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ORIGINAL CONTRIBUTION

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Raman scattering study of polyaminopropylsiloxane and its compounds for characterization of 3-aminopropylsilane-modified silica gel. Utility of the CH_2 rock and skeletal stretch modes

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Abstract The Raman scattering spectra for polyaminopropylsiloxane (poly-APS) samples in the solid state and in aqueous solution and for the related compounds, γ-aminobutyric acid (GABA) and its hydrochloride salt (GABA · HCl), have been examined in the CH_2 rock and skeletal stretch region. The Raman spectrum of the solid poly-APS sample may be accounted for by direct combination of the Raman spectra for GABA and GABA · HCl, whose crystal structures have been elucidated by a single-crystal X-ray diffraction study, suggesting that the APS segments of poly-APS in the solid state are in a conformationally ordered state. It has also been found that the Raman spectra of the solid and aqueous poly-APS samples in this region are useful for diagnosing the conformations of APS moieties bound onto the surface of silica gel.

Key words Raman – polyaminopropylsiloxane – GABA – CH_2 rock and skeletal stretch

Introduction

Extensive studies have been made to try and elucidate the structure of the aminopropyl silane layer bound onto the surface of substrates. In particular, it has been recognized that vibrational spectroscopic methods are a powerful tool for investigating the chemical structure and interaction of a silane layer bound onto surfaces [1–13].

Following the pioneering study of Shih et al. [5] on the molecular structure of aminosilanes using laser Raman spectroscopy, Ishida et al. [8] utilized a combination of FTIR and laser Raman spectroscopy in order to study the structures of amine and silanol groups in greater detail.

Davis et al. [12] studied silylation reactions of the surface of silica using laser Raman spectroscopy and demonstrated that the implementation of organosilane synthetic routes for surface modification can be monitored at near-monolayer resolution.

Recently, we have reported a Raman scattering study of the kinetics of interaction of 3-aminopropyltriethoxy silane on silica gel [14], for the silica gel samples prepared by sequentially sampling the substrate from the reaction vessels at various short-time intervals. The results revealed that time-dependent variation of the ν(CH) band intensity is followed by reaction of APTS with the silica gel and that the reaction induces local conformational changes of bound aminopropyl segments.

The conformation of aminopropylsilyl moieties coated onto the surface plays an important role in the reinforcement mechanism of silane-modified materials. However, such conformational studies are rare. Lippert et al. [15] investigated the Raman-active vibrations of long-chain fatty acids in detail, and elucidated the Raman bands which were sensitive to conformationally ordered or

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disordered states. Rosenholm et al. [16] successfully used the Raman bands in the 1000–1200 and 2800–3000 cm^{-1} region to discuss the hydrocarbon structure of short-chain carboxylates (C_1–C_8) in the micellar state. In our preceding papers [17–19], which discuss the properties of a homologous series of sodium *n*-alkylsulfates and potassium *n*-alkylcarboxylates, we demonstrated that the all-trans form of the hydrocarbon chain is preferentially stabilized upon micellization.

In the present study, the Raman spectra of poly-aminopropylsiloxane (poly-APS) in the solid state and in aqueous solution have been measured in the 700–1100 cm^{-1} region, which is sensitive to the conformational change of a hydrocarbon chain. In order to assist the assignment of Raman bands of poly-APS in this region, it was necessary to record the Raman spectra of γ-aminobutyric acid (GABA) and its hydrochloride salt under our experimental conditions, although these spectra have been reported by Tanaka et al. [20]. The crystal structures of GABA and its hydrochloride salt have been elucidated by a single-crystal X-ray diffraction study [21, 22] and the skeletal structure of GABA is quite different from that of its hydrochloride salt. Therefore, this difference in conformation should be reflected in the Raman bands in the CH_2 rock and skeletal stretch region. Accordingly, the Raman spectra of these related compounds assist us in understanding not only the origin of the Raman bands of poly-APS but also that of aminopropylsilane-modified silica gel.

Experimental

Materials

3-Aminopropyltriethoxy silane (APTS) was purchased from Shinetsu Chemical Industry Ltd., and was used without purification for the reaction with the silica gel and for preparation of poly(3-aminopropyl) siloxane. Super Micro Bead Silica Gel B-5 (SMBS), with a particle size distribution of $d_{10}/d_{90} = 1.5$, average particle diameter 5 μm, and pore diameter $\phi = 5.5$ nm, was purchased from Fuji Silysia Chemical Co.

