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# Synthesis of colloidal polyoxazoline/silica hybrids prepared in an aqueous solution

Tomoki Ogoshi, Yoshiki Chujo *

*Department of Polymer Chemistry, Graduate School of Engineering,*
*Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan*

## Abstract

New colloidal polymer hybrids with polyoxazolines such as poly(2-methyl-2-oxazoline) (PMeOZO) and poly(2-ethyl-2-oxazoline) (PEtOZO) were obtained in an aqueous solution as a sol–gel solvent. The polyoxazoline segment was incorporated into the siliceous particle and formed strong hydrogen bonds with silanol moieties, judging from TGA and FT-IR studies. Colloidal polymer hybrids exhibited no glass transition temperature of the polyoxazoline and showed excellent thermal stability and solvent-resistant property. Porous silica obtained by charring the colloidal polymer hybrids at 600 °C exhibited the peak at 3.5 Å. These results strongly indicate the homogeneous molecular scale dispersion of polyoxazoline in the colloidal silica gel matrix.

*Keywords:* Polymer hybrid; Colloidal materials; Sol–gel reaction

## 1. Introduction

Sol–gel technology has been widely used for the preparation of organic–inorganic hybrid materials due to the formation of inorganic solid under ambient condition [1–10]. The elaborated hybrid materials show not only both organic and inorganic features but also unique properties resulted from the miscibility between organic and inorganic components at the level of nanometer. The introduction of high affinity into the interface between organic and inorganic phases accomplishes the preparation of the nanometer scale hybrid matters with both organic polymer and inorganic solid by means of sol–gel reaction. One of the approaches for the preparation of transparent polymer hybrids is using covalent bonds between the organic polymer and inorganic solid [11–17]. The other methodology for the construction of the polymer hybrids is employing physical interactions [18–28] such as hydrogen bonding [18,19], ionic [20] and aromatic [21] interactions.

Here in this paper reports the colloidal polymer hybrids with polyoxazolines such as poly(2-methyl-2-oxazoline) (PMeOZO) and poly(2-ethyl-2-oxazoline) (PEtOZO). Previously, we succeeded in the preparation of transparent polyoxazoline/silica hybrids by using methanol as a sol–gel solvent (Scheme 1a) [18]. The strong hydrogen bonding interactions between amide groups of polyoxazolines and silanol groups from sol–gel reaction gave the transparent polymer hybrids. In the present study, however, when water was used as a sol–gel solvent instead of methanol, white precipitates appeared during the preparation of polyoxazoline/silica hybrids (Scheme 1b). The obtained colloidal state polymer hybrids with polyoxazoline showed excellent solvent-resistant property and thermal stability compared with the previously reported transparent polymer hybrids. We discuss here such a difference from the results of nitrogen adsorption porosimetry study. From a viewpoint of the application of the colloidal polymer hybrids, the obtained hybrids can be expected as the column packing material because they formed spherical shape and exhibited excellent solvent-resistant property. The process of the formation of colloidal polymer hybrids is also discussed in details by TEM study in this research.

## 2. Experimental section

### 2.1. Materials

Tetramethoxysilane (TMOS) was distilled and stored under nitrogen atmosphere. Preparation procedure of poly

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* Corresponding author. Tel.: +81 75 383 2604; fax: +81 75 383 2605.
*E-mail address:* chujo@chujo.synchem.kyoto-u.ac.jp (Y. Chujo).

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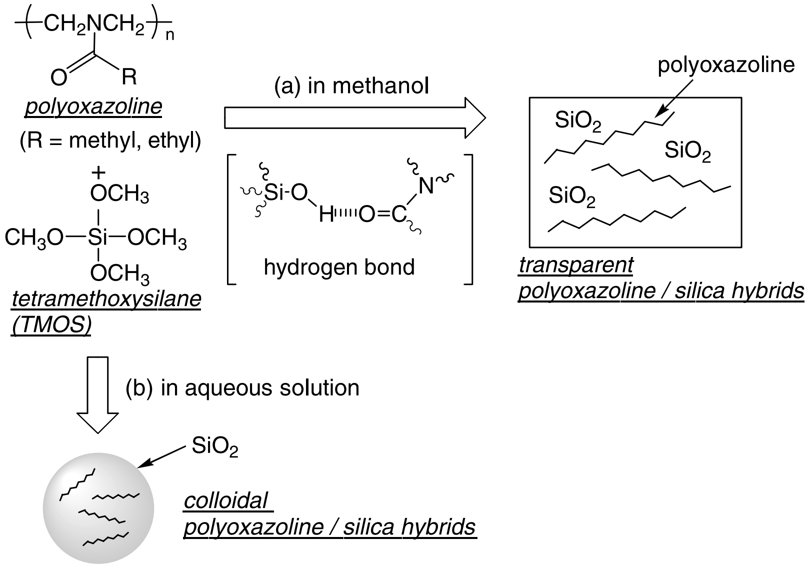


Scheme 1.

