A New Amphiphilic and Thermoresponsive Polysilsesquioxane Having Alkoxyethylamide Group

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(Received April 23, 2008; CL-080426; E-mail: moriyaos@nda.ac.jp)

The polysilsesquioxanes (PSQ) having alkoxyethylamide groups were prepared from the silane coupling reagents, prepared by addition reaction of alkoxyethylamines to (3-isocyanatopropyl)triethoxysilane, by condensation under acidic conditions. In the obtained PSQs, those having bis(methoxyethyl)amide or bis(ethoxyethyl)amide group showed reversible thermoresponsive phase separation in an aqueous solution. The PSQs formed by the co-condensation of such silane coupling reagents, the feed mole ratio of which were changed, also showed the thermoresponsive aggregation at the temperatures reflected with the ratios of alkoxyethyl groups.

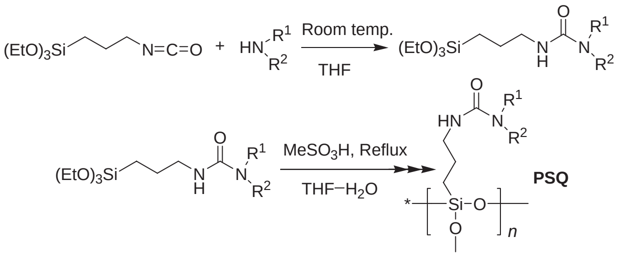
Recently, the investigations concerning thermo-responsive phase separation of polymeric compounds in an aqueous solution have been widely developed from the interests in the use of various material scenes such as microencapsulation, biosensor, and drug delivery.[1,2] We also have reported the syntheses of thermoresponsive hybrid polymers containing polysilsesquioxane (PSQ) structure, in which the grafted poly(*N*-isopropylacrylamide) is utilized for providing the property.[3] The thermoresponsive derivatives of PSQ seem to be a useful functional material showing the improved durability for heat and weatherability.[4] On the other hand, the introduction of an appropriate functional group into PSQ main chain is expected to be another practical method for providing the thermoresponsive property and lead to a variety of useful hybrid materials. The synthetic polymers usually contain several common structures which bring the thermoresponsivility besides amphiphilicity. The representative structures are consisted of hydrophilic amide and/or ethyleneoxy groups with hydrophobic alkyl groups.[5,6] By considering such previous information, alkoxyethylamide group is thought to be a promising functional group to present the properties to PSQ. Fortunately, the starting silane coupling reagents for the formation of the modified PSQs are thought to be readily prepared from the simple addition reaction using commercially available (3-isocyanatopropyl)triethoxysilane and amines.

The silane coupling reagents having alkoxyethylamide group could be prepared efficiently in the high yields over 80% as supposed above.[7] The obtained triethoxysilanes were transformed into the PSQ derivatives through condensation reaction in the mixed solvents of tetrahydrofuran and water with a catalytic amount of methanesulfonic acid. The results of the condensation and synthetic route were shown in Table 1 and Scheme 1.

Table 1. Condensation of silane coupling reagent

PSQ	R^1	R^2	Yield[a] /%	M_n[b] (M_w/M_n)
1	H	CH_2CH_2OMe	Gel	—
2	Me	CH_2CH_2OMe	98	3500 (1.25)
3	CH_2CH_2OMe	CH_2CH_2OMe	89	4400 (1.05)
4	CH_2CH_2OEt	CH_2CH_2OEt	75	3700 (1.07)
5	CH_2CH_2–O–CH_2CH_2		92	4200 (1.02)

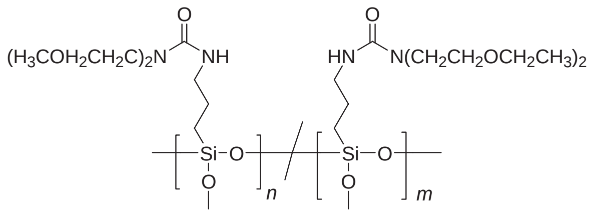
[a]Based on the content of functional group, which was estimated from ^{1}H NMR spectral data. [b]Estimated by GPC based on poly(methyl methacrylate) standards.



Scheme 1.

Five kinds of the silane coupling reagents were prepared and employed here for the condensation to give the PSQs. However, the reagent having mono-methoxyethyl group gave gel product **1**. While, other four PSQ derivatives **2**–**5** were successfully obtained as the viscous oils soluble in toluene, chloroform, THF, and water, but insoluble in diethyl ether. The contents of the functional groups in the PSQs were calculated by the spectral data of ^{1}H NMR, in which hexamethyldisiloxane was used as an internal standard.[8] The yields listed in Table 1 were based on the contents of the functional groups. The number-average molecular weight (M_n) was estimated by GPC using poly(methyl methacrylate) standards. In the measurements, the M_ns of the products were indicated to be in the range from 3500 to 4400. Further, in the respective GPC chromatogram of the PSQs, a unimodal peak was observed. Thus, the four PSQs were employed for the measurement of turbidity in an aqueous solution.

