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ORIGINAL CONTRIBUTION

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Surface structure of silica gel reacted with 3-mercaptopropyltriethoxysilane and 3-aminopropyltriethoxysilane: formation of the S–S bridge structure and its characterization by Raman scattering and diffuse reflectance Fourier transform spectroscopic studies

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Abstract Silica gel samples, modified with 3-mercaptopropyltriethoxysilane, and their S–S-bridged samples have been prepared. In order to characterize the microstructure of the surface of these silica gel samples, Raman scattering and diffuse reflectance Fourier transform IR spectra of these samples have been examined by comparison with Raman spectra of various *n*-alkyl disulfides and their related silane polymers. The S–S and C–S stretch modes characteristic of the CH_2SSCH_2 segment, in addition to the SH and C–S stretch modes of the CH_2SH segment, have been assigned for these silica gel samples. It has been found that, even on the surface of the silica gel, a specific conformer is stabilized about the CH_2SSCH_2 segment.

Keywords 3-mercaptopropyltriethoxy silane-modified silica gel · S-S bridge structure · Raman and DRIFT spectra

Introduction

The surface properties of silica gel and its interactions with various organofunctional silanes have been extensively examined for more than 4 decades. Many analytical techniques have been used in attempts to characterize the surface of silica gel modified with organic silanes, and details have already been reviewed in books [1–3]. Research developments in the field of organosilane-modified silica gel are still underway.

Of the large variety of organofunctional silanes which have been industrially produced and are of wide interest the most commonly used silanes may be classified as chloro-, alkenyl-, aryl-, epoxyfunctional-, N-functional-, S-functional- and Cl-functional silanes [3]. S-functional silanes, like 3-mercaptopropyltriethoxysilane (McPTS), which have been extensively utilized in the reinforced rubber industry [4], easily form a bridge structure by formation of a disulfide bond. This characteristic should lead to the molecular design of a new organofunctional silane incorporating the disulfide structure [5]. To this end, further investigation of the S–S bridge modification on the surface of silica gel is therefore highly desirable. However, quantitative and detailed surface structural studies of McPTS-modified silica gel are few in number.

Fourier transform (FT) IR, and particularly diffuse reflectance FTIR (DRIFT), [6–10] and Raman scattering spectra [11–13] have been recognized as powerful tools for the study of the chemical structure and interactions of a silane layer coated onto a surface. In the present study, we used these spectroscopic techniques in order to characterize the structure of a silica gel surface modified with McPTS, in particular focusing on the structure of the silica gel surface with S–S bridges resulting from interaction between –SH groups.

Experimental

Materials

McPTS and 3-aminopropyltrimethoxysilane (APTS) were purchased from Shinetsu Chemical Industry. *n*-Hexane-1-thiol, *n*-octane-1-thiol, *n*-decane-1-thiol and *n*-dodecane-1-thiol (all special grade) were purchased from Wako Pure Chemical Co. APTS was used without further purification, but McPTS was used after distillation in vacuo.

Poly(3-mercaptopropyl)siloxane [poly(MCP)] was synthesized as follows. Distilled water (8 g) was added to McPTS (5 g) and the reaction mixture was refluxed for 24 h at 383 K. The products of condensation (water and methanol) were removed by evaporation until the IR bands for methanol could no longer be detected. The solid poly(MCP) thus obtained was dried over P_2O_5 in a desiccator. Poly(3-aminopropyl)siloxane [poly(APS)] was synthesized by the method described in Ref. [14].

Copoly(3-mercaptopropyl-3-aminopropyl)siloxane [copoly-(MCP–APS)] was synthesized as follows. Water (10 g) was added to the McPTS–APTS mixtures (total weight: 5 g) at different molar ratios (1:1 and 4:1), which had been stirred for 6 h at room temperature (about 298 K), and each McPTS–APTS–water mixture was further stirred for 6 h. The products of condensation (water and methanol) were removed by evaporation. The copoly(MCP–APS) thus obtained was dried over P_2O_5 in a desiccator.

The S–S bridge formation of poly(MCP) and copoly(MCP–APS) was carried out as follows. The solid poly(MCP) or copoly(MCP–APS) (0.5 g) was dispersed in dichloromethane (50 g), and 10% $KHCO_3/H_2O$ (50 g) and I_2 (0.1 g) were added to the poly(MCP)- or copoly(MCP–APS)-dispersed system. The reaction mixture was stirred for 24 h. Dichloromethane and water in the reaction mixture were removed under vacuum. The solid S–S-bridged polymer thus obtained was washed with water, in order to remove $KHCO_3$, and dried over P_2O_5 in a desiccator. The treatment for copoly(MCP–APS) was similar. The two samples of S–S-bridged poly(MCP) and copoly(MCP–APS) are abbreviated as SSP and SSCP.

Supermicro bead silica gel B-10 (SMBS), with a particle size distribution, d_{10}/d_{90}, of 1.44, an average particle diameter of 5.7 μm and a pore diameter of 7.0 nm was purchased from Fuji Silysia Chemical Co. Surface areas (508 m^2/g) were determined by the Brunauer–Emmett–Teller method using nitrogen adsorption (a surface area of 16.2 Å was assumed for molecular N_2). The number of SiOH groups on the surface of SMBS, which was determined by the ignition loss method, was 6.

The SMBS sample systems (MCP-modified SMBS, SI) were modified with McPTS as follows. SMBS (10 g) was refluxed in toluene (40 ml) and then stirred at constant temperature (383 K). Weighed amounts of McPTS were added and the mixtures were further refluxed at 383 K for 6 h. The solid reaction mixture was washed with toluene in order to remove the unreacted McPTS, and then the hydrolysis reaction was quenched by washing the reaction mixture with methanol. Ethoxy groups remaining unreacted in the substrate were hydrolyzed in water–methanol (1:1) solution for 2 h at room temperature, and then the MCP-modified SMBS particles were again washed with methanol. The four SI samples (SMBS3, SMBS6, SMBS7 and SMBS9) thus prepared were dried at 383 K under vacuum for 12 h.

The SMBS sample system (MCP–APS-modified SMBS, SII) was also modified with the McPTS–APTS mixture (mixing weight ratios McPTS:APTS = 1:1 and 4:1) using the same method as described earlier. The abbreviations for the SII samples with ratios 1:1 and 4:1 are SMBS(S1N1) and SMBS(S4N1), respectively. The elemental analysis data of the SI and SII samples are listed in Tables 1 and 2, respectively. The S–S-bridged SI and SII samples were prepared by the same methods used for preparation of the SSP and SSCP polymers.

