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Synthesis of poly[(methylsiloxane)-*co*-(dimethylsilazane)] copolymers as precursors of ceramic materials

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Summary

A series of new crosslinked poly[(methylsiloxane)-*co*-(dimethylsilazane)] copolymers were synthesized by cationic ring opening polymerization of the cyclic monomers 1,3,5,7 – tetramethylcyclotetrasiloxane and 2,2,4,4,6,6 - hexamethylcyclotrisilazane. These copolymers contain different concentrations of methylsiloxane and silazane comonomer units. The thermal stability is strongly related to the concentration of methylsiloxane co-units in the copolymers. The weight loss curve of the copolymers lies in a temperature range between its two homopolymers. FT-IR studies are in good agreement with the proposed structure, either for the copolymers or for the residual powder ceramic obtained by pyrolysis. Two cured processes (thermal and UV) were used. The pyrolysis of the copolymers were carried out under argon atmosphere at 1200°C and in air at 1000 °C. Kinetic decomposition parameters of the copolymers such as a pre-exponential factor, the decomposition reaction orders and the activation energies were determined. The molecular weights were determined by osmometry.

Introduction

An important application of polysiloxane is in reinforced ceramic or metallic matrices at elevated temperature where high strength and fracture toughness are required [1]. Polysiloxanes can be synthesized by cationic or anionic ring opening polymerization of cyclic siloxane monomers [2,3]. Mineral acids, Lewi's acids and organic acids are used as cationic initiator [4-6]. Polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H) by triflic acid has given high molar mass polymers and small cycles [6]. Besides, there are a lot of possible functional groups, which can be incorporated in the cyclic siloxane monomers [7]. The polysilazanes are usually synthesized by polycondensation [8]. Cyclotrisilazane polymerize under different conditions. The lineal polymer is preferably obtained by cationic polymerization by using mineral acids (H_2SO_4, HNO_3) and NH_4I [9,10] as initiators. The polysilazanes can be synthesized by ring opening polymerization of cyclosilazanes [11], too. In the case of cyclodisilazane polymerization gives a mixture of high molar mass linear polymers and small cycles

[12,13]. Duguet et al., in the cationic ring-opening oligomerization of 2,2,4,4,6,6-hexamethylcyclotrisilazane (SZ) obtained both linear oligomers and macrocycles [14]. The aim of this work was to obtain poly[(methylsiloxane)-*co*-(dimethylsilazane)]s, by copolymerization of D_4^H and SZ because both monomers can be polymerized cationically. This synthetic way is an alternative for to the polymerization by hydrosilation, polycondensation or living anionic polymerization [15,16]. The crosslinking reactions occur in the reaction medium, due to the labile hydrogen atoms bonded to silicon and nitrogen atoms. The polymers containing labile Si-H bonds are highly interesting since they can be easily crosslinked [17].

Our interest was also to synthesize organosiloxanes derived polymers from silazanes, because this kind of polymers represent an attractive area of the preceramic polymers chemistry [17-19]. The route of the precursor polymers has been used almost entirely to prepare advanced ceramic materials (SiC, Si_3N_4 fibers) or amorphous silicon carbonitride with excellent thermal stability. Nowadays, it's very well known that polymers, which contain silicon, nitrogen, oxygen and carbon atoms, are described as a possible fiber precursor of ceramic materials [19,20]. Also, polymers formed by silazane units [-$Si(CH_3)_2NH$-], are used in refractory production and in the dielectric recover of microelectronic materials [21].

