

Highly Heat and Oxidation-Resistant Materials Prepared Using Silicon-Containing Thermosetting Polymers with [Si(H)~C≡C] Units

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Abstract: Highly heat and oxidation-resistant materials prepared using the silicon-containing thermosetting polymer, poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [-Si(Ph)(H)-C≡C-C₆H₄-C≡C-] are summarized. This polymer is light, moldable, soluble in solvent, and highly heat resistant. It is prepared by the dehydrogenative cross-coupling reaction of the Si-H bond of phenylsilane and the C-H bond of 1,3-diethynylbenzene in the presence of base catalysts. Applications of the polymer to particularly composite and ceramic materials are reviewed. Other polymers with molecules containing [Si(H)~C≡C] units are discussed. The chemistry and possible applications of the [Si(H)~C≡C] unit are also discussed.

Keywords: Silicon containing polymer, thermosetting polymer, heat-resistance, dehydrogenative coupling reaction, glassy carbon, composite material.

1. INTRODUCTION

Thermosetting resins such as phenol, epoxy, urea-melamine, and silicone resins have been developed and used for many applications. In this paper, new silicon-containing thermosetting polymers having molecules with [Si(H)~C≡C] units are reviewed. Preparations, properties, thermosetting mechanisms and applications of the thermosetting polymers are discussed.

Metals such as iron (specific gravity 8) and titanium (specific gravity 4.3) are highly heat resistant and tough, but heavy. Aluminum (specific gravity 2.7) is light but has heat resistance (ca. 300°C). Ceramics such as SiC, Si₃N₄, and silica glass (SiO₂) are lighter (specific gravities 2-3) than metals and highly heat resistant, but are not robust or moldable. Many light (specific gravities 1-1.5), moldable engineering plastics with good mechanical properties have been synthesized. Polyimide (Vespel from DuPont) has the highest heat resistance of all plastics with a heat-distortion temperature of 360°C. Several polymers have been developed, such as polybenzylimidazole, polybenzothiazole, and polybenzoxazole, which have a higher heat resistance than the polyimide [1,2], but they are flammable and not moldable.

Our objective is to prepare new materials that combine the best properties of both plastics and ceramics, that is, materials that are highly heat and combustion resistant as ceramics and moldable and light as plastics. We believe that an organic polymer that can be cross-linked like metals or ceramics would serve as such a material. The Si-H bond is very reactive to many chemical bonds such as C=C, C≡C, C=O, O-H, N-H, and C≡N, and the Si atom forms thermally

stable inorganic compounds such as SiC and SiO₂. Therefore, we postulated that a silicon-based organic polymer would be favorable for producing such a material by cross-linking. On the basis of this concept, we designed and prepared several polymers that contained a Si-H bond and another functional group in a molecule. As a result we found that poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene], [-Si(Ph)(H)-C≡C-C₆H₄-C≡C-] (abbreviated as MSP, Fig. 1), which is prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and 1,3-diethynylbenzene in the presence of base catalysts, has extremely high thermal stability [3-5].

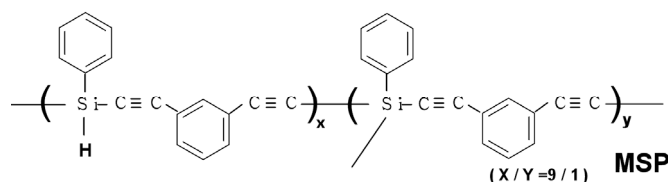


Fig. (1). Poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene].

MSP is a highly heat-resistant thermosetting polymer that has some branches and Si-H and C≡C bonds, as shown in Fig. (1). In recent years, many studies of silicon-containing polymers composed of [-SiR₂-C≡C-] (R = alkyl or phenyl) units have been reported because of their potential application in ceramic precursors and conducting materials. There are a few reported cases in the literature of a polymer containing the Si-H bond (R=H) in a molecule. Poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene], [-Si(Ph)(H)-C≡C-C₆H₄-C≡C-] [6]; poly[(phenylsilylene)diethynylene], [-Si(Ph)(H)-C≡C-C≡C-] [7], and poly[(methylsilylene)ethynylene], [-Si(CH₃)H-C≡C-] [8] have been used, but there is almost no information about the properties of the polymer, except that in our reports.

We successfully prepared MSP on a bench scale and investigated its properties. In addition, we proposed the intermolecular cross-linking reactions concerning the Si-H

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and C≡C bonds, which formed a thermally stable structure at high temperature. This paper reviews MSP's 1) preparation, 2) properties, 3) thermosetting mechanisms, and 4) its applications to structural materials. Moreover, other silicon-containing polymers having the Si-H and C≡C bonds as in MSP, which have been prepared, and the chemistry and the possibility of applications of [Si (H)-C≡C] unit are reviewed.

2. POLY[(PHENYLSILYLENE)ETHYNYLENE-1,3-PHENYLENEETHYNYLE] (MSP)

Preparation

Though some routes to prepare MSP had been considered, we adopted the dehydrogenative reaction route which includes no halogen, yields a more stable polymer, and is economical. MSP is prepared by the dehydrogenative cross-coupling reaction between the Si-H bond of phenylsilane and the C-H bond of m-diethynylbenzene in the presence of base catalysts such as metal oxides [9,10], metal hydrides [11,12], alkoxides [13], alkylmetals [13], and metalamides [13] of alkali metals or alkaline earth metals (Fig. 2). Barium alkoxide has the highest catalytic activity. However, at present, we think magnesia, which is a typical solid base catalyst [14], is the most advantageous in the industrial reaction process because the solid catalyst of magnesia is easily removed by filtration after the reaction and a highly pure polymer can be obtained. Less than 10 ppm of magnesia was found in MSP, and there is no problem storing the polymer for a long period in air. The reaction mechanisms of dehydrogenative cross-coupling using the base catalysts were proposed [13,15].

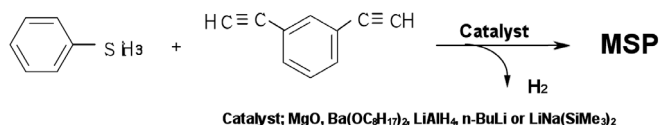


Fig. (2). Preparation of MSP in the presence of base catalysts.