Methods

Care was taken to protect the sample from moisture during preparation and spectral analysis.

Raman spectra were recorded with a PerkinElmer FT Raman spectrometer (4,000–150 cm^{-1}) using a Nd:YAG laser (CVI) excitation wavelength of 1,064 nm with a resolution of 4 cm^{-1} at room temperature. The reproducibility of the Raman band frequencies was ± 1 cm^{-1} for sharp bands and ± 2–3 cm^{-1} for broad bands. The Raman spectra of the samples were obtained from pressed solid samples in a sealed capillary tube with a laser power of 440 mW.

The DRIFT spectra were recorded using a Nicolet Magna 750 system at 4-cm^{-1} resolution using the Spectra Tech collector diffuse reflectance accessory at room temperature. The samples were mixed with dried KBr and were used to fill the DRIFT sample cup before measurement. All the DRIFT measurements were carried out in an atmosphere of dry nitrogen.

A PerkinElmer 2400II CHNS/0 was used for elemental analysis of the samples. The concentrations of APTS and McPTS which had reacted with the silica gel were determined by analyzing the nitrogen or sulfur content of the samples. The error of the estimate was ±0.3%. The nitrogen or sulfur content (C_N or C_S, respectively) data of the samples are listed in Table 1.

Table 1 Elemental analysis data and concentration of modified (3-mercaptopropyl)siloxane (*MCP*) for SI samples

SI	c_S (wt%)	c_{MCP} (μmol/m^2)	Molecules (MCP) (nm^2)
SMBS3	2.95 ± 0.3	27.75	167
SMBS6	1.54 ± 0.3	14.49	87
SMBS7	0.75 ± 0.3	7.06	46
SMBS9	0.17 ± 0.3	1.60	10

Results

S–S and C–S stretch vibrational modes of di-*n*-alkyl disulfides

The vibrational spectra of dialkyl disulfides in the 500–750-cm^{-1} region, in which the S–S and C–S stretch modes are reflected, have been investigated in detail by

Table 2 Elemental analysis data and concentration of modified MCP and APS for SII samples

SII	c_S (wt%)	c_N (wt%)	c_{MCP} (μmol/m^2)	c_{APS} (μmol/m^2)	Molecules (MCP) (μmol/m^2)	Molecules (APS)(nm^2)
SMBS(S1N1)	2.14 ± 0.3	1.48 ± 0.3	20.13	28.54	121	172
SMBS(S4N1)	3.75 ± 0.3	0.76 ± 0.3	35.28	14.66	213	88

Sugeta et al. [15]. The results showed that the frequencies of the S–S stretch mode (ν_{SS}) of disulfide groups are strongly dependent upon the molecular conformations about the two C–S bonds adjacent to the S–S bond. The characteristics of the ν_{SS} stretch modes of dialkyl disulfides may be summarized as follows.

The frequencies of the ν_{SS} modes of the *X*–C–S–S–C–*Y* fragment are specified by the atoms *X* and *Y*, which occupy the two trans positions with respect to the sulfur atoms (Fig. 1):

1. For the conformation with two hydrogen atoms at both trans positions [type (H, H)], the ν_{SS} mode lies at about 510 cm^{-1}.
2. For those with a hydrogen atom at one trans position and a carbon atom at the other trans position [type(H, C)] the ν_{SS} mode lies at about 525 cm^{-1}.
3. For those with two carbon atoms at both trans positions [type (C, C)] the mode is expected to appear at about 540 cm^{-1}.

For dimethyl disulfide and other disulfides [16], in which no rotational isomers are expected other than the conformation with the gauche S–S bond, only one ν_{SS} mode was observed; however, for other dialkyl disulfides, in which the rotational isomers about the C–S bonds are possible, two ν_{SS} modes were actually observed in the spectra.

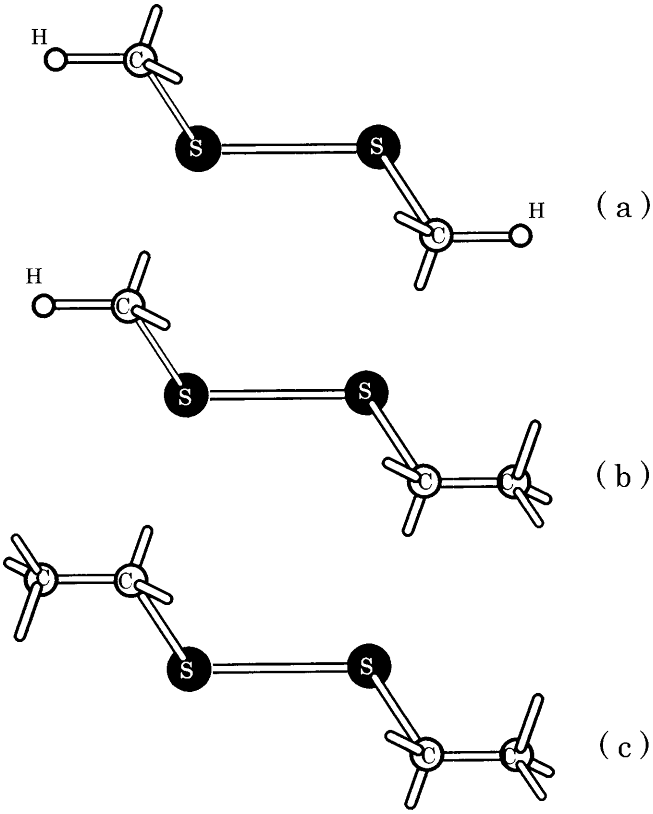


Fig. 1 Schematic models of possible three conformations: **a** type (H, H), **b** type(H, C) and **c** type(C, C) about the S–S bond

For di-primary-alkyl disulfides [16], two ν_{SS} stretch bands coming from the two conformers [type (H, H) and type (H, C)] were observed in the liquid state, indicating that the gauche–gauche–gauche (GGG) and the trans–gauche–gauche (TGG) forms for the CH_2–S–S–CH_2 segment coexist.

