

Formation and Characterization of Microemulsions Containing Polymeric Silicone

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We have prepared microemulsions consisting of water/[40 wt % polyoxyethylene (20 mol) glycerin isostearate (abbreviated as POE-GIS) + 60 wt % random copolymer of polyoxyethylene (POE, 38 mol)/polyoxypropylene (POP, 10 mol) pentaerythritol tetramethyl ether {abbreviated as PEPTME (38/10)}]/[polyoxyethylene (POE, 19 mol)/polyoxypropylene (POP, 19 mol) polydimethylsiloxane copolymer (abbreviated as POE/POP-PDMS)] and water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/[95 wt % POE/POP-PDMS + 5 wt % oleic acid (abbreviated as OA)] systems and characterized them with optical observation, rheometry, and freeze–fracture transmission electron microscopy (FF-TEM) images. Bicontinuous and droplet-type O/W (oil-in-water) microemulsions are formed depending on the volume fraction of water. The bicontinuous structure observed in the oil-rich region, upon successive dilution with water, is transformed into a droplet-type microemulsion without phase separation. The prepared droplet-type microemulsion containing polymeric silicone and random copolymer PEPTME (38/10) as a cosurfactant in the water-rich region has potential applications in cosmetics.

1. Introduction

Microemulsions are thermodynamically stable, isotropic, microstructured solutions of oil and water stabilized by an interfacial film of a suitable surfactant, usually in combination with a cosurfactant.^{1–4} They can have characteristic properties such as ultralow interfacial tension, large interfacial area, and the ability to solubilize both aqueous and oil-soluble compounds. The microemulsions can be of the droplet type, either with isolated water pools dispersed in a continuous oil phase (water-in-oil microemulsions, W/O) that usually occur in systems with high oil content or with isolated oil pools dispersed in a continuous water phase (oil-in-water microemulsions, O/W), typically occurring in water-rich region. Nondroplet-type microemulsions feature continuous oil and water phases intertwined in dynamic extended networks and are called bicontinuous microemulsions.

With progress in the study of microemulsions and their increased technical applications, knowledge of their microstructures has become more and more important. The unique stability, solubilization, and optical clarity of microemulsions make them very attractive for many industrial applications, for example, in the pharmaceutical fields as drug delivery systems,^{5,6} in cosmetics as skin and body care products,^{7–9} in

nanoparticles synthesis,^{10–12} and so on. Earlier papers mainly described the formation of microemulsions with hydrocarbon oils and alcohols with medium-length chains as cosurfactants.

However, because of their low surface tension and good spreading capacity on the substrates that results in the ability to protect skin and hair, silicone-based oils are receiving much attention in the cosmetic field.¹³ The structure and dynamic features of this oil differ from those of hydrocarbon oil in a number of fundamental respects, giving rise to important physical properties. The large Si–O–Si bond angle and absence of substituents on the bridging oxygen atom permits enhanced chain mobility, and the high methyl group density imparts highly hydrophobic character.¹⁴ Generally, because polymeric silicone chains spread, it is thought that the preparation of O/W droplet-type microemulsions of polydimethylsiloxane compounds is a difficult task. Although Aramaki et al. prepared a mixed micelle composed of hydrophilic poly(oxyethylene)-polydimethylsiloxane and poly(oxyethylene)dodecylether,^{15,16} to our knowledge, there is no report of the formation of droplet-type microemulsions of hydrophobic polymeric silicone having a very high molecular weight.

