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Original Scientific Paper

Transcription of Gel Assemblies of Bola Type Bis(oxalamide)-dicarboxylic acid and -diester Gelators into Silica Nanotubes and Ribbons under Catalyzed and Non-catalyzed Conditions*

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Assemblies of the bola type bis(oxalamide)-dicarboxylic acid and -diester gelators lacking any positive charges or amine groups can be transcribed into silica nanotubes and ribbons by sol-gel polymerizations of tetraethoxysilane (TEOS) either in the presence or absence of benzyl amine as solution catalyst.

INTRODUCTION

Nano-structured materials have attracted considerable attention owing to their novel properties that are opening exciting perspectives in technology.[1] Supramolecular approach to nano-structures is based on the self-assembly of predesigned organic building blocks. Numerous recent reports describe formation of organogels by low molecular weight organic molecules capable of unidirectional self-assembly into nano-dimensional fibrous aggregates.[2] Since the pioneering work of Shinkai *et al*.[3] from 1998, various gel superstructures have been more or less precisely transcribed into silica nano-dimensional superstructures such as nanotubes, helical ribbons or paper-roll-like structures. The transcription processes are based on amine catalyzed polycondensations of negatively charged precursors of inorganic material at the surface of templating gel fibers. The presence of positive charges or hydrogen bonding amine groups at the fiber surface was shown to be crucial for adsorption of inorganic precursors and successful transcription.[4] Thus far, transcription into silica structures was accomplished using gelators containing either positively charged groups such as quaternary ammonium groups[3] or crown units with bound metal cations[5] or primary or secondary amine groups that can be protonated,[6] providing positive charges, or can form hydrogen bonds[7] to ensure interaction between the negatively charged inorganic precursor and the fiber surface. In this paper, we report on the first successful transcription of gel fibers into silica structures using the bola type bis(oxalamide) gelator **2d** bearing terminal carboxylic acid groups and bis(oxalamide) dicarboxylic ester **2c** being neutral, thus both lacking any positively

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* Dedicated to Professor Nikola Kallay on the occasion of his 65th birthday.

** Author to whom correspondence should be addressed. (E-mail: zinic@irb.hr) charged or amine groups. With the first gelator, the transcription into silica nanotubes was performed in the presence of benzyl amine as a solution catalyst while silica ribbons were obtained with the second even in the absence of any catalyst, which shows that the presence of amide type hydrogen bonding units is sufficient for successful transcription.

EXPERIMENTAL

General

Melting points were determined on a Kofler stage and are uncorrected. Optical rotations were measured on an optical activity AA – 10 automatic polarimeter using the wavelength of 589.3 nm. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz, respectively, on a Varian XL–300 Gemini spectrometer, and at 600 MHz on a Bruker spectrometer (TMS was used as an internal standard). FTIR spectra were recorded on a Bomen MB 102 spectrometer. Thin layer chromatography (TLC) was performed on silica-gel-coated Merck 60 F_{254} silica plates, and spots were visualized using a UV lamp (254 nm) or I_2 vapors. All chemicals were of the best commercially available grade and were used without purification. Solvents were purified according to literature methods and stored over molecular sieves.

*Diethyl 2,2'-(nonane-1,9-diylbis(azanediyl))bis(2-oxoacetate)(**2a**)*

A solution of diaminononane (0.654 g, 4.13 mmol) in dry CH_2Cl_2 (30 mL) and TEA (1.21 mL, 8.68 mmol) were simultaneously added dropwise within 30 minutes to a cooled (–10 °C) solution of ethyl oxalylchloride (0.97 mL, 8.68 mmol) in dry CH_2Cl_2 (50 mL). Stirring was continued for 30 min at 0 °C and overnight at room temperature. CH_2Cl_2 (50 mL) was added and the mixture was washed with water, 1.5 % AcOH, 5 % $NaHCO_3$ and again with water. Organic layer was dried (Na_2SO_4) and the solvent was evaporated. Recrystallization (CH_2Cl_2 / light petroleum) gave **2a** (0.903 g, 61 %). ^{1}H NMR (d_6 – DMSO) δ/ppm: 1.21–1.25 (m, 16 H, $CH_{3(\mathrm{ethyl})}$, $CH_{2(5)}$, $CH_{2(4)}$, $CH_{2(3)}$), 1.41 (bs, 4H, $CH_{2(2)}$), 3.08 (m, 4H, $CH_{2(1)}$), 4.19 (q, 4H, J = 6.99 Hz, $OCH_{2(\mathrm{ethyl})}$), 8.83 (bs, 2H, $CONH_{\mathrm{linker}}$); ^{13}C NMR (d_6 – DMSO) δ/ppm: 13.9 ($CH_{3(\mathrm{ethyl})}$, 26.4 ($CH_{2(5)}$), 28.6 ($CH_{2(4)}$), 28.7 ($CH_{2(3)}$), 28.9 ($CH_{2(2)}$), 40.0 ($CH_{2(1)}$), 61.9 ($OCH_{2\,(\mathrm{ethyl})}$), 157.1 (CONH), 160.9 ($COO_{\mathrm{ester}}$).

