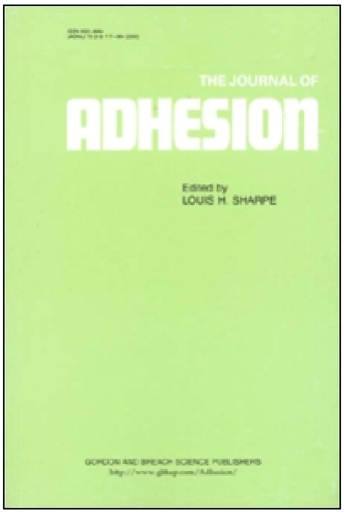

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Synthesis of amphiphilic copolymers having capability as emulsifiers and their surface chemical properties

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SYNTHESIS OF AMPHIPHILIC COPOLYMERS HAVING CAPABILITY AS EMULSIFIERS AND THEIR SURFACE CHEMICAL PROPERTIES

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Some comblike terpolymers composed of methyl methacrylate (MMA), methoxypolyethyleneglycol methacrylate (MPEGMA) as a hydrophilic component, and methoxypolypropyleneglycol methacrylate (MPPGMA) as a hydrophobic component were synthesized by both living radical photopolymerization and ordinary radical polymerization. Since these terpolymers showed a high surface activity, it was suggested that they could be utilized as good polymeric emulsifiers. The polymeric emulsions containing these emulsifiers also showed comparatively good emulsion and mechanical properties as an adhesive. From these facts, it was found that these terpolymers had almost the same emulsification capability as commercially available low molecular weight emulsifiers. Conversely, a difference in surface tension behavior of these terpolymers could be observed. We think that it was due to the chain arrangements (random or block sequence) of the terpolymer.

Keywords: Amphiphilic copolymer; Emulsion polymerization; Polymeric emulsifier; Micelle formation

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INTRODUCTION

We [1–5] have studied the surface properties of comblike polymers having hydrophilic and/or hydrophobic side chains and their applications to functional polymeric materials. In a recent report, we [6] synthesized some terpolymers composed of methoxypolyethyleneglycol methacrylate (MPEGMA) having hydrophilic side chains, methoxypolypropyleneglycol methacrylate (MPPGMA) having hydrophobic side chains, and ethyl acrylate (EA) and reported that these terpolymers could be applied to pressure-sensitive adhesives (PSA) and that they had significant blood compatibility. We think that the high molecular mobility of the side chains of these polymeric materials results in these good properties.

On the other hand, although these polymeric materials have been synthesized by radical polymerization in solution, recent environmental problems with the organic solvent used in the process have arisen. Therefore, the manner of polymerization of polymeric materials and their usage should, of necessity, be converted from an organic solvent to a waterborne system. Thus, we have synthesized these polymeric materials *via* emulsion polymerization and tried to apply them to adhesives. In this case, although the polymeric emulsions mainly composed of methyl methacrylate (MMA), MPEGMA, and MPPGMA showed good emulsion properties in some particular compositions, some improvements were required. One such improvement required modification with comonomer butyl acrylate (BA). Results of this modification have been reported on previously [7]. Another improvement was emulsion polymerization using synthesized polymeric emulsifiers. We are in agreement that using polymeric emulsifiers may reduce some problems related to a low molecular weight emulsifier.

In this study, polymeric emulsifiers were synthesized by both living radical photopolymerization and ordinary radical polymerization. In addition, a previously synthesized polymeric emulsifier with the same components as our synthesized polymeric emulsions was studied. The capabilities as an emulsifier of our synthesized copolymers were estimated from their surface chemical properties. Furthermore, we also polymerized emulsions containing our synthesized polymeric emulsifiers and measured several characteristics as well as the tensile adhesion strength and 90-degree peel strength for their adhesive properties.