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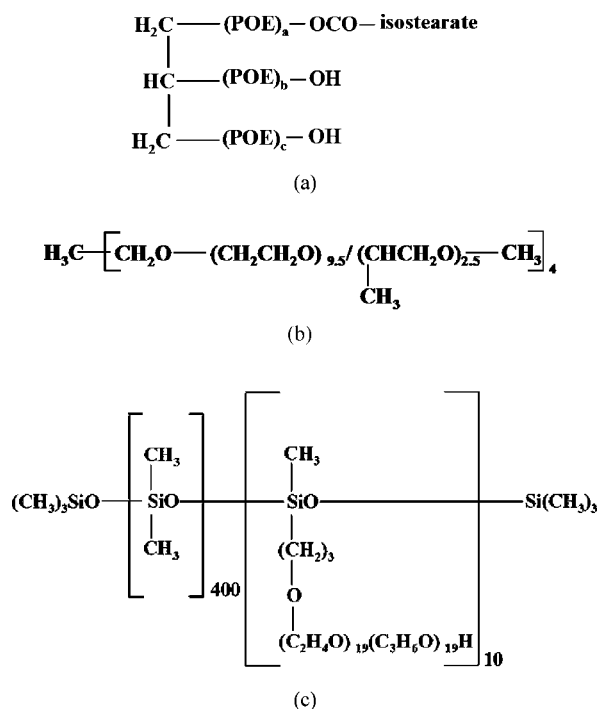
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Scheme 1. Schematic Molecular Structures of POE-GIS (a), PEPTME (38/10) (b), and POE/POP-PDMS (c)



Miyahara et al. prepared a highly concentrated O/W droplet-type microemulsion by using a random copolymer of polyoxyethylene/polyoxypropylene dimethylether (EPDME) as a co-surfactant.^{17,18} In this letter, we report a microemulsion that can occur in a system containing water, polyoxyethylene (20 mol) glycerin isostearate, a random copolymer of polyoxyethylene (POE, 38 mol)/polyoxypropylene (POP, 10 mol) pentaerythritol tetramethyl ether, which is an analog of EPDME, and a polyoxyethylene (POE, 19 mol)/polyoxypropylene (POP, 19 mol) polydimethylsiloxane copolymer with or without oleic acid. Microemulsion characterization has been performed by phase behavior, rheometry, and FF-TEM.

2. Experimental Section

2.1. Materials. A random copolymer of polyoxyethylene (POE, 38 mol)/polyoxypropylene (POP, 10 mol) pentaerythritol tetramethyl ether, PEPTME (38/10), was kindly supplied by Nichiyu, Japan. The number-average molecular weight of PEPTME (38/10) is 2300. Polyoxyethylene (20 mol) glycerin isostearate, POE-GIS, and polyoxyethylene (POE, 19 mol)/polyoxypropylene (POP, 19 mol) polydimethylsiloxane copolymer (POE/POP-PDMS) were purchased from Nikko Chemical Co., Japan, and Dow Corning Toray Co. Ltd., Japan, respectively. The number-average molecular weight of POE/POP-PDMS is 60 000. Oleic acid (OA) was a product of Nacalai Tesque, Japan. All chemicals were used as received. Deionized (Millipore-filtered) water was used to prepare the samples. Schematic molecular structures of POE-GIS, PEPTME (38/10), and POE/POP-PDMS are shown in Scheme 1.

2.2. Phase Diagrams. Samples for phase diagram construction were prepared by weighing the required amounts of reagents into screw-capped test tubes and mixing using a vortex mixture. The samples were kept in a water bath at 25 °C for equilibration. The phase boundaries were established by the observation of the turbidity-to-transparency transition and vice versa. The dotted lines were drawn where the exact boundaries were not clear. Finally, phases were identified by visual observation (through crossed polarizers).

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2.3. Rheometry. Samples for viscosity measurements were homogenized and kept in a water bath at a specified temperature for at least 24 h to ensure equilibration before performing measurements. The viscosity measurements were performed in a stress-controlled rheometer, AR-G2 (TA Instruments), using cone-plate geometries (diameters of 60 mm for the low-viscosity sample and 40 mm for the high-viscosity sample, each with a cone angle of 1°) with the plate temperature controlled by a Peltier unit. A sample cover provided with the instrument was used to minimize the change in sample composition by evaporation during the measurement.

2.4. FF-TEM. TEM observations of the sample were performed using the freeze-replica method. The sample was rapidly frozen in liquid propane using a cryopreparation system (LEICA EM CPC, LEICA microsystems), and the frozen sample was transferred into a freeze-replica preparing apparatus (FR-7000A, Hitachi Science Systems, Ltd.) and fractured with a glass knife at -120 °C. A replica film was prepared by evaporating platinum-carbon at 45° and then carbon at 90° on the fractured sample. The prepared replica film was washed several times with acetone and distilled water after being taken out of the freeze-replica preparing apparatus and transferred onto a 300 mesh copper grid. The replica thus prepared was observed with a transmission electron microscope (H-7650, Hitachi Science Systems, Ltd.) at an accelerating voltage of 120 kV.

