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Controlled synthesis of amphiphilic siloxane-siloxane block copolymers with carboxyl functions

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Summary

Poly[2-(carboxymethylthio)ethyl]methylsiloxane-block-polydimethylsiloxane, **1**, and poly{[2-(carboxymethylthio)ethyl]methylsiloxane-co-dimethylsiloxane}-block-polydimethylsiloxane, **2**, were synthesized by ene-thiol addition of mercaptoacetic acid to respective precopolymers **3** and **4**, containing vinyl groups bound to silicon. The precopolymers **3** and **4** were obtained by sequential anionic copolymerization of hexamethylcyclotrisiloxane, D_3, with 2,4,6-trimethyl-2,4,6-trivinyl-cyclotrisiloxane, **5**, and D_3 with 2,4,4,6,6,-pentamethyl-2-vinylcyclotrisiloxane, **6**, respectively. The method permits to synthesise the block copolymers with a narrow molecular weight distribution and a high block purity. The ene-thiol addition was performed on free radical route, using AIBN as initiator. The reaction proceeds selectively, leading to the transformation of vinyl groups in the precopolymers into the ß-adducts.

Introduction

Block copolymers, built of hydrophobic and hydrophilic segments, show a very interesting morphology, unique surface properties and an unusual solution behavior(1-4). The synthesis of well defined amphiphilic block copolymers has attracted considerable attention because of their growing application as surface active materials(1,2). These copolymers are broadly applied for the stabilization of emulsions and dispersions of hydrophobic substances in water or alcohols. They are often preferred over conventional low molecular weight ionic detergents in various emulsion polymerization systems, as they are very effective steric stabilizers(5,6). The surface activity of amphiphilic block copolymers is also used in surface modification, foaming, lubrication and formulation of cosmetics(1,2). Another application of these copolymers is connected with their ability to solubilize various hydrophobic compounds in water or in some other polar solvents. When an amphiphilic block copolymer is dissolved in a solvent, which is precipitant for the hydrophobic block and a good solvent for the hydrophilic part, the block copolymer may associate in solution to form micelles(6,7). The hydrophobic core of the micelle surrounded by hydrophilic shell serves as a microcontainer for various organic substances. This ability may be taken into account in various separation techniques, being the main feature of the mechanism of micellar catalysis(8,9).

An interesting aspect of the amphiphilic block copolymers with hydrophilic groups able to be proton-donors in hydrogen bond, is the possibility of formation of polymeric complexes with polymers having proton acceptor groups(10,11). The behaviour of these macromolecular complexes are strongly affected by environmental conditions, temperature, pH, and electric field. A reversible solution-gel transition may occur in response to an environmental stimulation.

In this paper we describe a synthesis of AB block copolymers having a polydimethylsiloxane hydrophobic sequence A and a hydrophilic sequence B formed by a polysiloxane bearing carboxyl groups pendant to the polysiloxane chain. The carboxyl group is bonded to silicon through a dialkylthioether bridge. The amphiphilic block copolymers built entirely of polysiloxane seem to

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be particularly interesting because of an unusually high mobility of the silicon-oxygen chain. These polymers should easily acquire various conformations and should be well soluble in various solvents, what can make them useful in many applications. The carboxyl group is also precursor to other functional groups(12).

The synthesis of the well defined siloxane block copolymers with carboxyl side groups is not an easy task. The best route for the controlled synthesis of the siloxane-siloxane block copolymers seems to be the sequential anionic copolymerization of cyclotrisiloxanes(13). However, a direct anionic polymerization of cyclosiloxane with carboxyl substituents is not feasible as these substituents do not tolerate anionic propagation centres. On the other hand, the cationic ring opening polymerization of cyclic siloxanes, as well as the polycondensation of difunctional silanes, are processes which are difficult to control. Thus, the copolymer was obtained in two steps. First, the block copolymer with precursor vinyl groups was produced by sequential anionic polymerization. The vinyl groups in copolymer were further used to introduce carboxyl functions by ene-thiol addition in the second step of the synthesis.