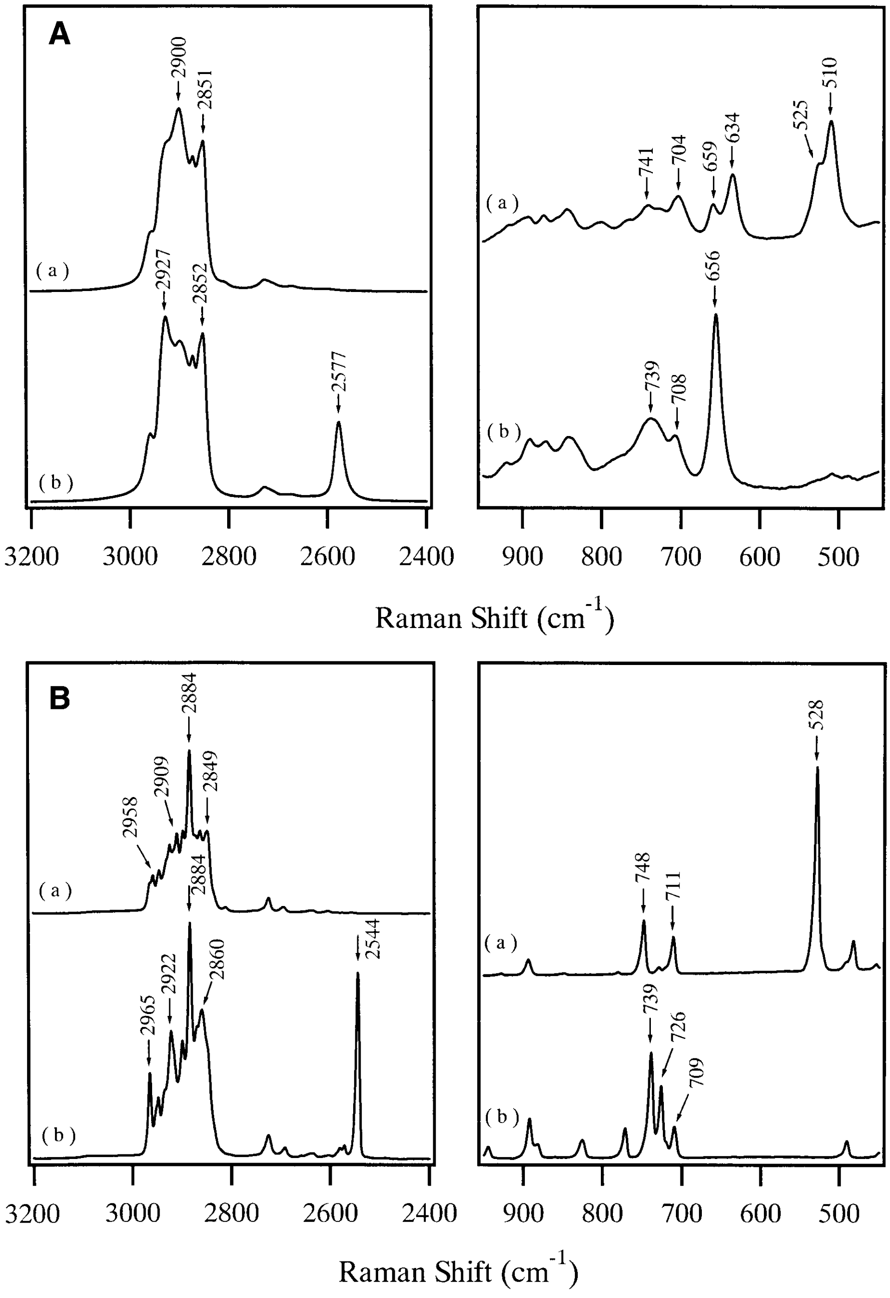
Sugeta et al. [16] made a detailed examination of the vibrational spectra of diethyl disulfides in the liquid state and suggested that for the CH_2–S–S–CH_2 segment a strong Raman band at 508 cm^{-1} may be assigned to the ν_{SS} mode of the GGG form and the band at 523 cm^{-1} may arise from the TGG form.

In the present study, the Raman spectra for di-*n*-alkyl disulfides with longer alkyl (*n*-hexyl, *n*-octyl, *n*-decyl and *n*-dodecyl) chains in the liquid state and in the solid state have also been examined. A representative Raman spectrum of di-*n*-octyl disulfide is shown in Fig. 2, and the characteristic bands of the S–S and C–S stretch modes, which have been observed in common for these longer di-*n*-alkyl disulfides, are listed in Table 3 together with the S–H and C–S stretch bands characteristic of *n*-octylthiol. For these di-*n*-alkyl disulfides, two Raman bands at 510–512 and 525–528 cm^{-1}, which closely correspond to the Raman bands of di-*n*-propyl (or diethyl) disulfides at 508–510 and 523 cm^{-1}, respectively, have been observed in liquid samples at room temperature and were assigned to the GGG and TGG forms for the CH_2–S–S–CH_2 segment, respectively. For the Raman spectra of these di-*n*-alkyl disulfides in the solid state (Fig. 2b), Raman bands were observed only at 525–528 cm^{-1}, indicating that the TGG form is predominantly stabilized in the solid state.

In the Raman spectra of these liquid samples, bands at 634–635, 658–659 and 703–705 cm^{-1} are observed in common. We may assign these bands to the C–S stretch modes coupled with the C–C stretch modes arising from some rotational isomers.

For primary alkyl disulfide groups, the frequency of the ν_{SC} mode strongly depends upon the molecular conformations about the C–C bonds adjacent to the C–S bond [16], similar to the C–Cl stretch frequencies of alkyl chlorides [17]. In particular, a species of the atom (*X*), which is in a trans position with respect to the sulfur atom (*X*–C–C–SS), strongly affects the frequency of the ν_{CS} mode [15]. For the conformation with $X = H$ (P_H type), we expect that the ν_{CS} value should lie at 630–670 cm^{-1}, whereas for that with $X = C$ (P_C type), it should lie at 700–745 cm^{-1}. In fact, in the Raman spectra of di-*n*-propyl sulfide [16], bands at 630, 656, 703 and 731 cm^{-1} were observed, and the two bands at 630 and 656 cm^{-1} were assigned to the

Fig. 2 Raman spectra of di-*n*-octyl disulfide (*a*) and *n*-octyl-1-thiol (*b*) at **A** room temperature and **B** 77 K



ν_{CS} modes of the P_H-type conformation and those at 703 and 731 cm^{-1} to those of the P_C-type conformation. Thus, the first two bands (634–635 and 658–659 cm^{-1}) may arise from the H-type conformation while the last one (703–705 cm^{-1}) arises from the P_C-type conformation.