Poly(3-aminopropyl) siloxane (poly-APS) was synthesized as follows. Distilled water (1.2 g) was added to APTS (5 g), and the reaction mixture was stirred for 24 h. The products of condensation (water and ethanol) were removed by evaporation until the IR bands for ethanol could no longer be detected. The solid poly-APS thus obtained was dried over P_2O_5 in a desiccator.

γ-Aminobutyric acid (GABA) was purchased from Tokyo Chemical Industry Co., Ltd., and was used without purification. GABA hydrochloride (GABA · HCl) was synthesized as follows. Hydrogen chloride ethyl acetate solution (4 mol l^{-1}, 25 ml) was added to GABA (5 g) and was stirred for 12 h. The mixture was evaporated and the products were washed and dried.

SMBS samples modified with APTS were prepared as follows. SMBS (40 g) in toluene (120 ml) was refluxed with stirring at 423 K. APTS was added to the preheated SMBS–toluene mixture, and refluxed for 6 h with stirring (under these conditions the reaction was completed). The concentration of APTS in the reaction mixture was varied over four concentrations within the range 0.72–0.19 mol l^{-1}. The SMBS–APTS–toluene mixture, separated from the reactor, was washed with methanol so as to quench the reaction. The unreacted ethoxy groups in the substrate were hydrolyzed in water–methanol (1 : 1) solution for 2 h at room temperature. The APTS-modified SMBS was again washed with methanol and dried at 388 K under vacuum. Thus, four samples modified with different APTS-concentrations were prepared (samples SI, SII, SIII and SIV). A sample of SMBS treated under the same conditions but in the absence of APTS was also prepared (sample S_0, control). These samples can be regarded as APS–SMBS complexes prepared under equilibrium conditions.

Method

Raman spectra were recorded with a Nicolet 950 Fourier transform Raman spectrometer (4000–150 cm^{-1}) using a Nd : YAG laser (CVI) excitation wavelength of 1064 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 and weak bands. The Raman spectra of the samples were obtained from pressed solid samples in a capillary tube with a laser power of 440 mW.

A Yanaco CN Coder MT 600 was used for elemental analysis of the samples. The concentration of APTS which had reacted with the silica gel was determined by analyzing the nitrogen (or carbon) content of the samples. The error of estimate was ± 0.3%. The nitrogen content data of the samples are listed in Table 1.

Table 1 Concentration of bound-APS (C (APS, μmol m^{-2}) determined by nitrogen content

Samples	C (APS, μmol m^{-2})
SI	3.36
SII	1.81
SIII	1.01
SIV	0.74

Results and discussion

Raman scattering spectra of poly-aminopropylsiloxane and its related compound (γ-aminobutyric acid)

The vibrational modes characteristic of the NH_2 (or NH_3^+) group in the 1500–1650 cm^{-1} region have previously been used successfully in discussion of the interaction of aminopropylsilane on a silica gel surface, and some important models have been proposed for the interaction between NH_2 and SiOH groups. Plueddemann proposed that NH_2 groups coordinated to the silicon atom to form cyclic inner complexes [23]. Moses et al. [24] suggested an internal hydrogen bonded six-membered ring structure for the aminosiloxane–water system, while Chiang et al. [7] also used a proton transfer model to propose the formation of an $SiO^- \cdots H \cdots NH_2^+$ group with a cyclic ring structure.

The formation of such a cyclic structure in an aminosiloxane solution or in the aminopropylsilane–silica gel system should be reflected in the CH stretch, CH_2 rock and skeletal stretch modes [25].

In the present study, we have assigned the bands in the Raman spectra of polyaminopropylsiloxane and its related compounds (GABA and GABA · HCl), and have discussed the CH_2 rock and skeletal stretch modes with respect to the conformation of the aminopropyl segment.

Within the vibrational spectra of polyaminopropylsiloxane in this region, a strong IR band at 1016 cm^{-1} and a strong Raman band at 1017–1025 cm^{-1}, arising from low molecular weight silane, are observed [7]. However, the corresponding Raman band in a sample of completely cured polyaminopropylsiloxane is weak [7] and we may therefore assume that the CH_2 rock and skeletal stretch modes of aminopropyl segments are the predominant contributors to this region.