Experimental

Monomers

2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane, **5**, was obtained as the 1:3 mixture of cis and trans isomers by a reaction of methylvinyldichlorosilane with zinc oxide in an analogous way to that described in Ref.(14). It was purified by distillation over an efficient column (b.p. 79.5-80°/20 mmHg), ^{1}H NMR ($CDCl_3$) δ(ppm): 0.245, 0.258, 0.273 [d+s, $SiC\mathbf{H}_3$ ($CH=CH_2$)], 5.81-6.10 [m, $SiCH_3$ ($C\mathbf{H}=C\mathbf{H}_2$)]; ^{13}C NMR ($CDCl_3$) δ(ppm): -0.90 [s, $Si\mathbf{C}H_3(CH=CH_2)$], 134.2, 134.3, 134.4 [d+s, $SiCH_3$ ($CH=\mathbf{C}H_2$)], 135.4, 135.5, 135.6, [d+s, $SiCH_3$ ($\mathbf{C}H=CH_2$)]; ^{29}Si NMR ($CDCl_3$) δ(ppm): -22.37 [s, $\mathbf{Si}CH_3(CH=CH_2)$]. 2,4,4,6,6,-pentamethyl-2-vinylcyclotrisiloxane, **6**, was obtained by condensation of 1,1,3,3,-tetramethyldisiloxanediol with methylvinyldichlorosilane according to the method described earlier(15). It was purified by distillation on an efficient column (b.p. 56°/23 mmHg), m.p. 27-29°C, ^{1}H NMR ($CDCl_3$) δ(ppm): 0.17, 0.18 [d, $Si(C\mathbf{H}_3)_2$], 0.23 [s, $SiC\mathbf{H}_3$ ($CH=CH_2$)], 5.80-6.08 [m, $SiCH_3(C\mathbf{H}=C\mathbf{H}_2)$]; ^{13}C NMR ($CDCl_3$) δ(ppm): -0.73 [s, $Si\mathbf{C}H_3(CH=CH_2)$], 0.88, 0.96 [d, $Si(\mathbf{C}H_3)_2$, 134.0 [s, $SiCH_3(CH=\mathbf{C}H_2)$], 135.9 [s, $SiCH_3(\mathbf{C}H=CH_2)$]; ^{29}Si NMR ($CDCl_3$) δ(ppm): -7.75 [s, $\mathbf{Si}(CH_3)_2$], -23.33 [s, $\mathbf{Si}CH_3(CH=CH_2)$]. All the cyclic monomers **5**, **6** and D_3 were additionally purified by distillation from CaH_2 on a high vacuum line to an ampoule with a Rotaflo stopcock from which they were distilled to a reactor installed on the vacuum line to prepare the solution for the polymerization experiment.

Precursor copolymers

Polydimethylsiloxane-block-polymethylvinylsiloxane, **3**. Prepurified D_3, 3.00 g (13.5 mmol) was distilled on a high vacuum line to a 50 ml glass reactor fitted with a magnetic stirrer and two stopcocks. THF (6 ml) prepurified (according to Ref.(16)) was subsequently distilled into the reactor. The reactor was filled with argon. Then 0.15 ml of 1.6 M solution of n-BuLi in n-hexane (0.24 mmol of BuLi) was introduced by means of a precision Hamilton syringe, while argon was streaming through the stopcock system. The polymerization proceeded in ambient temperature (22°C) and was followed by gas chromatographic analysis of the samples withdrawn after a time interval. After 3 hours, when 92% of D_3 was consumed, 2.9 g (11.0 mmol) of monomer **5** was introduced. After another 40 min. the reaction was quenched by introduction of 0.2 ml of Me_3SiCl in 1 ml of n-heptane. About 90% of monomer **5** was converted, while 7.5% of the initial D_3 remained unconverted. The copolymer was precipitated by introduction of the copolymer solution to 60 ml of methanol. The polymer was dried under vacuum. 3.8 g of the polymer was obtained - 76% yield (regarding samples withdrawn). SEC: $\overline{M}_n$ = 17000, $\overline{M}_w$ = 18700, $\overline{M}_w/\overline{M}_n$ =

1.1, $\overline{M}_n$(theor) = 23000. The molecular weights of blocks, calculated from ^{1}H NMR spectra were following: $\overline{M}_n$ (Me_2SiO-block) 8900, $\overline{M}_n$ (MeViSiO-block) 8100. ^{1}H NMR (solution in $CDCl_3$) δ(ppm): 0.11 [s, $Si(C\mathbf{H}_3)_2$], 0.17 [s, $C\mathbf{H}_3SiCH{=}CH_2$], 5.79-6.07 [m, $C\mathbf{H}_2{=}C\mathbf{H}Si$]. ^{29}Si NMR ($CDCl_3$) δ(ppm): -21.72 [s, $\mathbf{Si}(CH_3)_2$], -34.71 [s, $\mathbf{Si}CH_3(CH{=}CH_2)$].