(2-methyl-2-oxazoline) (PMeOZO) and poly(2-ethyl-2-oxazoline) (PEtOZO) was reported previously [29].

### 2.2. Measurements

Thermogravimetric analysis (TGA) was performed using a TG/DTA6200, SEIKO Instruments, Inc., with heating rate of 10 °C min$^{-1}$ in air. Scanning electron microscopy (SEM) measurements were conducted using a JEOL JNM-5310/LV system. The surface images were measured using a tapping mode atomic force microscopy (TM-AFM) (SPA 400, SEIKO Instruments) operating at room temperature. Height and phase images were recorded simultaneously. Nanoprobe cantilevers (SI-DF20, SEIKO Instruments) were utilized. The FT-IR spectra were obtained using a Perkin–Elmer 1600 infrared spectrometer. Nitrogen adsorption porosimetry was conducted with a BEL Japan Inc.

### 2.3. Synthesis of colloidal polyoxazoline/silica hybrids

A typical procedure of the colloidal polyoxazoline/silica hybrids is as follows. To water (9.0 ml), the prescribed amount of TMOS was added. Since the solubility of TMOS in water was very low, two separated TMOS/water phases were observed. The phase separated solution became transparent and homogeneous solution after vigorous stirring for several minutes. After stirring for 10 min, 50 mg of polyoxazoline in water (1.0 ml) was added to the mixture. After vigorous stirring for 20 min, the solution became translucent. The white precipitate was obtained after 24 h. The obtained colloidal polymer hybrid was collected by centrifugation, washed with methanol several times and dried under reduced pressure.

### 2.4. Solvent-resistant property of colloidal polyoxazoline/silica hybrids

The powdered hybrids were extracted with methanol using a Soxhlet apparatus for 1 week. After the solvent-extraction, the samples were dried in a vacuum oven at 100 °C. The amount of the remained organic component in the hybrids was measured by TGA in air.

### 2.5. Nitrogen adsorption porosimetry

The powder of the colloidal polymer hybrid was heated at 600 °C in an ambient atmosphere for 24 h to remove organic components. After the calcination, the sample was dried in a vacuum oven at 100 °C. The sample was dried at 150 °C for 2 h at reduced pressure before porosimetry measurements. The surface area was calculated with the Brunauer–Emmet–Teller (BET) equation [30] in the range of 0.05–0.30 ($p/p_0$) and the pore size distribution was estimated by the MP method [31].

## 3. Results and discussion

The results of the preparation of organic–inorganic polymer hybrids with polyoxazolines such as poly(2-methyl-2-oxazoline) (PMeOZO) and poly(2-ethyl-2-oxazoline) (PEtOZO) depending on the solvent are summarized in Table 1. The polymer hybrids using methanol (run 8, 9) formed completely transparent and homogeneous films as reported in the previous paper [18] on the other hand, the white precipitate was observed during the preparation of the polymer hybrids with polyoxazoline using water (run 1–6). The obtained materials without polyoxazoline using water formed transparent silica glass (run 7). These observations indicate that: (i) using water for the sol–gel solvent and (ii) adding polyoxazoline are necessary for the formation of the white precipitate. The shape

Table 1
Synthesis of colloidal organic–inorganic polymer hybrids in aqueous solution