Raman spectra of poly(MCP) and SSP

For the Raman spectra of the solid poly(MCP) and SSP samples, bands characteristic of the S–H, S–S and C–S single bonds are listed in Table 3. In the spectrum of poly(MCP), the Raman band at 2,568 cm^{-1} is assigned to the S–H stretch (ν_{SH}) mode. The bands at 653 and 694 cm^{-1} may be assigned to the ν_{CS} modes of the CH_2–CH_2–SH segment. We may assign the two bands at 512 and 521 cm^{-1} to the ν_{SS} modes of the SSP polymer, which was produced in the polymerization process of McPTS.

In the Raman spectrum of the SSP sample, the band corresponding to the 2,568 cm^{-1} band of poly(MCP) was not observed, indicating that the S–H groups were consumed in formation of the S–S bonds. The band at

Table 3 Band frequencies, ν_{SS} and ν_{CS}, of dialkyl disulfides. Dihexyl disulfide: *DHeD(S–S)*; dioctyl disulfide: *DOcD(S–S)*; didecyl disulfide: *DDeD(S–S)*; didodecyl disulfide: DDoP(S–S); diethyl disulfide: *DED(S–S)*

Characteristic band		DHeD(S–S)			DOcD(S–S)			DDeD(S–S)			DDoD(S–S)			DED(S–S)[a]	
ν_{SS}	25 °C	512		525	510		525	511		525	511		525	–	523
	−170 °C	–		528	–		528	–		527	–		526	509	–
ν_{CS}	25 °C	634	659	703	634	659	704	635	658	704	635	659	705	642	668
	−170 °C	–	–	712	–	–	711	–	–	710	–	–	708	641	–

[a] Data cited from Ref. [16]

509 cm^{-1} and shoulder band at about 520 cm^{-1} may be assigned to the ν_{SS} modes coming from the CH_2–S–S–CH_2 segments, which were formed in the SSP sample. On the basis of the Raman spectral data of the various di-*n*-alkyl disulfides described earlier, we may assign the bands at 509 and 520 cm^{-1} to the GGG and TGG forms of the CH_2–S–S–CH_2 segment, respectively. The intensity of the 509 cm^{-1} band is greater than that of the 520 cm^{-1} band, indicating that the GGG form is preferentially stabilized in the solid sample.

The Raman band at 634 cm^{-1} closely corresponds to the Raman band at 642 cm^{-1} for diethyl disulfide and the band at 630 cm^{-1} for di-*n*-propyl disulfide; thus, this band may be assigned to the ν_{CS} mode of the GGG form for the CH_2–S–S–CH_2 segment. The presence of a very broad band at 692 cm^{-1} may imply that the P_C-type conformation is induced by formation of the S–S-bridged structure.

We may emphasize that a marked difference in the spectral feature of the CH stretch region between poly(MCP) and SSP exists. For poly(MCP), four Raman bands, at 2,865, 2,889, 2,922 and 2,975 cm^{-1}, were clearly observed; however, formation of the disulfide bond brings about the disappearance of the bands at 2,889 and 2,922 cm^{-1} and the appearance of a broad band at 2,908 cm^{-1}. Simultaneously, it was also found that the bands at 2,865 and 2,975 cm^{-1} were reduced to very weak shoulders. In fact, it was found that the spectral feature of the SSP polymer in the CH stretch region is very similar to that of a dilute aqueous poly(APS) sample [14], indicating that formation of the S–S bridge induces an increase in the populations of bent or cyclic structures in the mercaptopropyl segment.

In a previous report [14] on the Raman spectra of aqueous poly(APS) siloxane samples we showed that the Raman spectral features in the CH stretch region change markedly upon dilution, resulting from an increase in the populations of rotational isomers (TG or GG or GG′ about the propyl segment) other than the TT form. Therefore, in the case of the SSP polymer, we may assume that formation of the CS–SC structure brings about an increase in the populations of rotational isomers other than the all-trans form about the segment.

Raman spectra of copoly(MCP–APS) and SSCP polymers

The Raman spectra of the solid copoly(MCP–APS) sample were been examined and the characteristic S–H and C–S bands are listed in Table 3. It is evident that the bands at 2,568–2,573 cm^{-1} arise from the S–H stretch mode of the $CH_2CH_2CH_2SH$ segment and that those at 3,303–3,311 and 3,358–3,370 cm^{-1} arise from the NH_2 stretch of the aminopropyl segment of poly(APS). The Raman bands at 510–511 and at about 520 cm^{-1}, observed in common for copoly(MCP–APS), can be assigned to the S–S stretch bands for the spectra of the copolymer, implying the existence of the S–S-bridged structure which was already formed during the polymerization of McPTS. The band at 635 cm^{-1} may also be assigned to the ν_{CS} mode of the CS–SC segment; however, the 652 cm^{-1} band may contain a large contribution from the ν_{CS} mode of the unreacted CH_2SH groups.

The SS and CS characteristic bands, which were observed in the Raman spectra of the SSCP copolymer, are listed in Table 3. We may note that the characteristic bands of the CH_2SH group at 2,568–2,573 cm^{-1} and the 652 cm^{-1} band also disappear or decrease in intensity and that the Raman bands at 510–512 cm^{-1} are intensified, indicating the formation of S–S bonds, even in the copolymer. In particular, it has been confirmed that formation of the S–S disulfide bond induces a broadening of the NH_2 stretch bands. In the Raman spectra of the SSCP copolymers in the NH_2 stretch region, it was found that Raman bands, which correspond to the bands at 3,303–3,311 and 3,358–3,365 cm^{-1} for copoly(MCP–APS), disappeared, implying that the NH_2 stretch bands were broadened too much for them to be detected. Thus, we may expect that the 3-amino- and 3-mercaptopropyl segments should be very flexible in the reaction mixtures of the copolymers. Accordingly, formation of the S–S bridge structure probably results in an increase in proximity between these segments, changing the environment of the NH_2 groups by enhancing the rigidity of the hydrogen-bonded structure between them [14].

