Synthesis of Organic–Inorganic Polymer Hybrids from Ammoniumpropyl-Functionalized Polyhedral Oligomeric Silsesquioxane

Kaoru Adachi, Ryo Tamaki, and Yoshiki Chujo*

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

Received March 19, 2004; E-mail: chujo@chujo.synchem.kyoto-u.ac.jp

Organic–inorganic polymer hybrids were prepared from ammoniumpropyl-functionalized polyhedral oligomeric silsesquioxane, octa(3-chloroammoniumpropyl)octasilsesquioxane (OCAPS), and several organic polymers such as poly(*N*-vinylpyrrolidone) (PVP), poly(*N*,*N*-dimethylacrylamide) (PDMAAm), and poly(vinyl alcohol) (PVA). The polymer hybrids obtained were optically transparent and soluble in methanol or water. The results of IR spectra of the organic polymers and the polymer hybrids indicate an interaction between the organic component and the inorganic one in the homogeneous polymer hybrids.

Organic–inorganic hybrid materials have recently attracted much attention because of their characteristic properties.[1–5] The sol–gel reaction of metal alkoxide is one of the most effective methods for the preparation of hybrid materials because of the low reaction temperature. When alkoxysilanes are used as precursors, Si–OH groups are formed by hydrolysis of alkoxy groups and, with condensation of hydroxy groups, Si–O–Si linkage should be obtained. With further hydrolysis and condensation, a siloxane network evolves via crosslinking of oligomers. After the solvent is removed, xerogel can be obtained. We have recently investigated the preparation of homogeneous polymer hybrids of organic polymers such as poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone) as well as poly(*N*,*N*-dimethylacrylamide) and silica gel utilizing the sol–gel reaction of alkoxysilanes. In the polymer hybrids described above, hydrogen bonding interactions between residual silanol groups and amide groups of organic polymers were confirmed by FT-IR. We speculated that such hydrogen bonding interactions were strong enough to integrate the organic polymers and silica gel at the molecular level. The organic–inorganic polymer hybrids prepared by the sol–gel reaction of alkoxysilanes in the presence of organic polymers are known to have good properties such as high thermal stability and high strength.[5] However, because of the sol–gel reaction, the silica gel in the hybrids is amorphous and the hybrids thus obtained are not soluble in any organic solvents. Due to this insoluble property, it is impossible to reform the gel after it once forms. In addition, the homogeneity of the hybrids is dependent on the sol–gel reaction conditions. One of the answers to these problems is a utilization of polyhedral oligomeric silsesquioxanes as inorganic starting material for the preparation of the hybrids.

Silsesquioxanes are materials with the formula of $RSiO_{1.5}$. Among various silsesquioxanes, polyhedral oligomeric silsesquioxanes, which are prepared by the sol–gel reaction under the specific condition, have recently attracted much attention because of their solubility and thermal stability.[6–12] The polyhedral oligomeric silsesquioxanes have also received much attention as inorganic precursors because they are the smallest particles of sand and can easily be functionalized with organic moieties.[13–17] J. D. Lichtenhan and co-workers have developed a technique to utilize polyhedral oligomeric silsesquioxanes as a building unit in organic polymers.[8] The group of R. M. Laine reported organic–inorganic hybrids prepared from functionalized polyhedral oligomeric silsesquioxanes by covalent bonding; such hybrids showed remarkable mechanical properties and high thermal stability.[18–21] The hybrid materials containing polyhedral oligomeric silsesquioxanes without any covalent bonding between organic polymer and silsesquioxanes would show good performance, such as good thermal stability and mechanical properties, as the polymer hybrids from the sol–gel method utilizing various physical interactions. Here, the synthesis and properties of the organic–inorganic polymer hybrids prepared from polyhedral oligomeric silsesquioxanes are reported.

Experimental

Materials. Methanol (MeOH) was used after distillation with magnesium and iodine under nitrogen. Chloroform, 1,2-dichloroethane, allyl cyanide, and 1,2-dimethoxyethane were used after drying and distillation under nitrogen. Ammoniumpropyl-functionalized polyhedral silsesquioxane (OCAPS) was prepared from 3-aminopropyltriethoxysilane using the detailed experimental procedure described in a previous report.[22] Octahydridosilsesquioxane (Cube-H) was prepared according to the literature.[23] Octacyanopropylsilsesquioxane (Cube-CN) was synthesized by the procedure described in the following. Poly(*N*-vinylpyrrolidone) (MW av. 630000) was purchased from Tokyo Kasei Kogyo Co., Ltd. Other reagents were used as supplied.

