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POLYMERIZATION OF ISOBUTYLENE INDUCED BY RF-PLASMA-GENERATED Cl_xSi^+ SILYLIUM IONS

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ABSTRACT

Isobutylene was polymerized by Si_2Cl_6-RF-plasma-generated silylium ions. Initiation is due to Cl_xSi^+ in-situ adsorbed on frozen isobutylene surfaces at liquid nitrogen temperature. The polymerization of isobutylene occurs in the absence of counterions. According to survey and high resolution ESCA spectra, silicon is present in the resulting polymers, which suggests initiation by Cl_xSi^+. FT-IR, ^1H- and ^{13}C-NMR spectroscopies, GC-MS, high resolution pyrolysis MS, as well as FAB and FI-MS analyses indicate that plasma-polymerized isobutylenes are linear oligomers of broad molecular weight distribution. DTA-TG analyses substantiate the conclusion that the average molecular weight of plasma-polymerized isobutylene is low. The findings demonstrate the usefulness of RF-plasma for generating silylium ions and silylium ions-mediated cationic polymerization. The possibility of producing novel polyisobutylene/polysiloxane block copolymers is suggested.

INTRODUCTION

Trigonal planar silylium ions (R_3Si^+) [1-3] are known to be stable in the gas phase [4]. However, despite many attempts [5, 6], they have not yet been produced in the condensed phase. Strong evidence has been presented that R_3Si^+ exists as a reactive intermediate in solution [7].

While the average C—Si—C bond angle and the out-of-plane displacement are related, the changes from the ideal trigonal planar geometry relative to the bond angle are not linear. For instance, a distortion of only 3° from the ideal $C-Si^+-C$ angle of 120° produces more than half of the total out-of-plane displacement of the silicon on going from the trigonal planar to the tetrahedral structure [1].

Similarly, Cl_3Si^+ ions are planar trigonal, which accounts for their instability and high reactivity. The incorporation of Cl_xSi^+ into polymers by cationic polymerization would lead to new functional polymers. In comparison to the C—Cl bond, the Si—Cl bond is extremely labile, for example, CCl_4 and $SiCl_4$ behave totally differently toward water. Even though CCl_4 and $SiCl_4$ are tetrahedral due to sp^3 hybridization, the presence of d oribitals (dsp^3 and d_2sp^3 hybridization, trigonal bipyramidal and octahedral structures) render silicon compounds much more reactive. Indeed, all Group 4A elements can form four covalent bonds with nonmetals and can react with Lewis bases (by forming two additional covalent bonds) except carbon-based structures. The high reactivity of $SiCl_4$ with water (relative to that of CCl_4) may be attributed to the ability of silicon to expand its valence beyond 4. This may become important since $Si-Cl_x$ head groups arising from silylium ion-initiated cationic polymerizations may lead to polyhydrocarbon-polysiloxane-type block copolymers, for instance, by coupling in the presence of moisture.

This paper concerns isobutylene polymerization induced by RF-plasma-generated Cl_xSi^+ ions.

EXPERIMENTAL

Materials and Methods

High purity isobutylene (Aldrich, lecture bottle) was used. The monomer container was connected by a micrometric needle-valve, a measuring trap, and Tygon tubing to the plasma reactor. Prior to the experiment the connecting line was evacuated to avoid environmental contamination. Hexachlorodisilane (HCDS) (Aldrich, 1 g sealed vials) was handled in a glove-box under an argon blanket. Heavy-duty aluminum foil was used to cover the parallel plate electrodes to avoid the direct deposition of polymer on the electrodes and to facilitate cleaning. High purity argon (Liquid Carbonic) was employed to clean the reactor before each experiment (argon-plasma: argon pressure = 200 mT; RF power = 300 W; argon flow rate = 8 sccm; reaction time = 5 minutes) and to sustain the plasma under low temperature conditions.

The IR spectra of polyisobutylene (PIB) films synthesized by plasma-generated silylium cations and deposited on KBr pellets were recorded by a Mattson Galaxy Series FTIR-5000 instrument. The measurements were carried out under a moisture and CO_2-free nitrogen atmosphere.

The surface atomic composition of plasma-produced PIB films and the relative ratios of nonequivalent C_{1s} carbon linkages were analyzed using survey and high resolution (HR) x-ray photoelectron spectroscopy (ESCA-Perkin Elmer Physical Electronics O 5400 Small Area System; Mg source; 15 kV, 300 W; pass energy = 89.45 eV; angle = 45°). ESCA analyses involved the determination of carbon (C_{1s}), silicon (Si_{2p}) and oxygen (O_{1s}). To minimize moisture adsorption and postplasma oxidation, samples were stored under argon until measurements.

Plasma fragmentation of Si_2Cl_6 was simulated under various MS-electron energy conditions. The purity of HCDS and the identity of molecular-ion fragments were analyzed by GC-MS (GC-Carlo Erba Fractovap 4162; MS Kratos MS-25; experimental conditions: column-fused silica, length = 30 m, ID = 0.32 mm, coating = 0.25 μm of 5% phenyl and 95% vinyl polysiloxane, injector-splitter temperature = 25°C; temperature profile of the column: 2 minutes at room temperature then heated to 160°C at 15°C/min; electron energy = 32, 30, 50, and 70 eV).

Plasma-generated PIB was analyzed by HR-MS assisted pyrolysis (HR-MS, Kratos MSx80, experimental conditions: electron energy = 50 eV) at 400°C. Both MS instruments were double focusing mass spectrometers (electrostatic analyzer and magnet) provided with electron impact ion sources.

Additional structural information was obtained by ^1H- and ^{13}C-NMR spectroscopy by using a AMX360, 300K instrument and deuterated chloroform ($CDCl_3$) as solvent.

Fast atom bombardment (FAB) MS (VG ZAB-SE double focusing mass spectrometer; 8 kV Xe atoms) and field ionization (FI) mass spectrometry (MAT 731 and VG 70-VSE double focusing instruments; acceleration potential = 8 kV, electron plate potential = 4kV) investigations were carried out to gain insight into the macromolecular nature and the polydispersity of PIB.

Thermal properties of plasma-generated PIB in comparison to high molecular weight conventional PIB (Aldrich) were estimated by differential thermal analysis (TG; DTA) using a TG-DTA Seiko apparatus (100 mL/min nitrogen; 20-600°C; reference: alumina; heating 5°C/min).