*2,2'-(nonane-1,9-diylbis(azanediyl))bis(2-oxoacetic acid) (**2b**)*

A solution of **2a** (0.835 g, 2.33 mmol) was dissolved in 10 % KOH / CH_3OH (134 mL). The reaction mixture was stirred overnight at room temperature. Methanol was evaporated, water was added and the solution was acidified with 1 mol dm^{-3} HCl until pH = 2 when precipitation occurred. The precipitate was filtered off, washed with water and methanol, dried under reduced pressure. Yield: (0.600 g, 86 %). ^{1}H NMR (d_6 – DMSO) δ/ppm: 1.20 (bs, 10H, $CH_{2(5)}$, $CH_{2(4)}$, $CH_{2(3)}$), 1.40 (m, 4H, $CH_{2(2)}$), 3.09 (m, 4H, $CH_{2(1)}$), 8.80 (t, 2H, J = 5.65 Hz, $CONH_{\mathrm{linker}}$); ^{13}C NMR (d_6 – DMSO) δ/ppm: 26.4 ($CH_{2(5)}$), 28.7 ($CH_{2(4)}$), 28.8 ($CH_{2(3)}$), 29.0 ($CH_{2(2)}$), 40.0 ($CH_{2(1)}$), 158.3 (CONH), 162.4 (COOH).

*1,9-*N,N'*-bis[oxalyl-(L-leucin-methyl ester)] Diaminononane (**2c**)*

A solution of $SOCl_2$ (2.7 mL, 36.72 mmol) was added dropwise within 30 minutes to a cooled (–10 °C) solution of **2b** (0.555 g, 1.86 mmol) in dry CH_2Cl_2 (20 mL) containing a catalytic amount of DMF (4 drops). Stirring was continued for 2 hours under reflux at 40 °C. The solvent and residual HCl were evaporated under reduced pressure. The remaining product was dissolved in dry CH_2Cl_2 (80 mL) and simultaneously added dropwise within 30 minutes to a cooled (–10 °C) solution of H-Leu-OMe · HCl (0.743 g, 4.092 mmol) and TEA (1.09 mL, 7.81 mmol) in CH_2Cl_2 (50 mL). Stirring was continued overnight at room temperature. CH_2Cl_2 (50 mL) was added and the mixture was washed with water, 1.5 % AcOH, 5 % $NaHCO_3$ and again with water. Organic layer was dried (Na_2SO_4) and the solvent was evaporated. Recrystallization (CH_2Cl_2 / *n*-hexane) gave the title compound: (0.550 g, 53 %); m.p. = 163–165 °C; $[\alpha]_D$ = –10 (c = 1 in CH_2Cl_2); IR (KBr) ν_{max}/cm^{-1}: 3295 (NH), 1746 (COOMe), 1656 (amide I), 1523 (amide II); ^{1}H NMR (d_6 – DMSO) δ/ppm: 0.93 (d, 12 H, J = 5.5 Hz, $CH_{3(\delta,\mathrm{Leu})}$), 1.29 (bs, 10H, $CH_{2(3)}$,$CH_{2(4)}$, $CH_{2(5)}$), 1.55 (m, 4H, $CH_{2(2)}$), 1.68 (m, 6H, $CH_{2(\beta,\mathrm{Leu})}$ $CH_{(\gamma,\mathrm{Leu})}$), 3.30 (m, 4H, $CH_{2(1)}$), 3.73 (s, 6H, $CH_{3(\mathrm{OMe})}$) 4.58 (m, 2H, $CH_{(\alpha,\mathrm{Leu})}$), 7.57 (m, 2H, NH_{linker}), 7.87 (d, 2H, J = 8.79 Hz, NH_{Leu}); ^{13}C NMR (CD_3OD) δ/ppm: 21.5, 22.6 ($CH_{3(\delta,\mathrm{Leu})}$), 24.6 ($CH_{(\gamma,\mathrm{Leu})}$), 26.5 ($CH_{2(3)}$), 28.8, 28.9, 28.9 ($CH_{2(2)}$, $CH_{2(3)}$,$CH_{2(4)}$), 39.5 ($CH_{2(1)}$), 41.0 ($CH_{2(\beta,\mathrm{Leu})}$), 50.9 ($CH_{(\alpha,\mathrm{Leu})}$), 52.3 ($CH_{3(\mathrm{OMe})}$), 159.0 ($CONH_{\mathrm{linker}}$), 159.6 ($CONH_{\mathrm{Leu}}$), 171.9 ($COO_{\mathrm{ester}}$); Anal. Calcd. for $C_{27}H_{48}N_4O_8$ (M_r = 556.69): C 58.25, H 8.69, N 10.07 %; found: C 58.52, H 8.57, N 10.13 %.

