (m, 2 H); ^{13}C NMR δ −5.07, 9.83, 18.42, 18.76, 23.92, 70.57, 114.46, 120.42, 129.38, 159.06; ^{29}Si NMR δ 2.25; IR ν 3062, 3040, 2913, 2874, 2795, 1601, 1587, 1498, 1472, 1456, 1435, 1413, 1386, 1336, 1302, 1289, 1246, 1172, 1141, 1079, 1035, 1016, 993, 943, 909, 805, 752, 692 cm^{-1}; UV λ_{max} nm (ϵ) 279 (14 420), 272 (16 780), 221 (54 720). Elemental Anal. Calcd $C_{13}H_{20}OSi$: C, 70.88; H, 9.15. Found: C, 71.58; H, 9.15.

Poly(1-methyl-1-(4′,7′,10′-trioxaundecanyl)-1-silabutane) (IV). The reaction of poly(1-methyl-1-silabutane) (0.5 g, 5.8 mmol), allyl diethylene glycol methyl ether (Aldrich) (1.86 g, 11.6 mmol), 110 mg of Pt complex, and 20 mL of THF was carried out as above. After workup, the residue was dissolved in a minimum amount of THF and IV was precipitated from pentane. The process was repeated twice. IV was dried under vacuum. A sticky material, M_w/M_n = 27200/16900, T_g = −85 °C, 1.27 g, 90% yield, was obtained: TGA, onset 375 °C, 50% dec 445 °C, residue 6%; ^{1}H NMR δ −0.099 (s, 3 H), 0.47 (m, 6 H), 1.25 (m, 2 H), 1.54 (m, 2 H), 3.38 (m, 5 H), 3.58 (m, 8 H); ^{13}C NMR δ −5.23, 9.61, 18.30, 18.74, 23.98, 58.95, 69.92, 70.46, 70.58, 71.88, 74.47; ^{29}Si NMR δ 2.14; IR ν 2913, 2873, 1455, 1413, 1352, 1251, 1200, 1113, 1029, 991, 942, 909, 809 cm^{-1}. Elemental Anal. Calcd $C_{12}H_{26}O_3Si$: C, 58.51; H, 10.64. Found: C, 58.05; H, 10.65.

Poly[1-methyl-1-(4′,7′,10′,13′-tetraoxatetradecanyl)-1-silabutane] (V). The reaction of poly(1-methyl-1-silabutane) (0.5 g, 5.8 mmol), allyl triethylene glycol methyl ether (Aldrich) (2.4 g, 11.6 mmol), 110 mg of Pt complex, and 20 mL of THF was carried out as above. After workup, the residue was dissolved in a minimum amount of THF and V was precipitated from pentane. The process was repeated twice. V was dried under vacuum. A sticky material, M_w/M_n = 28600/14200, T_g = −84 °C, 1.48 g, 89% yield, was obtained: TGA, onset 385 °C, 50% dec 415 °C, residue 5%; ^{1}H NMR δ −0.099 (s, 3 H), 0.45 (m, 6 H), 1.24 (m, 2 H), 1.50 (m, 2 H), 3.35 (m, 5 H), 3.56 (m, 8 H); ^{13}C NMR δ −5.14, 9.59, 18.31, 18.75, 23.98, 58.97, 69.91, 70.45, 70.55, 71.87, 74.49; ^{29}Si NMR δ 1.22; IR ν 2913, 2872, 1455, 1413, 1350, 1329, 1301, 1251, 1200, 1112, 989, 942, 910, 808 cm^{-1}. Elemental Anal. Calcd $C_{14}H_{30}O_4Si$: C, 57.91; H, 10.41. Found: C, 57.34; H, 9.93.