Plasma Reactions

Plasma reactions were carried out in a parallel plate cylindrical reactor (Fig. 1) with an electrode diameter of 20 cm and spacing of 3 cm. The upper electrode (17) was connected to a matching network and a RF generator (30 kHz), and the lower electrode (25) was grounded, assuring the existence of self-bias. The hollow lower electrode (25) was connected to a liquid nitrogen supply for cooling it to −195°C. A thermocouple (27) allowed the monitoring of the electrode temperature. Specially designed ring-shaped aluminum thermal barriers (23) assured monomer deposition only on the upper surface of the lower electrode (the sharp edge of the ring was in touch only with the low temperature electrode so that monomer deposition outside of the upper surface of the lower electrode was avoided). The reactor was equipped with two vacuum lines connected by 1″ stainless steel tubing (28) to the reaction chamber and positioned through the center of the lower electrode. In this way the gas flows symmetrically into the discharge zone between the electrodes. The major vacuum line, comprised of a large cross-section valve (29), liquid nitrogen trap (30), and high capacity vacuum pump (33), facilitated quick reaction evacuation to base

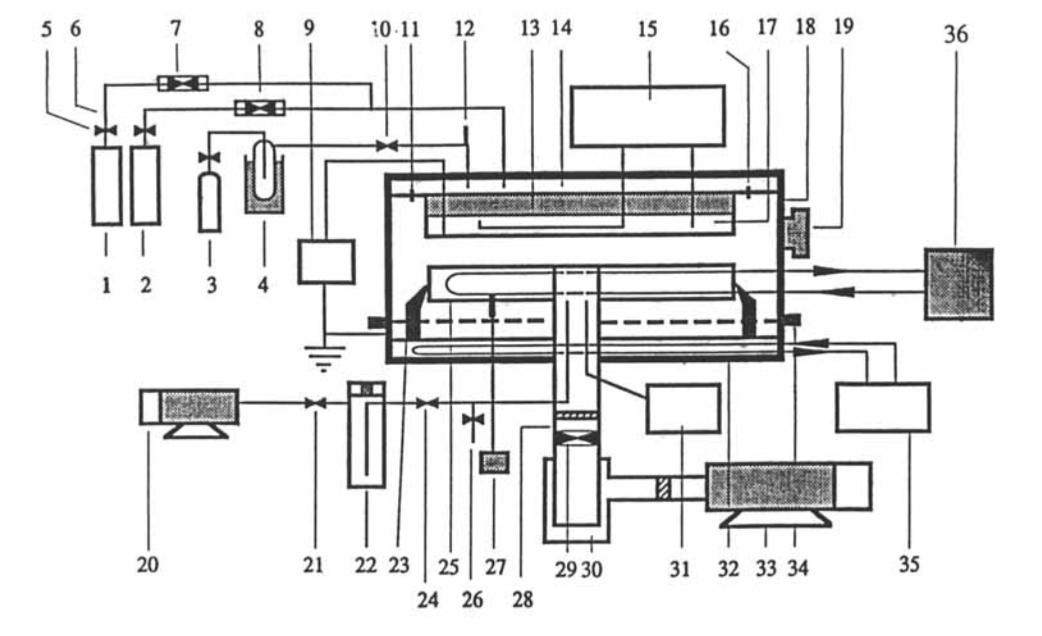


FIG. 1. Parallel plate, capacitively coupled, cylindrical stainless steel RF-plasma reactor. 1, 2: Argon and HCDS reservoirs; 3: Isobutylene (lecture bottle); 4: Isobutylene measuring trap; 5, 6, 10, 21, 24, 26: Needle valves; 7, 8: Flow controllers; 9: RF power supply; 11, 16: Monomer and gas inlet orifices located around the upper electrode; 12: High pressure vacuum gauge; 13: Insulator disk; 14: Gas-mixing chamber; 15: Thermostated recirculator; 17: Drum-type stainless steel upper electrode; 18: Cylindrical-shaped upper part of the reactor; 19: Observation port; 20: Mechanical vacuum pump; 22: Liquid nitrogen trap for collecting the plasma-generated species under vacuum conditions; 23: Ring-type thermal barrier; 25: Grounded hollow stainless steel electrode; 27: Thermo couple; 28: One inch diameter stainless steel connecting tubing; 29: Large cross-section butterfly-type valve; 30: Stainless steel liquid nitrogen trap for connecting vacuum pump; 31: Vacuum gauge; 32: Cylindrical stainless steel lower part of the reactor; 33: High capacity mechanical vacuum pump; 34: Rubber O-ring mediated circular vacuum-tight sealing; 35: Refrigerated recirculator; 36: Liquid nitrogen supply.

pressure and protected the pump from contamination. A valve (29) also permitted equilibrium to be established between the incoming and outgoing gas flows. The second vacuum system, comprised of stainless steel needle valves (21, 24, and 26), a specially designed liquid nitrogen trap (22), and a mechanical pump (20), assured the collection of neutral molecules arising from the recombination of active species outside the discharge zone. The latter line was not in operation during polymerization. A needle valve (26) was used as a vent. The lower electrode (25) was covered with aluminum foil (heavy-duty Reynolds-brand) to avoid polymer deposition on the electrode and to facilitate cleaning. The aluminum foil also served as the substrate for monomer and polymer deposition. Gaseous isobutylene (IB) was introduced into the reaction chamber from a lecture bottle (3) equipped with a needle valve through a specially designed measuring glass trap (4, Fig. 2) and needle valve (10). Argon and HCDS were led into the reactor from reservoirs (1) and (2) through

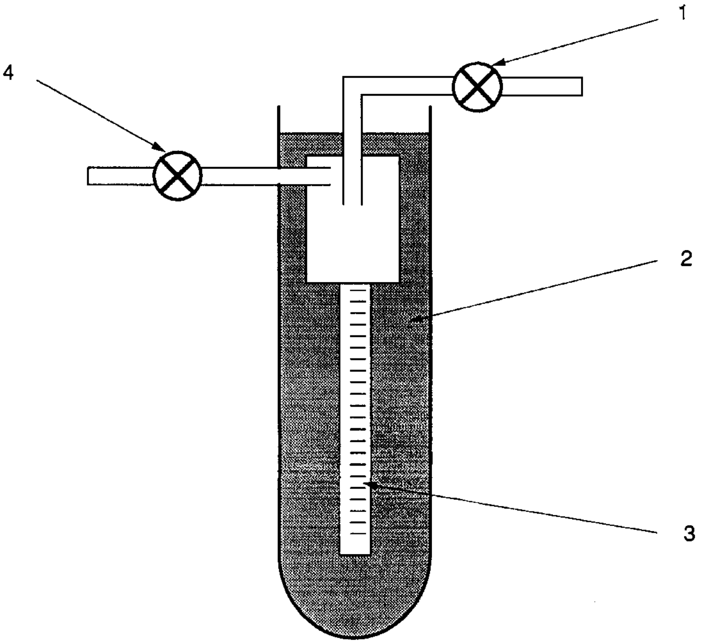


FIG. 2. Measuring glass trap for isobutylene. I, 4: Needle valve. 2: Liquid nitrogen trap. 3: Pyrex measuring trap.

the corresponding leak valves (5 and 6) and flow controllers (7 and 8). HCDS was degassed by freezing at liquid nitrogen temperature, vacuumed to ground pressure, and isolated by closing a needle valve (6). During the experiment the HCDS reservoir was kept at room temperature. The IB connecting line was also evacuated and isolated by closing a valve (10).