Experimental

Materials and copolymerization procedure

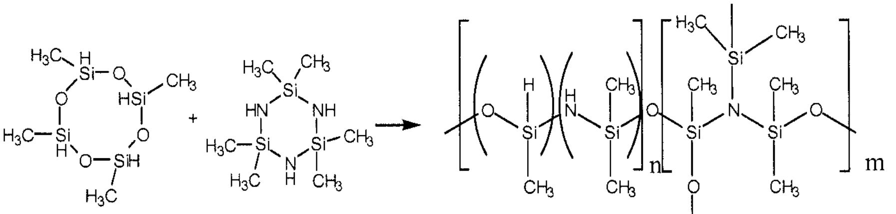
A series of new crosslinked poly[(methylsiloxane)-*co*-(dimethylsilazane)] copolymers were synthesized by cationic ring opening mass copolymerization of D_4^H and SZ using triflic acid as initiator (added as CH_2Cl_2 solution) at 30 °C. The cyclic monomers (UCT, United Chemical Technologies, Inc.) were purified by refluxing over molecular sieves for 48 h. D_4^H was additionally dried with CaH_2 and then distilled in vacuum in a nitrogen atmosphere before the copolymerization reactions. CH_2Cl_2 was purified by refluxing over $AlLiH_4$ for 72 h. The copolymerizations were carried out in nitrogen atmosphere to avoid the presence of water. The series of copolymers was obtained upon variation of the initial stoichiometric quantities. In all copolymerizations, the initiator concentration was $2.5x10^{-3}$ mol/L. The experimental work was carried out as described previously for another similar copolymerization [22,23]. The reactions were stopped by adding a small amount of triethylamine in methanol. The copolymers were washed with CH_2Cl_2 and dried in vacuum at room temperature. The yield obtained, after 10 days of polymerization time, indicates that the polymerization reached the expected thermodynamic ceiling-equilibrium (see Table 1). The concentration of the methylsiloxane (-$OSiHCH_3$-) and dimethylsilazane (-$Si(CH_3)_2NH$-) comonomer units on the copolymers depends on the monomer concentrations in the initial reaction mixture . The composition was determined by elemental analysis expressed as the molar fraction of SZ units in the copolymers, X_{SZ}, (Table 1).

Measurements

Fourier-transform infrared spectra were obtained on a Nicolet Magna-550 instrument in KBr pellets. The TGA were performed in samples obtained directly from the reaction medium. Thermogravimetric data were obtained using a thermobalance Polymer Laboratories STA 625. Samples (2-12 mg) were placed in aluminium pans and heated under flowing nitrogen (50 cm^3 min^{-1}) at a rate of 10 °C min^{-1} between 25 and 550 °C. The thermal and UV curing were carried out at 250 °C for 2 h and by using a Minerallight Lamp (UV Gl-58, 254/366 nm) for 2 h, respectively. The pyrolysis was carried out in a high temperature tube Furnace Thermolyne 59300 in argon atmosphere (gas flow of 1 L min^{-1}) at 1200 °C and in air at 1000 °C. The molecular weights were determined by osmometry (acetone as solvent at 37 °C) on a Knauer instrument. The partially soluble copolymers were first filtered and then the molecular weights were determined.

Results and discussion

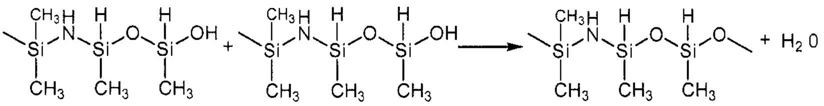
Crosslinked copolymers, poly[(methylsiloxane)-*co*-(dimethylsilazane)]s, were synthesized according to the following reaction :



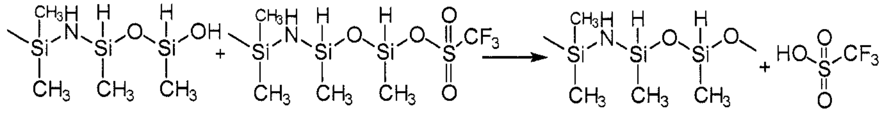
D_4^H SZ Random lineal segments Crosslinked segments

The copolymer chains grow by direct addition of the cyclic monomers to the cationically active chain ends and by a simultaneous polycondensation [24,25]; this explains the formation of siloxane-silazane chain segments. In the homopolymerization of SZ by using triflic acid as initiator was observed a molar mass increase of the reaction products due to both ring-opening polymerization and polycondensation through trisilylation of the nitrogen atoms [26,27]. So, the following growth sequence for the poly[(methylsiloxane)-*co*-(dimethylsilazane)] copolymers is discussed, on the basis to the simultaneous cationic and condensation polymerization mechanism of cyclosiloxane monomers:

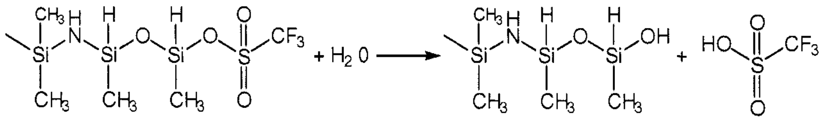
1. Homocondensation



2. Recovery of the initiator



3. Heterocondensation and recovery of the initiator.



In the cationic ring-opening polymerization of SZ and cyclodisilazanes, cyclic-quaternary "silazammonium" salt are assumed to be the active centres, and mechanisms of both propagation, cyclization and back-biting reactions were proposed [13].