We stress that formation of the disulfide structure changes the environment of the propyl segments. When we compare the CH stretch Raman bands of the copoly(MCP–APS) with those of the SSCP polymer, we find that the band at about 2,860 cm^{-1}, observed in common for copoly(MCP–APS), becomes very weak in intensity and the spectral feature in this region closely resembles that of dilute aqueous polyAPS [14]. This fact may imply that S–S bridge formation induces an increase in the population of the gauche conformers of the propyl segment.

Raman scattering spectra of MCP- and MCP–APS-modified SMBS particles and the formation of an S–S-bridged structure

The Raman spectra of the MCP-modified SMBS samples are shown in Fig. 3. On the basis of the assignment of the Raman bands of related compounds, described earlier, some of the bands can be easily assigned, and we can use these Raman bands in the discussion of the surface structure of these MCP-modified particles.

The Raman band at 2,584 cm^{-1}, which was observed in common, is ascribed to the ν_{SH} mode of the SH groups, and the bands at 652 and 685 cm^{-1} may be assigned to the ν_{CS} modes of the 3-mercaptopropyl segments, indicating that these segments are modified onto the SMBS-surface. It should be noted that the Raman spectral feature in the CH stretch region depends upon the concentration of the MCP segments bound onto the surface (discussed in detail later).

The Raman spectra of the S–S-bridged SMBS complex systems are shown in Fig. 4. It is evident that the formation of the S–S-bridged structure brings about the disappearance of the ν_{SH} band at 2,584 cm^{-1} and the ν_{CS} band at 652 cm^{-1} and the appearance of the bands at 633, 520 and 510 cm^{-1}, indicating that S–S disulfide bonds are formed on the surface of these SMBS complex particles.

The Raman spectra of the MCP–APS-modified SMBS and of their S–S-bridged complex systems are shown in Figs. 5 and 6. For the spectra of the MCP–APS-modified SMBS (Fig. 5), the ν_{SH} band at 2,583 cm^{-1} and the ν_{CS} band at 652 cm^{-1}, characteristic of the mercaptopropyl segment, are observed in common, indicating that the MCP segments are bound onto the surface of the SMBS particles. Furthermore, in these Raman spectra, bands at 3,313 and 3,370 cm^{-1} are also found in common and should be ascribed to the symmetric and antisymmetric stretch modes, respectively, of the NH_2 group. This assignment is based on the Raman spectral data of the APS-modified silica gel [10], and provides ample evidence for the existence of the aminopropyl segments on the SMBS particles. These results reveal that the MCP and APS segments coexist on the surface of the particles. As shown in Fig. 6, upon formation of the S–S-bridged structure, the ν_{SH} and ν_{CS} bands disappear and the characteristic ν_{SS} and ν_{CS} bands at 506–520 and 634 cm^{-1} of the CS–SC segment weakly appear. Therefore, it may be assumed that the formation of the S–S-bridged structure occurs on the surface of an MCP–APS–SMBS particle; however, a small number of the SH groups probably remain unreacted on the surface of the MCP–APS-modified particles, since extremely weak bands at about 2,583–2,585 cm^{-1} and a shoulder

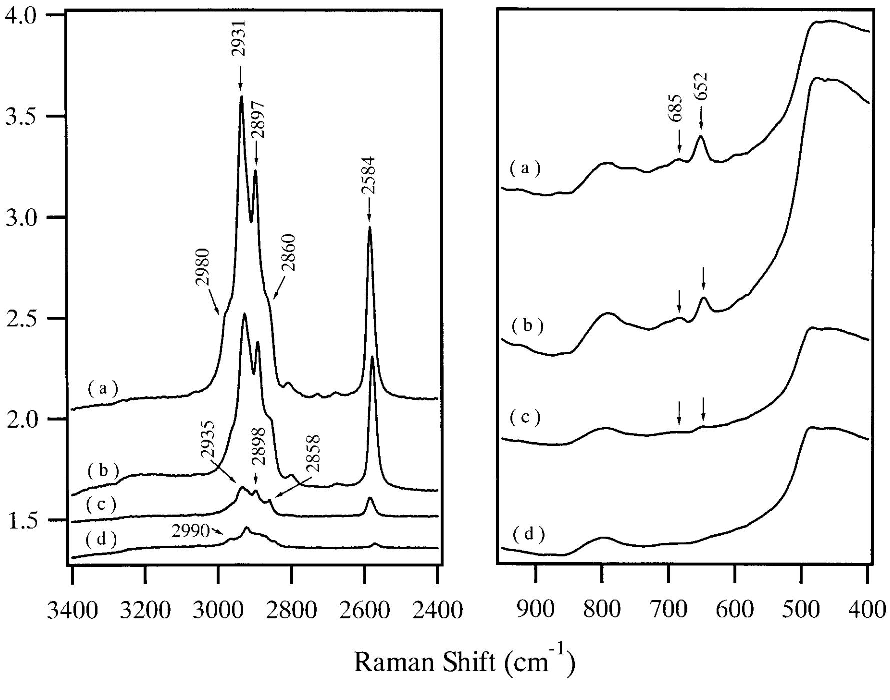


Fig. 3 Raman spectra of the SI samples: SMBS3 (*a*), SMBS6 (*b*), SMBS7 (*c*) and SMBS9 (*d*)