Poly(dimethylsiloxane-co-methylvinylsiloxane)-block-polydimethylsiloxane, **4**, was obtained in an analogous way by anionic sequential polymerization of D_3 with 2,4,4,6,6-pentamethyl-2-vinylcyclotrisiloxane, **6**. Using 4.53 g (20.5 mmol) of D_3 in 9 ml of THF and 1.12 mmol nBuLi, after 2 hrs at 22°C, 91% of D_3 was converted and 1.5 g of monomer **6** was introduced. The reaction was quenched after additional 80 mins, when 98% of **6** was converted and 5% of D_3 remained unconverted. SEC $\overline{M}_n$ = 8600, $\overline{M}_w$ = 9400, $\overline{M}_w/\overline{M}_n$ = 1.1, $\overline{M}_n$(theor) = 7500. $\overline{M}_n$ (Me_2SiO-co-MeViSiO-block) = 4400, $\overline{M}_n$ (Me_2SiO-block) = 4200.^{1}H NMR ($CDCl_3$) δ (ppm): 0.07-0.13 [m, $Si(C\mathbf{H}_3)_2$], 0.16-0.19 [m, $C\mathbf{H}_3SiCH{=}CH_2$], 5.78-6.05 [$C\mathbf{H}_2{=}CHSi$]. ^{29}Si NMR ($CDCl_3$) δ (ppm): -20.74 to -21.71 [m, $\mathbf{Si}(CH_3)_2$], -35.25 to -35.61 [m, $\mathbf{Si}CH_3(CH{=}CH_2)$].

Poly[methylvinylsiloxane-alt-bis(dimethylsiloxane)], **8**, polymer of regular alternating structure was synthesized by polycondensation of 1,1,3,3-tetramethyl-1,3-diol with methylvinyldichlorosilane in the presence of DMAP/Et_3N in an analogous way to that described in Ref.(15). Since molecular weight of **8** was relatively low the polymer was not isolated by precipitation in methanol, but only lower cyclics were distilled off the polymer under vacuum (10^{-3} mmHg).. SEC: $\overline{M}_n$ = 3600, $\overline{M}_w$ = 13800, $\overline{M}_w/\overline{M}_n$ = 3.8. ^{1}H NMR (toluene-$CDCl_3$) δ (ppm): 0.12 [s, $(C\mathbf{H}_3)_2Si$], 0.18 [s, $C\mathbf{H}_3SiCH{=}CH_2$], 5.8-6.1 [m, $\mathbf{Si}CH_3(CH{=}CH_2)$].

Copolymers with carboxyl side groups

Synthesis of poly[2-(carboxymethylthio)ethyl]methylsiloxane-block-polydimethylsiloxane, **1**. 1.50 g of block copolymer **6** containing 9.4 mmol of vinyl groups, 1.03 g (11.2 mmol) of mercaptoacetic acid and 0.03 g of azodiizobutyronitrile (AIBN) in 20 ml of prepurified toluene was placed in a 50 ml glass reactor fitted with a magnetic stirrer, two stopcocks and a reflux condenser. The reactor was purged with argon. The mixture was heated at 80°C for 5 hrs with stirring in the atmosphere of argon. Toluene and the excess of mercaptoacetic acid were removed under vacuum (up to 10^{-3} mmHg). The ^{1}H NMR analysis showed that over 98% of vinyl groups were converted. ^{1}H NMR ($CDCl_3$), δ (ppm): 0.07 [s, $Si(C\mathbf{H}_3)_2$], 0.15-019 [m, $SiC\mathbf{H}_3CH_2$], 0.84-0.96 [m. $CH_3SiC\mathbf{H}_2$], 2.66-2.78 [m, $SiCH_2C\mathbf{H}_2S$], 3.23-3.34 [m, $SC\mathbf{H}_2COOH$], 7.6 [broad s, $COO\mathbf{H}$]. ^{29}Si NMR ($CDCl_3$): -21.9 [s. $\mathbf{Si}(CH_3)_2$], -23.9 [b.s. $\mathbf{Si}CH_3CH_2$]. Elemental Anal.; % S 11.8 (theor. 12.7) - (polymer contained a small amount of toluene). IR (cm^{-1}): 3060 s. [O-H stretching H-bonded] 2962 m (C-H); 2918 w (C-H); 1707 s (C=O); 1415 m ($Si{-}CH_3$); 1261 s ($Si{-}CH_3$); 1092 s (Si-O); 1020 s (Si-O); 799 s (Si-C).