Figure 1A shows the Raman spectrum of poly-APS in the solid state in the 400–1800 cm^{-1} region and assignment of the observed band frequencies is listed in Table 2. The spectrum for APTS in the liquid state is shown in Fig. 1B and assignment of the bands in this spectrum is given below. The present discussion concentrates on the 800–1100 cm^{-1} region in Fig. 1A which mainly reflects the CH_2 rock and skeletal stretch modes of the *n*-propyl segment [15, 26]. The Raman bands at 997, 1010, 1026 and 1074 cm^{-1} may be assigned to the mixed modes of skeletal C–N stretch and C–C stretch for the APS segment. The probable assignment of the bands at 866, 937 and 963 cm^{-1} is to modes of CH_2 rock heavily mixed with skeletal stretch. We may assume that these Raman bands reflect the conformationally ordered APS segments which are characteristic of solid poly-APS.

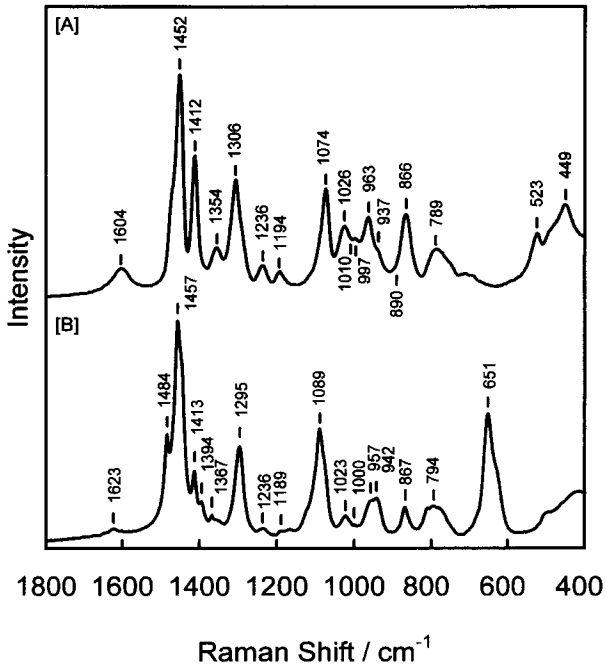

Fig. 1 Raman scattering spectra of polyaminopropylsiloxane in the solid state (A) and 3-aminopropyltriethoxysilane in the liquid state (B)

Table 2 Observed Raman band frequencies for solid poly-APS, GABA and its hydrochloride salt in the crystalline state

GABA (gauche–trans)	GABA · HCl (trans–trans)	Poly-APS	Assignment[a]
		1604	NH_2 bend
1448	1448	1452	CH_2 bend
1400	1404	1412	$Si–CH_2$ bend
1342		1354	CH_2 wag
1313	1309	1306	CH_2 twist
		1236	
		1194	
1066	1072	1074	Skeletal stretch
1028		1026	
1009	1013	1012	
995		997	
	982		
	958	963	Skeletal stretch + CH_2 rock
		937	
885	887	890	
868		866	

[a] Based on assignments made in ref. [7].

Figure 2 shows the concentration dependence of the Raman spectrum for polyaminopropylsiloxane in aqueous solution. For the concentrated sample solutions, Raman bands at 866, 968, 997, 1007 and 1074 cm^{-1} correspond

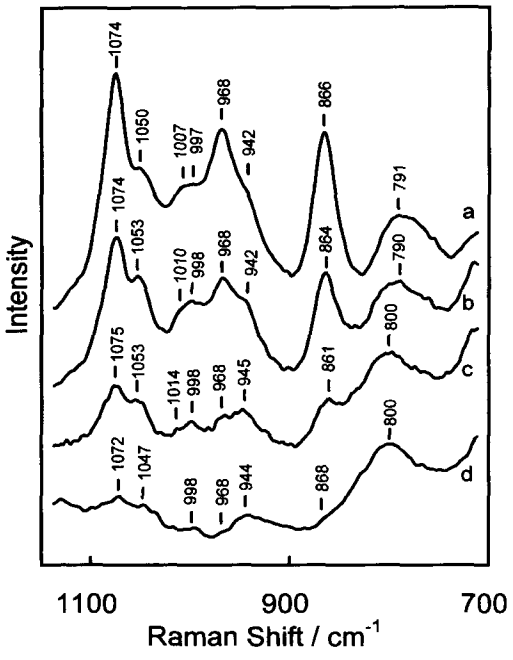

Fig. 2 Concentration dependence of the Raman scattering spectrum of polyaminopropylsiloxane–H_2O solution (a 50 wt%; b 17 wt%; c 6 wt%; d 2 wt%) in the 700–1100 cm^{-1} region