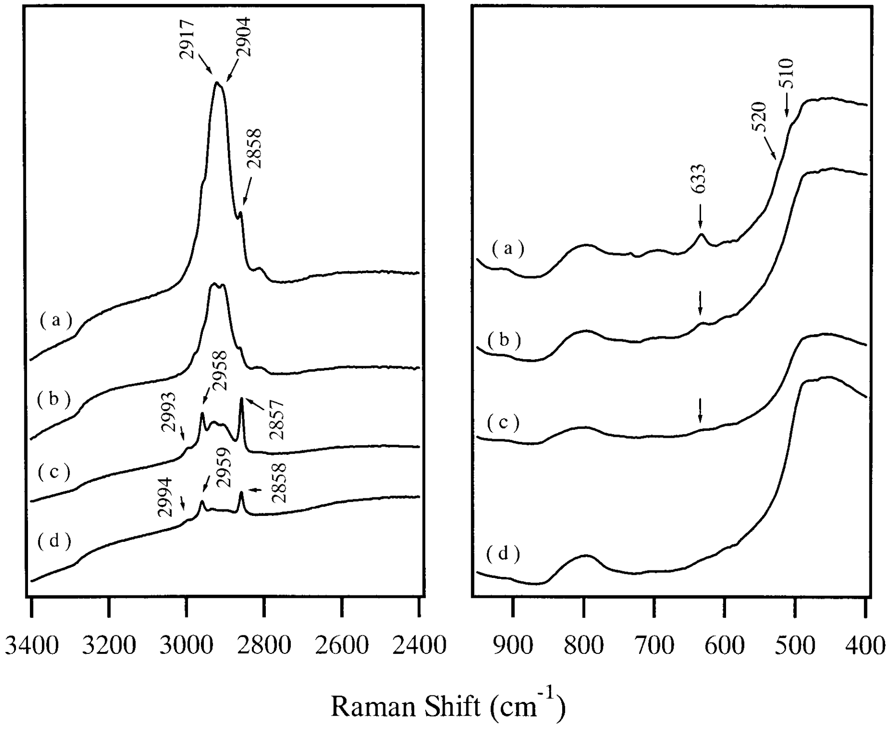


Fig. 4 Raman spectra of the S–S-bridged SI samples: (SS)SMBS3 (*a*), (SS)SMBS6 (*b*), (SS)SMBS7 (*c*) and (SS)SMBS9 (*d*)

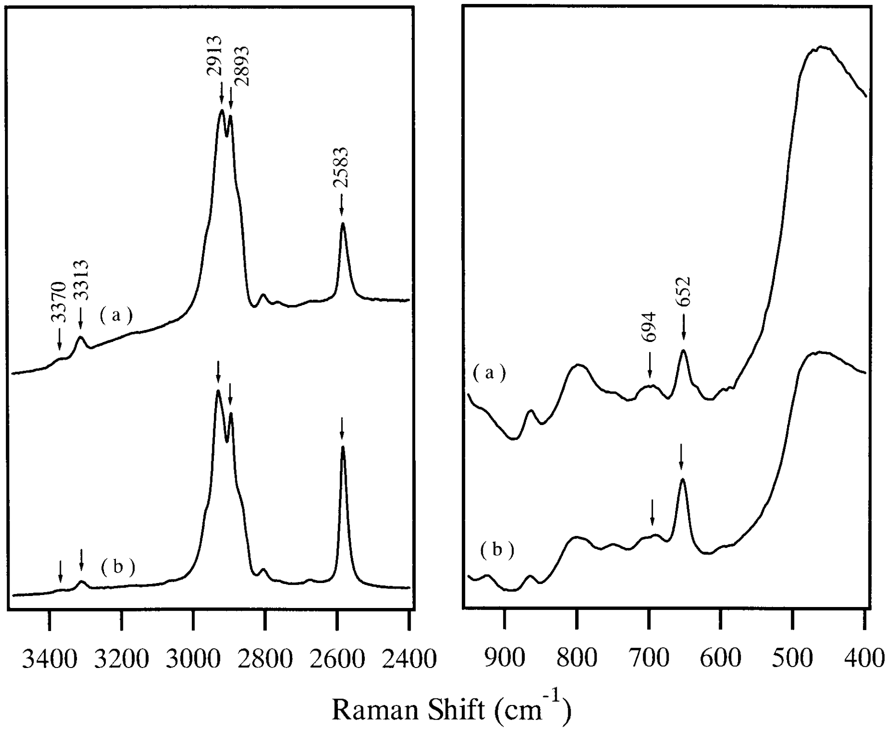


Fig. 5 Raman spectra of the (3-mercaptopropyl)siloxane (*MCP*)–(3-aminopropyl)siloxane (*APS*)-modified supermicro bead silica gel B-10 (*SMBS*) systems: SMBS(S1N1) (*a*), SMBS(S4N1) (*b*)

band at about 650 cm^{-1} are still apparent in the Raman spectra of these samples.

The Raman spectral feature in the CH stretch region depends upon the concentration of the MCP segments modified onto the SMBS particles. In the spectra of concentrated MCP-modified samples (Fig. 3), predominant Raman bands at 2,897 and 2,931 cm^{-1} are observed, in addition to shoulder bands at about 2,860

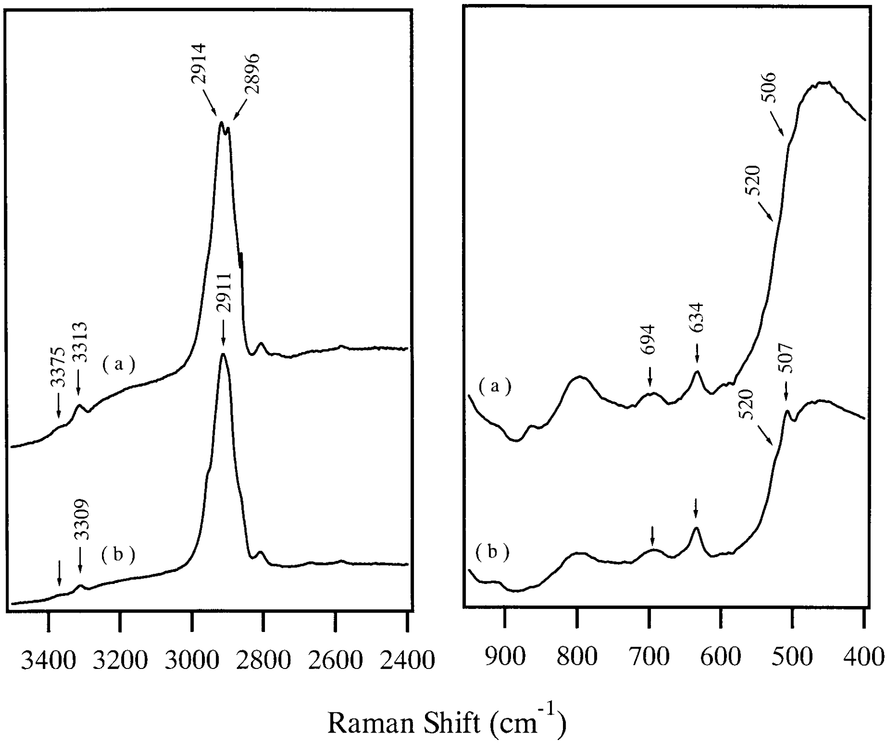


Fig. 6 Raman spectra of S-S-bridged MCP–APS-modified SMBS systems: (SS)SMBS(S1N1) (*a*), (SS)SMBS(S4N1) (*b*)

and 2,980 cm^{-1}; however, in the spectra of dilute MCP-modified samples, the band at 2,897 cm^{-1} becomes very weak in intensity, while a new band at 2,990 cm^{-1} appears. This observation reveals that for a mercaptopropyl segment the population of the conformations containing the gauche form with respect to the $SCH_2CH_2CH_2Si$ segment probably becomes predominant, a judgment based on the Raman spectral results for the interaction of APTS on silica gel [13].