In a typical experiment, after covering the lower electrode with aluminum foil, the upper part of the reactor was locked and the system was evacuated through opening a valve (29) to base pressure by the high capacity vacuum pump (33). The second vacuum line was isolated by closing a valve (24) and a vent (26). Molecular fragment trapping was not performed during this experiment. Argon was then introduced into the system and plasma cleaning was performed for 5 minutes, followed by reevacuating the system to base pressure. The measuring trap (4) was then cooled by liquid nitrogen, and the preselected amount of solid IB was collected in the trap by operating the valve of the lecture bottle. Next, the lower electrode (25) was cooled to liquid nitrogen temperature by admitting liquid nitrogen (36), and the IB was slowly admitted into the reactor by opening a valve (10) and a heating trap (4). During the transfer of IB into the reactor, a valve (29) and the argon supply valve were closed. The deposition of IB on the lower electrode surface (25) was monitored through a porthole [19] (the presence of a uniform white film was observed at the end of the deposition). At the end of monomer deposition, the IB valve (10) was closed and argon was introduced into the reactor at the preselected pressure by operating a valve (5) and a flow controller (7). The plasma state was then initiated; the preselected partial pressure of HCDS was quickly established (about 5 seconds) in the reactor with the aid of a valve (6) and a flow controller (8), then the argon valve (5) was closed. This operation prevented the very fast deposition of unfragmented HCDS on frozen IB which would have led to a significant pressure drop. The discharge was sustained for 1 minute, then the RF power supply was disconnected, and the reactor was isolated from the HCDS line by closing a valve (6). Basic pressure was reestablished and the reactor was closed under vacuum by operating a valve (29). The cooling of the lower electrode was then discontinued by closing the liquid nitrogen valve; the reactor was not opened until the system reached room temperature. During heating up, both the low- (31) and the high-pressure (12) vacuum gauges were closely monitored.

Experimental conditions used during plasma treatment were as follows:

Monomer: Isobutylene
Cation source: HCDS
Inert gas (employed both for cleaning and for sustaining the discharge at low temperature conditions): Argon
Base pressure: 50 mtorr
Pressure in the presence of argon plasma: 100 mtorr
Pressure in the presence of argon plus HCDS plasma: 500 mtorr
Flow rate of argon: 2 sccm
Flow rate of HCDS: 2 sccm
Substrate: Heavy-duty aluminum foil
Temperature of the lower electrode and substrate during plasma treatment: −195°C
Quantity of IB deposited on the substrate at liquid nitrogen temperature: 0.5 mL
RF power: 50 W
Reaction period (plasma treatment): 1 minute
Heating period: 90 minutes.

RESULTS AND DISCUSSION

The extremely high reactivity of silicon-based cations opens up the possibility for silylium-ion-initiated carbocationic polymerization.

The cold plasma technique offers a novel approach for creating silylium ions in the gas phase and trapping them on frozen monomer surfaces under vacuum. Cold-plasma-induced molecular fragmentation can be simulated by low electron-energy mass spectroscopy (LEE-MS) [8–10] to predict predominant ion-molecular fragments. By trapping the neutral species arising from the recombination of plasma-generated active species and analyzing them by GC-LEE-MS, feedback can be established for a better understanding of plasma-induced ion and free-radical generation mechanisms. Recently it has been demonstrated that $SiCl_4$-RF plasmas generate predominantly Cl_3Si^+ ions, and that these extremely reactive species are capable of interacting with polymeric surfaces, i.e., polypropylene and polytetrafluoroethylene [11, 12].

Based on LEE-MS estimations, HCDS was selected as the RF-plasma-mediated silylium ion generator. Figure 3 shows molecular ion compositions at

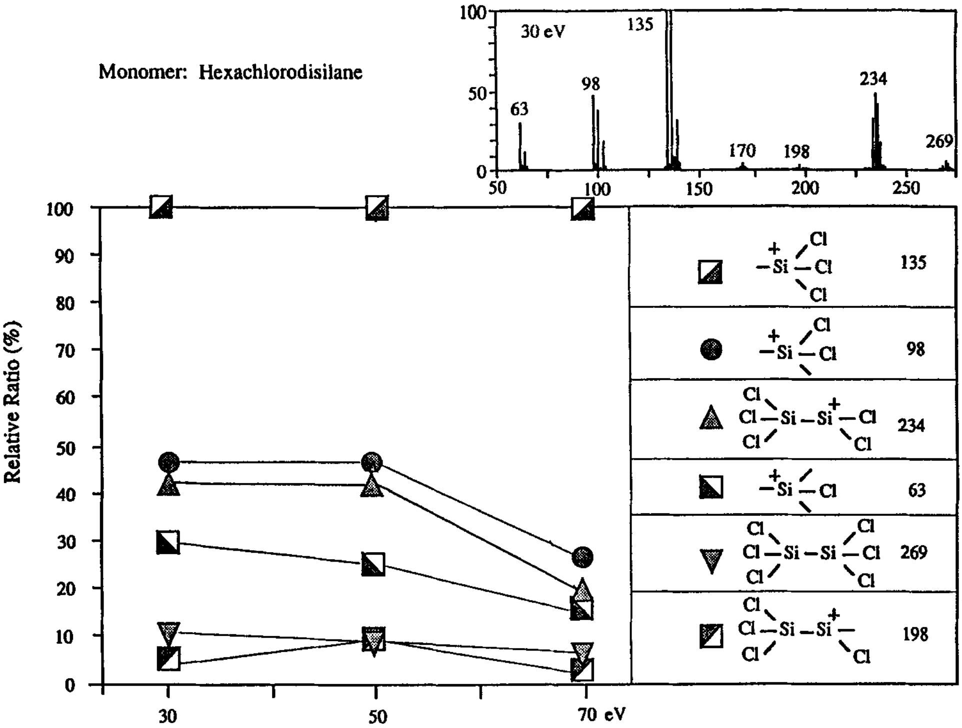


FIG. 3. Molecular-fragment ion composition at various MS-electron energy levels, and a typical MS spectrum of HCDS recorded at 30 eV.

different electron energy levels and a typical MS spectrum of HCDS recorded at 30 eV. Evidently Cl_3Si^+ (m/e = 135) is the predominant species, and even very high electron energy levels (70 eV) do not influence significantly the relative composition of the molecular ion fragments. HCDS is almost completely fragmented (the relative ratio of this molecular ion is 10%), probably due to the weakness of the Si—Si bond (3.3 eV) in comparison to the Si—Cl linkage (4.2 eV). The standard enthalpies of formation of Cl_xSi free radicals (Cl_3Si = −3.3 eV; Cl_2Si: = −1.7 eV; ClSi: = +2.0 eV) also indicate that Cl_3Si should be the predominant species subject to ionization (most of the electrons of cold plasmas have energies between 0.5 and 4 eV). Ionization of Si requires 8.15 eV, while halosilicon derivatives are ionized even at higher energies (e.g., Cl_2Si: = 10.9 eV and $SiCl_4$ = 11.8 eV). These energies are available only for a small number of electrons, specifically for the tail region of the electron energy distribution function of RF discharges. The bulk electron energy region of plasma induces intense fragmentation and free-radical formation, while the tail energy zone leads to the formation of silylium ions. Thus, in addition to silylium-ion-mediated processes, free-radical recombination may also be present. Since IB polymerizes exclusively by a cationic mechanism [13, 14], the presence of free radicals will not influence cation-induced processes. Relatively small quantities of Cl_2Si^+ (m/e = 98), $Cl_5Si_2^+$ (m/e = 234), and $ClSi^+$ (m/e = 63), possibly present in the mixture in addition to the predominant molecular-ion fragment (m/e =

135), may also contribute to initiation. The resulting multifunctionality may lead to reactive surfaces which in turn may lead to further possibilities such as grafting, crosslinking, etc.