Synthesis of Octacyanopropylsilsesquioxane (Cube-CN). Octahydridosilsesquioxane (Cube-H) (0.50 g, 1.18 mmol) was dissolved in 1,2-dichloroethane (30 mL). To the solution, allyl cyanide (1.14 mL, 14.2 mmol) and 2.33 mM 1,2-dimethoxyethane solution of $H_2PtCl_6 \cdot 6H_2O$ (0.5 mL) were added. The mixture was

Published on the web November 11, 2004; DOI 10.1246/bcsj.77.2115

heated at 80 °C under nitrogen for 24 h. After removal of the solvent, a clear oily product was obtained and used directly for the following experiments. ^{1}H NMR (DMSO-d_6); δ 2.43 (t, 2H), 1.79 (m, 2H), 0.88 (t, 2H).

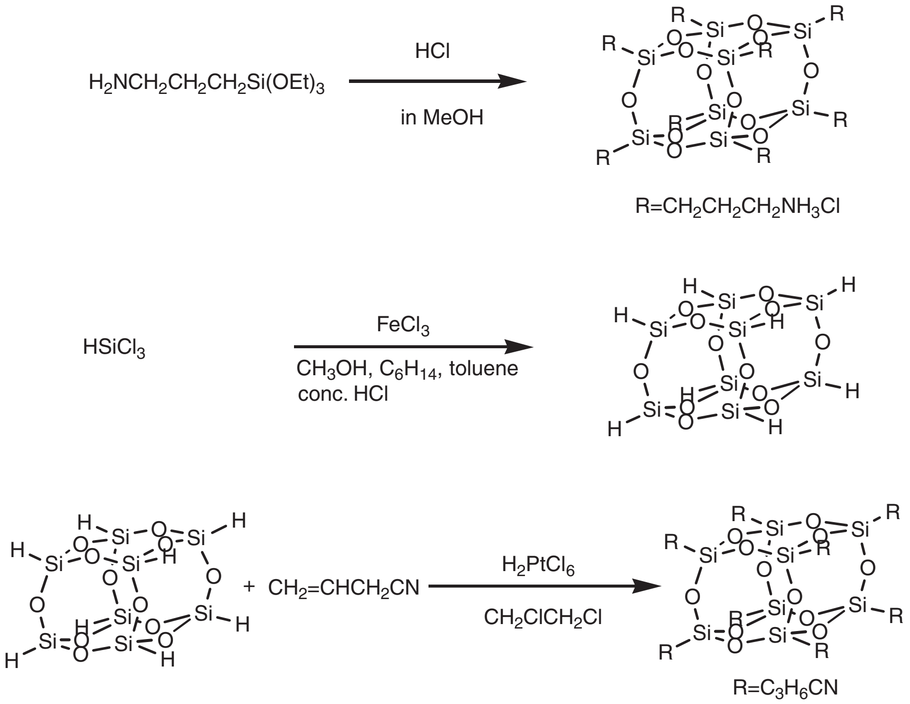
Synthesis of Silsesquioxane Polymer Hybrids. A prescribed amount of organic polymer was dissolved in dry solvent with silsesquioxane. In the cases of Cube-H polymer hybrids and Cube-CN, chloroform was used. After stirring at room temperature for 1 h, the mixture was placed in a plastic container and heated in air at 50 °C.

Measurements. Differential scanning calorimetry (DSC) was performed on a SEIKO DSC200 with a heating rate of 10 °C/min in air. DSC thermograms were measured after the samples were heated from room temperature to 250 °C with a heating rate of 10 °C/min. Thermogravimetric analysis (TGA) was performed on a SEIKO TG/DTA 6200 with a heating rate of 10 °C/min in air. Scanning electron microscopy (SEM) measurements were conducted with a JEOL JSM-5130LV. The samples for SEM were taken by breaking monolith hybrids; a piece with the size about 5 mm × 5 mm × 0.5 mm was used for the measurement. ^{1}H NMR spectra were measured on a JEOL EX270 spectrometer with dimethyl sulfoxide-d_6.