*1,9-*N,N'*-bis[oxalyl-(L-leucine)] Diaminononane (**2d**)*

To a solution of **2c** (0.450 g, 0.81 mmol) in dry CH_2Cl_2 (6 mL), MeOH (6 mL) and 1 mol dm^{-3} LiOH (2.7 mL) were added. The reaction mixture was stirred overnight at room temperature. The solvent was evaporated, water was added and the solution was acidified with 1 mol dm^{-3} HCl until precipitation occurred. The precipitate was filtered off, washed with water and dried under reduced pressure. Yield: (0.348 g, 82 %); m.p. = 149–151 °C; $[\alpha]_D$ = –7 (c = 1 in EtOH); IR (KBr) ν_{max}/cm^{-1}: 3303 (NH), 1728 (COOH), 1659 (amide I), 1518 (amide II); ^{1}H NMR (d_6 – DMSO) δ/ppm: 0.81, 0.85 (2d, 12 H, J = 5.86 Hz, $CH_{3(\delta,\mathrm{Leu})}$), 1.22 (bs, 10H, $CH_{2(3)}$, $CH_{2(4)}$, $CH_{2(5)}$), 1.43 (m, 4H, $CH_{2(2)}$), 1.52 (m, 4H, $CH_{2(\beta,\mathrm{Leu})}$), 1.74 (m, 2H, $CH_{(\gamma,\mathrm{Leu})}$), 3.10 (m, 4H, $CH_{2(1)}$), 4.24 (m, 2H, $CH_{(\alpha,\mathrm{Leu})}$), 8.70 (d, 2H, J = 8.57 Hz, NH_{Leu}), 8.77 (t, 2H, J = 6.03 Hz, NH_{linker}); ^{13}C NMR (CD_3OD) δ/ppm: 22.0, 23.5 ($CH_{3(\delta,\mathrm{Leu})}$), 26.2 ($CH_{(\gamma,\mathrm{Leu})}$), 27.9 ($CH_{2(3)}$), 30.2, 30.5 ($CH_{2(2)}$, $CH_{2(3)}$,$CH_{2(4)}$), 40.7 ($CH_{2(1)}$), 41.6 ($CH_{2(\beta,\mathrm{Leu})}$), 52.4 ($CH_{(\alpha,\mathrm{Leu})}$), 161.4 ($CONH_{\mathrm{linker}}$), 161.8

(CONH$_{Leu}$), 175.2 (COO$_{ester}$); Anal. Calcd. for $C_{25}H_{44}N_4O_8 \cdot 1/2\ H_2O$ (M_r = 537.64): C 55.85, H 8.44, N 10.42 %; found: C 55.74, H 8.33, N 10.54 %.