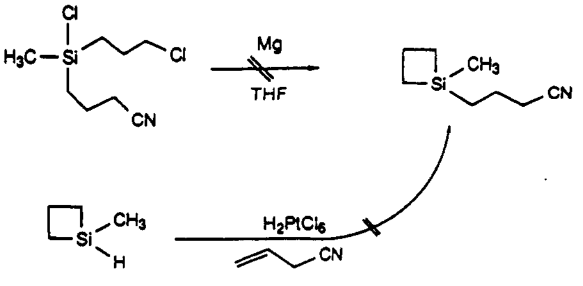
Poly[1-methyl-1-[3′-(glycidyloxy)propyl]-1-silabutane] (VI). The reaction of poly(1-methyl-1-silabutane) (0.5 g, 5.8 mmol), allyl glycidyl ether (Aldrich) (1.3 g, 11.6 mmol), 110 mg of Pt complex, and 20 mL of THF was carried out as above. After workup, the residue was dissolved in a minimum amount of THF and VI was precipitated from pentane. The process was repeated twice. VI was dried under vacuum. A sticky material, M_w/M_n = 38000/19500, T_g = −64 °C, 1.05 g, 90% yield, was obtained: TGA, onset 385 °C, 50% dec 445 °C, residue 10%; ^{1}H NMR δ −0.099 (s, 3 H), 0.47 (m, 6 H), 1.23 (m, 2 H), 1.53 (m, 2 H), 2.57 (dd, 1 H, J = 4.9, 2.6 Hz), 2.76 (t, 1 H, J = 4.4 Hz), 3.12 (m, 1 H), 3.38 (m, 3 H), 3.65 (dd, 1 H, J = 11.5, 2.9 Hz); ^{13}C NMR δ −5.17, 9.73, 18.36, 18.76, 24.12, 44.29, 50.84, 71.42, 74.59; ^{29}Si NMR δ 2.15; IR ν 2996, 2913, 2872, 1414, 1337, 1251, 1136, 1108, 1024, 944, 908, 804, 699, 668 cm^{-1}. Elemental Anal. Calcd $C_{10}H_{20}O_2Si$: C, 59.97; H, 10.07. Found: C, 58.61; H, 9.99.

Poly[1-methyl-1-[3′-(triethoxysilyl)propyl]-1-silabutane] (VII). The reaction of poly(1-methyl-1-silabutane) (0.5 g, 5.8 mmol), allyltriethoxysilane (Aldrich) (2.4 g, 11.6 mmol), 110 mg of Pt complex, and 20 mL of THF was carried out as above. The residue was dissolved in a minimum amount of THF, and VII was precipitated from pentane. The process was repeated twice. VII was dried under vacuum. A sticky material, M_w/M_n = 38200/11100, T_g = −90 °C, 1.48 g, 88% yield, was obtained: TGA onset 375 °C, 50% dec 480 °C, residue 15%; ^{1}H NMR δ −0.11 (s, 3 H), 0.52 (m, 4 H), 0.66 (t, 2 H, J = 7.9 Hz), 1.20 (t, 9 H, J = 7.0 Hz), 1.40 (m, 2 H), 3.79 (q, 6 H, J = 7.0 Hz); ^{13}C NMR δ −5.19, 15.10, 17.50, 18.32, 18.43, 18.98, 58.23; ^{29}Si NMR δ 0.97, −45.21; IR ν 2973, 2916, 2879, 1450, 1411, 1395, 1336, 1295, 1251, 1104, 1080, 956, 912, 862, 781, 671 cm^{-1}. Elemental Anal. Calcd $C_{13}H_{30}O_3Si_2$: C, 53.77; H, 10.41. Found: C, 53.33; H, 10.37.

Results and Discussion

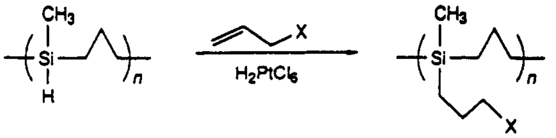
We report the preparation and properties of a number of saturated carbosilanes which have pendant functional groups. From an architectural point of view, these will be comb polymers. A key difference between these polymers and the corresponding siloxane polymers is the polymer backbone. A saturated carbosilane backbone is chemically quite inert. On the other hand, the Si–O bonds of siloxanes are susceptible to both acid- and base-catalyzed hydrolysis as well as to thermal redistribution reactions. Further, the glass transition temperatures of functionally substituted saturated carbosilane polymers are expected to be higher than the corresponding functionally substituted siloxane polymers since the glass transition temperature of poly(1-methyl-1-silabutane) (T_g = −85 °C)[6] is higher than that of poly(methylhydrosiloxane) (T_g = −120 °C).

While 1,1-dimethyl-1-silacyclobutane undergoes anionic,[25] thermal,[26] and platinum-catalyzed[27] ring-opening polymerization to yield poly(1,1-dimethyl-1-silabutane), ring-opening polymerization of functionally substituted silacyclobutanes is not suitable for the preparation of many functionally substituted poly(1-silabutanes). This limitation results from the fact that the synthetic methodology (Grignard cyclization)[28] necessary to prepare silacyclobutanes is not compatibile with many functional groups: amino, cyano, ester, epoxy, and trifluoromethyl among others. Further, attempts to carry out hydrosilation reactions between 1-methyl-1-silacyclobutane and various functional alkenes to yield functionally substituted 1-silacyclobutanes resulted in competitive platinum-catalyzed polymerization.[29]



The desired systems have been prepared by the chloroplatinic acid catalyzed reaction of poly(1-methyl-1-silabutane), prepared by anionic ring-opening polymerization of 1-methyl-1-silacyclobutane,[6] with functional alkenes. No evidence for unreacted Si–H bonds in the product polymers was detected by infrared spectroscopy. For this reason, we believe that the graft hydrosilation reactions proceed quantitatively. Yields have been calculated on this basis. For example, poly[1-(3′-cyanopropyl)-1-methyl-1-silabutane] (I) has been prepared by the hydrosilation reaction between poly(1-methyl-1-silabutane) and allyl cyanide. Similarly, poly[1-3′-(pentafluorophenyl)propyl]-1-methyl-1-silabutane] (II) and poly[1-(3′-phenoxypropyl)-1-methyl-1-silabutane] (III) have been prepared by platinum-catalyzed hydrosilation graft reactions between poly(1-methyl-1-silabutane) and 3-(pentafluorophenyl)propene and allyl phenyl ether, respectively.