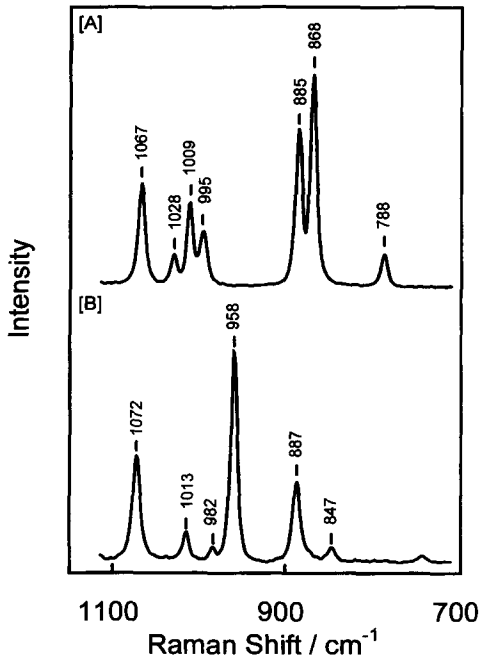

Fig. 3 The Raman scattering spectra of GABA (A) and GABA · HCl (B) in the 700–1100 cm^{-1} region

well in frequency to the bands for the solid poly-APS, at 866, 963, 997, 1010 and 1074 cm^{-1}, respectively. This result shows that the conformations of the *n*-propyl segments which are characteristic of solid polyaminopropylsiloxane are stabilized even in aqueous solution. However, the band at 1050 cm^{-1} is not found in the Raman spectrum of the solid sample, while the 942 cm^{-1} band, corresponding in frequency to the 937 cm^{-1} band for the solid polymer, is intensified. Therefore, we may assume that these two bands reflect the conformationally disordered state of APS segments in aqueous solution. As the sample solution is diluted, the intensities of the bands at 942–945 and 1047–1053 cm^{-1} increase while those of the 866 and 968 cm^{-1} bands decrease and finally disappear. Thus, it seems that for the aqueous polymer sample the Raman bands at 866 and 968 cm^{-1} reflect the conformationally ordered state of the aminopropyl segments while the bands at 942–945 and 1047–1053 cm^{-1} reflect the disordered state, indicating that these bands are useful as indicators for investigation of the conformations of the aminopropyl segments.

The Raman spectra of GABA and its hydrochloride salt are useful models for understanding the conformation of the aminopropyl segment of the polymer samples in the solid state and in aqueous solution. The crystal structures of GABA and its hydrochloride salt [21, 22] show that the conformation of the C_α–C_β–C_γ–N skeleton of GABA hydrochloride is all trans (TT) while that of GABA in its free form is gauche (73.6°) about the C_α–C_β bond and trans about the C_β–C_γ bond (GT).

Tanaka et al. [20] have reported the Raman spectra of GABA and its hydrochloride salt in the crystalline state and aqueous solution and have shown that the CH_2 rock and skeletal stretch region is sensitive to the conformational change of the GABA molecule.

Figure 3 shows the Raman spectra of GABA and its hydrochloride salt in the crystalline state in the 700–1100 cm^{-1} region and the observed band frequencies are also listed in Table 2. We can now see that the observed Raman band frequencies of solid poly-APS in this region can all be accounted for by direct combination of the observed band frequencies of GABA and GABA · HCl.