EXPERIMENTAL

Materials

Monomers used for the polymeric emulsifier were methyl methacrylate (MMA), MPEGMA and MPPGMA. MPEGMA and MPPGMA were macromonomers having hydrophilic and hydrophobic side chains, respectively. The chemical structures of these macromonomers are shown in Figure 1. The molecular weight and the number of repeating units in the side chains of MPEGMA and MPPGMA are shown in Table 1. In addition, the surface tension of the side chains in the macromonomers are listed in the table [8]. MPEGMA and MPPGMA were supplied by Shin-Nakamura Chemicals Co. (Tokyo, Japan) and were used as received. Methyl ethyl ketone (MEK) and p-xylene were used as solvents for polymerization. These solvents were purified by distillation.

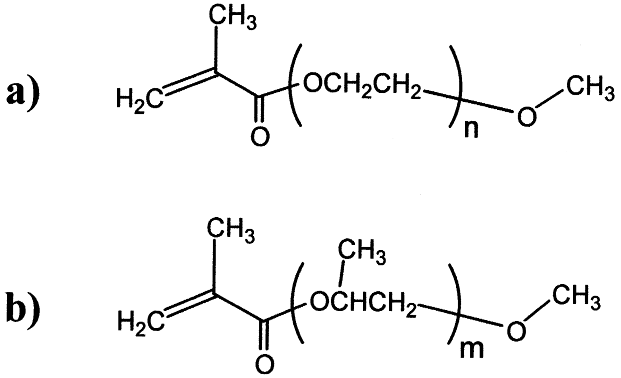


FIGURE 1 Chemical structures of monomers (a) methoxypolyethyleneglycol methacrylate (MPEGMA) and (b) methoxypolypropyleneglycol methacrylate (MPPGMA).

TABLE 1 Characteristics of Monomers MPEGMA and MPPGMA

Monomer	Mn($\times 10^{-2}$)	Mw/Mn*[1]	Number of *[2] repeating units	Surface tension*[3] at 25°C (mN/m)
MPEGMA	10.4*[1]	1.08	21.4	43
MPPGMA	9.24*[2]	—	14.2	31

*[1] Determined by GPC; *[2] Determined by ^{1}H-NMR; *[3] See Kasemura and Hata [8].

Monomers used for the emulsion polymerization were the same as mentioned above. In this case, acrylic acid (AA) as a comonomer was added in order to increase cohesion. Comonomer BA was used for modifying the emulsions. 1-dodecanethiol and ammonium peroxodisulfate (APS) were also added as a chain transfer agent and initiator, respectively. These monomers and reagents were of commercially available grade and were purified *via* normal methods. In order to compare the capabilities of the synthesized polymeric emulsifiers, two kinds of surfactants were used as low molecular weight emulsifiers. Polyoxyethylene polycyclicphenylether sulfuric acid ester salt (Newcol-707SF) as an anionic emulsifier and ethylene oxide/propylene oxide/ethylene oxide triblock copolymer (Pluronic-F68, MW = 8350) as a nonionic emulsifier were supplied by Nippon Nyukazai Co. (Tokyo, Japan) and Asahi Denka Kogyo Co. (Tokyo, Japan), respectively. These surfactants were used without further purifications.

Preparation of Polymeric Emulsifier

Polymeric emulsifiers were prepared by means of the following two techniques. Terpolymers P(MMA-co-MPEGMA-co-MPPGMA) {a} and P(MMA-co-MPEGMA)-b-PMPPGMA {b} were synthesized by living radical photopolymerization under irradiation by a UV light source. Photopolymerization was carried out in MEK at room temperature for $6 \sim 8$ hours in a sealed bottle of argon atmosphere using benzyl N, N-diethyldithiocarbamate (BDC) or p-xylylene bis (N, N- diethyldithiocarbamate) (XDC) as a photoiniferter [9]. The molecular structures of these photoiniferters are shown in Scheme 1. Samples {a} and {b} were found to be random and block copolymers, respectively. Block copolymers {b} were polymerized *via* the two-step method. The second monomer, MPPGMA, was copolymerized successively after copolymer P(MMA-co-MPEGMA) was prepared first. These samples were precipitated from MEK solution by n-hexane. However, since it proved to be difficult to produce complete isolation of a pure block copolymer {b}, they could not subsequently be sufficiently purified.