We succeeded in preparing MSP on a bench scale using a

magnesia catalyst, although some problems are still to be solved. The preparation flow chart is shown in Fig. (3) [15]. Advantages of the process are 1) easy separation of the catalyst, and 2) yielding a pure and very stable polymer in air. The problem with the process is the need of a large amount of magnesia and a decrease in the polymer yield due to adsorption on the magnesia surface (about 20% of the produced polymer is adsorbed on the magnesia surface). The improvement of reaction conditions and recycling of the catalyst must be studied.

Other preparation routes, adaptable to MSP synthesis, such as Grignard addition reactions using chlorosilanes [4, 15, 16] and dehydrogenative cross-coupling reaction between phenylsilane and m-diethynylbenzene in the presence of some transition metal complexes [5, 6,17-22], were also examined. Other routes were not industrially viable and could not yield pure and stable polymers. A similar polymer has been obtained by a dehydrogenative coupling polymerization reaction between phenylsilane and 1,3-diethynylbenzene by using CuCl/amine as a catalyst. In that case, the polymer had a wider molecular weight distribution, and the Si-H bond was easily hydrolyzed in the presence of moisture to form a siloxane bond in air when the polymer was contaminated with the amine of the catalyst ($2 \text{ Si-H} + \text{H}_2\text{O} \rightarrow \text{Si-O-Si} + 2\text{H}_2$) [6].

Subsequently, Baba et al. and Takaki et al. reported that KNH₂ loaded on Al₂O₃, which is a solid base, and Y-imine complex showed catalytic activity for the dehydrogenative coupling between Si-H and H-C≡C bonds, respectively [23,24].

Properties

MSP with a molecular weight (M_w) above 2000 was a pale yellow amorphous solid, and MSP with M_w below 2000 was a viscous yellow liquid ((a),(b) in Fig. 4). The solid polymer was highly soluble in benzene, toluene, tetrahydrofuran (THF), and N-methylpyrrolidone (NMP). The glass transition temperature (T_g , determined by

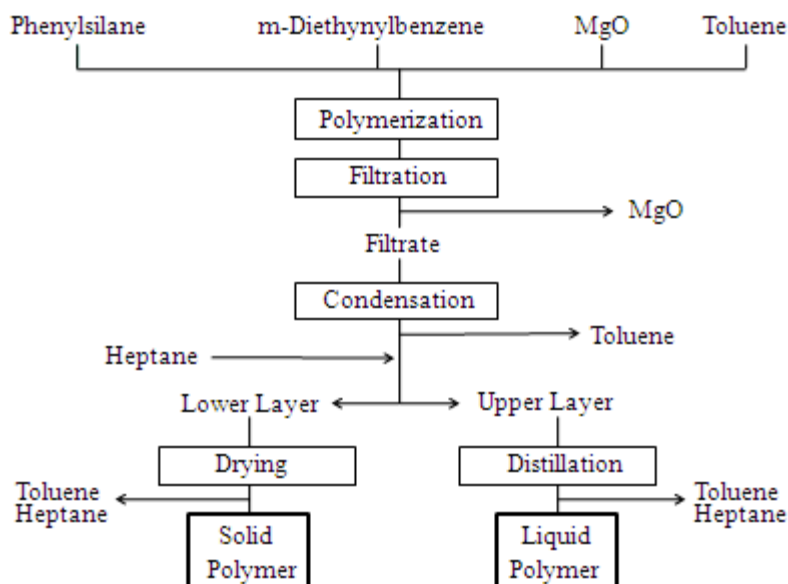


Fig. (3). Preparation flow chart of MSP in bench test.

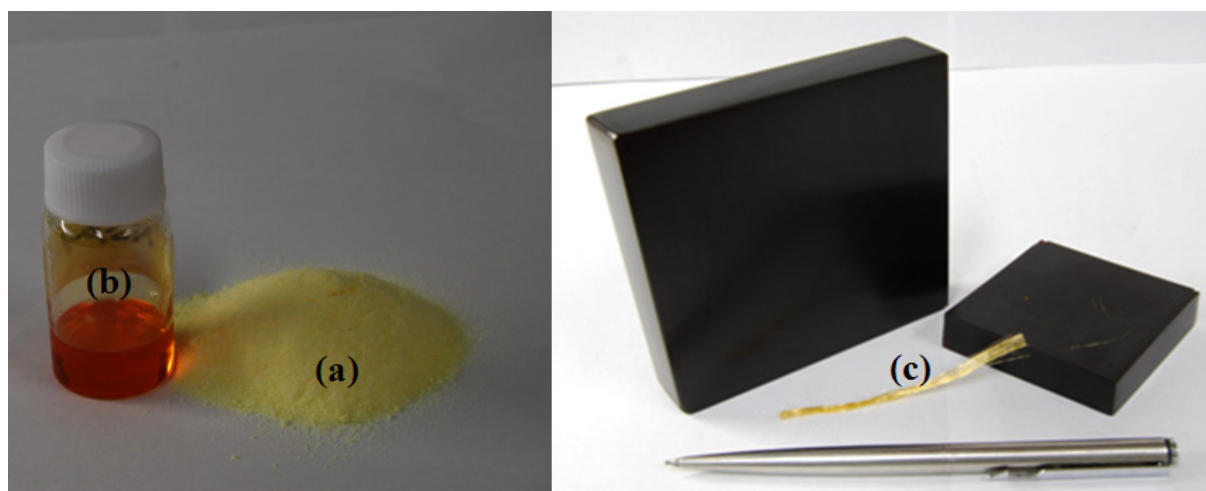


Fig. (4). (a) solid MSP, (b) liquid MSP, and (c) molding products of MSP.

differential scanning calorimetry, (DSC)) of the polymer ($M_w=5000$ to 6000) was about 50°C . The polymer was fusible and moldable, and it was possible to melt-spin the polymer at $100\text{--}150^\circ\text{C}$ (Fig. 4(c)). The polymers are also stable for long periods in air. The polymer gradually changed black and cured above 200°C (curing temperature was $150\text{--}210^\circ\text{C}$). The melt viscoelasticity and a complex elastic modulus spectrometer (Rheometrix Inc. RDS-II $^\circ\text{C}$) are shown in Fig. (5).