We have therefore used the Raman spectral data for GABA and its hydrochloride to assign the band frequencies of poly-APS in the solid state. On this basis, the bands at 866, 997 and 1026 cm^{-1} may be assigned to the gauche–trans form of the aminopropyl segment. The bands at 963 and 1074 cm^{-1} arise from the all-trans form, although the latter band may be superimposed upon the 1066 cm^{-1} band of the gauche–trans form. The shoulder band at 937 cm^{-1}, observed for the polymer sample in the solid state, is intensified for the aqueous sample. Moreover, since the corresponding band within the Raman spectra of crystalline GABA and its hydrochloride salt disappears, while for GABA · H_2O it is observed at 942–945 cm^{-1}, we may assign this 937 cm^{-1} band within

the poly-APS spectrum to another conformer (TG or GG) of an amino-propyl segment.

The Raman spectrum of APTS in the liquid state is shown in Fig. 1B. The bands at 867, 1000 and 1023 cm^{-1} correspond well to those at 866, 997 and 1026 cm^{-1} for poly-APS in the solid state and may be assigned to the gauche–trans form. The 957 cm^{-1} band may be ascribed to the all-trans form and the band at 942 cm^{-1} may arise from another conformer. This assignment is tentative, since the vibrational modes arising from the three ethyloxy groups are also included within the Raman spectrum.

Thus, we may conclude, for the conformations of APS moieties of poly-APS in the solid state, that the all-trans and gauche-trans forms are predominant, but that a small population of other conformers (TG and GG) may coexist.

For the Raman spectra of poly-APS in concentrated aqueous solutions, the Raman bands at 866 and 968 cm^{-1} and the 1074 cm^{-1} band (which may be superimposed upon the 1066 cm^{-1} band) become more intense. This fact reveals that both the gauche–trans and trans–trans forms are preferentially stabilized. Conversely, in dilute solution, the intensities of these three bands become very weak, while the bands at 942–945 and 1047–1053 cm^{-1} are intensified compared with those at 791–800 cm^{-1} (or 1072–1075 cm^{-1}). Since the Raman bands at 942–945 and 1047–1053 cm^{-1} may arise from the other rotational isomers (trans–gauche or gauche–gauche) (for the correct assignment of these two bands, further study of related compounds may be required), this observation indicates that the populations of the gauche–trans and trans–trans forms become extremely small and that the other conformers are stabilized.

Raman scattering spectra of APS-modified silica gel

Figure 4 shows the Raman scattering spectra of the APS-SMBS complex samples in the 700–1100 cm^{-1} region, together with that of the control SMBS sample. These spectra are very similar to those of the aqueous poly-APS samples (Fig. 2) and do not all reflect the spectrum of poly-APS (Fig. 1). However, for the SI sample (with the highest concentration of bound APS), the Raman bands at 865, 960, 996, 1005 and 1066 cm^{-1} correspond closely to those at 866, 963, 997, 1007 and 1074 cm^{-1} for solid poly-APS, indicating that the APS segments of the APS–SMBS complex may be in an ordered state similar to that of poly-APS in the solid state. However, as the concentration of bound-APS decreases, the intensities of the Raman bands at 940 and 1050 cm^{-1} (which are characteristic of the aqueous poly-APS solution) increase, while those characteristic of solid poly-APS decrease. It should be noted

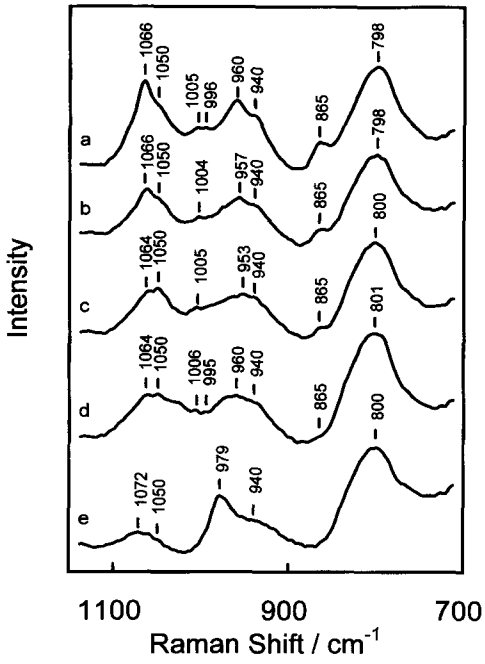

Fig. 4 The Raman scattering spectra of APS-SMBS complexes (a sample I (C(bound APS, $\mu mol\,m^{-2}$) = 3.36); b sample II (C = 1.81); c sample III (C = 1.01); d sample IV (C = 0.74); e S_0) in the 700–1100 cm^{-1} region

that the 865 cm^{-1} band almost disappears in the Raman spectrum of the SIV sample (with the lowest concentration of bound APS). This observation shows that the conformationally ordered or disordered state of the aminopropyl segment for the APS–SMBS complexes is obviously reflected in the 800–1100 cm^{-1} region. We may therefore conclude that analysis of the CH_2 rock and skeletal stretch region within the Raman spectrum of the APS-modified silica gel is a useful tool for diagnosing the conformations of the APS segments.