Syntheses of poly{[2-(calboxymethylthio)ethyl]methylsiloxane-co-dimethylsiloxane}-block-polydimethylsiloxane, **2**, and poly[2-(carboxymethylthio)ethyl]methylsiloxane-alt-bis(dimethylsiloxane), **7**, were performed in an analogous way. The reaction proceeded more slowly than the modification of polymer **3**. After heating under the same conditions for 12 hrs, about 20% of the vinyl groups remained in copolymer **2**.

2: ^{1}H NMR (CDCl3), δ (ppm): 0.05-0.10 [m, $Si(C\mathbf{H}_3)_2$], 0.10-0.14 [m, $SiC\mathbf{H}_3CH_2$],0.85-0.95 [m, $CH_3SiC\mathbf{H}_2$], 2.7-2.8 [m, $SiCH_2C\mathbf{H}_2S$], 3.2-3.3 [m, $SC\mathbf{H}_2COOH$], 10.2 [b.s. O-**H**]. ^{29}Si NMR ($CDCl_3$), δ (ppm): -20.8- -21.8 [m, $\mathbf{Si}(CH_3)_2$], -24.85- -25.4 [m, $\mathbf{Si}CH_3CH_2$]. IR (cm^{-1}): 3420, 3450 w [O-H, H-bonded], 2962 m (C-H), 2906 w (C-H), 1711 s (C=O); 1415 m ($Si{-}CH_3$); 1261 s ($Si{-}CH_3$), 1166 w (CH_2CH_2), 1093 s (Si-O), 1024 s (Si-O), 845 w ($Si{-}CH_3$), 802 s (Si-C).

7: ^{1}H NMR ($CDCl_3$), δ (ppm): 0.12 [s, $Si(C\mathbf{H}_3)_2$], 0.15 [s, $SiC\mathbf{H}_3CH_2$], 0.86-0.90 [m, $CH_3SiC\mathbf{H}_2$], 2.71-2.74 [m, $SiCH_2C\mathbf{H}_2S$], 3.24-3.29 [m, $SC\mathbf{H}_2C{=}O$]. ^{29}Si NMR ($CDCl_3$), δ (ppm): -20.8 [s, $\mathbf{Si}(CH_3)_2$, -25.3 [s, $\mathbf{Si}CH_3CH_2$]. IR (cm^{-1}): 3095 s [O-H, H-bonded], 2962 m (C-H), 1711 s (C=O), 1417 m (Si-CH_3), 1296 m (Si-CH_3), 1261 s (Si-CH_3), 1093 s (Si-O), 1024 s (Si-O), 848 m (Si-CH_3), 802 s (Si-C).

Analyses

^{1}H and ^{29}Si NMR spectra were taken with a Bruker MSL working at 300 and 59.6 MHz for ^{1}H and ^{29}Si, respectively. SEC analyses were performed with a LDC-Analytical, refracto Monitor IV using a baterry of two phenogel columns covering the MW range 10^2-10^5 g·mol^{-1}. Calibration was made on polystyrene, solvent was toluene. IR spectra of copolymer films were taken with an ATI MATTSON INFINITY FTIR 60. Gas chromatographic analyses were performed with a Hewlett Packard HP 6890 using TCD detector and HP.1 column, length 30 m, diameter 0.53 mm.

Results and discussion

Two types of block copolymers differing in the structure of the hydrophilic sequence were synthesized; the one having the carboxyl function in every siloxane unit of the hydrophilic block and the other of a lower hydrophilicity with the hydrophilic block being a copolymer of the carboxyl containing siloxane with dimethylsiloxane, the respective siloxane unit ratio was 1:2. The synthesis was performed according to scheme 1. The precopolymers containing vinyl groups were obtained in a one pot procedure. In the first step, lithium silanolate ended polydimethylsiloxane was obtained by a careful polymerization of hexamethylcyclotrisiloxane (D_3) initiated by butyl lithium in THF solution. When the concentration of D_3 dropped below 10% of its initial value, the vinyl-containing comonomer, i.e., 2,4,6-trimethyl-2,4,6-trivinylcyclotrisiloxane, **5**, or 2,4,4,6,6,-pentamethyl-2-vinylcyclotrisiloxane, **6**, was introduced. The polymerization was quenched by trimethylchlorosilane at a high conversion of the vinyl-containing monomer. The SEC chromatogram showed that the molecular weight distributions were unimodal and the heterogenity factor was very low, see Fig. 1. The formation of the PDMS block in the first stage is advantageous as it ensures a better control over the structure of the block formed in the second stage. In order to keep the molecular weight heterogenity at a low level, the first step should not be carried out to more than about 90-95% of monomer conversion. Thus, the polymerization system in the second stage, in addition to the introduced second comonomer, contains considerable amounts of the first monomer which did not enter the polymerization in the first stage. If this remaining comonomer is D_3, it is much less reactive compared to **5** or even to **6**, thus it has a low propensity to enter into the vinyl containing block of the copolymer. Consequently, the purity of blocks was high. The block built of monomer **5** contained less than 1% of D_3 units, while that one built of **6** contained 4% of D_3.