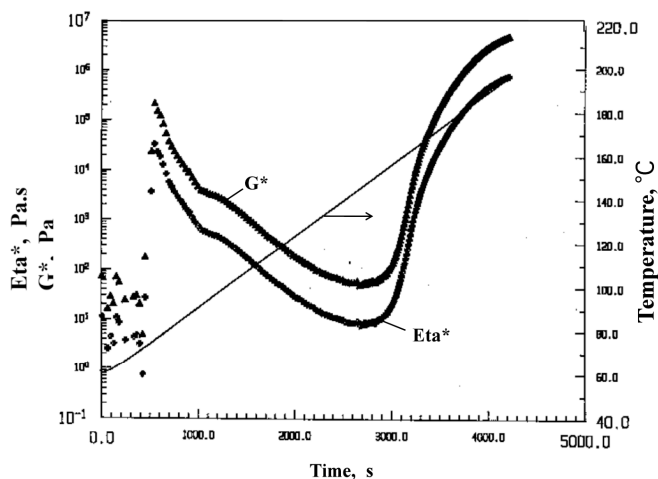


Fig. (5). Melt viscoelasticity (Eta^*) and complex elastic modulus (G^*) of MSP.

From thermogravimetric analysis (TGA), we detected very little weight loss during thermal cracking under argon. The T_{d5} (temperature of 5% weight loss) is 860°C and the residue at 1000°C is 94%. These values are much higher than those of polyimide (Kapton; DuPont, T_{d5} is 586°C and the residue at 1000°C is 55%). An exothermic peak at 210°C is observed by DSC. This could be caused by intermolecular cross-linking reactions (curing reactions) between the Si-H and $\text{C}\equiv\text{C}$ bonds, which are addition reactions and produce no by-product as described later [25]. No change in size of the molded test piece is observed up to 500°C . MSP is an insulator similar to other plastics and hard and fragile similar to glass.

The T_{d5} (567°C) of MSP under air is nearly equal to that of Kapton (polyimide). The limiting oxygen indices (LOI: minimum oxygen concentration for the polymer to continue combustion) of MSP cured at 400°C and 500°C are 40-42 and 54, respectively (LOI of Vespel (polyimide) is 53). MSP is noncombustible in air. In a flame produced by a gas burner, the molded MSP test piece turns red but does not burn and has no smoke. When the flame is removed, the test piece recovers its original black surface [26].

MSP has an extremely high ceramics yield (94%, Kapton 55% and phenol resin ca.50%), as shown above. As the content of hydrogen in MSP is 4.4%, so the yield is almost a theoretical one. The specific gravity is 1.14, constant in the range of 150°C to 500°C , and the value gradually increases to above 500°C . The value at 1000°C is about 1.5, which is nearly equal to that of glassy carbon prepared from an organic compound such as phenol resin. The materials obtained by 1000°C or 2000°C for several hours under argon are glassy and hard. A molded block of MSP pretreated at 400°C contracts by about 10% in every dimension when heated at 1000°C and 2000°C for several hours. It is confirmed that the material is composed of carbon with silicon carbide particles (SiC 17-18%) from X-ray diffraction patterns, and Raman spectra suggest that the material is difficult to change into a crystal graphite [26,27].

The heat distortion temperature is above 470°C (Vespel 360°C) and demonstrates high radiation resistance. The thermal, combustible, dynamic, and electric properties of MSP are summarized in Table 1.

Thermosetting Mechanism Study

T_{d5} values of some polymers under argon and air are shown in Table 2. T_{d5} of MSP under argon is much higher than those of poly[(diphenylsilylene)ethynylene-1,3-phenyleneethynylene] ($T_{d5} = 547^\circ\text{C}$) [3], which has no Si-H bond, poly(methylsilylene)ethynylene-1,4-phenylene] ($T_{d5} = 320^\circ\text{C}$) [28], and poly(silylene-1,3-phenylene) ($T_{d5} = 295^\circ\text{C}$) [29], which has no $\text{C}\equiv\text{C}$ bonds. MSP had an exothermic peak at 210°C in the DTA curve. The infrared adsorption bands characteristic of the Si-H and $\text{C}\equiv\text{C}$ bonds of MSP were reduced to half the initial absorption band

Table 1. Properties of MSP

Soluble in THF, Toluene, Benzene	
Moldable	100-150°C
Temperature of 5% weight loss (Td ₅)	860°C(in argon) 567°C(in air)
Heat distortion temperature (HDT)	> 470°C
Oxygen index	40-42 ^a 54 ^b
Bending modulus ^a	5.5GPa
Bending strength ^a	10MPa
Density	1.14 (Curing temp. 150~400°C)
Coefficient of linear thermal expansion ^a	2 x 10 ⁻³ /°C
Thermal conductivity ^a	0.2-0.4 W/Mk
Volume specific resistance ^a	3 x 10 ¹⁶ Ωcm
Specific dielectric constant ^a	3.77
Gel time	8min/180°C 3.5min/200°C 1min/220°C

^aSample were heated for 2 h under argon at a) 400°C or b) 500°C.

when the polymer was treated at 240°C for 4h [3]. Moreover, here was no weight loss and gases were not detected under 500°C. These facts suggest an additional cross-linking reaction involving the Si-H and C≡C bonds that may have occurred to form a highly thermally stable structure.

Based on the results of ¹³C and ²⁹Si solid-state NMR methods and computational chemistry, we concluded that the intermolecular cross-linking reactions of MSP due to 1) the Diels-Alder reaction between Ph-C≡C and C≡C and 2) the hydrosilylation reaction between Si-H and C≡C took place proceed at 150-200°C, and a very highly thermally stable structure formed. Above 300°C, only the hydrosilylation reaction occurs and the intermolecular cross-linking proceeds further (see Fig. 6) [25].

Applications of MSP

Functional materials using MSP, have been studied. In this review, (1) composite materials, (2) ceramic materials, and (3) other materials are described.

(1) Composite Materials

Many types of polyimides have been developed as the matrix resin for fiber-reinforced plastics (FRPs), and they are generally soluble only in a polar solvent of high boiling point

such as NMP or dimethyl sulfoxide. In the case of the condensation-type polyimides, the polyamic acids are used as precursors for molding, and they are cured for a long time at high temperatures (usually 300-400°C) accompanied by the generation of water. Therefore, it takes a long time to produce FRPs. As mentioned above, MSP is highly heat resistant, non-flammable, and has a reactive Si-H bond that would be able to bond with many reinforcing materials. Moreover, MSP is moldable, soluble in many solvents of low boiling point, and can be cured at low temperatures with no generation of by-products. When we use an oily oligomer, no solvent is needed in preparing the reinforced material. These characteristics of MSP are more advantageous for preparing reinforced materials than those of polyimides.