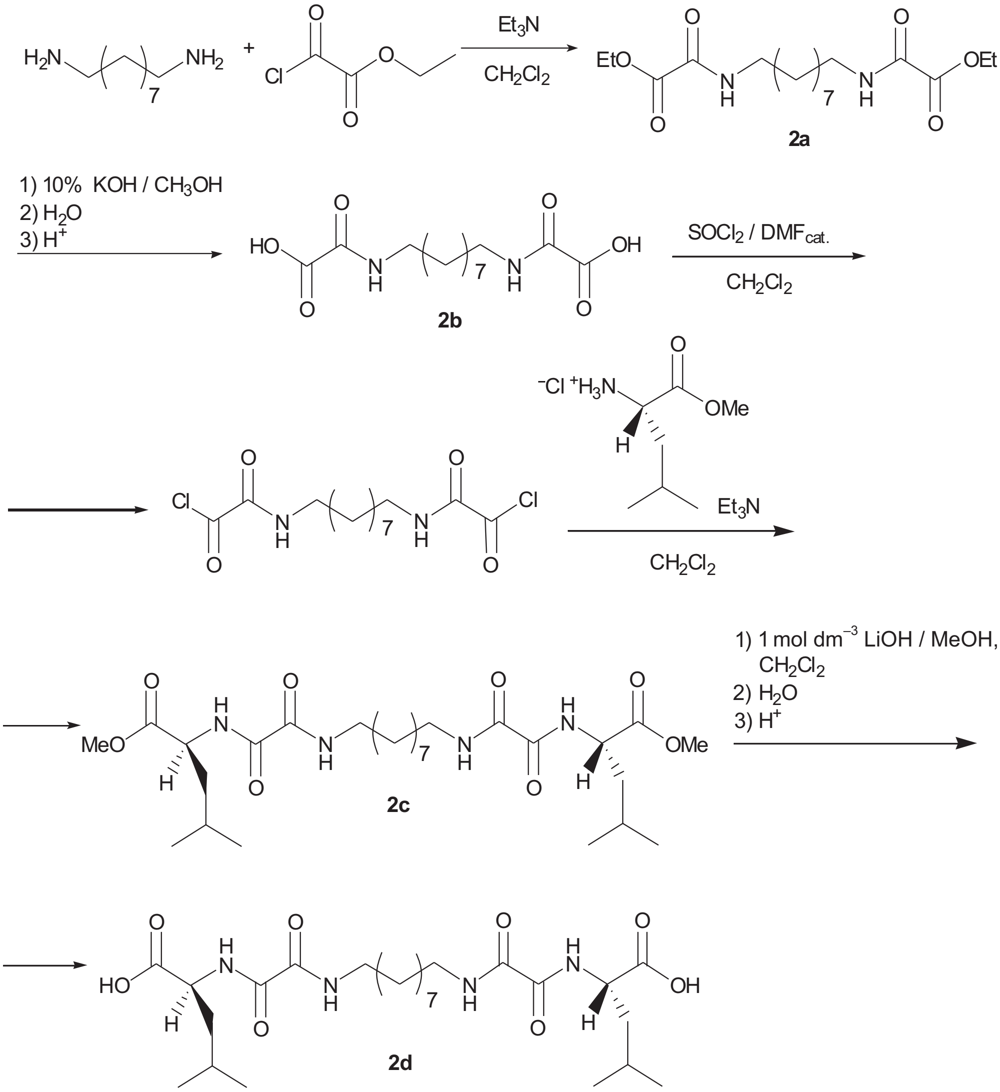
Gelation Experiments. – The experiments were performed by dissolving a weighed amount of the selected gelator (10 mg) in a measured volume of the selected solvent or solubilizing component. In the first case, heating of the sample is needed to produce solution. Cooling to room temperature produced gels. In the second case, the measured volumes of another solvent were added and the sample was heated and cooled to room temperature until gel was produced. To determine maximal volumes of gelation, each procedure was repeated until the solution was formed, instead of gel, at room temperature.

TEM and SEM Investigations. – Transmission electron micrographs were negatively stained by dipotassium polytungstate or Pd shadowing. JOEL JSM-5800 scanning electron microscope was used to take SEM pictures. The sample was shielded by gold (10 Å). The accelerating voltage of SEM was 20 kV.

RESULTS AND DISCUSSION

Bis(L-Leu) bis-oxalamide compounds with nonamethylene spacer between two oxalamides have been prepared. The bisoxalamides were prepared starting with the reaction of the respective diamine and ethyl oxalylchloride, which gave diester **2a** in 61 % yield. The ester was hydrolyzed with methanolic KOH and free acid **2b** (86 % yield) was isolated after acidification. In the next step, diacid **2b** was transformed to the respective diacid chloride and reacted with L-LeuOMe, giving diester **2c** in 53 % yield. The subsequent alkaline hydrolysis of **2c** gave the diacid product **2d** in 82 % yield (Scheme 1).

The bola type chiral leucine containing gelators **2c** and **2d** were designed by oligomethylene bridging of two self-complementary oxalamide units, which were found earlier to strongly promote the unidirectional self assembly by intermolecular oxalamide-oxalamide hydrogen bonding in other types of gelators.[8] Compound **2d** is capable of



Scheme 1. Synthetic route to bisoxalamide derivatives **2c** and **2d**.

TABLE I. Gelation efficiency of various solvents and solvent mixtures toward 10 mg of **2c** and **2d**, expressed as the maximal volume (V_{max}) of gelled solvent or solvent mixture (in mL)

Solvent	V_{max} / mL	
	2c	**2d**
DMSO – H_2O[a]	2.8 (DMSO) + 0.8 (H_2O) opaque gel	2.0 (DMSO) + 1.5 (H_2O) translucent gel
DMF – H_2O[a]	0.9(DMF) + 0.9 (H_2O) opaque gel	1.0(DMF) + 1.05 (H_2O) opaque gel
ethanol	1.2 opaque gel	ng [b]
2-propanol	0.5 opaque gel	ng
2-octanol	1.0 translucent gel	ng
dichloromethane – *n*-hexane	0.3 (CH_2Cl_2) + 0.7 (*n*-hexane) transparent gel	ng
cis,trans-decaline	0.75 transparent gel	ng
benzene	0.4 transparent gel	3.0 transparent gel
toluene	0.7 transparent gel	1.20 transparent gel
p-xylene	1.5 transparent gel	1.5 transparent gel
tetralin	1.2 transparent gel	1.7 transparent gel
Super 98 (fuel)	ng	ng
Eurodiesel	6.0 transparent gel	ng

[a] **2c** and **2d** are soluble in DMSO and DMF and insoluble in water.
[b] ng = no gelation

gelling benzene, toluene, *p*-xylene, tetraline and also highly polar DMSO/water and DMF/water mixtures. Compound **2c** can gel the same solvents, however less efficiently, but also ethanol, 2-propanol, 2-octanol, highly lipophilic dichloromethane/hexane mixture and also the hydrocarbon Diesel fuel, giving stable and transparent gel (Table I).