In our previous study [27], we have reported the diffuse reflectance infrared Fourier transform spectra of the APTS–SMBS complexes. We may summarize as follows. For samples in which a smaller APTS concentration was used, the SiO $\cdots$ H^+NH_2-type structure is predominantly stabilized on the surface of the silica gel, and cyclic structures may be formed on the surface as consequence of the formation of NH_3^+ groups. Furthermore, as the APTS concentration in the reaction mixture increases, the population of the NH_2 groups in the silane layer coated onto the surface increases. Thus, the conformation of an aminopropylsilyl segment in the silane layer strongly depends on the concentration of APTS which is used for the APTS–silica gel reaction. This may cause a stepwise change of the Raman spectra for the APS–SMBS complexes.

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References

1. Ishida H, Koenig JL (1978) J Colloid Interface Sci 64:555; 64:565
2. Ishida H, Koenig JL (1978) J Appl Spectrosc 32:462; 32:469
3. Ishida H, Koenig JL (1978) J Polym Eng Sci 18:128
4. Tabb DL, Koenig JL (1975) Macromolecules 8:929
5. Shih PTK, Koenig JL (1975) J Mater Sci Eng 20:145
6. Ishida H, Koenig JL (1980) J Polym Sci Poly Phys Ed 18:1931
7. Chiang C-H, Ishida H, Koenig JL (1980) J Colloid Interface Sci 74:396
8. Ishida H, Chiang C-H, Koenig JL (1982) Polymer 23:251
9. Murthy RSS, Biltz JP, Leyden DE (1986) Anal Chem 58:3167
10. Murthy RSS, Leyden DE (1986) Anal Chem 58:1228
11. Vrancken KC, Van Der Voort P, D'Hamers IG, Vansant EF (1992) J Chem Soc Farad Trans 88:3197
12. Davis CA, Graves PR, Healy PC, Myhra S (1993) Appl Surf Sci 72:419
13. Vrancken KC, Coster LD, Van Der Voort P, Grobet PJ, Vansant EF (1995) J Colloid Interface Sci 170:71
14. Shimizu I, Okabayashi H, Taga K, Yoshino A, Nishio E, O'Connor CJ (1997) Vib Spectroscopy, in press
15. Lippert JL, Peticolas WL (1972) Biochim Biophys Acta 282:8
16. Rosenholm JB, Stenius P, Danielsson I (1976) J Colloid Interface Sci 57:551
17. Okabayashi H, Okuyama M, Kitagawa T, Miyazawa T (1974) Bull Chem Soc Jpn 47:1075
18. Okabayashi H, Okuyama M, Kitagawa T (1975) Bull Chem Soc Jpn 48:2264
19. Okabayashi H, Taga K, Tsukamoto K, Tamaoki H, Yoshida T, Matsuura H (1985) Chem Scripta 25:153
20. Tanaka K, Akutsu H, Ozaki Y, Kyogoku Y, Tomita K (1978) Bull Chem Soc Jpn 51:2654
21. Tomita K (1965) Jpn J Brain Physiol 51:1
22. Steward EG, Player RB, Warner D (1973) Acta Cryst B29:2825
23. Plueddemann EP (1974) Composite Materials, Vol 6, Chap 6. Academic Press, New York
24. Moses PR, Wier LM, Lennox JC, Tinklea HO, Lehard JR, Murray RW (1976) Anal Chem 50:576
25. McDermott DP (1986) J Phys Chem 91:2569
26. Snyder RG (1967) J Chem Phys 47:1316
27. Okabayashi H, Taga K, Shimizu I, Nishio E, O'Connor CJ (1996) Colloid Polym Sci, submitted