In particular, we note that S–S bridge formation induces a marked variation in the CH stretch spectral feature, as shown in Fig. 4. When the S–S bridges are formed on the surface of the concentrated MCP-modified SMBS system, predominant Raman bands at 2,897 and 2,931 cm^{-1} disappear and bands at 2,904 and 2,917 cm^{-1} first appear, followed by a shift of the latter bands to 2,925 cm^{-1}, while the position of the former band remains unchanged. However, for extremely dilute MCP-modified samples, very sharp and strong Raman bands at 2,857–2,858 and 2,958–2,959 cm^{-1} appear upon formation of the S–S bridge structure. Furthermore, bands at 2,993–2,994 cm^{-1}, which were not observed for concentrated MCP-modified samples, newly appear. Thus, the Raman spectral feature approaches that of dilute aqueous APS–water samples [14], revealing that S–S bridge formation strongly induces an increase in the population of the conformers containing the gauche form.

As shown in Fig. 7, S–S bridge formation gives liquidlike properties to the spectral feature in the CH stretch region, but does not affect markedly the environment in the hydrogen-bonding system, since Raman bands at 3,309–3,313 and 3,370–3,375 cm^{-1} are still observed. The MCP and APS segments bound onto the surface of the SMBS particles are likely to be fixed through siloxane bonds on the surface, bringing about a decrease in the rigidity and flexibility of these segments. In the case of the MCP–APS-modified SMBS particles, since an increase in proximity between these segments does not occur, S–S bridge formation probably occurs independently of the APS segments and therefore does not affect the NH_2 environment of these segments.

DRIFT spectra of MCP and MCP–APS-modified SMBS particles

The effect of S–S bridge formation on the structure of an MCP- or MCP–APS layer coated onto the surface of silica gel has been evaluated by using DRIFT spectra.

The CH stretch band features of MCP-modified samples are compared with those of S–S-bridged samples in Fig. 7. As the concentration of MCP modified onto the surface of SMBS particles decreases, the intensities of the bands at 2,859 and 2,984 cm^{-1} become stronger. This observation closely corresponds to that seen in the Raman spectral data (Fig. 5) and supports the conclusion that in the dilute MCP-modified sample, the rotational isomers of the propyl segments with gauche forms (that is, bent or cyclic structures) are

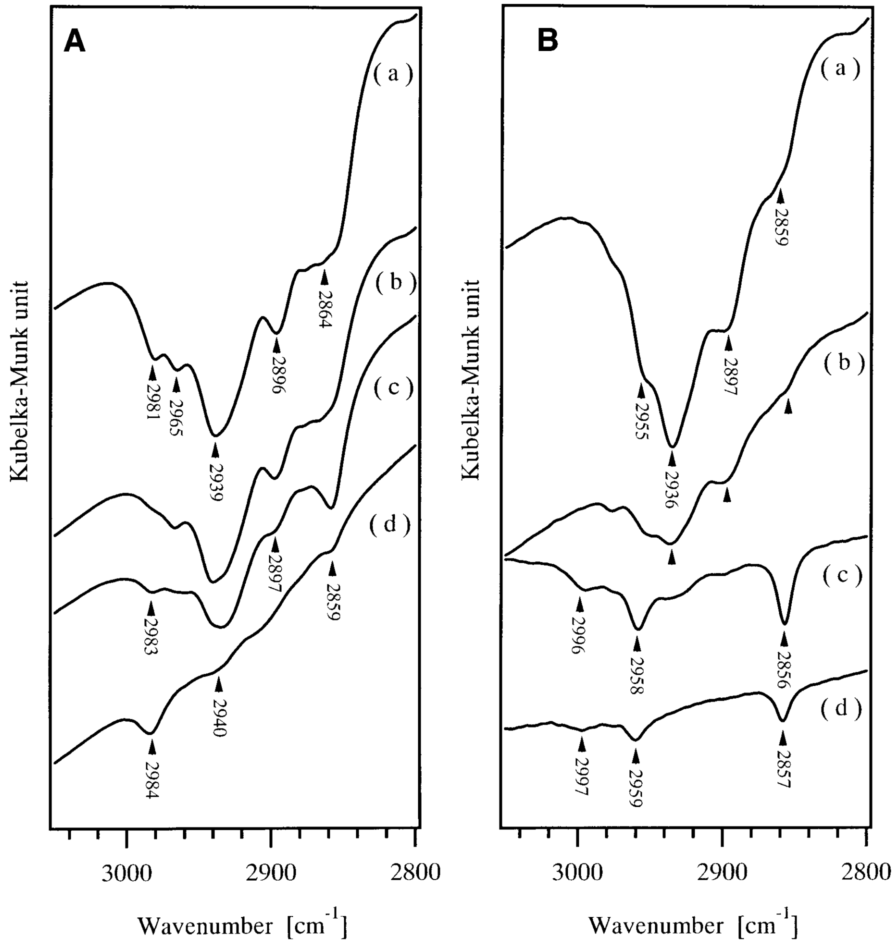


Fig. 7 Diffuse reflectance Fourier transform spectra of **A** the SI samples SMBS3 (*a*), SMBS6 (*b*), SMBS7 (*c*) and SMBS9 (*d*) and **B** the SS bridged SI samples (SS)SMBS3 (*a*), (SS)SMBS6 (*b*), (SS)SMBS7 (*c*) and (SS)SMBS9) (*d*)

predominantly stabilized. Furthermore, formation of the S–S bridge structure on the surface of the MCP–SMBS particles markedly changes the spectral feature of the CH stretch region in the DRIFT spectra, as shown in Fig. 7b. It is evident that a decrease in the concentration of the MCP segment results in an increase in intensity for the bands at 2,856–2,856, 2,959–2,955 and 2,996–2,997 cm^{-1}, supporting the results obtained from the Raman spectral data.