3. Results and Discussion

3.1. Phase Behavior. The isothermal pseudoternary phase diagrams constructed for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(POE/POP-PDMS) system and the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(95 wt % POE/POP-PDMS + 5 wt % OA) system at 25 °C are shown in Figure 1a,b, respectively. The chemical structure of PEPTME (38/10) is similar to that of the polyoxyethylene chain in polyoxyethylene nonionic surfactants. PEPTME (38/10) may thus be considered to be a hydrophilic cosurfactant like polyoxyethylene (POE)/polyoxypropylene (POP) dimethyl ether (EPDME)^{17,18} when the concentrations of both PEPTME (38/10) and polyoxyethylene nonionic surfactants are high and may possibly be distributed in the polyoxyethylene chain of the polyoxyethylene surfactant. Oleic acid is added to the oily phase (POE/POP-PDMS) to raise the curvature of an interfacial film by an electrostatic repulsion of carboxylate groups. The mixture [40 wt % POE-GIS + 60 wt % PEPTME (38/10)] is insoluble in both POE/POP-PDMS and (95 wt % POE/POP-PDMS + 5 wt % OA). For all [40 wt % POE-GIS + 60 wt % PEPTME (38/10)] to (POE/POP-PDMS) or (95 wt % POE/POP-PDMS + 5 wt % OA) weight ratios *R*, the turbidity was noted for low water content. As the amount of water increases, the system reaches a single-phase microemulsion, indicated as I in the diagrams. It is seen that the isotropic monophasic microemulsion domains extend over a wide range in the diagrams. The area occupied by the microemulsion region shrinks and extends sharply toward the oil corner when POE/POP-PDMS is mixed with oleic acid in a 19:1 (w/w) ratio (Figure 1b). Within the microemulsion domain, the region with high oil content has a high viscosity. The solutions in this region are isotropic at rest but are birefringent when applying a shear, such as a sudden jerk. The microstructure of a microemulsion in the high oil content region is thought to be bicontinuous and similar to that previously reported.¹⁹ Besides a single-phase microemulsion domain, liquid crystal was also observed. Additionally, a very small domain of a highly viscous isotropic gel was encountered in an oleic acid-incorporated system. Unfortunately, we could not identify the liquid crystal (LC) by both small-angle X-ray scattering and polarizing microscopy. However, by judging the position of formation and