Analysis of Thin Polyisobutylene Layers

After the reaction the reactor was opened and the aluminum foil coated with a uniform transparent polymer layer was removed from the lower electrode and stored in a vacuum desiccator until analyses.

It is noteworthy that no significant pressure change occurred during heating up in the reactor; this indicates a fast transformation of deposited IB to a low vapor pressure (polymeric) material.

Figures 4 and 5 show the FT-IR spectrum of a representative PIB (collected from three different locations of the aluminum foil; PIB deposited on KBr pellets) and that of a conventional PIB. In addition to the characteristic vibrations of PIB (CH stretching of CH_2 and CH_3: 2958 and 2888 cm^{-1}; C—H deformation of CH_2 and CH_3: 1472, 1388, and 1369 cm^{-1}; skeletal vibration in the presence of dimethyl groups: 1229 cm^{-1}), the former spectrum shows the presence of fairly intense Si—C vibration at 889 and 1274 cm^{-1} together with characteristic —OH (3436 cm^{-1}) and —C=C— stretching (1600-1660 cm^{-1}) absorptions. The existence of —OH functionalities is most likely due to hydrolysis of Si—Cl groups under open laboratory conditions. The presence of —C=C— groups may be due to dehydrochlorination and/or chain transfer to monomer.

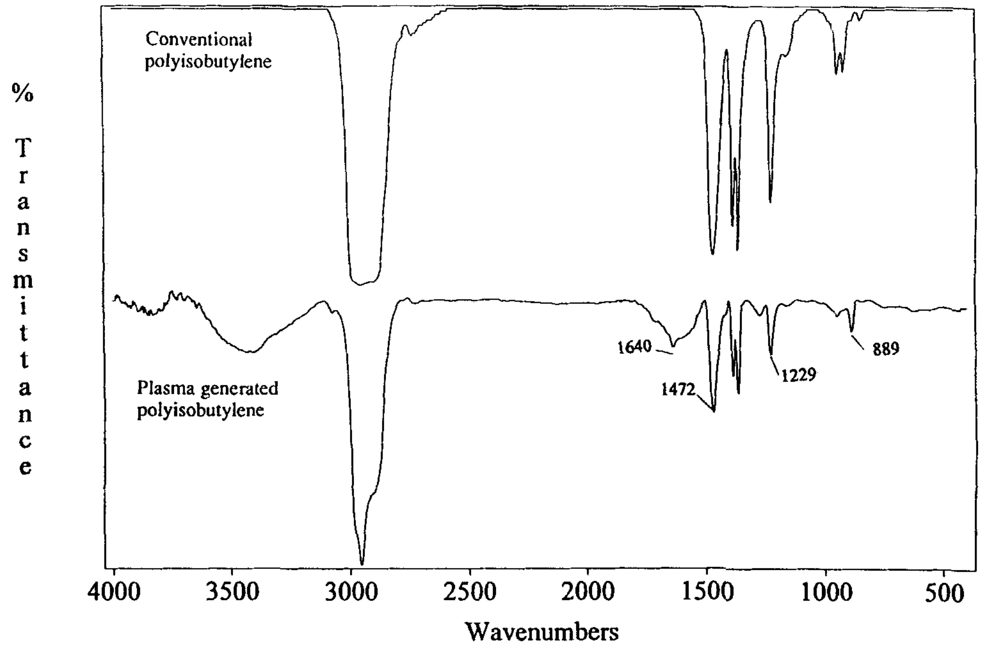


FIG. 4. FT-IR spectra of conventional polyisobutylene and plasma-generated polyisobutylene.

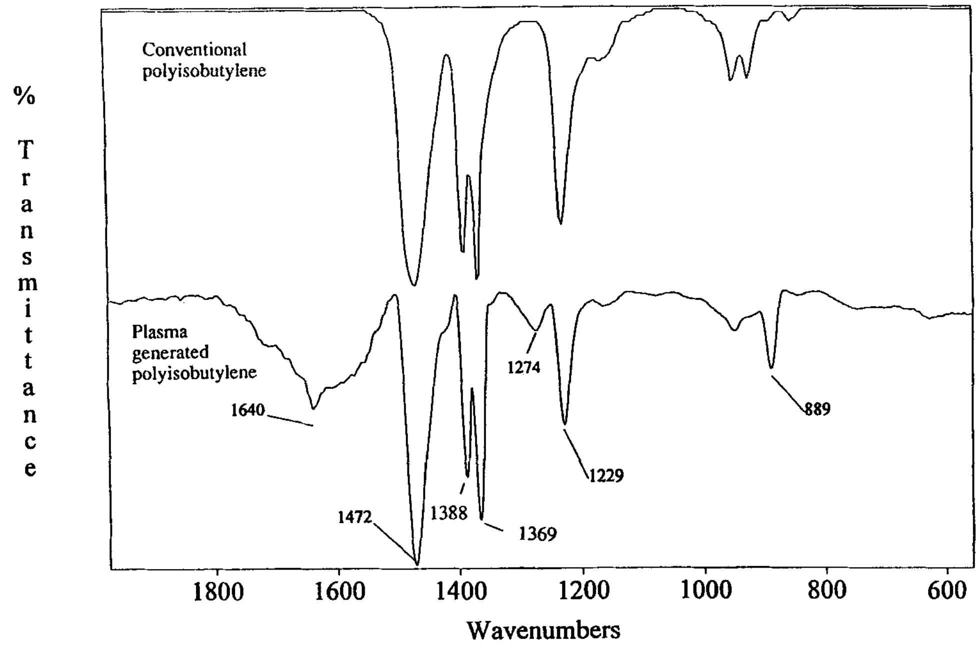


FIG. 5. High resolution FT-IR spectra of conventional polyisobutylene and plasma-generated polyisobutylene.

The ESCA survey spectrum of plasma-generated PIB in Fig. 6 shows, in addition to the characteristic C_{1s} (C—C and C—H; 285 eV) peak of hydrocarbons, the presence of oxygen (O_{1s}; 530 eV) and the two characteristic signals for silicon (Si_{2p}; 103 eV and Si_{2s}; 153 eV). The relative surface atomic composition (see table in Fig. 6) shows relatively low silicon (1.6%) and oxygen concentrations (8%). The presence of oxygen is most likely due to ex-situ postplasma hydrolysis of Si—Cl and/or to free-radical mediated postplasma oxidation. Further, high resolution ESCA evaluation of plasma-generated PIB surfaces, shown in Fig. 7, exhibit non-equivalent C_{1s} carbon linkages indicating the presence of Si—C (284.6 eV), and C—C and C—H (285 eV), and C—O—C (286.4 eV) linkages. The absence of higher binding energy peaks in the C_{1s} region suggest that the polymer is not intensively oxidized or chlorinated, and that the oxygens are probably due to Si—O linkages.

These data are in good agreement with those obtained by FT-IR analysis and substantiate the conclusion that Si—C and Si—O bonds are present in the surface of plasma-generated PIB. The absence of halogen incorporation is probably due to the very low temperatures (−195°C) employed during HCDS-plasma irradiation. Bond vibrations and molecular motions are extremely weak at these temperatures, so that plasma-induced dehydrochlorination, chlorination, and destruction are limited.