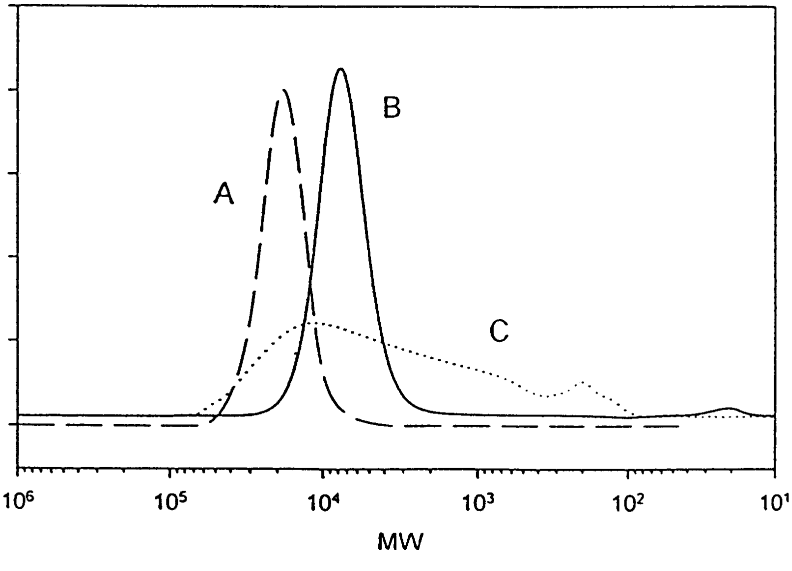
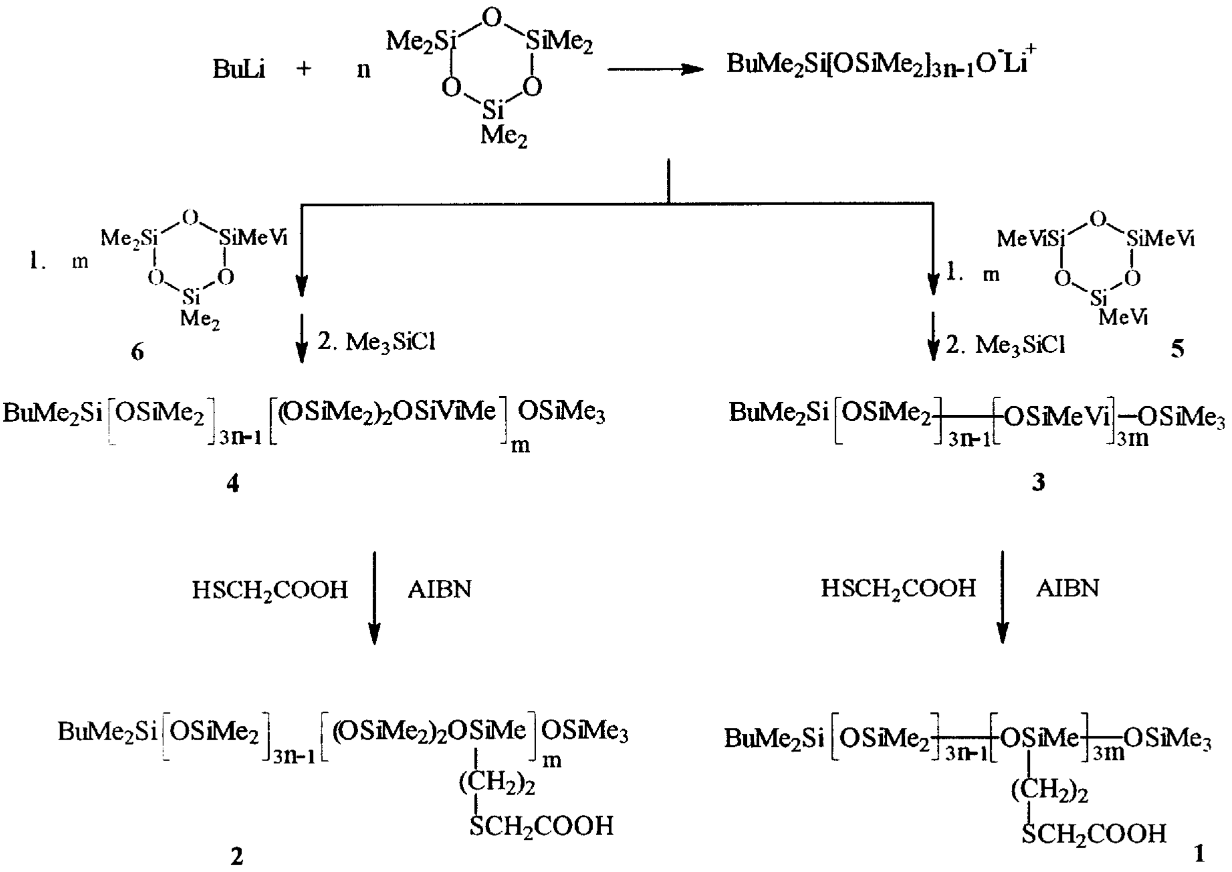