| Run | Poly(2-R-2-oxazoline) | | Solvent | TMOS (mg) | Appearance | Yield (mg, %) | Ceramic yield (wt%) | |
|---|---|---|---|---|---|---|---|---|
| | R | (mg) | | | | | Calcd. | Obsd.[a] |
| 1 | Methyl | 50 | Water | 1000 | Colloid | 141.0 (31.3) | 88.9 | 77.3 |
| 2 | Methyl | 50 | Water | 500 | Colloid | 122.7 (49.1) | 80.0 | 72.5 |
| 3 | Methyl | 50 | Water | 250 | Colloid | 128.2 (85.4) | 66.7 | 72.2 |
| 4 | Methyl | 50 | Water | 125 | Colloid | 35.3 (35.3) | 50.0 | 64.7 |
| 5 | Ethyl | 50 | Water | 500 | Colloid | 161.3 (64.5) | 80.0 | 71.4 |
| 6 | Ethyl | 50 | Water | 250 | Colloid | 131.1 (87.4) | 66.7 | 67.6 |
| 7 | – | – | Water | 250 | Transparent film | – | – | – |
| 8 | Methyl | 50 | MeOH | 250 | Transparent film | – | 66.7 | 59.6 |
| 9 | Ethyl | 50 | MeOH | 250 | Transparent film | – | 66.7 | 56.7 |

[a] Determined by TGA.

of the obtained white precipitate was examined by SEM study. Spherical particles having about 1 μm size were clearly observed (Fig. 1).

For the elucidation of the constituent of the particles, FT-IR and TGA measurements were carried out. In the colloidal polymer hybrid, the observation of the weight loss around at 200–400 °C by TGA and the amide–carbonyl peak in FT-IR indicated the presence of PMeOZO in the particles (Fig. 2). Furthermore, the C=O stretching band of the original PMeOZO positioned at 1634 $\mathrm{cm}^{-1}$ was clearly shifted to a lower wavenumber region (1622 $\mathrm{cm}^{-1}$) in FT-IR, which strongly indicates the formation of hydrogen bonds between amide groups of PMeOZO and silanol moieties from sol–gel reaction. The shift was also found as an evidence for the formation of the hydrogen bonds in the transparent polymer hybrid with PMeOZO using methanol.

The DSC and nitrogen adsorption porosimetry studies of the colloidal polymer hybrids were carried out for the estimation of the miscibility between PMeOZO and silica gel in the colloidal particles. Fig. 3 shows the DSC thermograms of the colloidal polymer hybrid. No glass transition temperature ($T_g$) was observed in the colloidal polymer hybrid, while $T_g$ at 72 °C was clearly observed in the bulk PMeOZO. These results strongly suggest that PMeOZO was dispersed in the colloidal silica gel matrix at the molecular level since the segmental motion of PMeOZO extremely decreased by the hard, reticular silica gel matrix. These observations are same as the transparent polymer hybrids with PMeOZO using methanol.

The obtained colloidal polymer hybrid was heated at 600 °C for 24 h for the complete removal of organic component as shown in Scheme 2. The silica matrix was so rigid and strong that the pore of the obtained porous silica reflected on the organic polymer domain. The methodology was justified in the previous papers [19,20,23]. The pore size distribution of the obtained porous silica was calculated by MP method. The porous silica exhibited strong peak at 3.5 Å, which strongly indicates the molecular scale miscibility between PMeOZO and silica gel in the colloidal hybrid. On the other hand, the porous silica prepared by the transparent polymer hybrid using methanol showed the peak at 1.8 nm described in the previous article [18]. Therefore, the miscibility of the colloidal polymer hybrid using water was angstrom/molecular level, while the

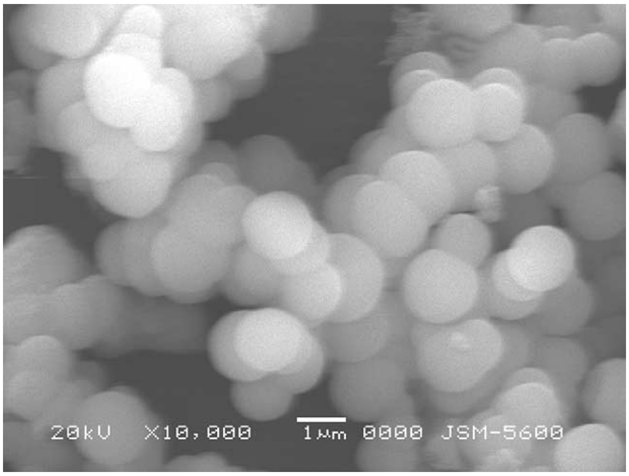


Fig. 1. SEM image of the colloidal PMeOZO/silica hybrid (run 4), the scale bar: 1μm.