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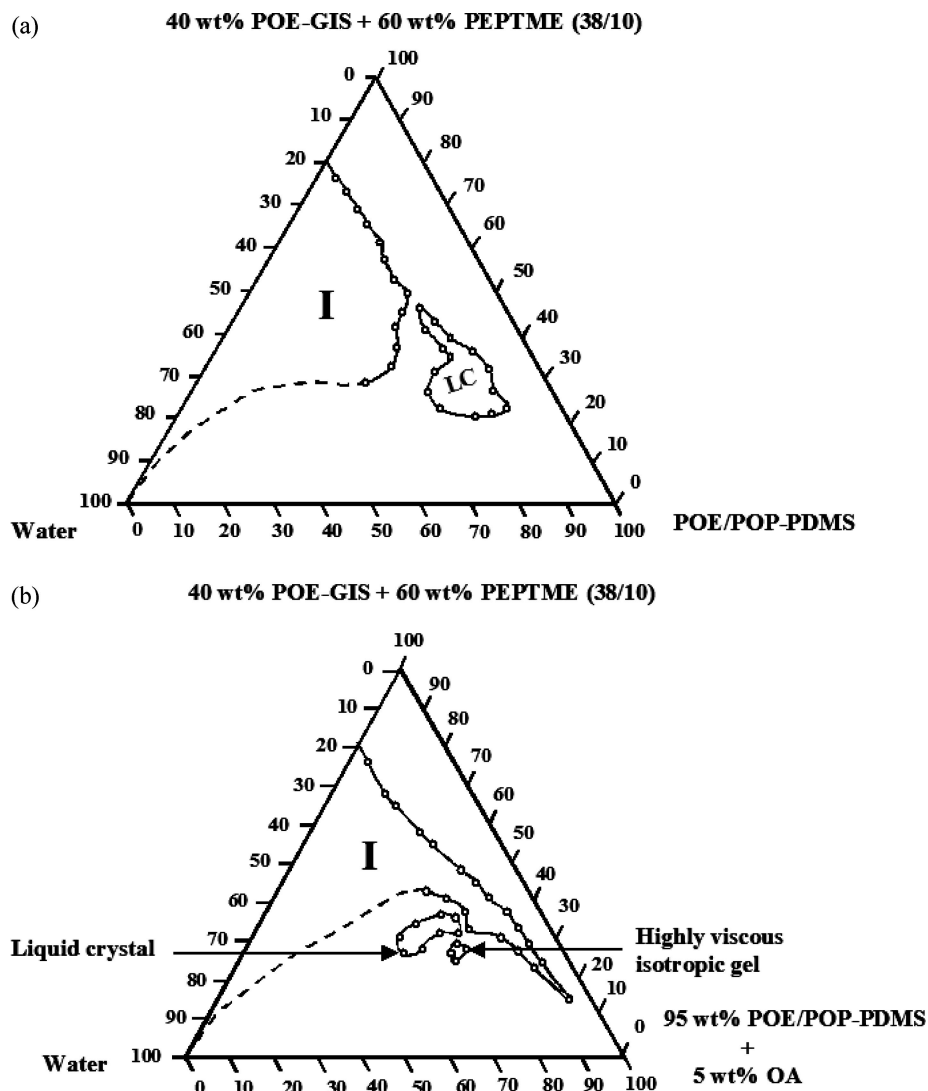


Figure 1. Pseudoternary phase diagrams of the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(POE/POP-PDMS) system (a) and the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(95 wt % POE/POP-PDMS + 5 wt % OA) system (b) at 25 °C.

the physical appearance of the LC, it can be concluded that the LC may be lamellar phase.

3.2. Rheometry. In microemulsions, viscosity is a macroscopic property that mainly depends upon the type and shape of aggregates present, the concentration, and the interaction between dispersed particles and hence can be used to obtain important information concerning microstructural changes. For example, the change in zero-shear viscosity provides valuable information regarding the transition of rodlike to globular micelles.²⁰ The steady shear rate versus viscosity curves for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(POE/POP-PDMS) system with $R = 1$ at different mixing fractions of water, expressed in weight fraction (W) at 25 °C, are shown in Figure 2. At a minimum water content of $W \approx 0.285$, the Newtonian behavior is limited to lower shear rate, and viscosity decreases gradually with increasing shear rate. The decrease in viscosity with increasing shear rate corresponds to shear-thinning behavior. The dispersions are organized at a lower shear rate and suffer fragmentation with increasing shear rate. With increasing water content up to $W \approx 0.305$, the shear-thinning behavior is still observed, but the viscosity at the lower shear rate decreases. However, with further increases in water content to $W \approx 0.391$,

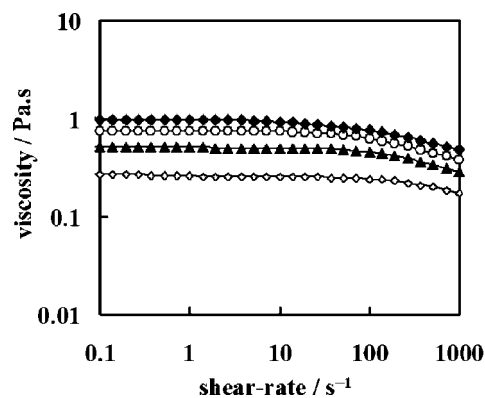


Figure 2. Steady shear rate versus viscosity curves for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(POE/POP-PDMS) system along $R = 1$ at various weight fractions of water, W : 0.285 (◆), 0.305 (○), 0.341 (▲), and 0.391 (◇) at 25 °C.

