Characterization of O/W Emulsions Prepared by PEG-Diisostearate Amphiphilic Random Copolymer

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Abstract: We have characterized an emulsion system stabilized by an amphiphilic random copolymer, methoxy polyethylene glycol-23 methacrylate/glycerol diisostearate methacrylate copolymer (MPM-GDM). The combined results of the static surface tension and transmission electron microscopy with freeze-fracture technique (FF-TEM) suggested that this copolymer forms aggregates in aqueous solutions. The membrane emulsification method produced an oil-in-water (O/W) emulsion in the mixture of squalane, water, and MPM-GDM, where the squalane concentration was set at 10 - 60 wt% and the MPM-GDM concentration was either 1 or 5 wt%. The prepared emulsion was stable against coalescence due to the formation of an adsorption layer of MPM-GDM. Based on the FF-TEM results, it is confirmed that a relatively large island-like structure is formed on the emulsion droplet surface. Furthermore, MPM-GDM can act as a thickening agent of the continuous liquid phase, which enhances the stability against creaming. The cooperative two effects improve the stability of the emulsion system without adding co-stabilizer such as low molecular-weight surfactants.

Key words: amphiphilic random copolymer, membrane emulsification, coalescence, thickening

1 INTRODUCTION

Emulsion is a colloidal dispersion system in which a liquid phase is dispersed in a continuous liquid phase. These two liquids are intrinsically immiscible with each other. Emulsion has wide range of industrial applications such as cosmetics, food, medical applications, etc. The cosmetic applications typically involve using oil-in-water (O/W) type emulsion as a substrate for skin-care products because of(i) its soft feeling that provided by the dispersed oil droplets(ii)its freshness that originated from the continuous water phase, and (iii)its skin protection capability.

In typical emulsion systems, low molecular-weight surfactants (called emulsifiers) are added in order to improve the dispersion stability. However, in the cosmetic applications, such low molecular-weight surfactants are not favored because of their skin irritant nature and uncomfortable feeling to the skin. Instead, water-soluble amphiphilic copolymers have been widely accepted. Historically, water-soluble amphiphilic copolymers have been used as a thickening agent in emulsion systems. They have attracted much attention since the 1990s due to their interesting aggregation properties in aqueous solutions¹⁻³. For example, they can improve the dispersion stability as a result of(i) the formation of an adsorption layer at the oil/water interface⁴⁻⁸, (ii) the adsorption of their aggregates due to the Pickering⁹⁻¹⁰ or three-phase emulsion¹¹⁻¹⁴ mechanism, and (iii) the association and network formation of hydrophobic moieties in the continuous water phase, which leads to holding the oil droplets¹⁵⁻²⁰.

From the standpoint of cosmetic applications, Akiyama et al. studied the emulsion system stabilized by a watersoluble amphiphilic copolymer, which is hydrophobically–hydrophilically modified hydroxyethylcellulose (HHM-HEC)¹⁹⁻²¹. The findings of their earlier study¹⁹ suggest that HHM-HEC can improve the dispersion stability of the emulsion system even without the addition of co-stabilizers (i.e., low-molecular weight hydrophilic surfactants). This emulsion system exhibits the properties mentioned above in Category(iii), i.e., the network structure consisting of the polymeric aggregates increases the viscosity of the continuous water phase. Furthermore, the effect of adding lipophilic small-molecular weight surfactants on the emulsion droplet size was investigated²⁰.

The current study employs methoxy polyethylene glycol-
23 methacrylate/glyceryl diisostearate methacrylate copolymer (MPM-GDM) as an amphiphilic copolymer sample. This copolymer sample is anticipated to form aggregates in aqueous media, and can act not only as a thickening agent for improving the stability against creaming but also as a stabilizer for the oil/water interface for achieving anti-coalescence. In addition, from the standpoint of cosmetic applications, MPM-GDM copolymer sample is also expected to offer the following three structural merits; (i) high safety of polyethylene glycol (PEG) to the skin, (ii) excellent soft feeling provided by the isostearic acid derivatives, and (iii) pH-insensitive nature to develop stable emulsion in a wide pH range. If this emulsion system does not require adding low-molecular weight surfactants to obtain a stable O/W emulsion, the MPM-GDM copolymer may contribute to improving the quality of the cosmetic products in terms of providing better feeling and eliminating skin irritations. The aim of this study is to understand the stabilization mechanism of the emulsion system stabilized by MPM-GDM copolymer sample.

2 EXPERIMENTAL METHOD

2.1 Materials

The MPM-GDM amphiphilic random copolymer was provided by NOF Co. The chemical structure of MPM-GDM is shown in Fig. 1. The average molecular weight of the copolymer sample used in this study was \(6.35 \times 10^5\), and the polydispersity index was 2.5. The weight ratio of the hydrophilic PEG unit to the hydrophobic diisostearyl unit was set at 7:3. Squalane was purchased from Nikko chemicals Co. The water used in this study was deionized using a reverse osmosis membrane equipped in a Millipore Direct-Q UV 5 water purification system.