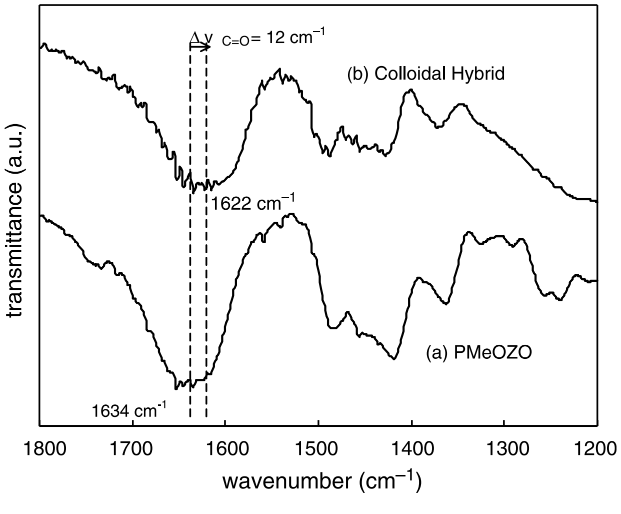


Fig. 2. FT-IR spectra of (a) the pristine PMeOZO and (b) the colloidal polymer hybrid (run 4).

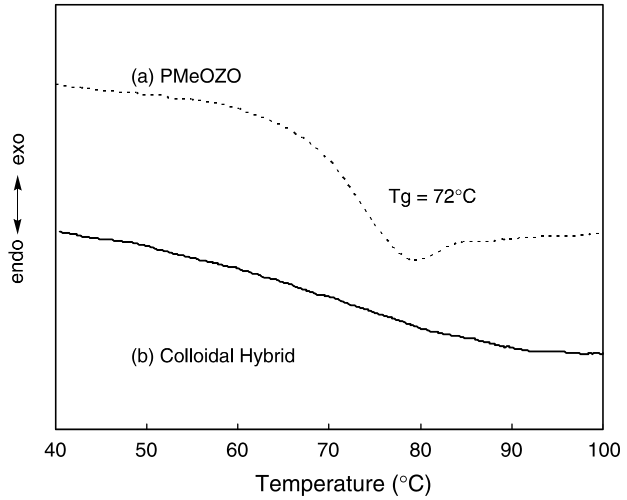


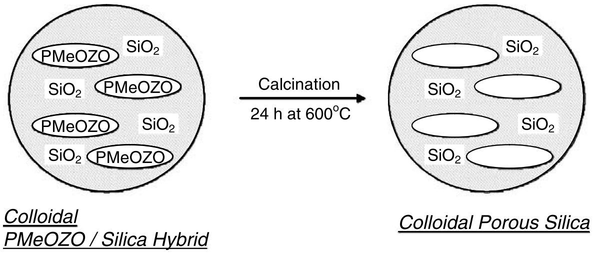
Fig. 3. DSC thermograms of (a) the pristine PMeOZO and (b) the colloidal polymer hybrid (run 4).

dispersion scale of the film state polymer hybrid using methanol was nanometer scale (Fig. 4).

The solvent-resistant property of the colloidal polymer hybrid was examined (Table 2). Surprisingly, little PMeOZO was extracted with methanol (run 3). In the colloidal polymer hybrid with PEtOZO, the solvent-resistance was also high (run 6), while 60–80% of polyoxazoline was extracted in the transparent polymer hybrid film using methanol (run 8). The excellent solvent-resistance in the colloidal polymer hybrids is almost same as that of the polymer hybrids having an interpenetrating polymer network structure [20,24,25,27,28]. The excellent solvent-resistance in the colloidal polymer hybrids should result from the molecular scale dispersion of polyoxazolines in a silica gel matrix, which was revealed by nitrogen adsorption study.

The thermal stability of the colloidal polymer hybrids was measured. Ten wt% decomposition temperature ($T_{10}$) of the colloidal polymer hybrid and the pristine PMeOZO was 319.5 and 124.5 °C, respectively, which indicates the improvement of the thermal stability of the PMeOZO by hybridization with silica gel (Fig. 5).

The process of the formation of the colloidal polymer hybrids in water was revealed by TEM measurement. In the homogeneous solution from TMOS and water after vigorous stirring for 10 min, the nanoparticles at 2–7 nm were clearly observed as shown in Fig. 6(a.). The nanoparticles should be



Scheme 2.