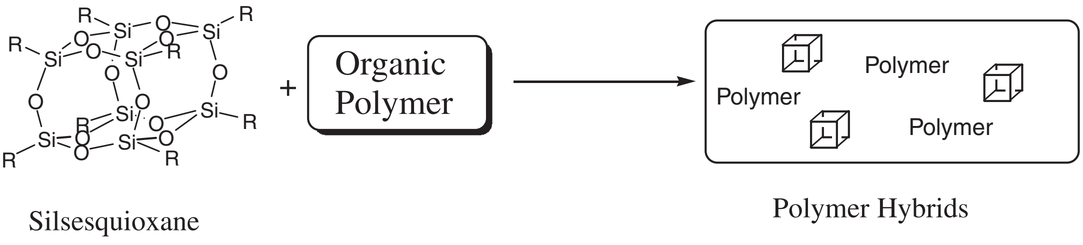
Results and Discussion

Preparation of Organic Polymer/Silsesquioxane Hybrids. OCAPS was prepared by the hydrolysis and condensation reactions of 3-aminopropyltriethoxysilane in methanol. For comparison with OCAPS, two silsesquioxanes having other functional groups were prepared. Cube-H was prepared by the hydrolysis and condensation reactions of trichlorosilane. Cube-CN was prepared by the hydrosilation reaction of allyl cyanide and Cube-H using a platinic acid catalyst (Scheme 1).

OCAPS/PVP hybrids were prepared by mixing both components in the solvent. The solvent was evaporated at 50 °C for 2 days (Scheme 2). Various ratios of the samples were examined to evaluate the effect of the ratio of organic polymer and OCAPS. Also to evaluate the effect of the organic polymer component, various polymers were used for preparation of polymer hybrids. As shown in Table 1, by using PVP as an organic polymer, the optically transparent polymer hybrids were obtained in a wide range of the ratio of PVP to OVAPS from 10:1 to 1:1. The obtained polymer hybrid materials were soluble in organic solvents such as methanol and dimethyl sulfox-



Scheme 1. Synthesis of functionalized silsesquioxanes.



Scheme 2. Synthesis of silsesquioxane/organic polymer hybrids.

Table 1. Preparation of PVP/Silsesquioxane Polymer Hybrids

Run	Functional group (R)	PVP/silsesquioxane (w/w)	Appearance
1	$(CH_2)_3NH_3Cl$	10/1	transparent
2	$(CH_2)_3NH_3Cl$	2/1	transparent
3	$(CH_2)_3NH_3Cl$	1/1	transparent
4	H	10/1	phase separated
5	$(CH_2)_3CN$	10/1	phase separated

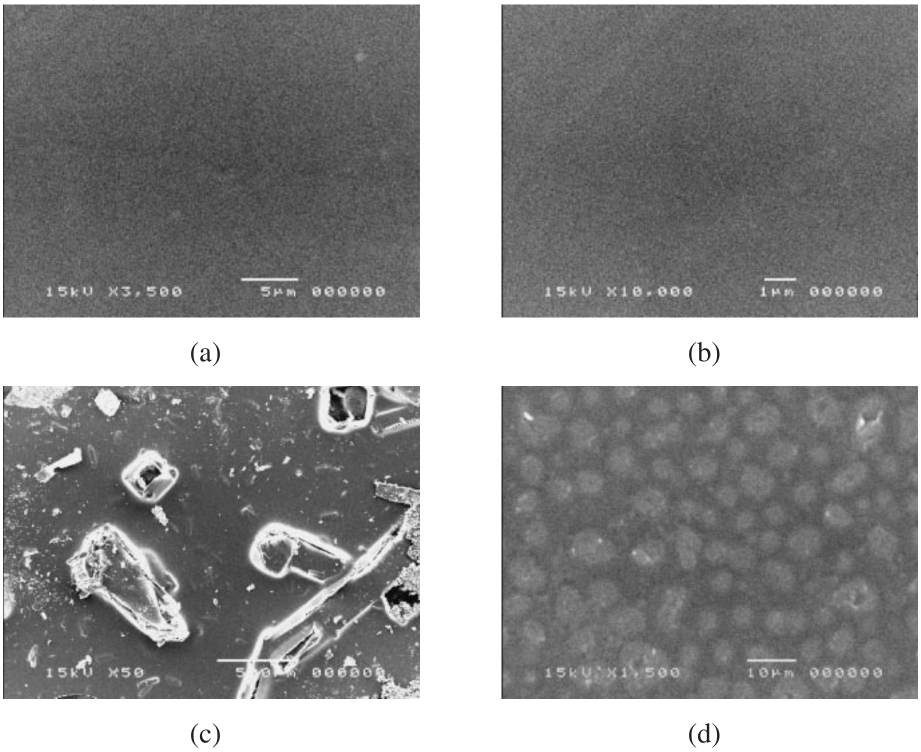


Fig. 1. SEM images of PVP–silsesquioxane hybrids. (a), (b) R = $(CH_2)_3NH_3Cl$, (c) R = H, (d) R = $(CH_2)_3CN$.