Figure 1. Comparison of SEC traces of vinyl containing polysiloxanes obtained by sequential anionic ROP of cyclotrisiloxane, traces A and B, with that obtained by polycondensation of tetramethyldi-siloxane-1,3-diol with methylvinyldichlorosilane, trace C (dotted line). A- polydimethylsiloxane-block-polymethyl-vinylsiloxane, **3**. B - poly(dimethylsiloxane-co-methylvinylsiloxane)-block-polydimethylsiloxane, **4**, C - poly[bis(dimethylsiloxane)-alt-methylvinylsiloxane], **8**.

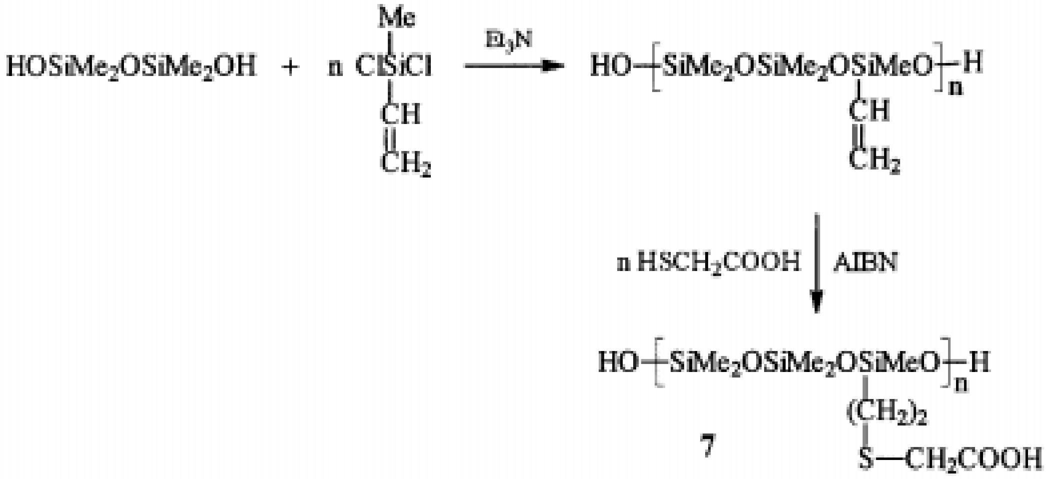
The synthetic strategy exploited here, i.e., the use of strained ring cyclotrisiloxane comonomers and of the lithium THF polymerization system (scheme 1), guaranteed a control of the molecular weight of copolymers, and a uniform spreading of the functional vinyl groups in the hydrophilic block. The copolymers are free of homopolymers and have a narrow molecular weight distribution. As it was shown earlier(15), the anionic polymerization of monomer **6** does not lead to a regular alternative structure of the copolymer as the monomer ring may be opened in various sites in the chain propagation reaction. However, since the processes leading to the chain cleavage are eliminated, the vinyl containing units are uniformly spread along the chain.