Additional structural information was obtained by ^1H- and ^{13}C-NMR spectroscopy (Figs. 8 and 9). The proton spectrum shows the presence of CH_2 (1.42 ppm) and CH_3 (1.11 ppm) groups, and the C-13 spectrum indicates the existence of

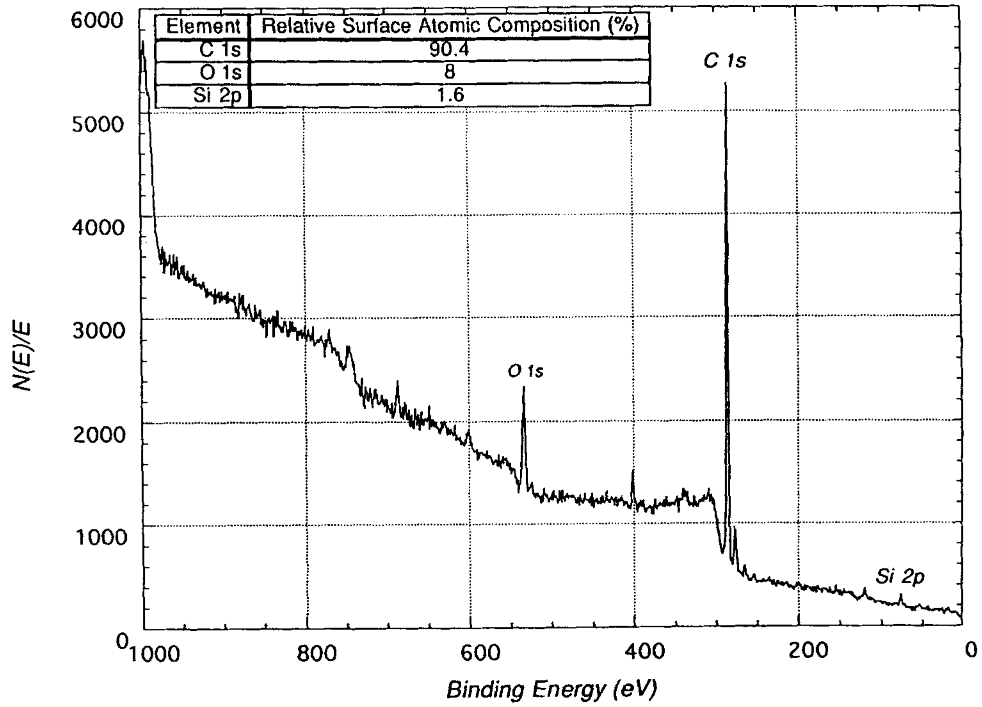


FIG. 6. Survey ESCA spectrum of plasma-generated polyisobutylene.

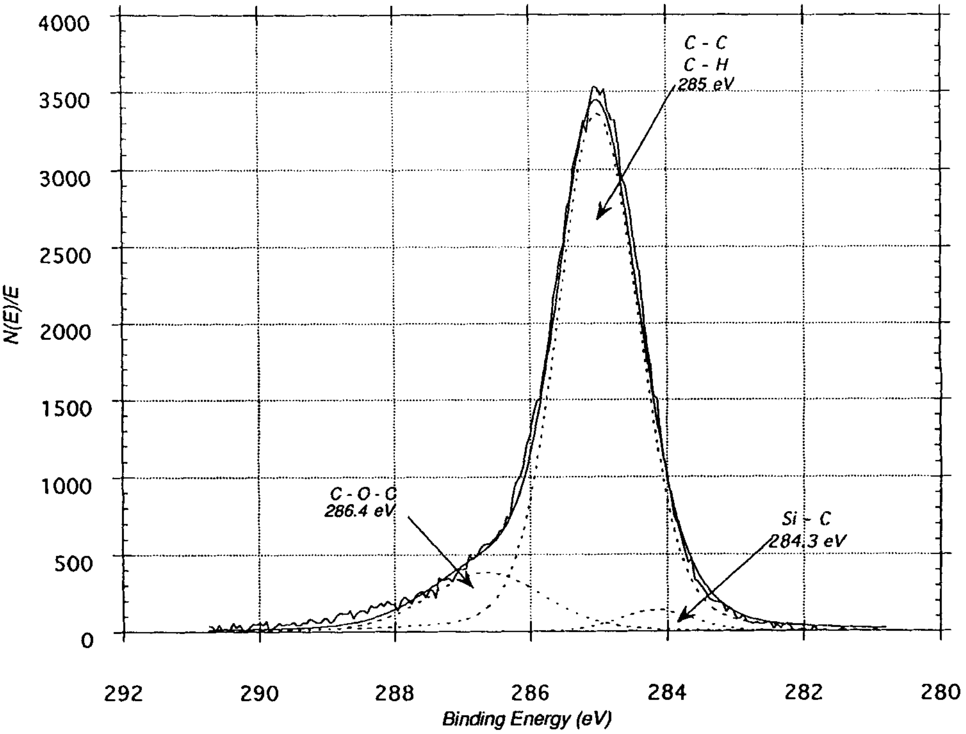


FIG. 7. High resolution ESCA spectrum of plasma-generated polyisobutylene.