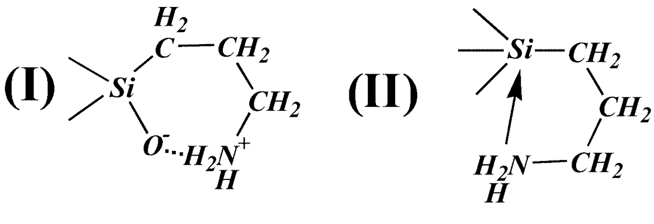
Similar observations were made in the DRIFT spectra of MCP–APS-modified SMBS particles.

Discussion

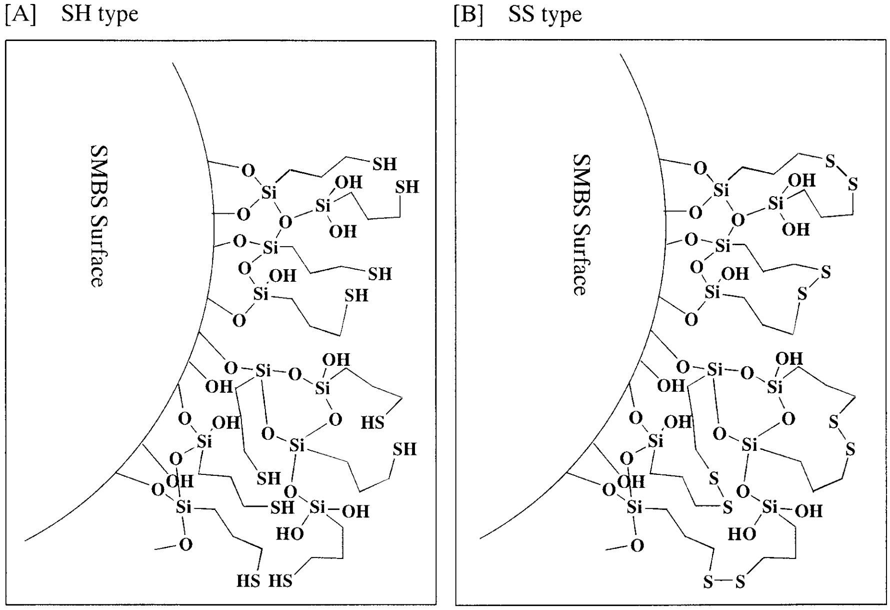
In previous work [14], the Raman spectra of poly(APS) in the solid and gel phases and in aqueous solution were investigated in detail. The results showed that there is preferential stabilization of the bent or cyclic structures of the aminopropyl segments resulting from the $NH_2 \rightarrow NH_3^+$ conversion at lower concentrations and lower pH. It was found that the Raman spectral behavior (in particular, in the CH stretch region) of poly(APS) is very similar to that of the SSP and SSS samples in the present study.

Evidence for a cyclic structure of the aminosilane layer has already been studied by many investigators. Plueddeman [18] proposed models of five- or six-membered rings in which the nitrogen atoms interact with either the Si atom or one of the SiOH groups. Boerio et al. [19] proposed two ring structures (I and II, Scheme 1) for an aminosilane layer coated onto the surface of electropolished metal.

Anderson et al. [20] found electron spectroscopy for chemical analysis (ESCA) evidence for the existence of a protonated amine in an aminosilane layer coated onto a



Scheme 1



[A] SH type

[B] SS type

Fig. 8 A possible schematic structure of **A** MCP-modified SMBS and **B** its S–S-bridged SMBS

silicone wafer. Moses et al. [21] proposed the existence of two six-membered ring models, containing either the $SiO^{-}\cdots NH^{+}H(R)$- or $SIOH\cdots NH(R)$ bonding structure, using results from an ESCA study of aminopropylsilane layers deposited onto the surface of an electrode.

Ishida et al. [22] investigated the FTIR and Raman spectra of APTS and its analogs in aqueous solution and in the solid state and concluded that the residual SiOH groups are strongly hydrogen-bonded to the amino groups in the form of $SiOH\cdots NH_2$, rather than as $SiO\cdots NH_3^+$.

When the mercaptopropyl segments of the poly(MCP) chains form an S–S bridge structure, it may be expected that the propyl segments of the MCP moieties should take up sterically bent structures involving gauche forms, as shown in Fig. 8. It has been established that the CH stretch modes of a polymethylene chain containing gauche forms appear at a higher frequency compared with those of extended polymethylene chains [14]. In particular, for compounds involving cyclic polymethylenes [23], the CH stretch modes of the CH_2 groups are usually found at a higher frequency, near 3,000 cm^{-1}; thus, if the formation of the S–S bridge structures occurs within the MCP segments, a cyclic structure should be reflected in the band frequency of the CH stretch modes.

In previous studies [13, 14] of the DRIFT and Raman spectra of aminopropylsilane-modified silica gel sample, the IR bands at 2,957 and 2,992 cm^{-1} and the corresponding Raman bands at 2,958–2,960 and 2,996 cm^{-1} were assigned to the CH stretch modes characteristic of a cyclic hydrocarbon structure, since corresponding IR and Raman bands have also been found for cyclic compounds such as butyrolactone and 2-pyrolidone [23].

Therefore, the bands at 2,958–2,959 and 2,993–2,994 cm^{-1}, for the Raman spectra of S–S-bridged dilute MCP-modified silica gel and the corresponding IR bands at 2,958–2,959 and 2,996–2,997 cm^{-1} in the DRIFT spectra of the same samples may be assigned to a cyclic structure formed on the surface of an SMBS particle. It has been confirmed that S–S bond formation induces bent or cyclic structures on the surface of an SMBS particle.

The numbers of 3-mercaptopropyl or 3-aminopropyl segments bound onto the surface of an SMBS particle, evaluated from the sulfur or the nitrogen content, are also listed in Table 1. We may assume that all silanol groups belonging to the SMBS particle were consumed by the reaction between the silanol and hydrolyzed silane, implying that silane layers thicker than a bilayer are formed on the surface.

Cyclic structures with various sizes, formed by S–S bridge formation, are shown in the schematic models of the surface structure (Fig. 8). It is seen that if we were to change the length of a polymethylene chain $[(CH_2)_n]$ in the molecular design of a silane coupling agent, we could control the size of the cyclic structure, thus leading to a change in the characteristics of the material.

Conclusion

3-Mercaptopropylsilane layers coated onto the surface or interface of reinforced materials may be converted to organosilane layers involving S–S bridge structures, which induce a bent or ring structure between side-chain segments. The size of the bent or ring structure may be controlled by changing the methylene number of the hydrocarbon portion.

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