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Synthesis of a Novel Silicone Monomer Bearing Amide Groups to Improve Compatibility with Hydrophilic Vinyl Monomers

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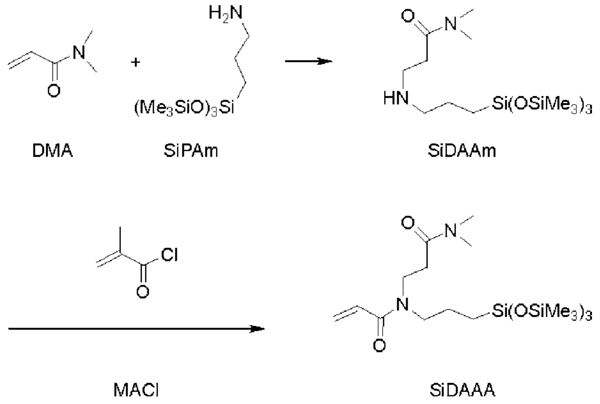
We designed a novel monomer bearing one organosiloxanyl group and two amide groups in order to improve its compatibility with hydrophilic vinyl monomers. The novel monomer, *N*-2-(*N*′,*N*′-dimethylcarbamoyl)ethyl-*N*-[3-tris(trimethylsiloxy)silylpropyl]acrylamide (SiDAAA) showed good miscibility with *N*-(hydroxyethyl)acrylamide (HEAA) and formed a transparent hydrogel with 2-hydroxyethyl methacrylate (HEMA) in the presence of a crosslinker. In contrast, the conventional monomer did not show transparency, such as tris(trimethylsiloxy)silylpropyl methacrylate (TRIS). These results validated our monomer design concept.

Silicone material has been attracting much interest due to its extremely high gas permeability. Therefore, it is widely used in medical devices, such as artificial lungs[1,2] and silicone elastomer contact lenses.[3,4] Such applications have been achieved by the modification of the hydrophobic nature of silicone into hydrophilic character. Thus, hydrophilicity is important for medical use of siloxane compounds. In fact, hydrophilic material like hydrogel[5–9] is abundantly used. So, silicone-containing hydrogel (silicone hydrogel) has received much attention for decades, possibly improving the poor gas permeability of the original hydrogels. For this purpose, small modifications of poly(dimethylsiloxane) (PDMS) are commonly carried out with poly(ethylene glycol) chains to transform the hydrophobic and lipophilic silicone character, in addition to the introduction of radically polymerizable groups into PDMS.[10–12] The reason for small modifications is that there are only a few methods to connect hydrocarbon groups and silicon, such as hydrosilylation. However this type of siloxane constituent (PDMS macromer) is compatible with only a limited number of hydrophilic monomers. This can lead to insufficient balance among the physical properties of silicone hydrogel.

To overcome the problems of PDMS macromers, some efforts have been focused on the synthesis of novel silicone-containing monomers which bear both organosiloxanyl and hydrophilic groups.[13,14] Considering the wide application of silicone hydrogels however, copolymerization with commercialized vinyl monomers could be an important approach, such as *N*,*N*-dimethylacrylamide (DMA) and HEMA. From this point of view, taking advantage of the high hydrophilicity of the amide group, and high activity for vinyl polymerization of the acrylamide group, we designed a novel silicone-containing vinyl monomer, which has one organosiloxanyl group and two amide groups, and then examined the characteristics of the resulting silicone hydrogel using this novel monomer.



Scheme 1. Synthesis of SiDAAA.

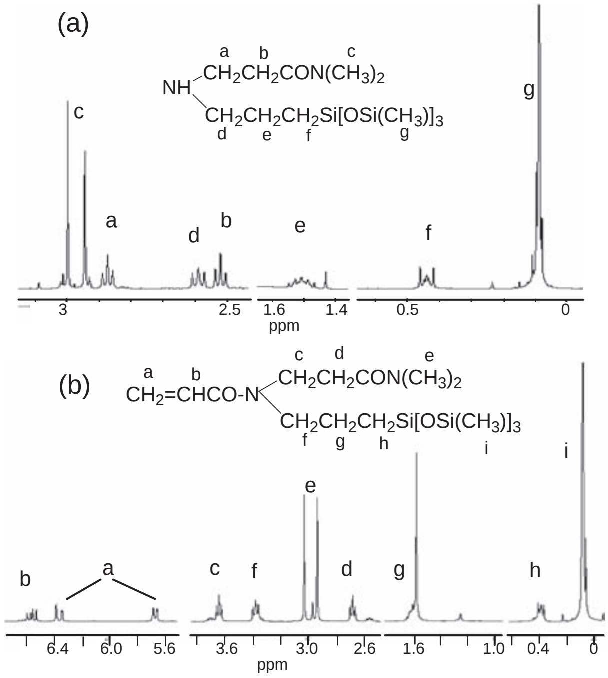


Figure 1. ^{1}H NMR spectra of SiDAAm (a) and SiDAAA (b).