The FRPs using MSP as the matrix resin, and carbon fiber, silicon carbide fiber or glass fiber as the reinforcement. The thermal and mechanical properties, dynamic viscoelasticity, and irradiation resistance were examined [30,31]. Prepregs were prepared by a molding or impregnation method, and were pressed for 12h at 150°C at a pressure of 9.8×10⁵ Pa to produce a FRP. There was little difficulty in fabricating the FRP laminates with the MSP resin (Fig. 7).

The fiber material was well impregnated with MSP, but some bubbles and cracks were observed in the resin layer. The bubbles could be removed by a resin transfer method (RTM) or autoclave method in mass-production. Further studies concerning the interface and adhesion between the fiber and MSP are needed to determine the optimum condition for the fabrication. The FRP was non-combustible in air. In the flame of a gas burner, the FRP turned red but did not burn or produce smoke (Fig. 8) as in the case of the molded sample of MSP [26].

The short term heat-resistant characteristics were evaluated by the bending strength and modulus at high temperature. Bending strengths and modulus of carbon, SiC or glass fiber reinforced MSP at room temperature, 200°C, and 400°C were almost equal, which suggests that the FRP prepared using MSP as a matrix resin could be used even at 400°C. The low bending strength could be improved by further studying the mechanical properties at high temperatures and by optimizing the preparation method of FRP. An FRP (Yokohama Rubber Co., Ltd.), which was prepared using polyimide resin (PMR-15); developed by NASA-Lewis Research Center [32] and a silicon carbide compact is shown on the graph below 300°C. Dynamic viscoelasticity and creep properties of MSP composite were

Table 2. Temperature of 5 % Weight Loss (Td₅) of Some Polymers Under Argon and Air

Polymer	Td ₅ (°C)	
	Under Argon	Under Air
poly[(phenylsilylene)etynylene-1,3-phenyleneethynylene] -Si(Ph)H-C≡C-C ₆ H ₄ -C≡C- (MSP)	860	567
poly[(diphenylsilylene)etynylene-1,3-phenyleneethynylene] -Si(Ph) ₂ -C≡C-C ₆ H ₄ -C≡C-	547	526
poly[(methylsilylene)-1,4-phenylene] -Si(CH ₃)H-C ₆ H ₄ -	320	551
poly(silylene-1,3-phenylene) -SiH ₂ -C ₆ H ₄ -	295	502
polyimide (Kapton; DuPoint)	567	565

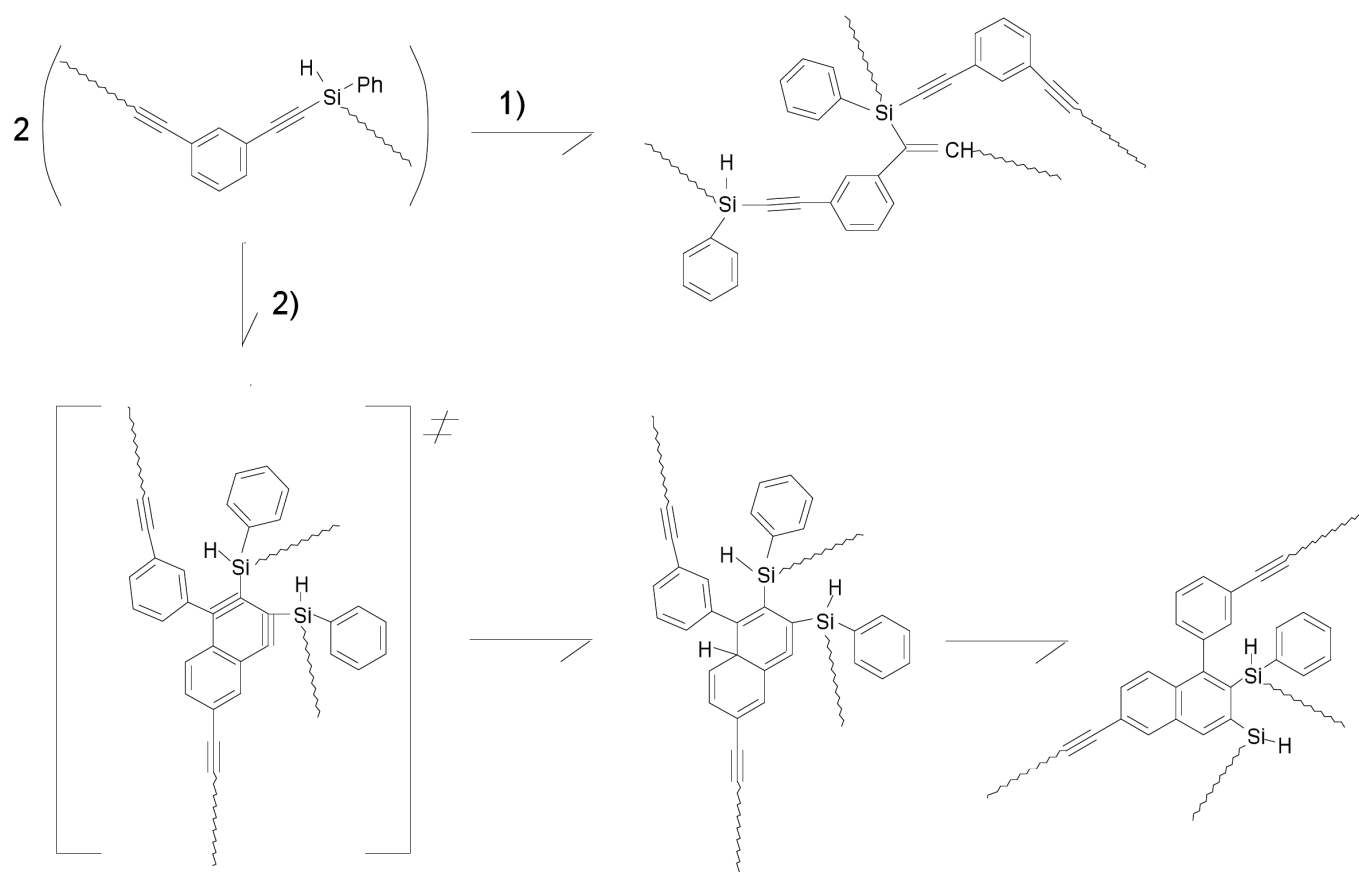


Fig. (6). Thermosetting mechanism of MSP based on solid-state NMR results: 1) the hydrosilylation reaction mechanism and 2) the Diels-Alder reaction mechanism.

determined and compared with those of a polyimide composite [30].