Table I
Glass Transition Temperature (T_g) and M_w/M_n of Functional Substituted Polycarbosilane



X	polymer	M_w/M_n (×10^{-3})	T_g, °C
CN	I	28.1/15.4	−53.0
C_6F_5	II	30.5/15.0	−39.0
OC_6H_5	III	56.2/20.9	−29.0
$(OCH_2CH_2)_2OCH_3$	IV	27.2/16.9	−85.0
$(OCH_2CH_2)_3OCH_3$	V	28.6/14.2	−84.0
$OCH_2H\overline{C{-}O{-}C}H_2$	VI	38.0/19.5	−64.0
$Si(OEt)_3$	VII	38.2/11.1	−90.0

We have also prepared polymers IV and V with a saturated carbosilane backbone and pendant oligo(oxyethylene) pendant groups by the platinum-catalyzed hydrosilation reaction of oligo(ethylene glycol) allyl methyl ethers with Si–H carbosilane polymers such as poly(1-methyl-1-silabutane). An epoxy-substituted carbosilane polymer (VI) was prepared by the hydrosilation reaction between allyl glycidyl ether and poly(1-methyl-1-silabutane). The epoxy functionalities of this polymer will provide multiple reactive sites for binding to polar surfaces and well as for incorporation of carbosilane polymers into epoxy network polymeric materials. In a similar manner, poly[1-[3′-(triethoxysilyl)propyl]-1-methyl-1-silabutane] (VII) will function as a multisite polymeric coupling agent.[9]

In several cases (I, II, VI) the elemental analysis results for carbon are low, 0.4%. This may result from a platinum-catalyzed side reaction between adventitious water and Si–H bonds of poly(1-methyl-1-silabutane). This would result in formation of silanol Si–OH bonds which would undergo dehydration to form siloxane bonds.[22,23] As expected, the molecular weight of the product polymers are greater than the starting polymer. In general, the ratio of M_w/M_n for the product polymers is approximately equal (1.6–2.0) to that of the starting polymer(1-methyl-1-silabutane) (M_w/M_n = 1.9). The high value for the ratio of M_w/M_n = 38200/11100 = 3.4 for VII suggests that a small amount of hydrolysis of the triethoxysilyl groups occurs to yield silanols which can undergo condensation, cross-linking, to form siloxane bonds. The ratio of M_w/M_n = 2.7 for VI is also high. We do not have any explanation in this case.

A general conclusion is that the T_g's of these polymers are quite low (Table I). In fact, the T_g's of IV, V, and VII are within a few degrees of that of poly(1-methyl-1-silabutane). The polymers also have quite high thermal

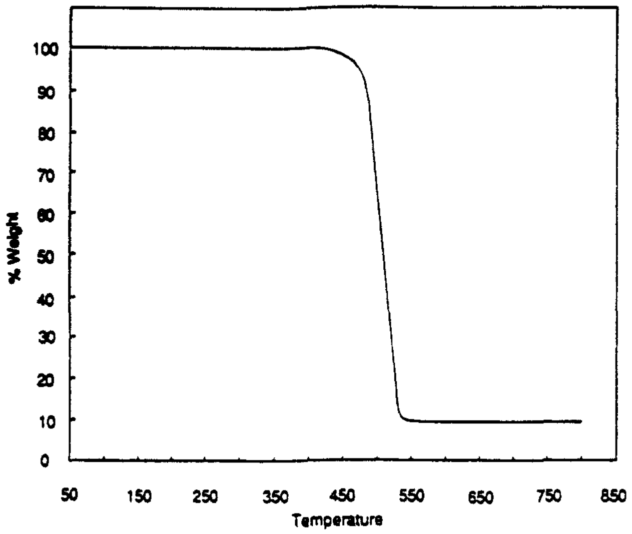


Figure 1. TGA of polymer III.

stabilities. The onset of thermal decomposition of the least stable of these derivative polymers, II, is 350 °C, while the most thermally stable III begins to decompose at 415 °C. See Figure 1 for the TGA of III. Additional studies on this new family of polymers are in progress.

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