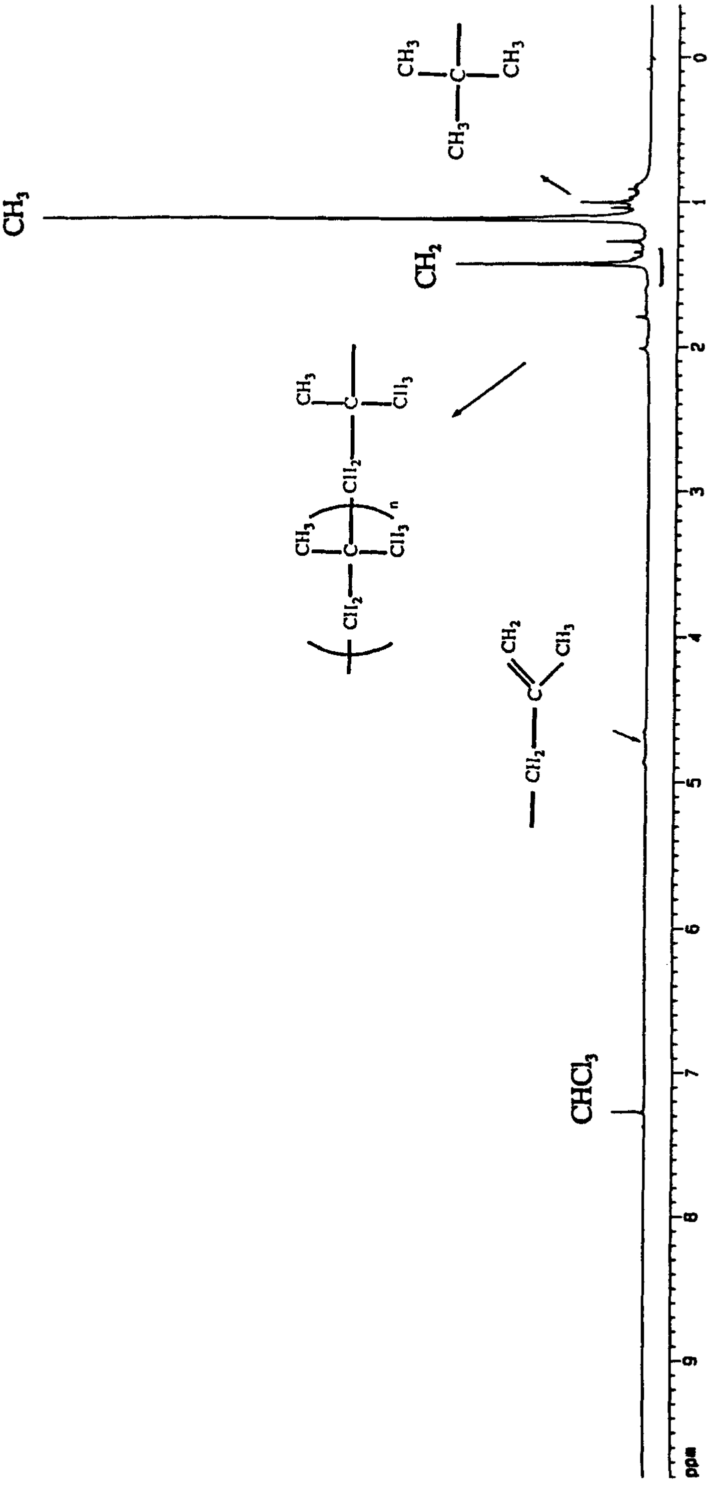


FIG. 8. ^{1}H-NMR spectrum of plasma-generated polyisobutylene.

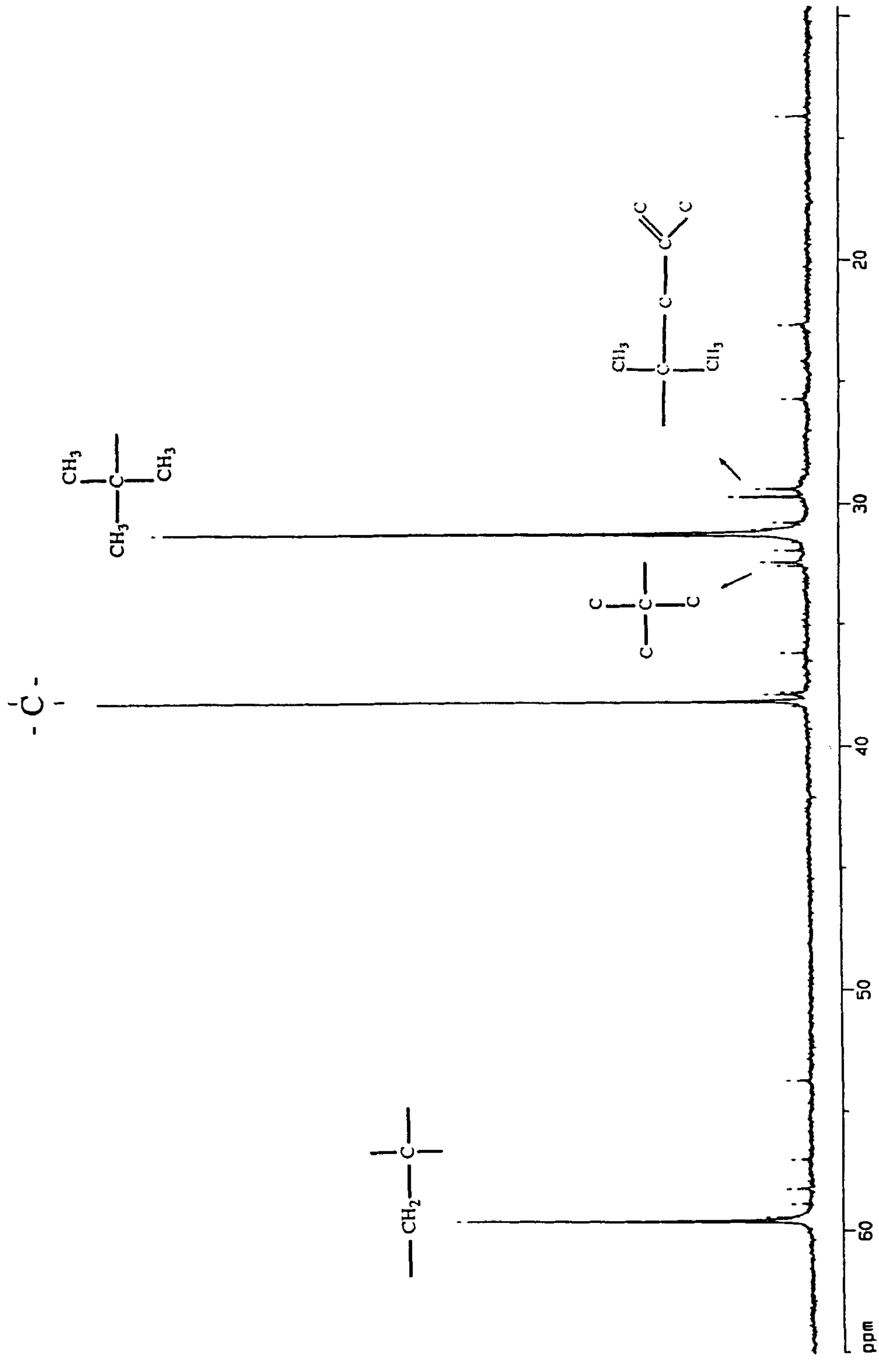
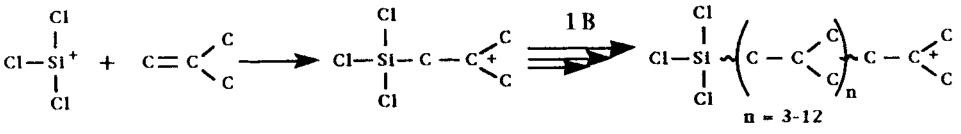


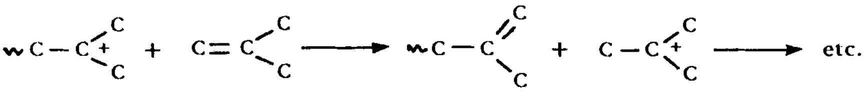
FIG. 9. ^{13}C-NMR spectrum of plasma-generated polyisobutylene.

primary (31.2 ppm), secondary (59.8 ppm), and quaternary (37.8 ppm) carbons. These data suggest that plasma-generated PIB is linear.

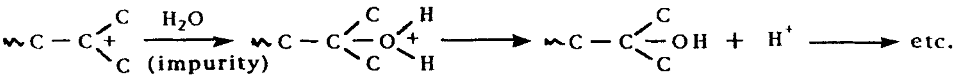
The following mechanism is suggested for possible initiation, propagation, chain transfer, and termination reactions:



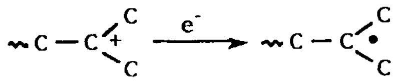
initiation propagation



chain transfer to monomer



chain transfer to moisture (impurity)



termination

A comparison of molecular fragments arising by in-situ HR-MS pyrolysis at 400°C of high molecular weight conventional and plasma-generated PIB indicate identical fragmentation patterns. The patterns in Fig. 10 exhibit the data. The almost identical ion-fragment distributions indicate similar structures. However, conventional PIB also yields small amounts of high molecular weight molecular-ion fragments which are absent in the MS spectrum of plasma-generated PIB.