Fig. (7). Fiber-reinforced plastics (FRP) using MSP as a matrix resin.

The bending strength and modulus of SiC fiber reinforced MSP cured at 400°C did not change with 100 MGy of irradiation (see Fig. 10). The bending strength and

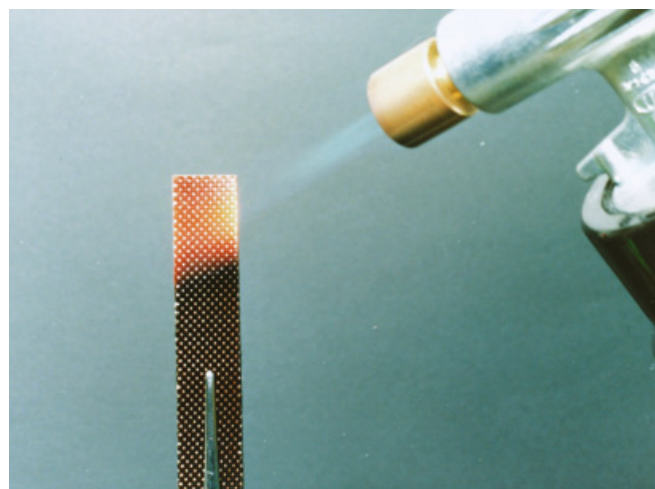


Fig. (8). Combustion test of the CFRP (MSP).

modulus cured at 200°C decreased by irradiation, which could be caused by the continued curing of the sample. The total amount of the irradiation is estimated to be 0.5 MGy in a light water reactor, and 50-100 MGy in fast breeder and nuclear fusion reactors. It is known that mechanical characteristics decrease under irradiation in many engineering plastics, such as polyimide materials [33]. It is clear that the highly cured SiC fiber reinforced MSP has higher radiation resistance than the FRPs used for many other engineering plastics. Cured MSP is surrounded by

electrons of the C=C and C=C bonds produced by a curing reaction and the phenyl group, and electrons of the silicon atom. The SiC fiber reinforced using MSP could show a high radiation resistance due to the shielding effects of these electrons.

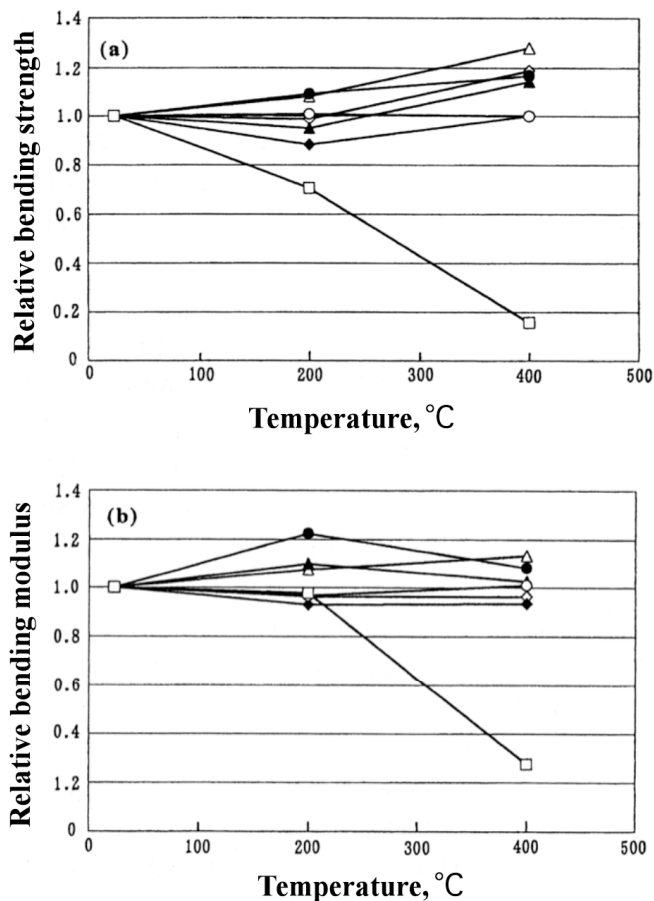


Fig. (9). Changes in the bending strength (a) and modulus (b) with the measuring temperature. FRPs were cured at 400°C (opened marks) or 600°C (closed marks). (Δ); MSP/carbon fiber, (\circ); MSP/SiC fiber, (\diamond); MSP/glass fiber (\square); PMR-15/SiC fiber.

Aerospace Plane Construction (Ablation Material) [34]

Thermal performance and ablation characteristics of a novel carbon composite with MSP polymer (CF/MSP) charred at 750°C were investigated under supersonic plasma air stream at an arc jet facility. An arc jet facility is used to simulate the aerodynamic heating conditions experienced by spacecraft during atmospheric re-entry. A conventional fiber phenolic composite (CF/PR) was tested under similar conditions for direct comparison. The mass loss of the CF/MSP composite was far less than that of the CF/PR composite. On the other hand, higher internal temperature was measured in the CF/MSP composite. Flexural strength of the CF/MSP composite after decomposition was considerably higher than that of the CF/PR composite. Therefore, it is thought that the CF/MSP composites are applied for full-charred heat shield system of a re-entry capsule, and a full-charred nozzle exit cone of a solid propellant rocket motor (Figs. 11,12 and Table 3).