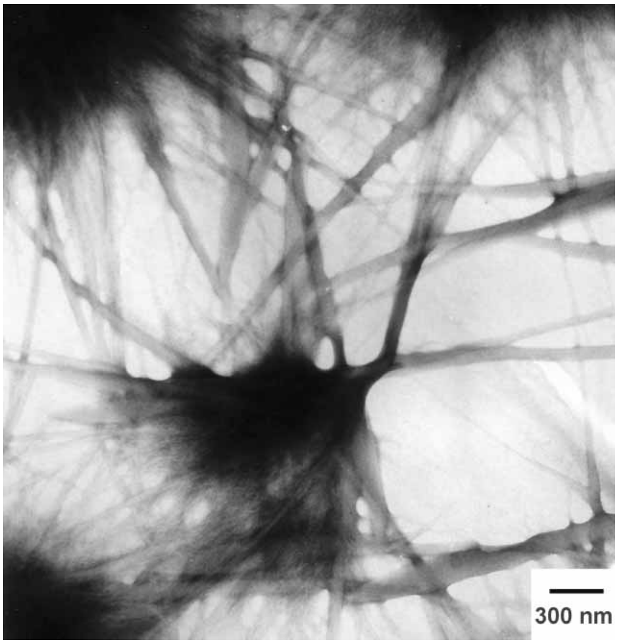


Figure 1. TEM image of **2d**-benzene gel stained with dipotassium polytungstate.

The TEM image of the **2d**-benzene gel network shows the presence of straight fibers with diameters in the range of 10–80 nm (Figure 1). To investigate transcription of the fibers, sol-gel polymerizations of $Si(OEt)_4$ (TEOS) were carried out using four different reaction conditions. Four benzene gel samples (**2d**, 5 mg; 9.46 μmol; solvent 0.5 mL) containing 18.72 mg (89.87 μmol) of $Si(OEt)_4$ and 9.94 mg (0.552 mmol) of H_2O were prepared. To each of the three samples, one of the following catalysts was added: hydrazine (4.49 mg, 0.08987 mmol), benzyl amine (9.62 mg, 0.08987 mmol) and citric acid (18.89 mg, 0.08987 mmol) while the fourth sample contained no catalyst. The samples were heated until sol was formed, followed by cooling to room temperature. Reformation of gel occurred in the sample without catalyst and in that containing benzyl amine. The samples with hydrazine and citric acid, upon cooling to room temperature, exhibited phase separation into precipitate and solution, showing that both latter catalysts prevented formation of gels. All prepared samples were then left at room temperature for 14 days. The solvent was removed under reduced pressure and the remaining solid was investigated by TEM. Only the sample containing benzyl amine showed successful transcription of gel fibers into silica nanotubes (Figure 2); in this system, the gel fibers present served as templates for polycondensation of inorganic precursor. In contrast, only compact blocks or granular silica particles could be observed for the remaining three samples. Apparently, destruction of gel by hydrazine and citric acid leaves the system without templating gel fibers, so that polycondensation results in formation of granular silica. It seems, however, that in the third gel system lacking any catalyst, polycondensation occurred without any interaction with gel fibers. This would suggest that the