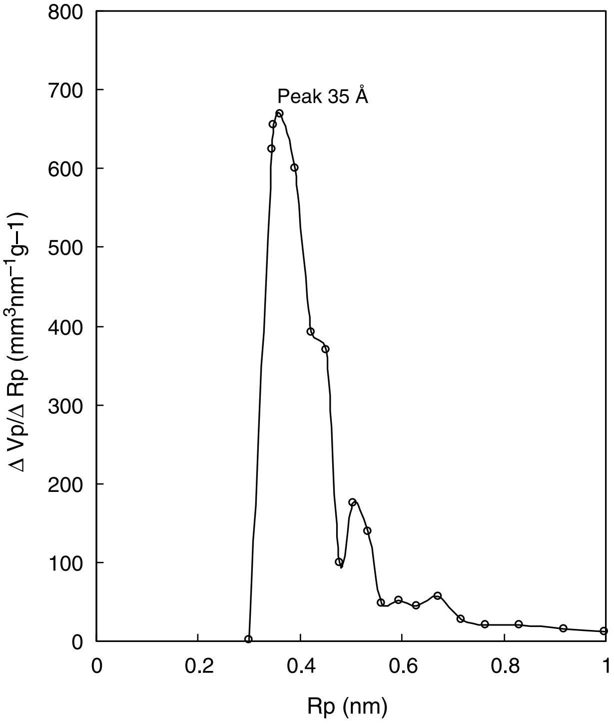


Fig. 4. Pore size distribution plot of the porous silica prepared from the calcination of the colloidal polymer hybrid (run 4).

Table 2
Solvent-resistant property of colloidal polymer hybrids

| Run | Poly(2-R-2-oxazoline) | | TMOS (mg) | Solvent extraction efficiency (%)[a] |
|---|---|---|---|---|
| | R | (mg) | | MeOH |
| 3 | Methyl | 50 | 250 | ∼0 |
| 6 | Ethyl | 50 | 250 | 23.2 |
| 8 | Methyl | 50 | 250 | 60.2 |

[a] The polymer content of the polymer hybrids before ($p_b$) and after ($p_a$) the extraction was calculated from TGA in air, and the solvent extraction efficiency ($E$) was calculated according to the equation: $E = 100(p_b - p_a)/p_b(100 - p_a)$.

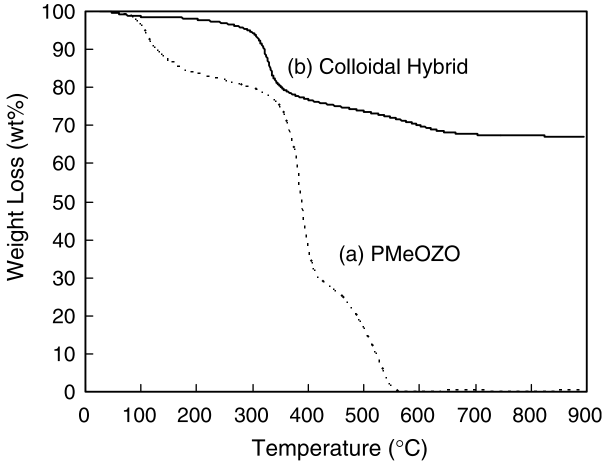
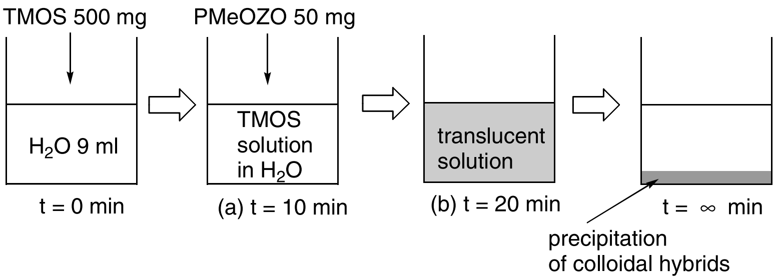


Fig. 5. TGA curves of (a) the pristine PMeOZO and (b) the colloidal polymer hybrid (run 4).