BDC; $C_6H_5CH_2S_2CN(C_2H_5)_2$

XDC; $C_6H_4(CH_2S_2CN(C_2H_5)_2)_2$

SCHEME 1 Chemical formula (see Eq. (9)).

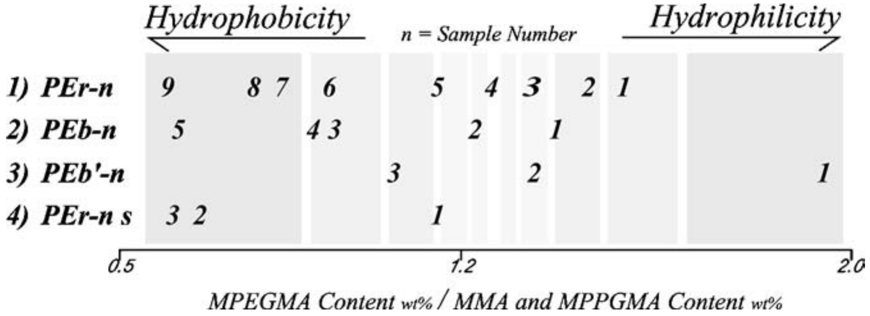


FIGURE 2 Nomenclature of synthesized polymeric emulsifiers.

Terpolymers P(MMA-co-MPEGMA-co-MPPGMA) {c} were synthesized by ordinary radical polymerization in MEK/p-xylene solution (1:1 volume ratio). This solution polymerization was carried out at 70°C for 6–8 hours using 2,2-azobis (isobutyronitrile) (AIBN) as an initiator. Samples {c} were found to be random copolymers. These samples were also precipitated from MEK/n-hexane solution by n-hexane.

The synthesized polymeric emulsifiers were denoted according to the following nomenclature: Terpolymers {a}, {b}, {b′}, and {c} were represented by PEr-1 to PEr-9, PEb-1 to PEb-5, PEb′-l to PEb′-3, and PEr-1s to PEr-3s, respectively. Samples {b} and {b′} are block copolymers to be synthesized using iniferter XDC and BDC, respectively. The samples were numbered according to the compositions of their terpolymers. This nomenclature is shown in Figure 2, *i.e.*, the hydrophobicity increases in the order of the sample number.

Preparation of Polymeric Emulsion

Polymeric emulsions used in this study were prepared by emulsion polymerization using the synthesized polymeric emulsifiers or two kinds of commercially available emulsifiers. Emulsion polymerization was carried out *via* the dropping method. Polymeric emulsions composed of MMA, MPEGMA, MPPGMA and AA, or MMA, MPEGMA, MPPGMA, AA, and BA were synthesized as follows. The feed composition of the monomers was set at 70 wt% of MMA, 15 wt% of MPEGMA, 15 wt% of MPPGMA and 3 wt% of AA and fixed. When the emulsion was modified, 5 wt% of BA was then added. These compositions have been reported on previously and their emulsions exhibited the best emulsion properties [7]. First, the pre-emulsified monomer emulsion for the dropping was prepared, *i.e.*, all of the monomers were emulsified successively in order of low polarity in a 2 wt% aqueous solution of the emulsifiers using a homogenizer (IKA Japan; ULTRA Turrax T25 Y.K., Nara, Japan). 1-dodecanethiol and an initiator APS were then added. Next, the pre-emulsified monomer emulsion was dropped at constant speed for $1.5 \sim 2.5$ hours, using a peristaltic pump, into water preheated to $72 \sim 75°C$, and the precursive emulsion was aged, maintaining a $72 \sim 75°C$ temperature for $1 \sim 2$ hours after the dropping into the system was completed. At this point, the progress of polymerization was terminated. All of the water used was deionized. The synthesized polymeric emulsions were adjusted to pH $7 \sim 8$ by aqueous ammonia and then filtered through a 200-mesh screen.