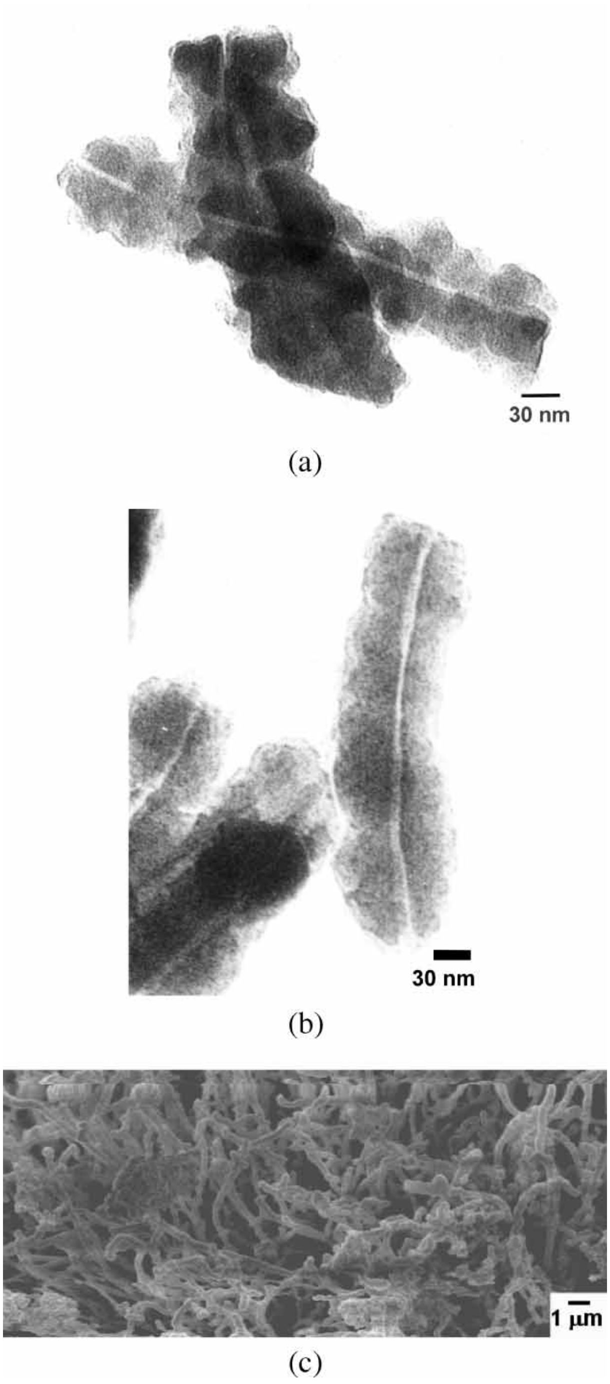


Figure 2. TEM images of silica nanotubes obtained from **2d**-benzene gel before (a) and after (b) calcinations, and (c) SEM image of silica nanotubes in the calcinated sample.

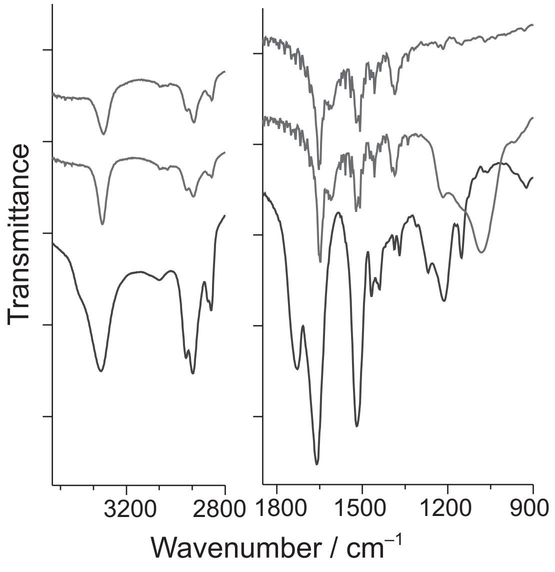


Figure 3. FTIR spectra of (up to down) benzylammonium salt of **2d**, the precalcinated sample after transcription and **2d**-benzene gel.

role of benzyl amine in the first sample is not only catalytic but also induces interaction of silica precursor with gel fibers. The silica tubes formed in the first sample have outer and inner diameters of 80–100 and 5–30 nm, respectively (Figure 2a). Calcination of the sample for 2 h at 200 °C, 2h at 500 °C under nitrogen atmosphere and 4 h at 500 °C under aerobic conditions gave silica nanotubes with dimensions similar to those of the precalcinated sample (Figure 2b). It should be noted that the TEM images of both precalcinated and calcinated samples show that the nanotubes have both ends open. The SEM image of the calcinated sample (Figure 2c) reveals that most of the material is present in the form of tubes.

To find an explanation for how the transcription took place in **2d**-benzene gel, the FTIR spectra of **2d**-benzene gel, the silica tubes before calcination and the dibenzylammonium salt of **2d** were taken (Figure 3). The spectrum of the gel shows the NH and amide I bands at 3303 and 1659 cm^{-1}, respectively, being characteristic of hydrogen bonded oxalamide units in the gel aggregates.[8] The carboxylic acid C=O band appears at 1728 cm^{-1}. The spectrum of the precalcinated sample shows that in addition to the Si-O stretching band at 1082 cm^{-1}, also the NH stretching band at 3297 cm^{-1} and the amide I band at 1649 cm^{-1} are present; however, the band of carboxylic acid C=O is shifted to 1609 cm^{-1} characteristic of the position of the C=O of carboxylate salts. The latter observation shows that in the formed silica hybrids organic aggregates are still stabilized by intermolecular oxalamide–oxalamide hydrogen bonding and that the carboxylic acid functions are converted into carboxylates. However, the positions of the bands fully correspond to those present in the FTIR spectrum of the separately prepared benzyl ammonium salt of **2d**. This observation suggests the presence of **2d**-benzylammonium salt in the precalcinated sample. Hence, the polycondensation of ≡Si-O- may occur at the surface of gel fibers containing some benzylammonium carboxylate groups, the latter being capable of electrostatic interactions and hydrogen bonding with negatively charged silica precursor species.