ide, which is in clear contrast to the insoluble polymer hybrids prepared by the sol–gel method. Furthermore, the obtained polymer hybrids showed good film-forming properties. These results indicate that OCAPS and PVP were dispersed in a scale smaller than the wavelength of visible light. Further fine phases of the obtained hybrids were observed by SEM measurement. Figure 1 shows the SEM images of PVP–silsesquioxane hybrids. No phase separation was observed in the PVP–OCAPS hybrids even at the magnification of 3500 and 10000 (Figs. 1a and 1b, respectively). These results mean that OCAPS was dispersed in PVP homogeneously.

Two other silsesquioxanes and PVP hybrid materials were prepared by the same method. Table 1 shows the results of the preparation of these hybrid materials. The composite from Cube-H was turbid even in the ratio of 1/10 to PVP. The composite from Cube-CN was also turbid. In the SEM image of the turbid composites, phase separation of the PVP and Cube-H can be observed; the domain of aggregation of this silsesquioxane was more than 500 µm (Fig. 1c). Also in the case of Cube-CN, the phase separation of the PVP and Cube-CN was confirmed; here, the domains of aggregation of this silsesquioxane were 5–10 µm (Fig. 1d).

Other organic polymers and OCAPS polymer hybrids were similarly prepared. Table 2 shows the solvents used and the results of the preparation of the hybrid materials. When poly(2-methyl-2-oxazoline) (POZO), poly(*N*,*N*-dimethylacrylamide) (PDMAAm), and poly(vinyl alcohol) (PVA) were used as organic polymers, optically transparent polymer hybrids were obtained. The PVA/OCAPS polymer hybrid materials were soluble in water. Other polymer hybrids were soluble in methanol and dimethyl sulfoxide. When poly(ethylene oxide) (PEO) was used, the phase separated composite was obtained. It can be considered that the crystallization of PEO caused the phase separated hybrid material.

The interaction between organic polymers and OCAPS was confirmed by FT-IR spectra. The carbonyl stretching vibration peak derived from the amide group in PVP was observed around 1650 cm^{-1}. In the case of PVP/OCAPS polymer hybrid (Fig. 2a), this peak was broadened and the shoulder peak of the lower wavenumber increased. In contrast, no peak shift was observed in the phase-separated composite prepared from PVP and Cube-H. Figure 2b shows the FT-IR spectra of PDMAAm/OCAPS homogeneous polymer hybrid. The shift of the absorption of carbonyl stretching peak to lower wave-

Table 2. Preparation of Polymer Hybrids Starting from OCAPS

Run	Organic polymer	Solvent	Organic polymer/OCAPS (w/w)	Appearance
1	PVP	MeOH	1/1	transparent
2	PDMAAm	MeOH	1/1	transparent
3	POZO	MeOH	1/1	transparent
4	PVA	H_2O	1/1	transparent
5	PEO	H_2O	1/1	phase separated