2.2 Preparation of MPM-GDM aqueous solutions

MPM-GDM and water were mixed in a glass test tube and allowed to stand for 1 day at room temperature. Then, the MPM-GDM/water mixture was heated up (above 40°C), mixed by a vortex mixer for several seconds, and finally cooled down to room temperature.

![Fig. 1 Chemical structure of MPM-GDM (m:n = 7:3 in weight ratio)](image)

2.3 Preparation of emulsion samples

The emulsion samples were prepared by a membrane emulsification method \(^{22}\) using a Shirasu Porous Glass (SPG) direct connector (SPG Technology, DC 01 N). First, the aqueous MPM-GDM solution was stirred in a glass beaker under magnetic stirring at 300 rpm. Then, squalane was added into the aqueous solution using a Terumo syringe at room temperature. During this stage, the oil passed through an SPG membrane film. The pore size of the SPG film was 1 µm and the flow rate was fixed at 0.5 mL/h. In this study, the squalane concentration was set at 10, 30, and 60 wt%, whereas the MPM-GDM concentration was set at 1 and 5 wt%.

2.4 Measurements

2.4.1 Surface tension and interfacial tension

The equilibrium surface tension was measured by the pendant drop method using a Kyowa Drop Master 500. The droplet volume was fixed at 10 µL and the equilibration time was set at 30 min. The measurement temperature was maintained at 25°C.

The squalane/water interfacial tension was also measured by the pendant drop method using the same instrument at 25°C. MPM-GDM was dispersed in pure water, and then a syringe was used to push the mixture (10 µL) into the squalane. The interfacial tension was monitored as a function of time and the equilibrium value was determined.

2.4.2 Transmission electron microscopy with freeze-fracture technique (FF-TEM)

The morphologies of the MPM-GDM aggregates in aqueous solutions and of the emulsion droplets were observed by means of transmission electron microscopy with freeze-fracture technique (FF-TEM). These samples were immediately frozen in liquid nitrogen (Leica EMCPG), and then the frozen sample was fractured in a freeze-replica apparatus (FR-7000A, Hitachi High-Technologies Co.) at −120°C. The sample replica was prepared using carbon shadowing, followed by initial platinum shadowing. After acetone and water cleaning, the replica was set on a TEM copper grid coated with a Holey carbon film. FF-TEM measurements were made using an H-7650 (Hitachi High-Technologies Co.) at an accelerating voltage of 120 kV under a low electron dose.

2.4.3 Optical microscopy

Optical microscope observations were performed using an Olympus IMT-2. A small amount of emulsion sample was placed on a glass slide and covered with a glass cover. The droplet size distribution of the emulsion was estimated by measuring the size of 100 droplets in the optical microscope images.

2.4.4 Shear viscosity

Shear viscosity measurements were performed using TA Instruments AR-G2 rheometer with the cone-plate geometry (cone angle = 2°, diameter = 40 mm) at 25°C. The
shear rate was controlled in the range of 10-1000 s⁻¹.

2.4.5 Turbiscan

The dispersion stability of the emulsion samples was evaluated using a Turbiscan™ Classic MA 2000 Stability Analyzer. The prepared emulsion sample was placed in a sample tube. The backscattered light intensity was measured as a function of storage time at 25°C.

3 RESULTS AND DISCUSSION

3.1 Aggregation of MPM-GDM in aqueous solutions

Figure 2 shows the static surface tension of the MPM-GDM aqueous solutions as a function of its concentration. The surface tension decreased gradually with increasing the MPM-GDM concentration and a break point was observed at around 0.02 wt%. Although the surface tension continued to decrease even above this concentration, the overall behavior was similar to the typical behavior of aqueous surfactant systems. The driving force for this adsorption may be a hydrophobic interaction, similar to the adsorption of conventional small molecular-weight surfactants. The surface tension result also indicates that MPM-GDM forms (micellar) aggregates in the concentration region above 0.02 wt%.

FF-TEM measurements were performed in order to confirm the formation of the aggregates. The results shown in Fig. 3 illustrate that spherical, elongated, and their aggregated morphologies were formed. The aggregation is more obvious at 10 wt% (b) than at 1 wt% (a). The size distribution of the aggregates was observed to be broad; however, the majority of the aggregates fall in the diameter range of 10 - 40 nm. The additional dynamic light scattering measurements support this result, as shown in Fig. S1.

![Fig. 2](image2.png)  
**Fig. 2** Surface tension of MPM-GDM in water as a function of MPM-GDM concentration.

![Fig. 3](image3.png)  
(a) 1 wt% and (b) 10 wt%.

**Fig. 3** FF-TEM images of MPM-GDM aggregates at different MPM-GDM concentrations; (a) 1 wt% and (b) 10 wt%.
We note that at the composition of squalane:MPM-GDM:water = 30:5:65 (in wt%) the emulsion droplet size was relatively small and their distribution was narrow. The emulsion droplet diameter was observed to be smaller than that at the MPM-GDM concentration of 1 wt%. For this reason, we hypothesize that the adsorption of MPM-GDM to the squalane/water interface is faster at 5 wt% than at 1 wt%. The slow adsorption rate at 1 wt% may lead to the coalescence of the emulsion droplets. Hence the droplet size was observed to be larger even just after preparation.