The emulsions, which were polymerized using synthesized polymeric emulsifiers, were denoted according to the following nomenclature: L-PEm-n and L-PEm-nB represents the synthesized polymeric emulsions, PEm-n represents the polymeric emulsifier used, and L-PEm-nB is the BA-modified emulsion.

Estimation of Polymeric Emulsifier

Molecular Weights and Their Polydispersities

The characteristics of the synthesized polymeric emulsifiers were determined by gel permeation chromatography (GPC, TOSOH-8020, TOSOH Co., Tokyo, Japan) *via* the polystyrene standard and proton-NMR (Varian 400 MHz NMR, Varian Inc., Tempe, Arizona, USA) using chloroform-d_1 as a solvent. In particular, the absolute molecular weights of these samples were measured by means of GPC (JASCO PU-2080 PLUS, JASCO Co., Tokyo, Japan), which was equipped with a Multi Angle Light Scattering (MALS) detector (DAWN®-EOS™, Wyatt Technology Co., Santa Barbara, California, USA).

Water Solubility and Emulsification Stability

Emulsifier capabilities were estimated *via* water solubility and emulsification stability to both lipophilic n-hexane and the target monomers for emulsion polymerization as follows: MMA, MPPGMA, and MPEGMA. Water solubility was observed, with the naked eye, in an aqueous solution of 2 wt% of the synthesized polymeric emulsifier. Emulsification stability was observed by looking at the status of the emulsion with the naked eye. The status of the emulsion was observed 5 h after emulsification with the above-mentioned n-hexane and/or monomers.

Surface Chemical Properties

Surface chemical properties were estimated experimentally as follows. The surface tensions of the aqueous solution of the synthesized polymeric emulsifiers were determined by Du Noüy (Pt-ring) method.

The interfacial tensions of the aqueous solution of polymeric emulsifier in contact with lipophilic n-hexane were also determined by the same methods as above. Here, n-hexane was used instead of a target monomer such as MPPGMA because of the difficulty of the measurement. Another reason for using n-hexane is that it exhibits an extremely low surface tension.

HLB and Cloud Point Calculated from Cloudy Number

The value of Hydrophile-Lipophile-Balance (HLB) and the cloud point (cp) were calculated from the cloudy number. The cloudy number was determined as follows [10]. First, 0.5 g of the emulsifier was dissolved in 5 ml of 98% ethyl alcohol. Next, this solution was titrated with 2 wt% of an aqueous solution of phenol at 25°C. The turbid point was prescribed as the end point of this titration. The volume (ml) which was required for titration was defined as the cloudy number (A). The titration for the cloudy number (A) was measured three times for each sample and the average value ($A_{av.}$) was used for the following calculations. The HLB value and the cp (°C) was calculated from Equation (1) and Equation (2), respectively [10].

$$\mathrm{HLB} = 16.02 \log \mathrm{A}_{\mathrm{av.}} - 7.34 \tag{1}$$

$$\mathrm{cp} = 163.4 \log \mathrm{A}_{\mathrm{av.}} - 115.9 \tag{2}$$

Estimation of Polymeric Emulsion

General Properties

The general properties of the polymeric emulsion were estimated *via* its viscosity, nonvolatile content, observation of surface morphology, and particle size distribution. The viscosity was determined by a rotational viscometer (Brookfield RVT, Brookfield Inc., Middleboro, Massachusetts, USA) according to Japan Industrial Standard (JIS) K6828. The nonvolatile content was also determined, according to the same standard as above, as follows. A dish made of aluminium foil containing approximately 1 g (w_1) of the polymeric emulsion was dried in an oven for 60 min at 104 ~ 106°C and then weighed (w_2). Then, the nonvolatile content was calculated from $w_2/w_1 \times 100$ (wt%).

Surface Morphology Observed by AFM

The surface morphology of the polymeric emulsion, which was diluted with deionized water, was observed by atomic force microscopy (AFM, SPA-300 Seiko Instruments, Chiba, Japan). AFM topographic images were recorded in contact mode under ambient conditions. A

Si_3N_4 cantilever with a nominal force constant of 0.09 N/m was used for measuring the contact mode. The scanning range and frequency were 500 ~ 10,000 nm and 1 ~ 2 Hz, respectively.

