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Diethynyl terminated siloxane bases (bisazomethine Schiff base)

Preparation and polymerization

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SUMMARY

Bis-4 ethynylbenziminopropyl-hexamethyldisiloxane was prepared and characterized. The flexible central unit of this product allows an easy and thorough polymerization of the ethynyl groups at a moderate temperature.

After thermal polymerization of the ethynyl groups, another reaction takes place upon curing, leading to a product presenting no detectable Tg.

This increase in crosslinking could be related to a diene synthesis involving both olefinic and imine double bonds.

INTRODUCTION

Most compounds containing both ethynyl and siloxane groups are described in the russian literature. Parnell and St Clair reported also on the subject (see reference in (1)).

Different scientists worked on the polymerization of trimethylsilylacetylene (2-4). A japanese team specialized itself in the polymerization of silyl-alkynes (5-12).

However, in all cases, these works were out of the scope of our study i.e. difunctionnal oligomers with a silicon atom not directly linked to the ethynyl group and thermal polymerization excluding all types of catalyst.

Reference 11 described the catalytic polymerization of 3-(trimethylsilyl)-1-octyn where the ethynyl group is not directly linked to a silicon atom. The results obtained in IR showed a weak absorption due to C=C stretching circa 1600 cm^{-1}. This observation was interesting as in most cases with aromatic structures, this band is hidden and cannot be detected.

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We recently prepared (1) a bis-ethynylbenzamide, the stability of which was limited, due to a thermal rearrangement at 250°C.

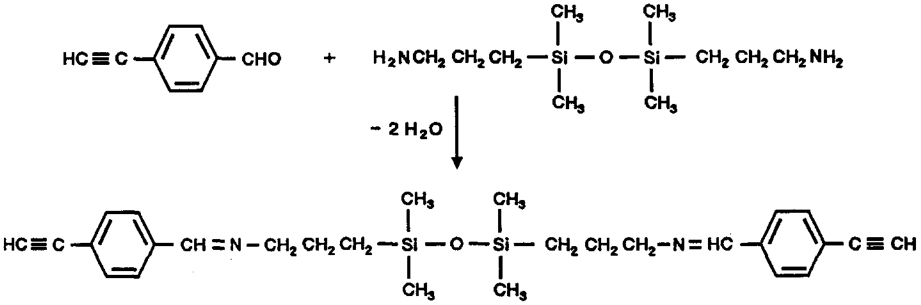
Starting from bis-γ-aminopropyltetramethyldisiloxane and 4-ethynyl benzaldehyde, we prepared the bis-ethynylazomethine and studied its thermal polymerization.

We combined by this procedure the advantages of a preformed acetylene group and easily accessible product (4-ethynylbenzaldehyde) with the flexibility of the siloxane linkage.

A paper dealing also with ethynyl Schiffs bases with a purely organic structure appeared recently (13).

RESULTS AND DISCUSSION

Bis-(γ-aminopropyl)-tetramethyldisiloxane was reacted with 4-ethynyl benzaldehyde according to the following scheme:



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The polymerization was followed by DSC (ΔH polymerization = 127 kJ/ ethynyl fonction) and by FTIR. The results are given on Figure 1. The results of both methods do not fit exactly. This could be an indication that different processes with different enthalpic effects take place during the thermal polymerization.

Assuming an Arrhenius dependance, the kinetic data lead to an activation energy of 79.7 kJ/mole.

DSC measurement performed at 10°C/min shows that the reaction takes place between 120 and 260°C with a maximum at 225°C.

The Tg of the final product was evaluated by thermomechanical analysis (TMA). According to the thermal cure treatment it increases from 260°C (100 min at 200°C) to 289°C (40 min at 200°C + 60 min at 250°C). It even disapears at a higher temperature cure (40 min. at 200°C + 60 min at 300°C) (Figure 2).

The thermal stability of the products after curing 1 hour at 140°C + 1 hour at 200°C was studied by TGA either in air or argon.

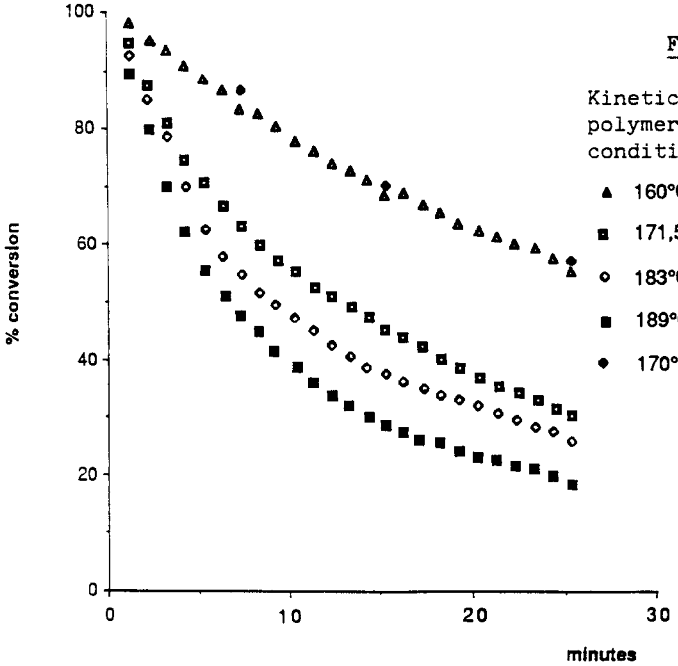

Figure 1

Kinetics of ethynyl group polymerization in isothermal conditions at:

▲ 160°C
◘ 171,5°C
○ 183°C
■ 189°C
◆ 170°C

followed by FTIR

followed by DSC

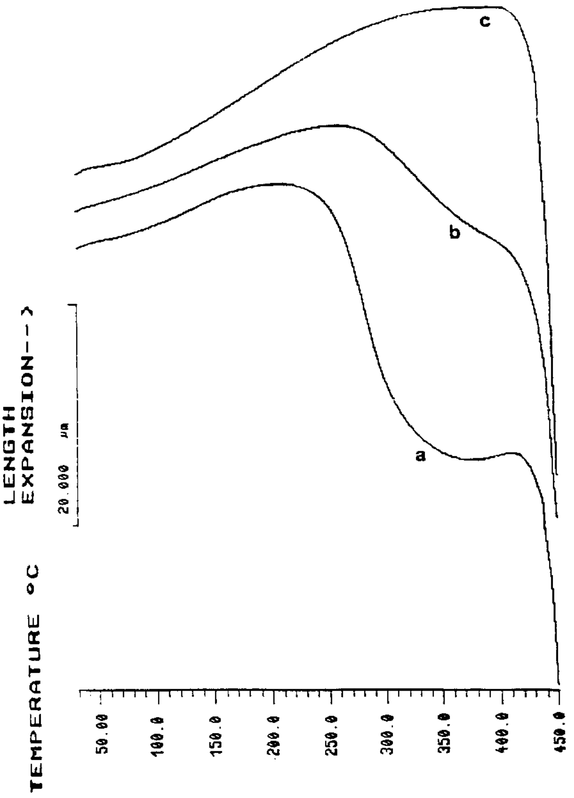

Figure 2

TMA analysis of resins after a cure cycle of:

a) 100 minutes at 200°C

b) 40 minutes at 200°C
+ 60 minutes at 250°C

c) 40 minutes at 200°C
+ 60 minutes at 300°C

Dynamic TGA carried out at 5°C/min heating rate shows an important weight loss at 400°C (Figure 3) as already observed in DSC.

Isothermal measurements were carried out at 300°C. The behaviour is the same in air or argon: 1% weight loss after 5.5 hours, 2% after 15 hours.

In both cases, the products exhibited a small nitrile band. However IR (Figure 4) shows that the structure of the product was partly changed. The intensity of the imine group decreases and -in the experiment carried out in air- a moderate oxydation takes place. The observed weight loss does not by far corresponds to this important structure change.

This very likely means that another process takes place. It could be a diene synthesis involving the conjugated olefinic double bonds created by the polymerization of the ethynyl groups and the imine double bond. The occurrence of such a reaction is reported in (14). It would explain the gradual disappearance of Tg observed by TMA (Figure 2) upon curing at 250°C and 300°C. It could also be at the origin of the discrepancy between the disappearance of the C CH observed by FTIR and the reaction course followed by DSC.

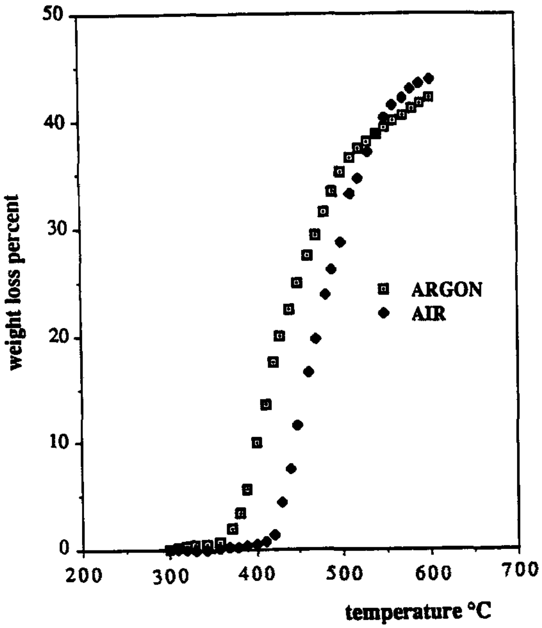

Figure 3

Dynamic TGA. Temperature increase speed:
5°C/minute weight loss percent vs temperature