The dynamic surface tension data shown in Fig. S2 support this hypothesis, although the data focus on the adsorption of MPM-GDM that occurs at the air/solution interface. Regarding the effect of squalane concentration on the emulsion droplet size, we found a larger size and wider distribution of the emulsion droplets prepared at 60 wt% than that at 10 and 30 wt% for a given MPM-GDM concentration. This suggests a relatively insufficient concentration of MPM-GDM against squalane (at 60 wt%) can be used to form a coalescence-resistible MPM-GDM interfacial film. The adsorption capability of MPM-GDM to the oil/water interface was further assessed by the squalane/water interfacial tensiometry by means of the pendant drop method.

The squalane/water interfacial tension value was measured as 32 mN/m in the absence of MPM-GDM, whereas the value was significantly decreased to 16 mN/m at the MPM-GDM concentration of 1 wt%.

In order to visualize the morphology of the oil/water interface, FF-TEM measurements were performed. For the purpose of these measurements, the squalane concentra-
tion was fixed at 30 wt%, while the MPM-GDM concentration was set at 1 or 5 wt%. Figure 5 shows the FF-TEM results. Small asperity on the droplet surface was observed at the MPM-GDM concentration of 1 wt%, whereas relatively large island-like morphology was seen at 5 wt%. Similar scanning electron microscope images were reported by Yi et al. and Destribats et al. These studies reported that the adsorption of "self-assembled polymeric micelles" or "micro-gel particles" was suggested to occur at the oil/water interface, and the prepared emulsions were stabilized through the Pickering mechanism. However, in this study, the diameter of the MPM-GDM aggregates formed in the aqueous solution is mainly in the range of 10 - 40 nm, which is much smaller than the size of the aggregates observed on the droplet surface. One possible interpretation for the observed morphology is the aggregation or growth of the solution aggregates into relatively large interfacial aggregates occurs on the emulsion droplet surface. This is not surprising because the MPM-GDM aggregates are not "frozen" in the aqueous solution and are deformable at the oil/water interface. The FF-TEM images also demonstrate the formation of a thin layer at the oil/water interface, supporting the growth or deformation of the solution aggregates at the interface. The other possibility to be considered is that MPM-GDM unimers are adsorbed to the oil/water interface and formed the interfacial thin layer. In this case, the amphiphilic nature of MPM-GDM may drive the adsorption. In either case, the adsorption layer of MPM-GDM stabilizes the interface against the coalescence between oil droplets.

3.3 Emulsion viscosity

Figure 6 shows a change in the viscosity of the emulsion samples as a function of shear rate. At the squalane concentration of 10 wt%, the viscosity was almost constant against the shear rate. This indicates that the emulsion samples are almost Newtonian fluids at this squalane concentration. The increased squalane concentration to 30 and 60 wt% led to the increased viscosity. Additionally, the viscosity is a large difference from the viscosity obtained from the Einstein equation (see Supporting Information), as shown in Table 1. In particular, a shear thinning behav-

![Fig. 6](image-url)  
Static viscosity data of the emulsion samples. These measurements were performed just after from the emulsion preparation. The composition ratio shows squalane:MPM-GDM:water in wt%.
ior was clearly observed at the composition of squalane:MPM-GDM:water = 60:5:35 in wt%. Such non-Newtonian flow behavior typically results from the interdroplet interaction dispersed in the continuous liquid phase. This justifies the differences between the experimental and calculated viscosity data. In the currently tested system, increasing the squalane concentration leads to increasing the number density of the dispersed droplets as well as increasing the viscosity of the continuous aqueous phase caused by the dissociation of the copolymer sample. Increasing the MPM-GDM concentration from 1 wt% to 5 wt% significantly increased the viscosity of the continuous phase (Table 2). Hence the emulsion viscosity was also increased for a given squalane concentration.

Based on the dispersion stability, FF-TEM, and viscosity results, we suggest that the tested emulsion system is stabilized by the following two mechanisms: (i) the adsorption of MPM-GDM to the oil/water interface, which enhances the stability of the oil droplets against coalescence, and (ii) the thickening of the continuous phase that enhances the stability against creaming. The latter effect was further verified by the Turbiscan backscattering results (shown in Fig. 7); i.e., the creaming rate was faster when the MPM-GDM concentration was 1 wt% than when it was 5 wt% at a given squalane concentration of 30 wt%.

### 4 CONCLUSIONS

In this study, we have characterized the emulsion system stabilized by the amphiphilic random copolymer, MPM-GDM. This copolymer forms aggregates in aqueous solutions. The membrane emulsification method can be used to prepare the O/W emulsion in the mixture of squalane, water, and MPM-GDM. The prepared emulsion was stable
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Supporting Information

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