Scheme 1

In contrast to the copolymers generated by the controlled sequential anionic polymerization, poly[bis(dimethylsiloxane)-alt-methylvinylsiloxane], 7, obtained by polycondensation of 1,1,3,3-disiloxano-1,3-diol with methylvinyldichlorosilane shows a very broad molecular weight distribution, $\overline{M}_w/\overline{M}_n = 3.8$, and a considerable amount of cyclic products. The broad distribution is partly due to different way of isolation of this polymer, see experimental section. On the other hand, the sequencing of siloxane units is more regular in the polycondensation polymer than in the copolymer obtained by ROP.

The ene-thiol addition to the vinyl group pendant to siloxane chains, has been exploited earlier to introduce thioether groups(15,17) and pyridyl groups(18) to polysiloxane chain. In those cases the reaction was selective, although, in the presence of pirydyl groups, it proceeded slowly. The reaction of vinyl-substituted polysiloxanes with mercaptoacetic acid was first studied by us on a model polysiloxane with regularly spaced vinyl groups. That polymer was synthesized by the polycondensation method, according to scheme 2.



Scheme 2

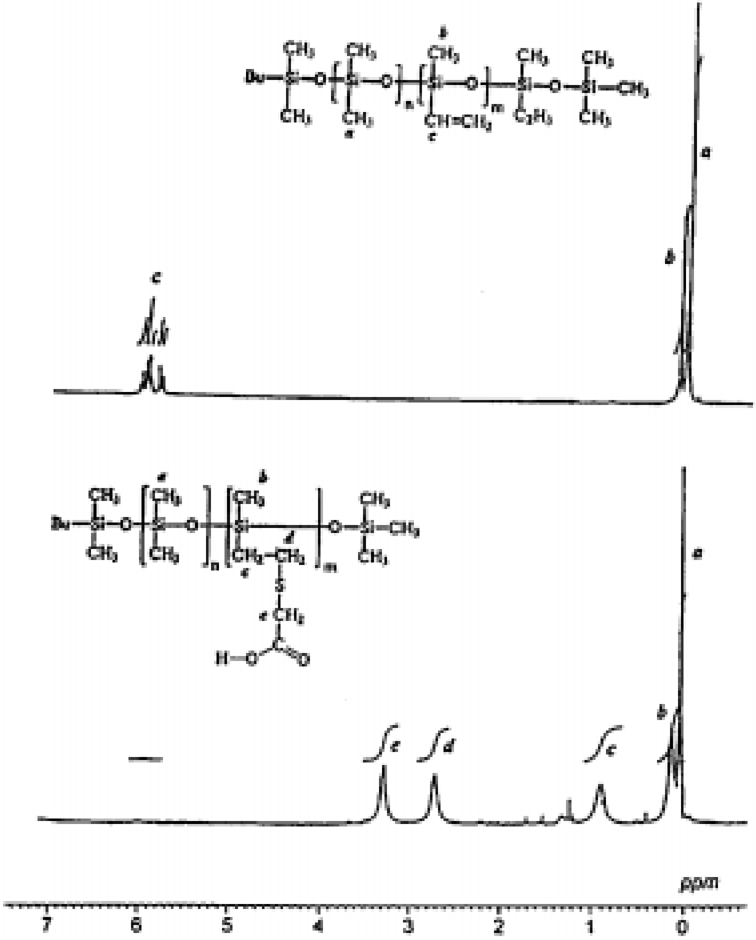


Figure 2. Comparison of ^{1}H NMR spectra of A - poly[2-(carboxymethylthio)ethyl]-methylsiloxane-block-poly-dimethyl-siloxane, **1**, and B - its precursor polydimethylsiloxane-block-polymethylvinylsiloxane, **3**.

The ene-thiol addition, initiated with azo-bis-(isobutyronitrile) (AIBN), proceeded smoothly and selectively, leading to transformation of vinyl groups into the anti-Markovnikov addition product (ß-adduct), ^{29}Si and ^{1}H NMR spectra of polymer **1** are compared with the spectra of the vinyl precopolymer substrate 3 on Fig. 2. Almost no vinyl groups are present in the modified polymer products. The addition reaction proceeds in accordance with a free radical mechanism(19), thus no polysiloxane chain cleavage occurs during the reaction(15). The SEC chromatogram of polymer **1** shows a unimodal peak. The molecular weight could not be directly deducted from the chromatogram because of different hydrodynamic properties of the amphiphilic block copolymers.