Particle Size Distribution

The particle size distributions of the pre-emulsified monomer emulsion and its polymeric emulsion were estimated *via* median and mode size and distribution pattern. These measurements were performed using a Laser Diffraction Particle Size Analyzer SALAD-2000 (Shimadzu Co., Kyoto, Japan).

Mechanical Properties as an Adhesive

The mechanical properties of the polymeric emulsion as an adhesive were estimated *via* tensile adhesion strength and 90-degree peel strength according to JIS A5536. The specimen for the tensile test was prepared by adhering an attachment (l: 40 mm, w: 40 mm) made of stainless steel SUS304 onto a floor tile made of polyvinyl chloride (PVC) having the same area with epoxy adhesives. The specimen for the peel test was a floor sheet (l: 200 mm, w: 25 mm) made of PVC. Next, the polymeric emulsion was coated on these specimens and kept for 3 days. The tensile adhesion strength was measured at 1 mm/min in tensile speed using a TENSILON testing machine (Orientec Co., Tokyo, Japan). The 90-degree peel strength was measured at 200 mm/min in peel speed using a AGS-1000A type peel testing machine (Shimadzu Co., Tokyo, Japan).

RESULTS AND DISCUSSION

Properties of Polymeric Emulsifier

Characteristics

The compositions and relative molecular weights of the synthesized polymeric emulsifiers are shown in Table 2. The compositions of the PEr and the PEr-s series determined by ^{1}H-NMR showed values close to their feed compositions. Contrarily, in the PEb and PEb′ series, a different tendency from the results of the PEr and the PEr-s series could be observed, *i.e.*, the introduced amounts of the hydrophobic MPPGMA component were found to be lower than those of the feed. This was due to the decrease in the block efficiency of MPPGMA as a second monomer. GPC size exclusion chromatography (SEC) profiles of the first (after 1st-step polymerization) and the final (after 2nd-step polymerization) product for PEb′-3 on block copolymerization are shown in Figure 3. The peak position of the final product shifted to the

TABLE 2 Characteristics of Synthesized Polymeric Emulsifiers

Polymeric emulsifier	Feed (wt%)	Composition* (wt%)	Mn# ($\times 10^{-4}$)	Mw# ($\times 10^{-4}$)	Mw/Mn#
PEr-1	5.0/48/47	18/60/22	1.1	1.3	1.2
PEr-2	10/55/35	14/59/27	1.2	1.5	1.2
PEr-3	10/50/40	7.0/57/36	1.0	1.2	1.2
PEr-4	15/55/30	9.0/56/35	1.2	1.4	1.2
PEr-5	10/45/45	9.0/53/38	1.0	1.1	1.1
PEr-6	10/48/42	15/49/36	1.1	1.3	1.2
PEr-7	5.0/45/50	8.0/47/45	1.2	1.4	1.2
PEr-8	10/40/50	16/42/42	1.4	1.6	1.2
PEr-9	10/42/48	15/39/46	1.3	1.5	1.2
PEb-1	11/38/50	23/59/18	1.2	1.3	1.1
PEb-2	12/38/50	35/55/10	1.0	1.2	1.1
PEb-3	12/38/50	34/48/18	1.1	1.2	1.1
PEb-4	10/40/50	33/48/19	1.0	1.2	1.1
PEb-5	13/37/50	45/41/14	0.9	1.0	1.1
PEb′-1	10/40/50	10/66/24	1.3	1.7	1.3
PEb′-2	10/40/50	20/57/23	1.0	1.2	1.2
PEb′-3	11/39/50	27/51/22	0.9	1.1	1.2
PEr-1s	10/55/35	16/53/31	0.9	1.0	1.1
PEr-2s	10/45/45	14/42/44	1.0	1.2	1.2
PEr-3s	10/50/40	25/39/36	0.8	0.9	1.1

*Determined by ^{1}H-NMR.
#Determined by GPC.

side of higher molecular weight when compared with that of the first product. Since this fact means the addition of the MPPGMA block as a second monomer to the P(MMA-co-MPEGMA) terminal, it is clear that block copolymerization proceeds normally. Furthermore, since these signals are almost the same profile, it is also shown that the amount of contaminants in the raw product are less than the allowable value for various estimations in this study.