the viscosity is nearly constant over a wide range of shear rate studied, but a slight shear-thinning effect is still noticed, which indicates that the system is becoming less structured. Ultimately, phase separation occurs on further dilution of the system with water. Previous work on microemulsion rheology has indicated that bicontinuous microemulsions may be weakly shear thinning,

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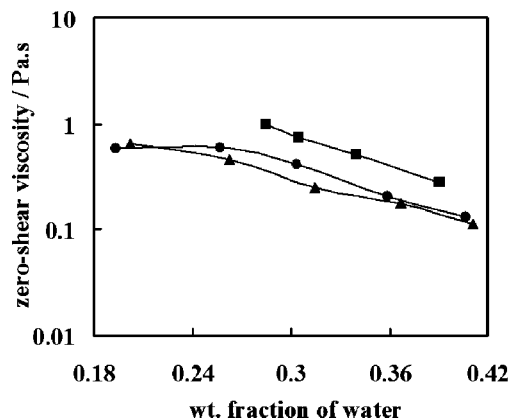


Figure 3. Variation of zero-shear viscosity as a function of the weight fraction of water for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(POE/POP-PDMS) system with different values of R : 1 (■), 1.86 (●), and 4 (▲) at 25 °C.

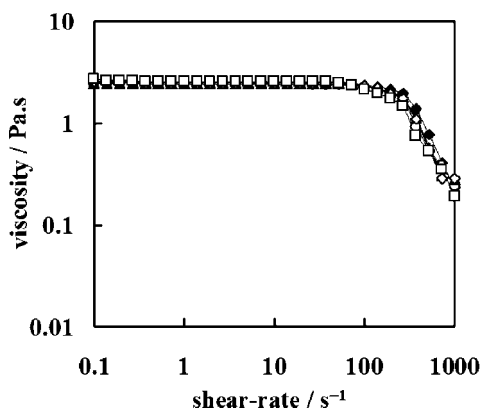


Figure 4. Steady shear rate versus viscosity curves for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(95 wt % POE/POP-PDMS + 5 wt % OA) system along $R = 1$ at various weight fraction of water, W : 0.133 (◆), 0.15 (○), 0.161 (▲), 0.179 (◇), and 0.195 (□) at 25 °C.

particularly if their low-shear viscosities exceed about 10 cP,²¹ which suggests that the microemulsion formed along $R = 1$ is assumed to have a bicontinuous structure. We observed a very weak shear-thinning effect at high shear rate for low water content and Newtonian behavior (data not shown) over the wide range of shear rate studied up to 1000 s⁻¹ for high water content along $R = 1.86$ whereas only Newtonian behavior was noticed at various water contents over the entire range of shear rate studied along $R = 4$. The effect of water on the microstructures of the microemulsion described in Figure 2 can be seen more clearly in Figure 3 where zero-shear viscosity is plotted as a function of the weight fraction of water at different values of R . The values of zero-shear viscosity have been determined by extrapolating the viscosity to zero shear rate. With increasing water content, the zero-shear viscosity of the microemulsion decreases continuously. The trend of decreasing zero-shear viscosity with increasing water content suggests a structural change in the microemulsion. In the bicontinuous region, the interconnected channels increase molecular interactions and hence increase in zero-shear viscosity for microemulsions with low water content.²² With continuous dilution, the bicontinuous structure gradually disappears, and transition into the oil-in-water microemulsion