To substantiate the conclusion that plasma-generated PIB is oligomeric, fast atom bombardment (FAB) and field ionization MS measurements were performed. FAB allows intact molecular ions to be desorbed from large and complex organic molecules under the impact of particles possessing kilovolt translation energies. The resulting molecular ions are quite abundant in the FAB spectra, and coherent fragmentation occurs to only a moderate extent. FI-MS yields almost fragmentation-less ionization in a very intense electric field. The ion source in this case consists of an anode with a sharp point and a cathode very close to the anode (1 mm). An impressed voltage (5–20 kV) creates an intense electric field which leads to electron

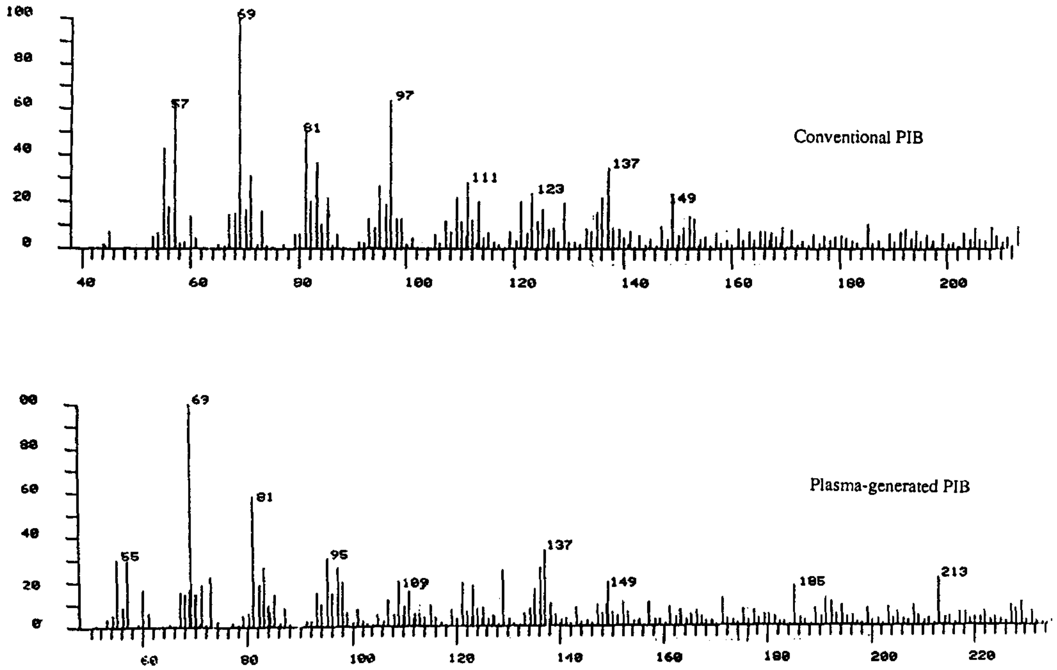


FIG. 10. High resolution MS-pyrolysis molecular-fragment ion-pattern of conventional and plasma-generated polyisobutylenes.

withdrawal and consequently to positive molecular ions. These techniques allow the evaluation of molecular weight distributions of polydisperse polymeric systems. Figures 11 and 12 show molecular ion distributions by FAB and FI-MS analysis. Both techniques showed relatively broad polydispersities with molecular weights mainly in the 200–700 *m/z* range. Plasma-generated PIBs are evidently low molecular weight oligomers of broad distribution.

Figures 13 and 14 show TG-DTA scans of conventional and plasma-generated IB. These data substantiate the MS findings that the latter PIB is of low molecular weight. While the thermal degradation of conventional PIB starts at ~350°C and occurs in a fairly narrow region (350–400°C), the TG-DTA scan of the plasma-generated PIB exhibits a much lower initial thermal decomposition temperature (around 250°C) and a much broader decomposition range (250–410°C).

Further investigations are required to establish the nature of structures arising from the attachment of Cl_xSi^+ ions to isobutylene during initiation.

CONCLUSIONS

- Si_2Cl_6-RF plasma produces active silylium ions (Cl_xSi^+) on low temperature surfaces.
- Silylium ions initiate the polymerization of IB, a monomer which can be polymerized only by a cationic mechanism.
- IB polymerization can be carried out by first adsorbing Si_2Cl_6-plasma-generated species on frozen (−195°C) IB surfaces and then gradually heating the dis-

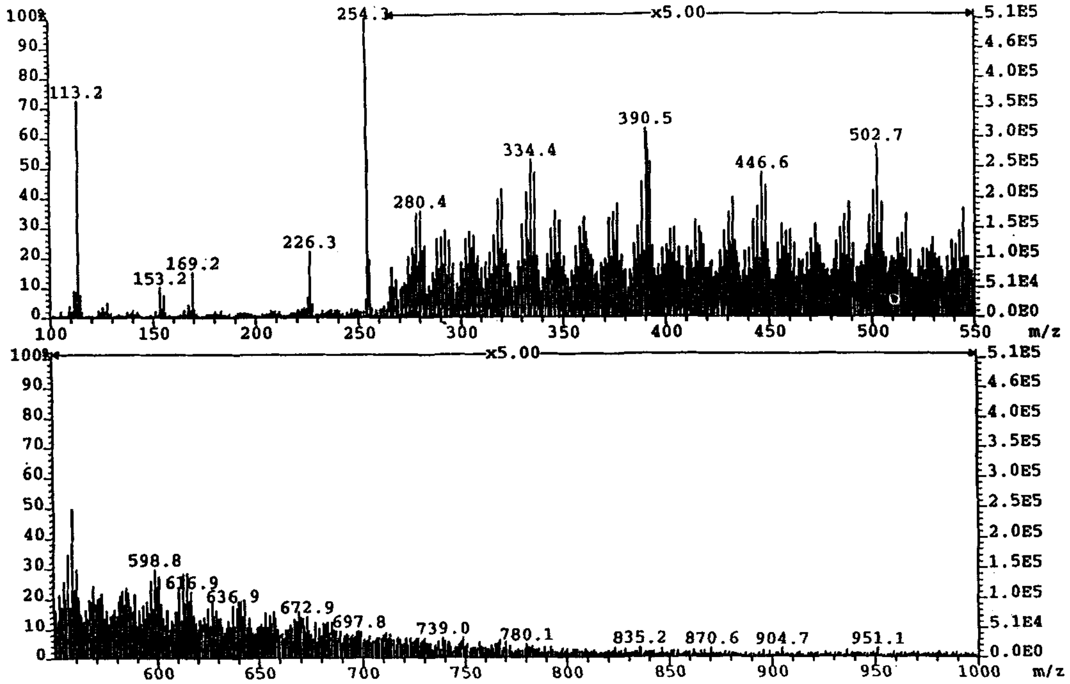


FIG. 11. Fast atom bombardment MS spectrum of plasma-generated polyisobutylene.