The relative molecular weight of all the samples was approximately 10,000. It has been difficult to synthesize a high molecular weight terpolymer. Since the reactivity of the polymerization of a macromonomer such as MPEGMA and MPPGMA is lower than that of low molecular weight monomers, it is presumed that an excessive feed of MPEGMA or MPPGMA to the MMA component is responsible for the decrease in the degree of polymerization. The absolute molecular weights of PEr-7, the first and the final product for PEb′-3 are shown in Table 3. The relative molecular weight and the absolute molecular weight of the three samples were very different. In addition, these absolute molecular weights were higher than the relative

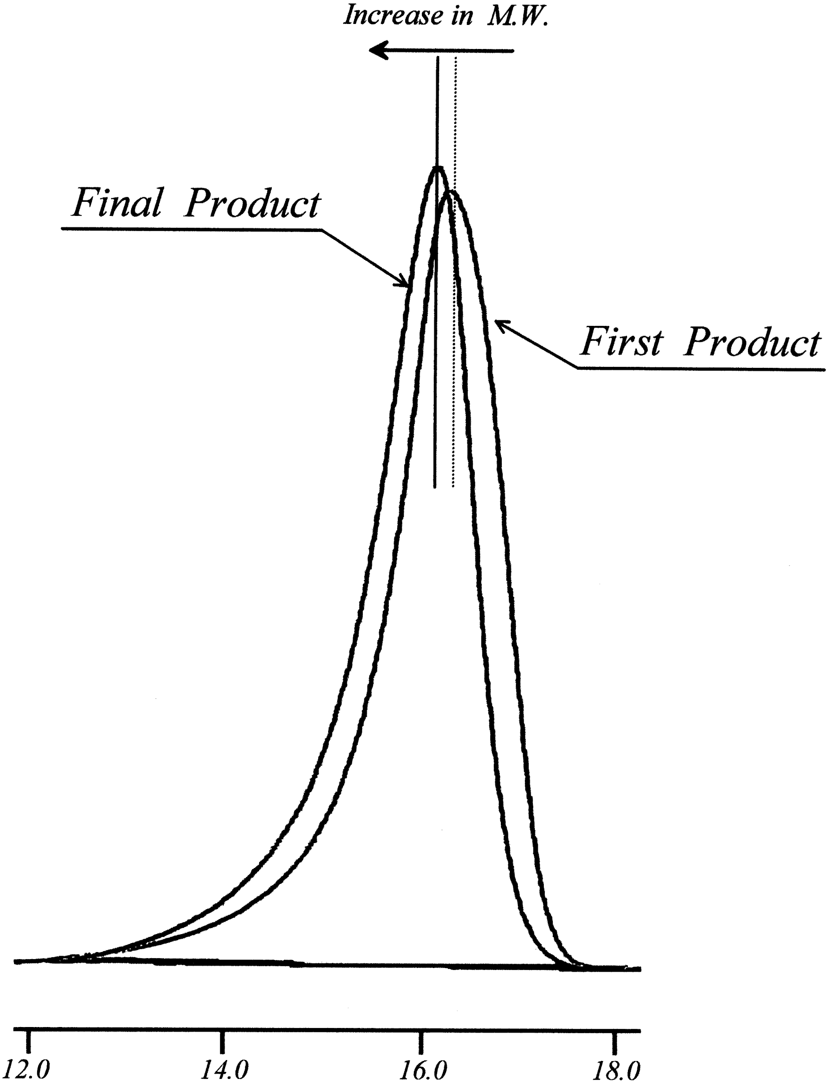


FIGURE 3 GPC profiles of first and final product for PEb′-3 on block copolymerization.