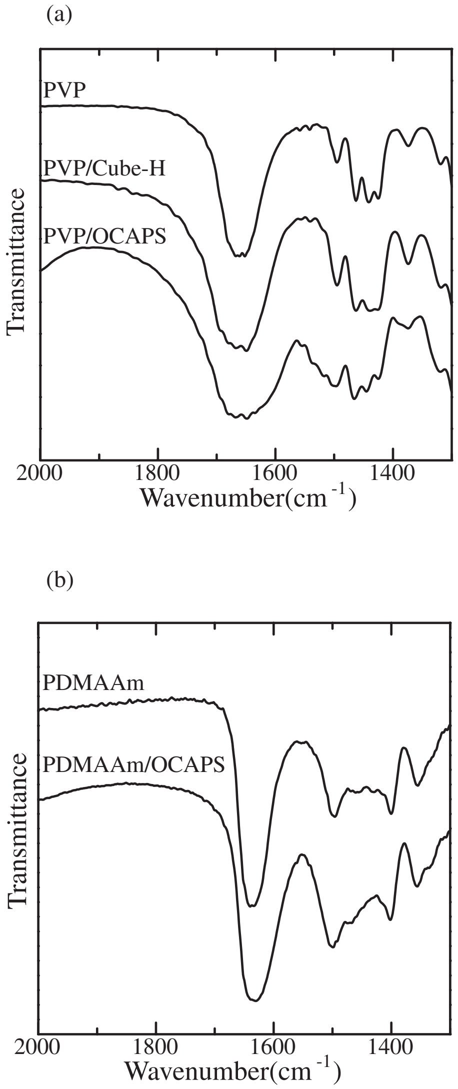


Fig. 2. FT-IR spectra of polymer hybrids. (a) PVP/OCAPS hybrid, (b) PDMAAm–OCAPS hybrid.

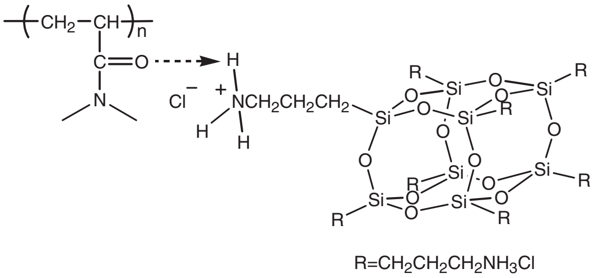


Fig. 3. Hydrogen-bond formation in polymer hybrids.

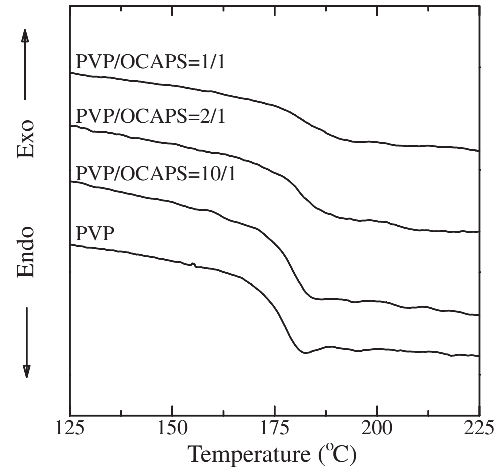


Fig. 4. DSC thermograms of PVP and PVP/OCAPS polymer hybrids.

number was also observed in this case. These results indicate that the amide carbonyl groups in the organic polymers contribute to the interaction between organic polymers and OCAPS. From these results, when the amide group containing polymer was used, one can presume a hydrogen bonding interaction as illustrated in Fig. 3 between carbonyl group and ammonium group in the polymer hybrid. Also in the case of PVA/OCAPS polymer hybrid, hydrogen bonding interaction might give the homogeneous polymer hybrids.

Thermal Properties of Organic Polymer/Silsesquioxane Hybrids. Figure 4 shows the DSC thermograms of PVP and PVP/OCAPS hybrids. The glass transition temperature (T_g) of PVP was observed around 175 °C. In the case of PVP/OCAPS hybrids, T_g becomes higher and unclear with an increase of the content of OCAPS; T_g was observed above 180 °C in the 1:1 hybrid. This result, which is similar to that for the polymer hybrids prepared from sol–gel reaction, suggests that the inorganic silsesquioxane prevents the mobility of the organic polymer, due to the specific interaction and bulky silsesquioxane cores.

Figure 5 shows the TGA traces of PVP and PVP/OCAPS hybrids. Generally, in the case of the polymer hybrids from sol–gel reactions, the thermal stability of the polymer hybrid is increased. Unfortunately, the observed decomposition temperature of the obtained hybrids becomes lower with the increase of the content of OCAPS. This result might be ascribed to the elimination of HCl after heating and this HCl might act as the catalyst for the decomposition of PVP.

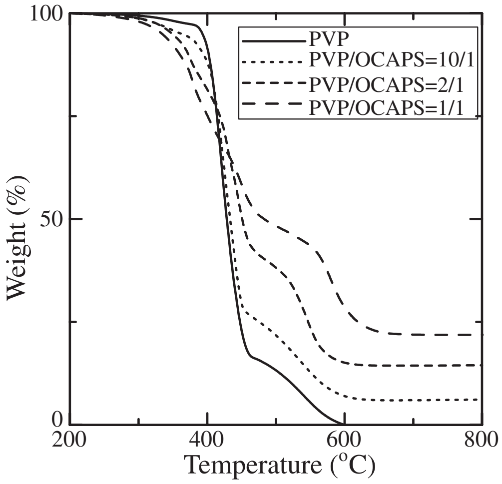


Fig. 5. TGA traces of PVP and PVP/OCAPS polymer hybrids.