Since the diester derivative **2c** exhibited gelation of ethanol, the solvent of choice for transcriptions using

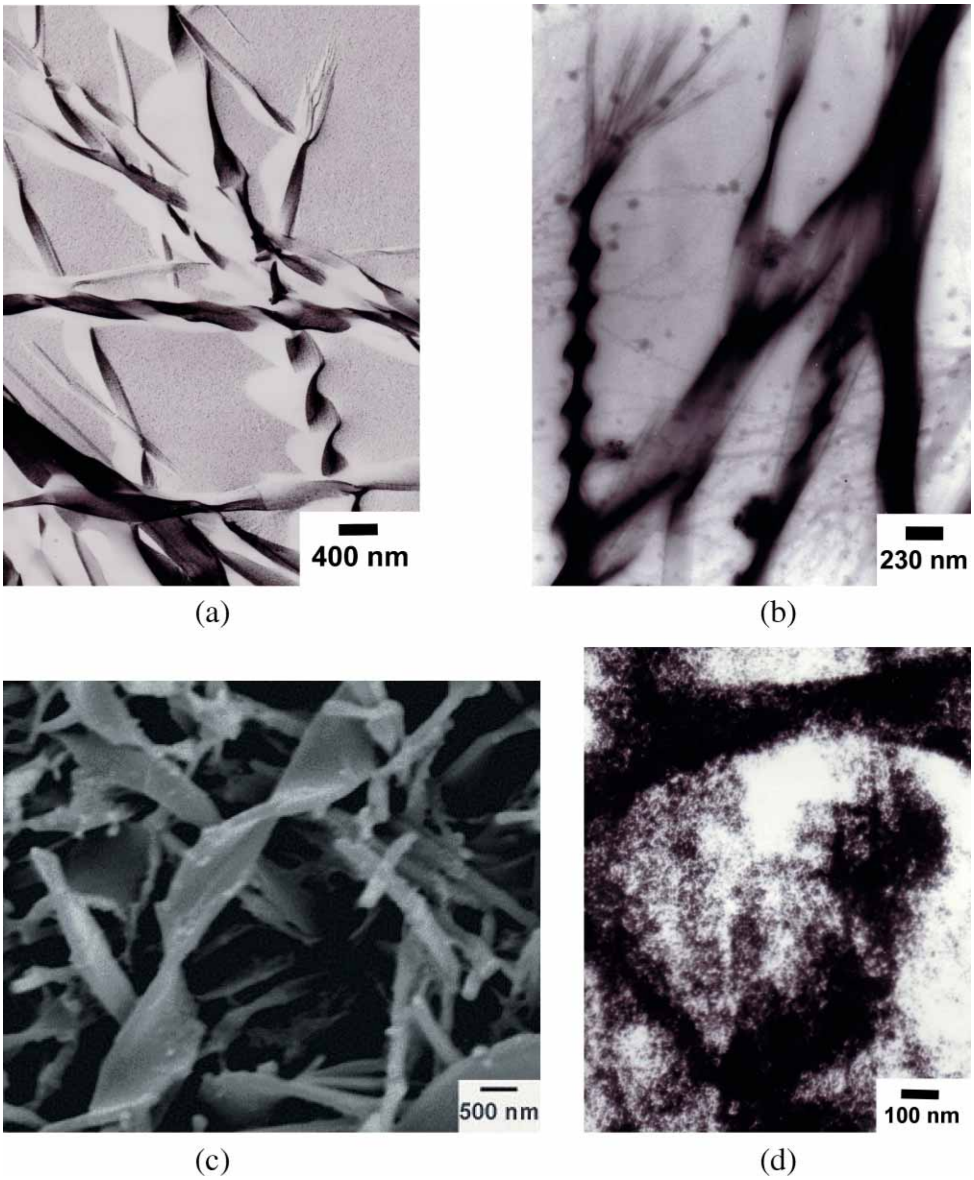
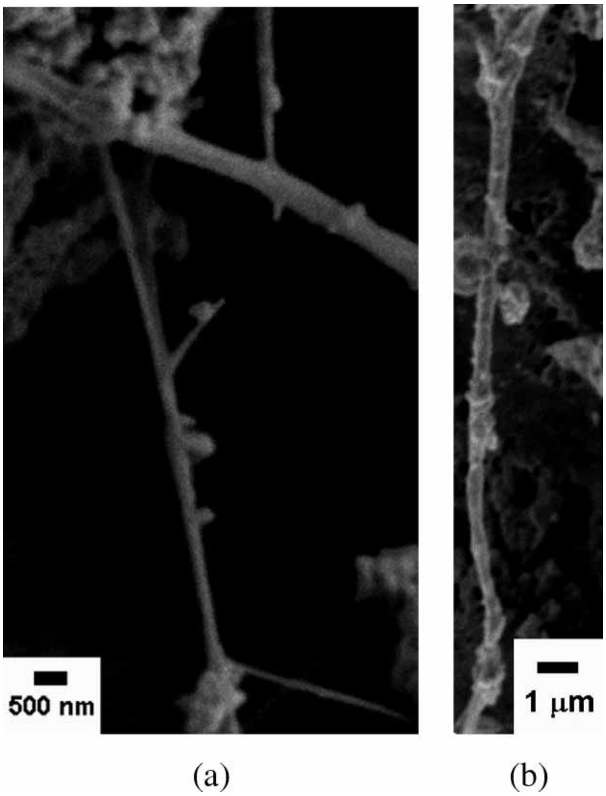