In our case, on the lineal copolymer segments partial crosslinked reactions take place, due to the labile hydrogen atoms attached to silicon and nitrogen atoms. The formation of small cycles by back-biting reactions is also possible.

The molecular weights of the soluble and partially soluble copolymers were determined by osmometry (acetone as solvent at 37°C) (Table 1).

The TG spectra presented decomposition temperature values between both homopolymers. The degradation observed at 100 °C of poly(dimethylsilazane) (PSZ) could be due to cyclic (or linear) products of small molecular weight. The thermal stability increases at higher concentration of methylsiloxane units in the copolymers (Figure 1, Table 1). Poly(methylsiloxane) (PMS) is described in literature as a crosslinked silico-

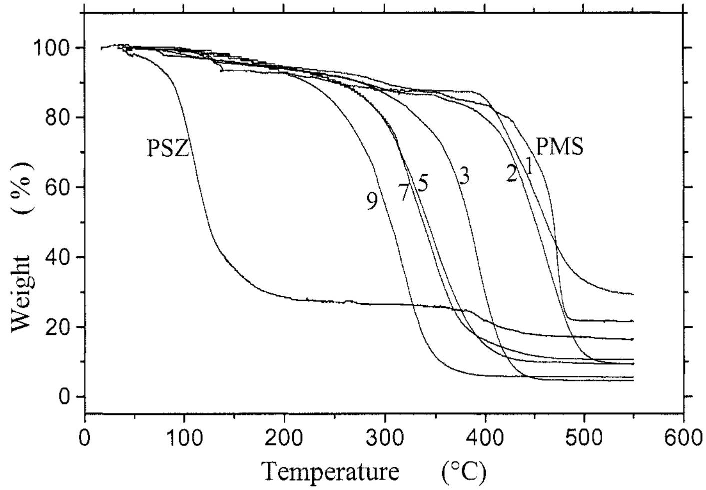


Figure 1. TG curves of poly[(methylsiloxane)-*co*-(dimethylsilazane)] copolymers recorded at a heating rate of 10 °Cmin^{-1}. PSZ : poly (dimethylsilazane), PMS : poly(methylsiloxane).

ne [23], and therefore it is thermally more stable than PSZ. In the anionic homopolymerization of N-methylcyclosilazoxane [28] and in the copolymerization of N-phenylcyclosilazoxane with hexamethylcyclotrisiloxane [29] yielded poly(silazoxane)s, i.e., polymers containing both N-methyl or N-phenylsilazane and dimethylsiloxane units in the main chain. These polymers present high thermal stability (up to 500 °C). In our case the samples 1 and 2 show a decomposition processes close to 500 °C. From the decomposition curves it was established that the molecular structure corresponds to block copolymers partially crosslinked, formed by random linear block segments, built by both comonomers units, which present a decomposition process between 25 and 550 °C. These blocks are covalently bonded to crosslinked block segments, in which the thermal decomposition process occurs at more than 550 °C , as we can concluded from the residual masses (see Table 1). Similar results have been obtained for another copolymer systems [30].

Table 1. Yields, molecular weights, initial and maximun thermal decomposition temperatures (T_i and T_D) and residual masses (r_m) for poly[(methylsiloxane)-*co*-(dimethylsilazane) copolymers.

Sample	X^o_{SZ}	X_{SZ}	Yield (%)	Mol.weight (g/mol) x10^3	T_i (°C)	T_D (°C)	r_m (%)
1	0.1	0.17	72	10.6	329.3	447.0	29.1
2	0.2	0.28	74	15.1	300.0	446.0	10.0
3	0.3	0.32	70	22.6	255.0	387.0	8.0
4	0.4	0.36	75	16.5	228.0	340.0	8.5
5	0.5	0.33	76	9.9	230.3	345.0	10.0
6	0.6	0.35	78	14.5	229.0	342.0	9.0
7	0.7	0.41	77	11.4	195.6	338.0	10.5
8	0.8	0.42	74	20.5	181.0	324.0	7.9
9	0.9	0.44	76	27.1	137.0	310.0	5.3

X^o_{SZ}: Mole fraction of SZ on the initial reaction mixture.
X_{SZ}: Mole fraction of SZ on the copolymers.