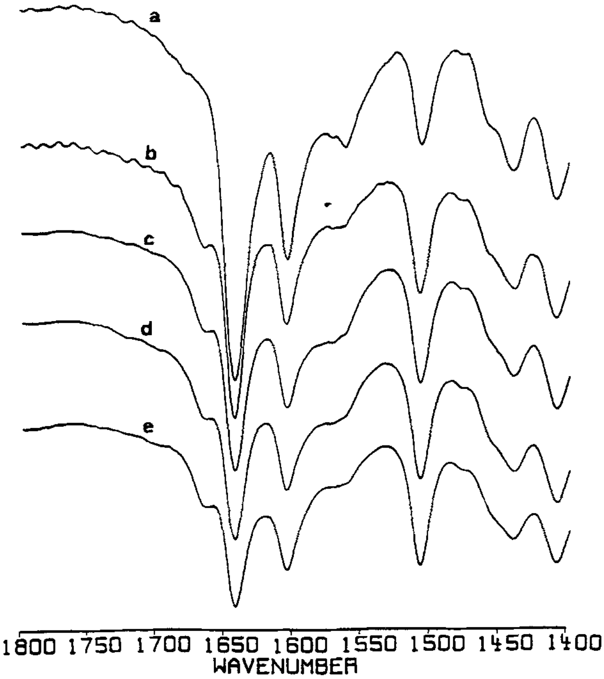

Figure 4

IR spectra of the polymerized resin and after different heating treatments at 300°C in argon

a) Polymerized resin
b) 1 h at 300°C
c) 2 h at 300°C
d) 7.5 h at 300°C
e) 10 h at 300°C

EXPERIMENTAL PART

4-[(trimethylsilyl)ethynyl] benzaldehyde

37.38 g (0.2 mol) 4-bromobenzaldehyde was dissolved in 130 ml anhydrous triethylamine. Argon was then flushed through during 30 minutes. A catalytic mixture containing 0.224 g (0.319 mmol), palladium (II) dichloro-bis-(triphenylphosphine), 0.4 g (1.52 mmol) triphenylphosphine, 0.074 g (0.38 mmol) copper (I) iodide was added and the temperature raised to 65°C. 25 g (0.25 mol) of ethynyl-trimethylsilane was introduced. Heating at 65°C under stirring was continued for 3.5 hours.

Upon cooling, triethylamine hydrobromide was filtered off. The solvent was distilled at room temperature under reduced pressure until precipitation occurred.

The solid residue was washed several time with water and dried at 50°C in vacuo.

26.4 g (65%) of a slightly coloured product mp 72°C, IR (KBr) cm^{-1} 2140, (-C≡C-), 1690 (C=O).

NMR ($CDCl_3$, CH_2Cl_2) δ (ppm) 9.9, (s, 1 H, $>\!\!-$CHO), 7.75 and 7.5 (4H, aromatic), 0.2 (s, 9 H, $(CH_3)_3Si$).

4-ethynylbenzaldehyde

The above product (22.5 g, 0.11 mol) was mixed with 1.42 g (10 mmol) of anhydrous potassium carbonate in 100 ml of methanol in argon at room temperature.

The mixture was stirred for 75 minutes. After filtration and concentration, the solid residue was washed several time with water and finally with methanol and dried in vacuo. 9.86 g (68%) of a nearly white product was obtained mp 94°C IR (KBr) cm^{-1}, 3200 (HC≡C-), 2100 (-C≡C-) 1680 (>C=O).

NMR ($CDCl_3$, TMS) δ (ppm) 10 (s, 1 H, -CHO) 7.8 and 7.6 (4 H, aromatic) 3.3 (s, 1 H, HC≡C-).

Ethynylation of bis-(3-aminopropyl)-tetramethyldisiloxane

5 g (0.0201 mol) of bis-(3-aminopropyl)-tetramethyldisiloxane (Petrarch) was dissolved in 12 ml methanol in argon. A few drops acetic acid were added. A solution of 5.243 g (0.0403 mol) of 4-ethynylbenzaldehyde dissolved in 70 ml ethyl acetate was then added dropwise under stirring. 10 ml additional ethyl acetate was finally added to dissolve the remaining unsolved solid. Stirring was continued for 2 hours.

The solvent was eliminated in vacuo first at 30°C and finally at 40°C 0.1 mm Hg.

9.4 g (100%) of a viscous yellow liquid having a tendency to precipitate is obtained.

IR (on NaCl pellet) cm^{-1}, 3300 (H-C≡) 2950, 2920, 2870, 2840 (CH_3-, -CH_2-) 2100 (-C≡C-) 1640 (-CH=N-) 1050 (>Si-O-)

NMR ($CDCl_3$, CH_2Cl_2) δ (ppm) 8.15 (s, 2H, CH=N) 7.6 and 7.45 (8 H, aromatic) 3.58 (t, 4 H, CH_2=N) 3.16 (s, 2H, HC≡C) 1.75 (m, 4H, CH_2-CH_2-N=) 0.58 (m, 4H, CH_2-Si) 0.13 (s, 12 H, CH_3-Si).

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