The novel monomer, *N*-2-(*N*′,*N*′-dimethylcarbamoyl)ethyl-*N*-[3-tris(trimethylsiloxy)silylpropyl]acrylamide (SiDAAA) was thus designed and synthesized according to Scheme 1. ^{1}H NMR spectra (Figure 1), FT-IR spectrum, elemental analysis, and mass spectrometry[15] (Supporting Information) were measured respectively.

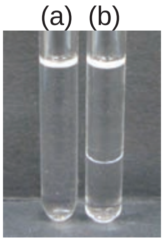


Figure 2. Comparison of miscibility between SiDAAA or TRIS and HEAA. (a) SiDAAA and HEAA. (b) TRIS and HEAA.

Table 1. Preparation of hydrogel[a]

Run	Silicone monomer		Hydrophilic monomer		Appearance
	SiDAAA	TRIS	DMA	HEMA	
1	60	0	40	0	Transparent
2	60	0	0	40	Transparent
3	0	60	40	0	Transparent
4	0	60	0	40	Opaque

[a]Number shows the parts by weight. Parts by weight was 1 for 3G, 0.2 for both V-65 and V-40.

To confirm the good compatibility and miscibility of SiDAAA with various types of hydrophilic monomers, we chose DMA, HEMA, and HEAA as typical hydrophilic monomers and studied the miscibility between these monomers and SiDAAA. Both SiDAAA and TRIS showed good miscibility with DMA and HEMA. However, there was a big difference in the case of HEAA as shown in Figure 2. SiDAAA was very miscible with HEAA (Figure 2a), whereas the combination of TRIS and HEAA showed phase separation (Figure 2b). This suggests that a wide variety of hydrophilic monomers can be used with SiDAAA for silicone hydrogel preparation.

Next, we compared the appearance of hydrogels. The results from the silicone hydrogel preparation using TRIS, SiDAAA, DMA, and HEMA are shown in Table 1. The conventional silicone monomer, TRIS, gave an opaque hydrogel when it was copolymerized with HEMA, although it was transparent after copolymerization with DMA. On the other hand, the novel monomer, SiDAAA, produced transparent hydrogels by copolymerization with HEMA, as well as with DMA. These results imply that the additional amide group in the SiDAAA monomer supports good miscibility during hydrogel preparation. The appearance of the hydrogels is shown in Figure 3. As expected from the miscibility test, SiDAAA gave a transparent polymer both before and after hydration of the hydrogel (Figures 3a and 3c). The difference in appearance between the TRIS and SiDAAA hydrogels may be due to the difference between the number and types of polar groups in each molecular structure, and this supports the validity of our approach to monomer design.

The copolymerized gels were also swollen in common organic solvents like tetrahydrofuran, chloroform, methanol, and dimethyl sulfoxide, implying the possibility of wide application. Measurement of the detailed physical characteristics, such as oxygen permeability and mechanical strength, are currently underway.

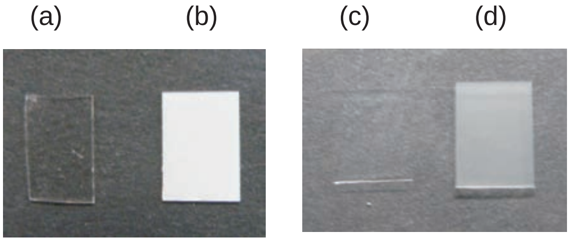


Figure 3. Comparison of appearance of hydrogel. (a) Polymer before hydration from SiDAAA and HEMA, (b) polymer before hydration from TRIS and HEMA, (c) hydrogel from SiDAAA and HEMA in water, and (d) hydrogel from TRIS and HEMA in water.

In conclusion, a novel silicone monomer bearing two amide groups (SiDAAA) was designed and synthesized. The design concept of this monomer was to improve its compatibility with various hydrophilic monomers, and thus two amide groups were introduced into the molecular skeleton. This monomer showed good miscibility with hydrophilic monomers bearing hydroxy group such as HEMA and HEAA. Furthermore, the hydrogel from SiDAAA and HEMA had good transparency. These results contrasted with those from hydrogel made with TRIS, conventional silicone monomer, and validated our monomer design concept.

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References and Notes

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15 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.