The FT-IR spectrum of the copolymers with different composition are in agreement with the proposed molecular structure. The infrared spectra from some of copolymers is shown in Figure 2. In Figure 2a the band at 2750-2950 cm^{-1} correspond to the stretching vibrations of the bond C-H (-CH_3). The band at 2144,2 cm^{-1} correspond to stretches of the Si-H bond and together with the signal of δ (NH) at 3377cm^{-1} it indicates the existence of the linear structure. This is confirmed with a strong Si-N-Si band between 970-1010 cm^{-1} of type δ[-(-Si(CH_3)$_2$-NH- Si(CH_3)$_2$-)-]. Also, it is well known that strong and complex absorption band around 1000-1200 cm^{-1} is assigned to –Si-O-Si- of polysiloxane, too. The band at 1261.8 cm^{-1} also indicates a small crosslinked fraction of the sample. Figure 2b shows the signal of δ (NH) at 3377 cm^{-1} and a complete disappearance of the δ (SiH) bond at 2144 cm^{-1}. This indicates that the sample is crosslinked. The crosslinked chain segments are confirmed with the strong band at 1261.8 cm^{-1}, which correspond to δ (Si-C) from tersiloxane groups.

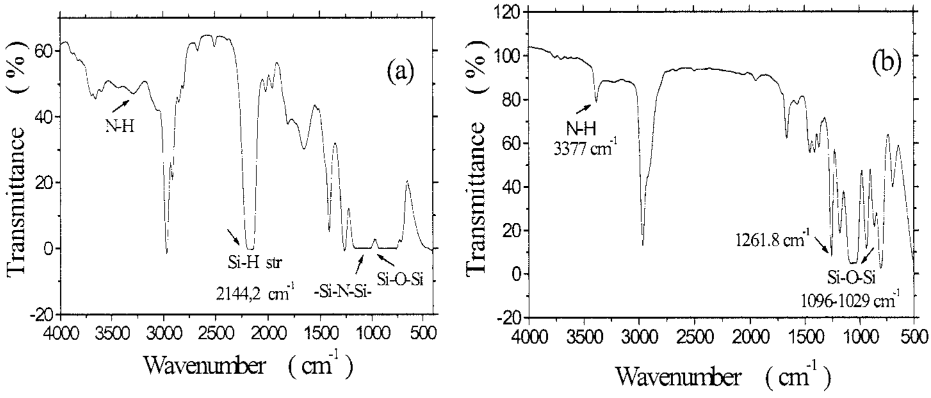


Figure 2. FT-IR spectra for the copolymers a) X_{SZ} = 0.28 and b) X_{SZ} = 0.42

The preparation of $Si_x N_y C_z$ powder ceramic was carried out by pyrolysis of the poly[(methylsiloxane)-*co*-(dimethylsilazane)] copolymers. Sample 3 was heated at 300 °C min^{-1} from 25 to 800 °C and then was heated at 10 °C min^{-1} from 800 to 1200 °C and held at this temperature for 2 h. Afterwards the sample was cooled at 10 °C min^{-1} from 1200 to 25 °C. The ceramic yield (65% at 1200°C) was obtained.

The FT-IR spectrum of residual powder ceramic of sample 3 is shown in Figure 3. These FT-IR spectra present a classic example of the residual material obtained from a preceramic polymer [31,32]. Figure 3a and b show the FT-IR spectra of the powder ceramic obtained by pyrolysis using two cured processes (thermal and UV) in air at 1000 °C, respectively. They show a strong broad band between 1000-1200 cm^{-1}, assigned to Si-O stretching (1080 cm^{-1}) and a typical ceramic absorption band (Si-C stretching) at 830 cm^{-1}. Figure 3c shows the FT-IR spectra of the powder ceramic obtained by pyrolysis in argon atmosphere at 1200 °C using a thermal cured process. The typical absorption bands for the silicon nitride (Si_3N_4) are found at 950 cm^{-1} (Si-N bonds) and at 3449.0 cm^{-1}. The band at 3449.0 cm^{-1} in the spectrum c was better observed than a and b because the pyrolysis was carried out in argon atmosphere. The FT-IR spectra finally shows the existence of a ceramic mixture formed by SiC, Si_3N_4 and SiO_2.