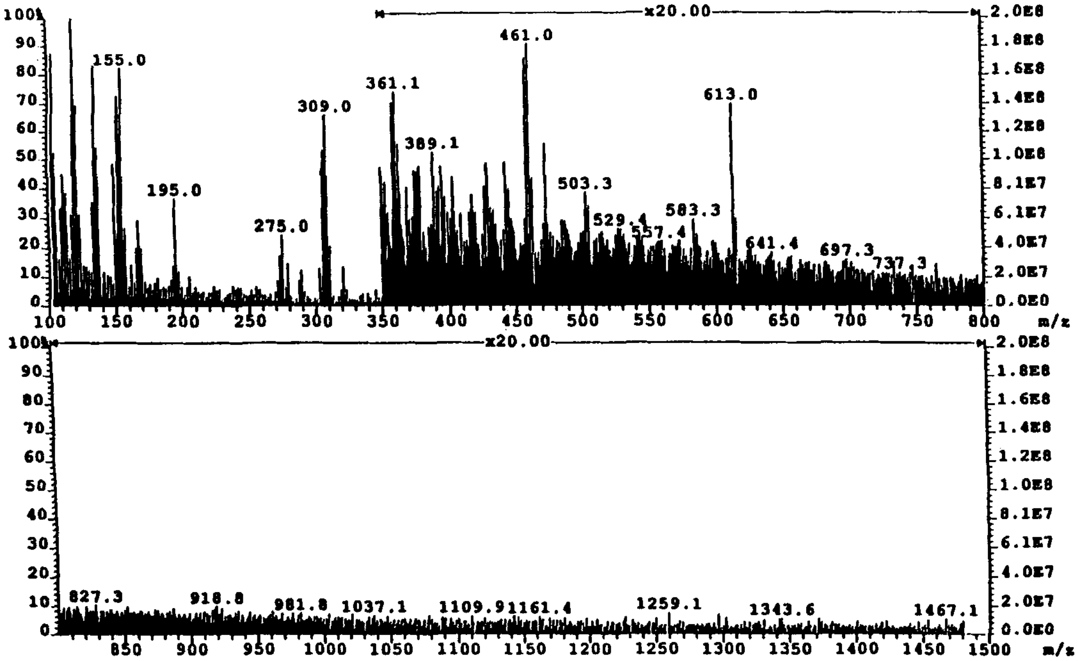


FIG. 12. Field ionization MS spectrum of plasma-generated polyisobutylene.

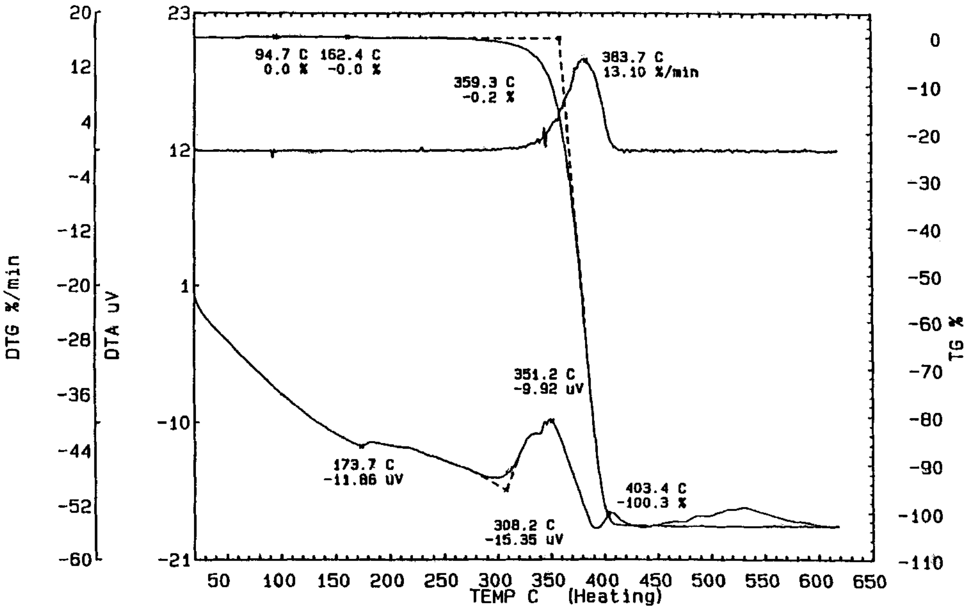


FIG. 13. TG-DTA scan of conventional high molecular weight polyisobutylene.

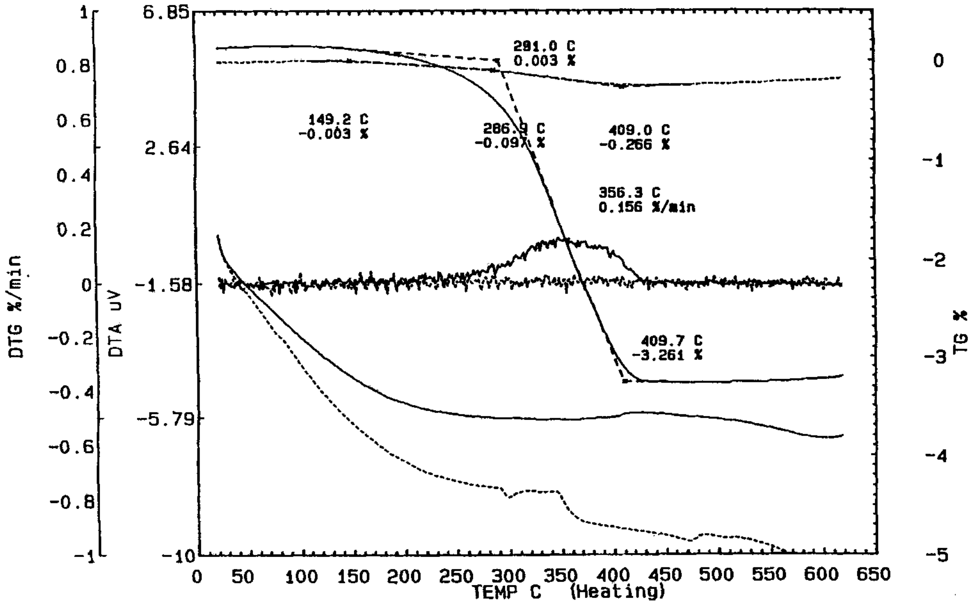


FIG. 14. TG-DTA scan of plasma-generated polyisobutylene.

charge-exposed monomer film under vacuum. The pressure change during heating is insignificant, which indicates the formation of low volatility oligomers.

- Silylium-ion-induced cationic polymerization of IB occurs in the absence of counterions and is mediated by high reactivity silicon-based cations. FT-IR and ESCA analyses of plasma-produced PIB indicate Si—C linkages in the macromolecule, which is regarded as strong evidence for initiation by Cl_xSi^+.
- High resolution MS pyrolysis, ^1H NMR, ^{13}C NMR, FAB, FI-MS, and TG-DTA analyses indicate that plasma-generated PIBs are linear oligomers of broad molecular weight distribution (m/z = 200–700); however, small fractions of higher molecular weight (m/z = 1000) products are also present. The low molecular weights are probably due to rapid deactivation (termination) of growing carbocations and not to frequent chain transfer.

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