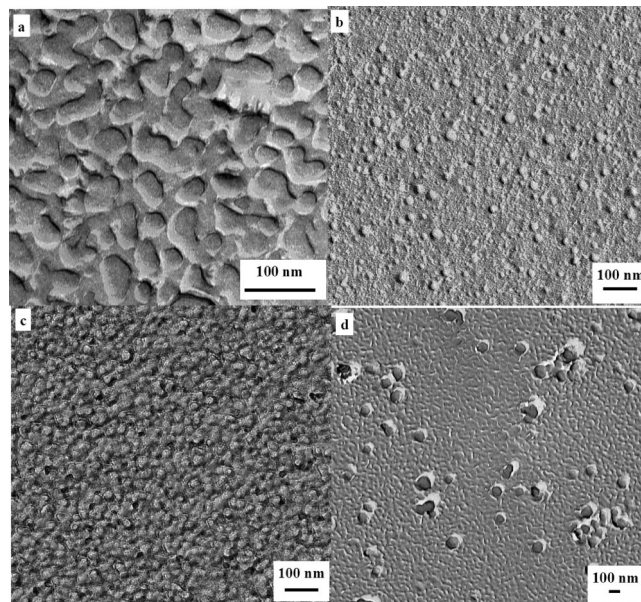


Figure 5. Freeze–fracture electron micrographs of microemulsions: (a) $W = 0.255$, $R = 1.5$; and (b) $W = 0.447$, $R = 4$ for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(POE/POP-PDMS) system. (c) $W = 0.291$, $R = 2.33$ and (d) $W = 0.448$, $R = 4$ for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(95 wt % POE/POP-PDMS + 5 wt % OA) system.

occurs, which is reflected in a sharp decrease in the zero-shear viscosity. The zero-shear viscosity continues to decrease as the nanodroplets decrease in number and size and become more and more diluted with water. The progressive dilution decreases the interdroplet interactions. We obtained a similar trend of decreasing viscosity (data not shown) with increasing water content along $R = 1.86$ and 4 for the oleic acid-incorporated system. However, a stronger shear-thinning effect is observed along $R = 1$, and the viscosity does not change with aqueous dilution as shown in Figure 4. The incorporation of OA may raise the curvature of an interface film, extend the microemulsion domain, and make the droplet size small. Therefore, strong entanglement is expected, leading to a viscosity increase. Further validation of the results can be obtained using the FF-TEM technique.

3.3. FF-TEM Observation. Freeze–fracture electron microscopy (FF-TEM) is one of the most advanced and powerful techniques used to characterize the size and shape of aggregates in microemulsions. The micrographs obtained by the FF-TEM technique are presented in Figure 5. A typical bicontinuous microemulsion texture can be observed in Figure 5a for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(POE/POP-PDMS) system at $W = 0.255$ along $R = 1.5$. Upon closer inspection, the image of the microstructure of the microemulsion shows a nearly zero mean curvature in the surfactant monolayers between the oil and water channels. The bicontinuous structure changes into oil-in-water droplets with increasing water content in the microemulsion. Droplet-type structures having diameters of less than 100 nm can be seen in Figure 5b for the same system at $W = 0.447$ along $R = 4$. Similar micrographs of bicontinuous and droplet-type microstructures having diameters of around 100 nm for microemulsions (Figure 5c,d) can be seen for the water/[40 wt % POE-GIS + 60 wt % PEPTME (38/10)]/(95 wt % POE/POP-PDMS + 5 wt % OA) system in low and high water content regions, respectively. These micrographs again reveal the transition from bicontinuous structure to oil-in-water droplets with aqueous phase dilution. This result is in agreement with the viscosity measurement.

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4. Conclusions

In this letter, we report for the first time the formation of a droplet-type microemulsion containing polymeric silicone by using a random copolymer of polyoxyethylene (POE, 38 mol)/polyoxypropylene (POP, 10 mol) pentaerythritol tetramethyl ether (PEPTME (38/10)) as a cosurfactant. The phase diagrams of the pseudoternary water/[40 wt % GWIS-120 + 60 wt % PEPTME (38/10)]/(POE/POP-PDMS) and water/[40 wt % GWIS-120 + 60 wt % PEPTME (38/10)]/(95 wt % POE/POP-PDMS + 5 wt % OA) systems present a wide one-phase microemulsion domain in which the structural transition from bicontinuous structure to oil-in-water droplets occurs continuously on dilution with the aqueous phase without phase separation. The transition from bicontinuous structure to oil-in-water droplets is easily detected by FF-TEM micrographs

and viscosity measurement. We believe that the prepared microemulsions using polymeric silicone oil would be potentially useful in the cosmetics field as a result of excellent spreading capacity on the substrate and the ability to protect skin and hair.

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Supporting Information Available: Plot of zero-shear viscosity versus weight fraction of water at $R = 1, 1.86,$ and 4 for the oleic acid-incorporated system. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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