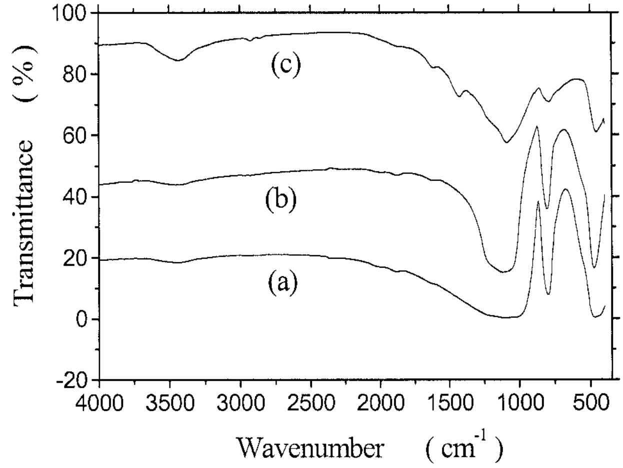


Figure 3. FT-IR spectra of powder ceramic obtained from sample 3. Pyrolysis: a) in air at 1000 °C (thermal cured), b) in air at 1000 °C (UV cured) and c) in argon at 1200 °C (thermal cured)

Kinetic parameters

The thermal decomposition reaction of the copolymers is irreversible and the rate-dependent parameters such as activation energy and reaction order can be calculated from a single experimental curve [33]. The thermal decomposition kinetics of the thermogravimetric weight loss data were assumed to the kinetic equation

$$- (d\alpha/dt) = K\,(1 - \alpha)^n \qquad (1)$$

where α is the fraction of sample weight reacted at time t, n is the reaction order and K is the specific rate constant The reaction rates, $d\alpha/dt$, were calculated by using a differential technique with the heating rate (v =10 °Cmin^{-1}) incorporated directly in the data of temperature versus sample weight fraction, according to the method developed by Wen and Lin [34]. The specific rate constant, K, was obtained from the Arrhenius equation

$$K = Z \exp (- E / RT) \qquad (2)$$

where E is the activation energy, Z the pre-exponential factor, T the absolute temperature and R the gas constant. After combining eq. (1) and (2) and using the logarithmic form we obtained

$$\beta = \ln [-v (d\alpha/dT) / (1 - \alpha)^n] = \ln Z - E /RT \qquad (3)$$

A computer linear multiple-regression program was used to calculate the kinetic parameters E and Z linear least-squares fit of the data in a semilogarithmic plot of β versus 1/T. The Arrhenius plot of some copolymers are shown in Figure 4. Plotting β against 1/T should give a straight line, and E and Z are determined from slope and intercept. They show a very good correlation and the coefficients of linear correlation varied from 0,993 to 0,998. The kinetic parameters n, E and Z calculated from these plots are summarized in Table 2.

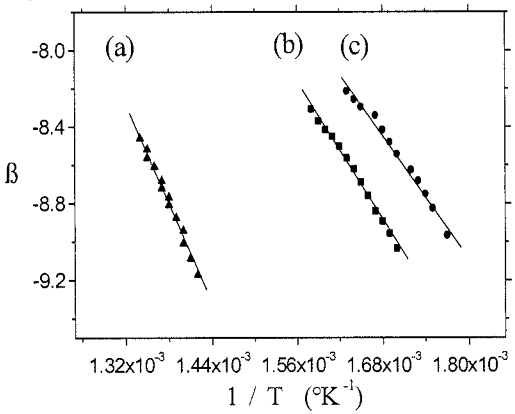


Figure 4. Arrhenius plots for the thermal degradation of poly [(methylsiloxane)-*co*-(dimethylsilazane)] copolymers according to eqn.(3): plot a, sample 2; plot b, sample 5 and plot c, sample 9.

Table 2. Kinetic parameters of poly[(methylsiloxane)-*co*-(dimethylsilazane)] copolymers

Sample	X_{SZ}	n	Z (min^{-1})	E (Kcal mol^{-1})
1	0.17	0	0,181	10,51
2	0.28	0	0,189	10,57
3	0.32	0	0,020	6,56
4	0.36	0	0,119	9,77
5	0.33	0	0,209	9,04
6	0.35	0	0,033	7,39
7	0.41	0	0,029	6,44
8	0.42	0	0,134	8,84
9	0.44	0	0,206	8,39

The linear relationships obtained indicated that the reactions are of zero order. It seems likely that they exhibit a complex decomposition kinetics because of their mixed molecular structures. In general, the activation energies increase at higher frequency factor.

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