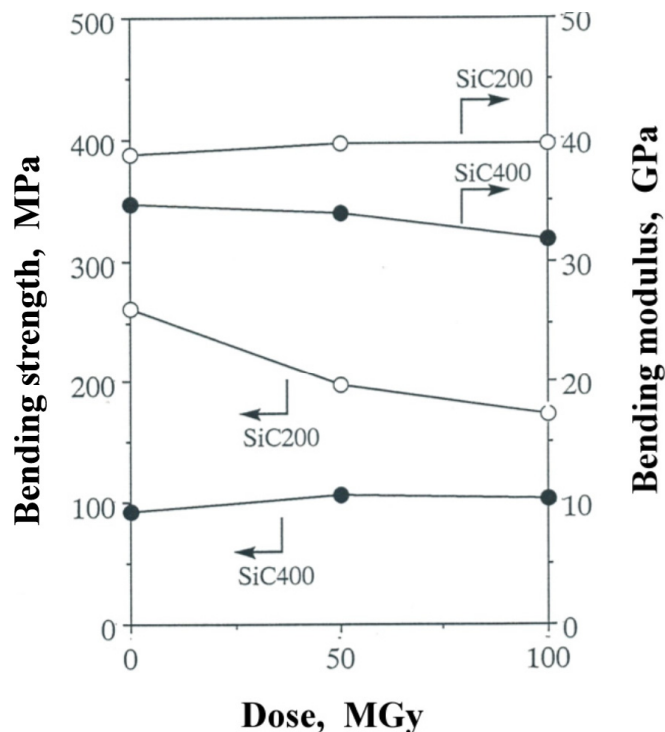


Fig. (10). Radiation property of FRP (MSP-SiC fiber). SiC200 : cured at 200°C Electron beam : 2MeV, 6Ma, 6kGy/sec.

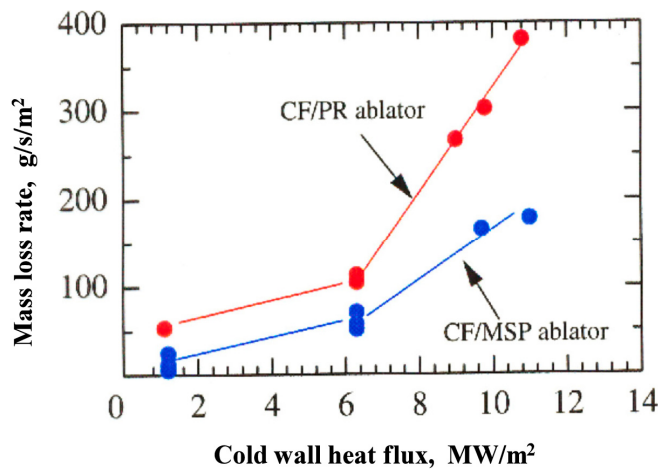


Fig. (11). Mean mass loss rate during arc jet testing of the CF/MSP and CF/PR composites (exposure time 30s).

(2) Ceramic Materials

Glassy Carbon [26,27]

MSP has an extremely high ceramics yield (94%) as shown above. The specific gravity gradually increased to above 500°C and up to the value of 1000°C. It was about 1.5, which is nearly equal to that of glassy carbon prepared from an organic compound such as phenol resin. The chemical bonds of MSP gradually changed to an inorganic compound above 500°C. The materials obtained by heating MSP at 1000°C or 2000°C under argon are glassy and hard substances. A block of MSP pretreated at 400°C contracted

by ~10% in every dimension when heated at 1000°C and 2000°C. From the X-ray diffraction patterns and Raman spectra, the material was composed of carbon and silicon carbide (17-18% SiC) ((a) in Fig. 13). In the Raman spectrum, a strong absorption band 1360cm^{-1} , which is assigned to the non-crystalline part of graphite, was observed in addition to that at 1580cm^{-1} assigned to the crystalline graphite [35,36]. The values of the intensity ratio I_{1360}/I_{1580} , which indicates the ratio between the non crystalline parts, are 2.3 (1000°C) and 1.4 (2000°C), respectively. These values are larger than those of graphites prepared from an organic compound such as phenol resin ($I_{1360}/I_{1580} = 0.2$ to 1.5, see Fig. 14). A material of a peculiar structure, which is difficult to change into a crystalline graphite, is formed from MSP. Moreover, a highly pure ceramic (C-SiC) was prepared from the pure MSP. Many fine and functional C-SiC materials, e.g., fibers, films, have been synthesized [26,27].

Table 3. The Combustion Test of the Nozzle Components of a Rocket Motor

Material	Nozzle Throat		Erosion (mm)	Erosion (mm/s)
	Diameter (mm)			
	Before	After		
CF/MSP	14.95	25.44	10.49	0.405
CF/PR	14.93	26.45	11.52	0.457



Fig. (12). Nozzle components of rocket motor.

Above amorphous carbon obtained by pyrolyzing MSP showed higher oxidation-resistance than commercial amorphous carbon (GC-10) obtained by pyrolyzing phenol resin. The carbon-silicon- B_2O_3 hybrids (B_2O_3 8%) obtained by pyrolyzing the molding sample of MSP/ B_2O_3 at 1000°C showed much higher oxidation-resistance than the carbon derived from MSP (Fig. 15).

By using high solubility of MSP, the hybrids of MSP with various metal oxides (Si, Ti, Ta, Zr and Al) were prepared in THF solvent by a Sol-Gel method. The resin with alkoxide was gelled after casting the solution and drying it slowly. After the pyrolysis of the gel sheet at 1000°C, the

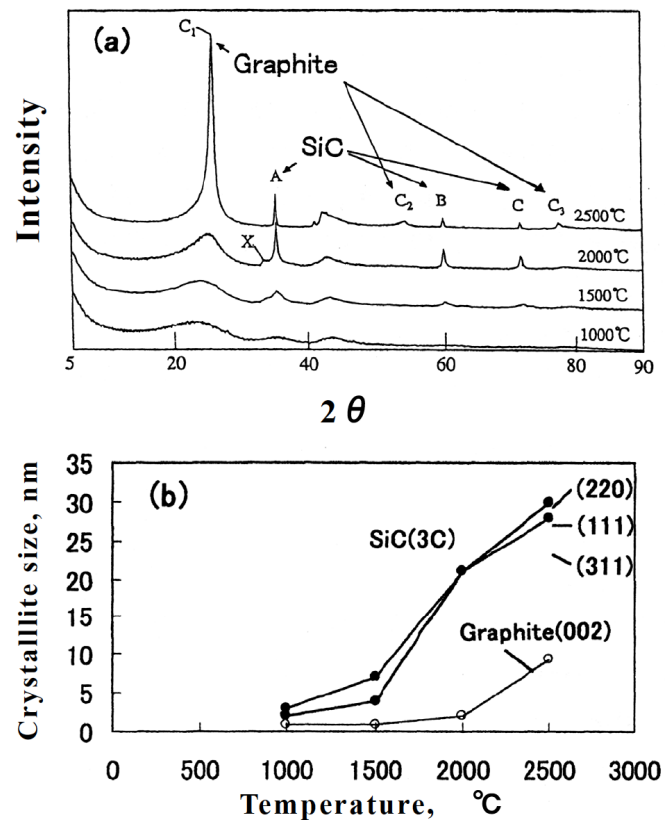


Fig. (13). X-ray diffraction patterns (a) and crystallite size (b) of the materials obtained by heating MSP at high temperatures under argon.