The copolymers are stable if kept for several days in room temperature. However, SEC chromatogram of the copolymers taken after 100 days showed some symptoms of cleavage of the siloxane bond by carboxyl groups.

Copolymer **1** is of a soft waxy consistence. Its DSC trace taken during heating shows a distinct sideslip at -123°C corresponding to the glass transition point, Tg, of polydimethylsiloxane and a strong endothermic peak with its maximum at -40°C corresponding to the melting point of the PDMS. On the other hand, a distinct leap observed at -19°C may be attributed to Tg of the carboxyl-substituted polysiloxane. Thus, the copolymer shows the microphase separation.

IR spectrum of the film of copolymer **1** exhibits a broad band of OH stretching vibration with the maximum at about 3060 cm^{-1}, Fig. 3. This band is characteristic for the hydrogen bond between carboxyl groups.

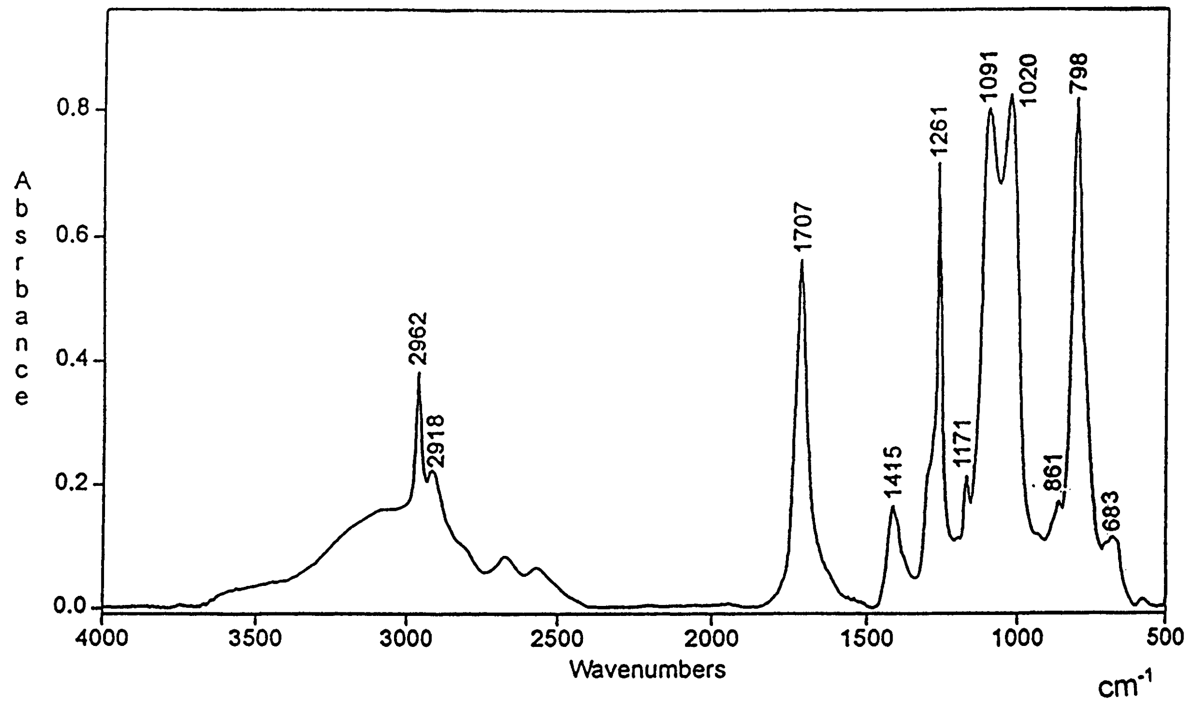


Figure 3. **IR-spectrum of poly[2-carboxymethylthio)ethyl]methylsiloxane-block-polydimethylsiloxane, 1.**

Block copolymer **1** can be dissolved in water, alcohols and in other polar solvents, such as ketones, acetonitrile, chlorinated hydrocarbons. It is also soluble in hydrocarbons and ethers. In water it forms micelles what was demonstrated by the solubilization of pyrene(20) by the copolymer in its solution in water. When the concentration of pyrene was about 10^{-5} M the solution irradiated with UV light (332 nm) exhibited fluorescence at 370-390 nm characteristic for excited pyrene monomer. At a higher pyren concentration the fluorescence shifted to 430-500 nm thus showing the formation of excimer. The block copolymer **2** is not soluble in water, but it is soluble in alcohols including methanol, ketones, ethers and hydrocarbons.

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