Figure 4. TEM images of (a) **2c**-ethanol gel (Pd shadowed), (b) sample after TEOS polymerization in the absence of benzyl amine, showing ribbons with adsorbed silica, (c) SEM image of the precalcinated sample of transcribed **2c** obtained without any catalyst, and (d) calcinated sample obtained by TEOS polymerization with benzyl amine, showing only the presence of granular silica.

TEOS and water, the transcription was investigated from ethanol gel. The TEM micrograph of the gel (Figure 4a) shows a completely different morphology compared to **2d**-benzene gel; here, the coexisting straight and twisted ribbons can be observed. Two gel samples were prepared (**2c**, 5 mg; 8.98 μmol; ethanol 0.5 mL) containing $Si(OEt)_4$ (13.12 mg, 0.063 mmol), and H_2O (8.09 mg, 0.449 mmol); to one of the samples, benzyl amine (6.74 mg, 0.063 mmol) was added as the solution catalyst. The samples were heated until sol was formed, followed by cooling to room temperature. In the sample without catalyst, reformation of gel occurred; however, in the sample with benzyl amine, a precipitate was formed that prevented gel formation. After two weeks and removal of the solvent, the remaining solid was investigated by TEM and SEM. The TEM image of the benzyl amine containing sample showed, after calcinations, only the presence of granular silica (Figure 4d). In the latter system, benzyl amine induced polycondensation of silica precursors, which occurred in the absence of templating gel fibers and gave granular silica as well as in the cases of **2d** benzene systems in the presence of hydrazine and citric acid, respectively. However, the TEM image of the sample lacking any benzyl amine revealed the presence of **2c**-silica hybrids with silica adsorbed on the organogel ribbons (Figure 4b and 4c). Upon calcinations, the SEM micrographs (Figure 5a,b) show the presence of silica ribbons having dimensions comparable to those of the pre-



(a) (b)

Figure 5. SEM images of selected silica ribbons found after calcination (a) and (b); the characteristic terminal branching is seen in (b) as observed also in the TEM image (Figure 4b) before calcination.

calcinated sample (Figure 4b) and showing also the characteristic terminal branching. Apparently, in this system the transcription occurred despite the absence of benzyl amine as the catalyst commonly used in the polycondensation of silica precursors.

CONCLUSIONS

The presented results demonstrate that in contrast to previous reports,[4] also the assemblies of gelators lacking any positive charges or amino groups can be used in sol-gel polymerizations of TEOS. In the case of the dicarboxylic acid gelator **2d,** formation of benzyl ammonium carboxylates at the surface of gel fibers is postulated to help adsorption of negatively charged silica precursors and allow their transcription into silica nanotubes. In the case of the neutral gelator **2c,** the presence of hydrogen bonding oxalamide groups seems to be sufficient for adsorption of negatively charged silica precursors, enabling transcription of gel's twisted ribbons into twisted silica ribbons. These results extend the structural types of gelators that can be used as templates and endow new possibilities to prepare nano-dimensional silica superstructures.

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SAŽETAK

Prijepis samoudruženih gelnih agregata bola gelatora bis(oksalamid)-dikarboksilne kiseline i -diestera u silikatne nano-cjevčice i trake u kataliziranim i nekataliziranim uvjetima

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Organizirane gelne agregate samoudruženih bola gelatora, bis(oksalamid)-dikarboksilnih kiselina i diestera, koji ne posjeduju pozitivan naboj ili amino skupine, moguće je sol-gel polimerizacijom tetraetoksisilana (TEOS) prepisati u silikatne nanocjevčice i izvijene trake u prisutnosti ili bez benzilamina kao katalizatora.