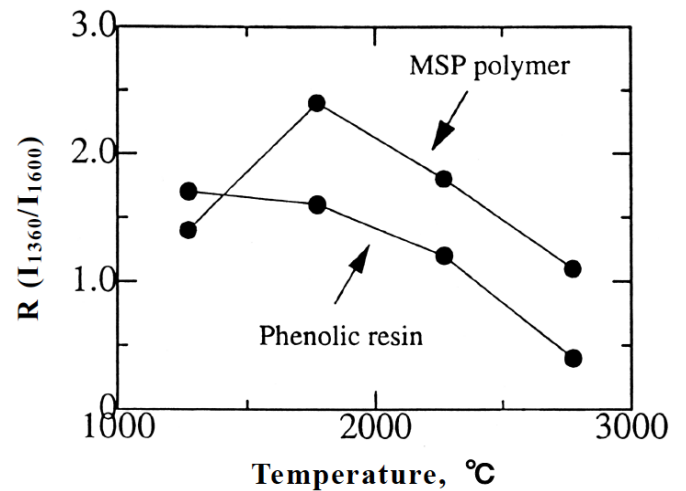


Fig. (14). The values of the intensity ratio I_{1360}/I_{1580} in the Raman spectra.

carbon base hybrid materials containing metal oxide-metal carbides were synthesized. Nano-structures were investigated by using the small angle X-ray scattering (SAXS) analysis. In addition, some of the starting resin-alkoxide mixture solutions were available to coat a transparent precursor layer on steel (SUS 316). These coating layers can be pyrolyzed without cracks up to 800°C. The corrosion resistance after pyrolysis was estimated by electrochemical measurements in terms of potentiodynamic polarization curves [37,38].

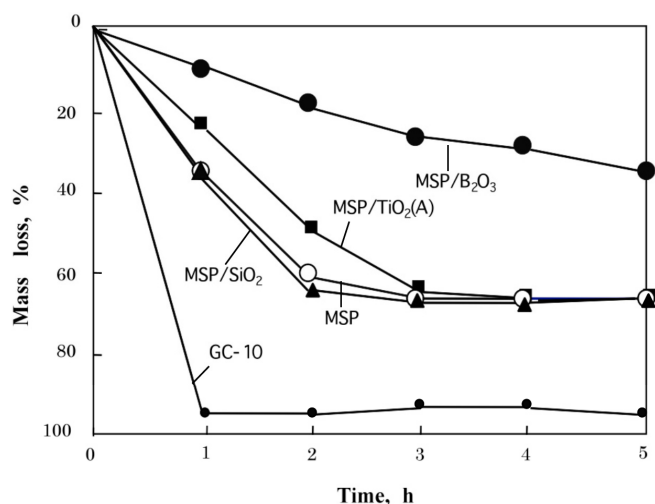


Fig. (15). The mass loss at 800°C in air of the pyrolysis products at 1000°C. The samples were prepared by a blending method.

Synthesis of Amorphous Carbon Fiber [39]

Synthesis of amorphous carbon fiber with atomic scale dispersed silicon obtained by melt-spinning and pyrolyzing MSP at 1000-1800°C was investigated. For the fiber curing, γ -ray irradiation previous to pyrolysis in an O₂ atmosphere was available.

(3) Other Materials

MSP has good compatibility with aromatic resins. Initiation temperatures of degradation and T_{d5} (temperature of 5% weight loss) of polystyrene increased by 50°C and 37°C, respectively, by adding 10% MSP to polystyrene.

3. VARIOUS SILICON-CONTAINING POLYMERS WITH [Si(H)~C≡C] UNIT

Nine new types of thermosetting polymers with the [Si(H)~C≡C] units were synthesized by dehydrogenative cross-coupling reactions between hydrosilanes and diethynyl compounds in the presence of a magnesia catalyst [40]. All the polymers were thermosetting, highly heat resistant, easily soluble in a solvent, and moldable. In particular, [-Si(R)(H)-C≡C-C₆H₄-C≡C-] (R=H or CH=CH₂) showed high thermal stability, the temperature of 5% weight loss was greater than 800°C, and the residue at 1000°C was over 90%. The thermal stabilities of the polymers were attributed to the cross-linking reaction of the Si-H and C≡C bonds (see Fig. 16).

Subsequently, Hayashi et al. reported some high heat-resistant polymers having the Si-H and C≡C bonds ((a) and (b) in Fig. 17) [41,42], (a) was prepared by the dehydrogenative cross-coupling reaction between poly(methylhydrosiloxane) and propargyl alcohol in the