The thermoresponsive aggregation behavior of 1 wt % aqueous solution of PSQs **2**–**5** was evaluated by the transmittance (%T) at 800 nm under heating and cooling, the rate of which was adjusted to be 1 °C/1 min. The PSQ having *N*-(2-methoxyethyl)methylamide group **2** showed a good solubility in water, but too hydrophilic to present the aggregation. On the other hand, the PSQ having morpholino group **5** was hardly soluble in water as shown in 27% of %T. Among the PSQs, those having bis(2-methoxyethyl)amide **3** and bis(2-ethoxyethyl)amide group **4** showed the reversible aggregation according to temperature. The lowest critical solution temperature (LCST) of **3** was 66 °C and that of **4** was 26 °C, respectively. Such difference of LCST was understandable. Since, the PSQ **4** had ethoxy groups, which should be more hydrophobic than methoxy groups contained in **3**. This also seemed to be linked with a relatively good response of the aggregation to temperature as



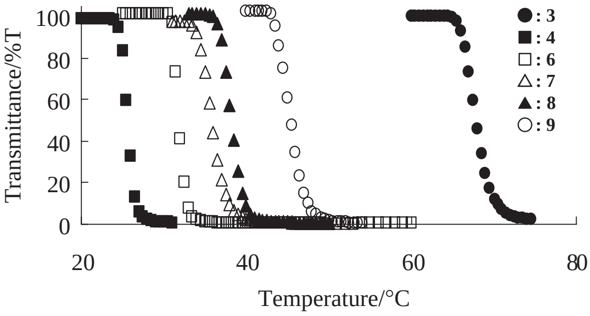


Figure 1. Temperature dependence of optical transmittance (%T) at 800 nm for 1 wt % aqueous solution of PSQ under heating (1 °C/min).

observed in the behavior of **4**. Such thermoresponsive aggregations of the PSQs were shown in Figure 1. The thermoresponsive aggregations of the PSQs were reversible, but the results of the measurements under cooling were skipped to avoid complexity.

Next, the co-condensations of the corresponding silane coupling reagents were conducted to form the PSQs having both bis(2-methoxyethyl)amide and bis(2-ethoxyethyl)amide groups. Four PSQs, which contained 0.5 (**6**), 0.9 (**7**), 1.9 (**8**), and 3.3 (**9**) of unit ratios of bis(methoxyethyl) group/bis(ethoxyethyl) group, were prepared over 80% yields for the evaluation of thermoresponsive behavior. The contents of the functional groups in the obtained PSQs were almost in accord with the feed mole ratios of the corresponding silane coupling reagents. The values of M_n for the obtained PSQs were estimated to be the almost same values such as 3700. In the resulting PSQs, two kinds of the functional groups were supposed to be randomly located along with the polysilsesquioxane main chain. The reversible thermoresponsive aggregation behavior of the co-condensated PSQs was also shown in Figure 1, although the behavior under cooling was excluded. The PSQ, **7**, containing the almost same unit ratio of ethoxy group/methoxy group such as 0.9, showed 33 °C of LCST. Even in the case of **9** containing 3.3 times unit ratio of bis(2-methoxyethyl) group to bis(2-ethoxyethyl) group, 45 °C of LCST was recorded. Such behavior was interpreted that the aggregation of bis(ethoxyethyl)amide group stimulated or enhanced that of bis(methoxyethyl)amide group. In other words, the aggregation of the former groups, occurred at the lower temperature, might remove water molecules and form a hydrophobic environment around the later groups. This should result in the unexpected lower LCST of the PSQs **8** and **9** in spite of the larger content of bis(methoxyethyl)amide group.

Thus, the new thermoresponsive PSQs, which had the functional groups showing reversible thermoresponsive aggregation behavior in an aqueous solution, were successfully prepared. On the other hand, the detailed structure control of polysiloxane unit has been continuously examined. The thermoresponsive behavior of the PSQs demonstrated that aggregation temperature was controlled by the combination of the functional groups, but the change of LCST was not in proportion to the content of the alkoxyethyl groups. In addition, the starting silane coupling reagents were regarded as the useful building blocks for the preparation of multifunctional PSQ derivatives. The combination with various silane coupling reagents having other functional groups should be available for the preparation of new hybrids.

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7 The reaction was carried out as follows: the solution of (3-isocyanatopropyl)triethoxysilane and an equimolar amount of the amine with 5 mol % of triethylamine in THF was stirred over night at ambient temperature under argon atmosphere. After evaporation to remove solvent, the residual silane coupling reagent was isolated by distillation under reduce pressure such as 170–210 °C/3 mmHg, respectively.

8 For the calculations of content of the functional groups, the peak areas of the signals at 3.44 ppm assigned to methylene protons of alkoxyethyl group bonded to nitrogen were compared to that of methyl protons of hexamethyldisiloxane appeared at 0 ppm.