Conclusion

Transparent polymer hybrids based on ammoniumpropyl-functionalized silsesquioxane were prepared. The polymer hybrids showed processability and film-forming property. The polymer hybrids obtained were soluble in water, methanol, and dimethyl sulfoxide. The removal of the solvent from the hybrid solution gave the transparent hybrid film, in contrast to the polymer hybrids prepared by sol–gel reaction, that are insoluble in all solvents. FT-IR spectra showed the shift of the amide carbonyl stretching band to a lower wavenumber region; this result suggests the specific interaction between carbonyl groups and ammonium groups. The DSC analysis showed that T_g was increased by the addition of OCAPS. In our polymer hybrids, the thermal stability was unfortunately decreased, but this hybridization method would give many organic–inorganic hybrid materials and organic–inorganic nanocomposites only by mixing of organic materials and silsesquioxanes. Recently, various kinds of functionalized silsesquioxanes have been synthesized and studied. From a point of view of composites, silsesquioxanes can play a role of very small and easily functionalizable inorganic fillers in the silsesquioxane hybrids.

References

1 C. J. Brinker and G. W. Scherer, "Sol–Gel Science," Harcourt Brace & Co., Boston (1990).

2 Y. Chujo, E. Ihara, S. Kure, and T. Saegusa, *Macromolecules*, **26**, 5681 (1993).

3 Y. Chujo and T. Saegusa, *Adv. Polym. Sci.*, **100**, 11 (1992).

4 Y. Chujo, *Polym. Mater. Sci. Eng.*, **74**, 65 (1996).

5 Y. Chujo, H. Matsuki, S. Kure, T. Saegusa, and T. Yazawa, *J. Chem. Soc., Chem. Commun.*, **1994**, 635.

6 R. H. Baney, M. Itoh, A. Sakakibara, and T. Suzuki, *Chem. Rev.*, **95**, 1409 (1995).

7 D. A. Loy and K. J. Shea, *Chem. Rev.*, **95**, 1431 (1995).

8 J. D. Lichtenhan, A. Romo-Uribe, P. T. Mather, and T. S. Haddad, *J. Polym. Sci., Part B: Polym. Phys.*, **36**, 1857 (1998).

9 D. Herren, H. Bürgy, and G. Calzaferri, *Helv. Chim. Acta*, **74**, 24 (1991).

10 U. Dittmer, B. J. Hendan, U. Flörke, and H. C. Marsmann, *J. Organomet. Chem.*, **489**, 185 (1995).

11 E. C. Lee and Y. Kimura, *Polym. J.*, **29**, 678 (1997).

12 I. Hasegawa and S. Motojima, *J. Organomet. Chem.*, **441**, 373 (1992).

13 R. M. Laine, C. Zhang, and R. Baranwal, *Polym. Prepr.*, **36**, 342 (1995).

14 G. H. Mehl and J. W. Goodby, *Angew. Chem., Int. Ed. Engl.*, **35**, 2641 (1996).

15 S. E. Yuchs and K. A. Carrado, *Inorg. Chem.*, **35**, 261 (1996).

16 F. J. Feher and K. D. Wyndham, *Chem. Commun.*, **1998**, 323.

17 K. J. Shea, D. A. Loy, and O. Webster, *J. Am. Chem. Soc.*, **114**, 6700 (1992).

18 R. M. Laine, A. Sellinger, and C. Zhang, *Polym. Prepr.*, **36**, 282 (1995).

19 R. M. Laine and A. Sellinger, *Polym. Prepr.*, **35**, 665 (1994).

20 R. M. Laine and A. Sellinger, *Macromolecules*, **29**, 2327 (1996).

21 R. M. Laine and A. Sellinger, *Chem. Mater.*, **8**, 1592 (1996).

22 R. M. Laine and M. C. Gravel, *Polym. Prepr.*, **38**, 155 (1997).

23 P. A. Agaskar, *Inorg. Chem.*, **30**, 2707 (1991).