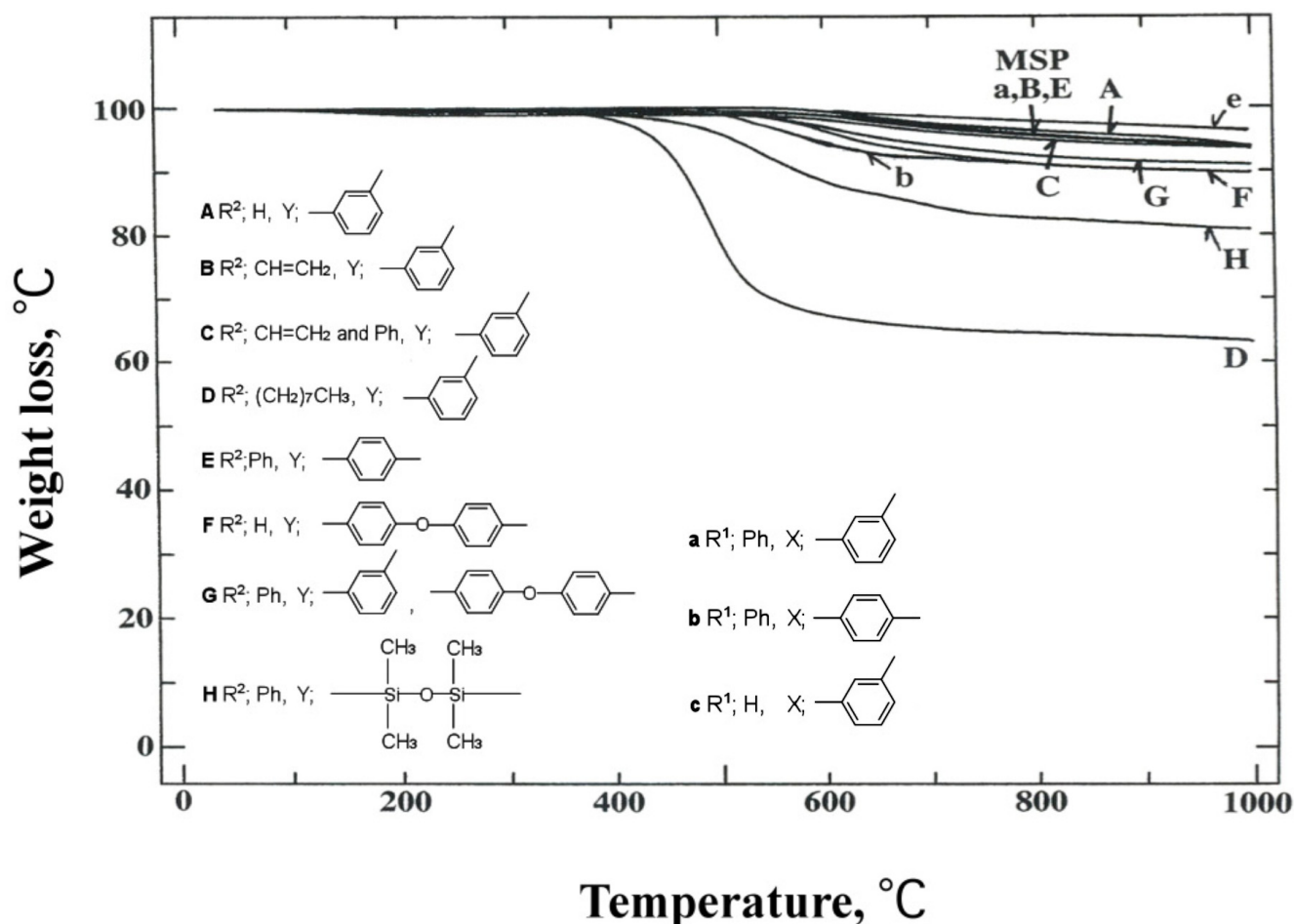


Fig. (16). TGA traces of polymers with [Si(H)~C≡C] unit. Polymer a,b,e : [-Si(R¹)(H)-C≡C-(X)-C≡C-]. Polymer A~H: [-Si(R²)(H)-C≡C-(Y)-C≡C-]_x[-Si(R²)(H)-C≡C-(X)-C≡C-]_y

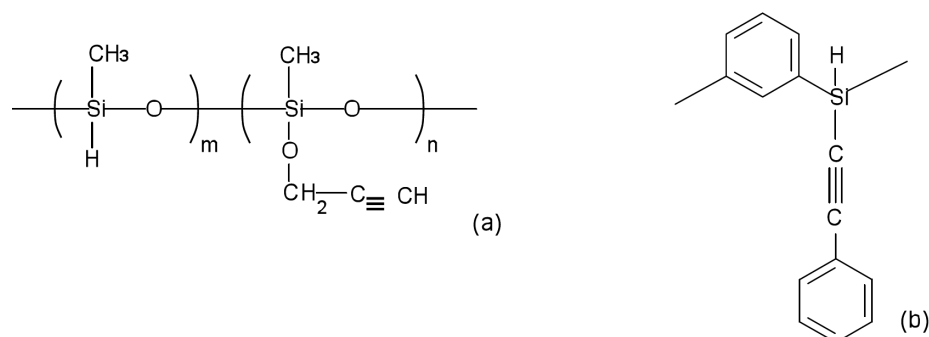


Fig. (17). High heat-resistant polymers having Si-H and C≡C bonds.

presence of $[\text{CuHPPH}_3]_6$. (a) having the ratio of Si-H to C≡C was 1/1 showed highest heat-stability.

Our study shows that Si-H and C≡C bonds are a useful couple to generate high heat resistance, which is caused by highly cross-linked structure. Many polymers could be designed and many polymers would be improved by introducing the two bonds into the polymers.

4. SUMMARY

- (1) We attempted to synthesize an organic polymer material, which can be highly cross-linked, poly [(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [-Si(Ph)(H)-C≡C-C₆H₄-C≡C-] (MSP). The small and reactive hydrogen and the C≡C bond in MSP forms a densely-packed cross-linked structure. Further study of the three-dimensional cross-linked structure is needed. Cured and cross-linked MSP has higher heat resistance and inflammability than other organic polymers, but is fragile as ceramics which is thoroughly crystallized.
- (2) The small amount of silicon in MSP (12%), especially Si-H bond, shows important rules in 1) dehydrogenative cross-coupling polymerization reaction, 2) cross-linking reaction, 3) heat, oxidation and irradiation-resistances, and 4) also shows difficulty in changing into a crystalline graphite when heated at elevated temperature.
- (3) The ceramics yield of MSP is 94%. As the content of hydrogen in MSP is 4.4%, MSP is an ideal ceramics precursor for C-SiC.
- (4) MSP has some excellent characteristics different from those of other polymer materials, and some applications have been considered. However, two monomers of phenylsilane and diethynylbenzene are needed for the preparation of MSP. The process to produce two monomers must be developed.
- (5) We have proposed that [Si(H)~C≡C] unit in macromolecules are useful for cross-linking and generation of heat resistance. The polymers having [Si(H)~C≡C] units and/or other units such as imide, amide and others could be synthesized.

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