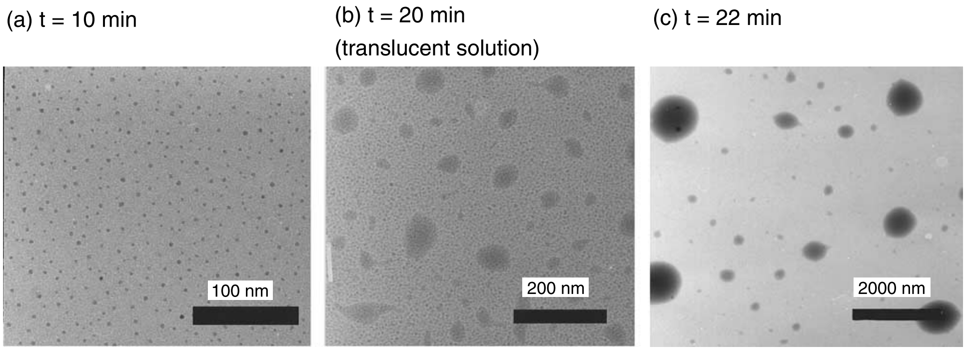
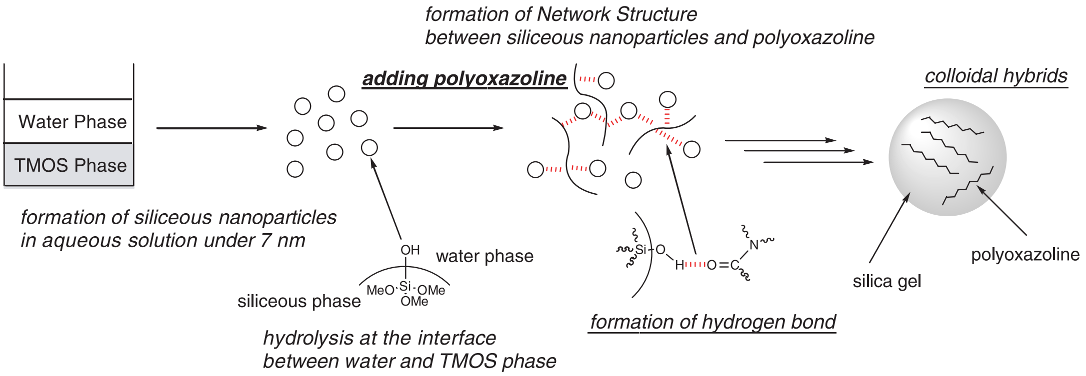


Fig. 6. TEM images of (a) the silica nanoparticles ($t = 10$ min, the scale bar: 100 nm), (b) the aggregations of the silica nanoparticles ($t = 20$ min, the scale bar: 200 nm) and (c) the aggregations of the silica nanoparticles ($t = 22$ min, the scale bar: 2 μm).

the micelle particles from TMOS. Then, the water solution containing PMeOZO was added to the mixture. After stirring for 20 min, the transparent solution was changed to the translucent one. The aggregations of the nanoparticles, observed in Fig. 6(a), were found around at 10–100 nm (Fig. 6(b)). Generally, the light scattering loss was observed in the presence of the particles over 30 nm, [32] thus the TEM image agreed with the change of the appearance of the reacting solution. The further aggregation of the nanoparticles took place after stirring for 22 min. The aggregations at 30–500 nm were presented as a result (Fig. 6(c)).

From these observations, the progress of the formation of the colloidal polymer hybrids can be proposed in Scheme 3. The nanoparticles from the formation of the micelle were initially formed in water by vigorous stirring of the phase-separated solution between TMOS and water. The formation of micelle is induced by the hydrolysis of the interface between TMOS and water phases. Then, three-dimensional network should be formed by addition of polyoxazoline. The driving force of the interaction between polyoxazoline and seed siliceous nanoparticles should be hydrogen bonding, which was directly estimated by the FT-IR study. Generally, the hydrogen bond interaction should be very weak in water, but it was known that the polymer–polymer complex via hydrogen bonds such as poly(*N*-vinylpyrrolidone)–poly(vinyl alcohol) and poly(acrylic acid)–poly(ethylene oxide) formed in an aqueous solution because the polymer complexes by the hydrogen bonding were enhanced by the hydrophobic interaction in the hydrophilic aqueous solution [33–35]. Therefore, PMeOZO should play a role as a cross-linker of



Scheme 3.

the siliceous nanoparticles in the present research. The progress of the three-dimensional network formation gave the colloidal polymer hybrids.

## 4. Conclusions

Colloidal organic–inorganic polymer hybrids with polyoxazolines were prepared in an aqueous solution. The polyoxazoline was completely dispersed in a colloidal silica gel matrix at the molecular scale, revealed by nitrogen adsorption porosimetry, DSC, solvent-resistance and TGA studies. The driving force of the formation of colloidal polymer hybrids was hydrogen bonds between polyoxazoline and siliceous phases identified by FT-IR measurement. The silica nanoparticles formed three-dimensional network by adding polyoxazoline because polyoxazoline acted as a cross-linker between siliceous nanoparticles.

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