molecular weights of those. On the other hand, since an absolute molecular weight of the final product was also higher than that of the first product, the progress of block copolymerization was found to be normal, as also supported by the data in Figure 3. In the case of

TABLE 3 Absolute Molecular Weights of PEr-7, First and Final Product for PEb′-3 Determined by MALS-GPC

Terpolymers (abbr.)		Mn ($\times 10^{-4}$)	Mw ($\times 10^{-4}$)	Mw/Mn
PEr-7		8.52	17.4	2.04
PEb′-3	First[#1]	6.43	7.76	1.21
	Final[#2]	15.4	17.8	1.16

[#1] Copolymer, which was produced after 1st-step polymerization.

[#2] Terpolymer, which was produced after 2nd-step polymerization.

linear polymers, the molecular weights obtained by means of GPC with a polystyrene standard (the relative molecular weights) are reasonable in terms of their hydrodynamic volume in solution. Contrarily, the relative molecular weights of comblike polymers, such as the synthesized terpolymer in the present study, are not reasonable because of the difference in the hydrodynamic volume in solution of their polymers and linear polymers. From these facts, it was proved that the synthesized terpolymers could be utilized as a polymeric material.

Water Solubility and Emulsification Stability

The experimental results on water solubility and emulsification stability of the synthesized polymeric emulsifiers are shown in Table 4. The polymeric emulsifiers of the PEr series, except PEr-7, exhibited excellent water solubility. The water solubilities of the PEr-s series decreased with an increase in hydrophobicity. From these results, it could be observed that a polymeric emulsifier maintaining excellent water solubility had compositions of 50 wt% or more of hydrophilic MPEGMA and 30 wt% or less of hydrophobic MPPGMA. In the case of the PEb and the PEb′ series, all of the aqueous solutions, except PEb′-1, exhibited a semitransparent dispersion. The water solubilities of the PEb series were poor in spite of high MPEGMA content and low MPPGMA content. This was due to a higher MMA content when compared with the others. Regarding water solubility, the polymeric emulsifiers of the PEr series had the best capability. Next, the emulsification stability to the target monomers for polymerization or lipophilic n-hexane exhibited excellent capabilities in all series. This result suggests that the interfacial tension of an aqueous solution of synthesized polymeric emulsifier in contact with lipophilic or hydrophobic materials such as MPPGMA could be sufficiently decreased. Furthermore, since these emulsifiers are considered polymeric

TABLE 4 Experimental Results of Water Solubility and Emulsification Stability of Synthesized Polymeric Emulsifiers

Polymeric emulsifier	Water solubility	Emulsification stability*
PEr-1	E	E
PEr-2	E	E
PEr-3	E	E
PEr-4	E	E
PEr-5	E	E
PEr-6	E	E
PEr-7	G	E
PEr-8	E	E
PEr-9	E	E
PEb-1	G	E
PEb-2	G	E
PEb-3	G	E
PEb-4	G	E
PEb-5	G	E
PEb′-1	E	E
PEb′-2	G	E
PEb′-3	G	E
PEr-1s	E	E
PEr-2s	G	E E#
PEr-3s	G	E E#

E, Excellent, G, Good.
*Emulsification of target monomers for polymerization.
Emulsification of lipophilic n-hexane.

materials, it appears that a membrane made of a polymeric emulsifier has a high mechanical toughness on the dispersed drop of the hydrophobic material. Thus, it can be shown that these polymeric emulsifiers had a high emulsification stability.

Surface Chemical Properties

The surface tensions of the aqueous solutions of the synthesized polymeric emulsifiers plotted against emulsifier concentration are shown in Figure 4. Figures 4a and 4b show the surface tension of random (PEr and PEr-s series) and block (PEb and PEb′ series) copolymerized emulsifiers, respectively. In both Figures 4a and 4b, the surface tensions decreased with an increase in emulsifier concentration. Consequently, it is clear that these two kinds of polymeric emulsifiers could be used as surface-active agents. In addition, critical

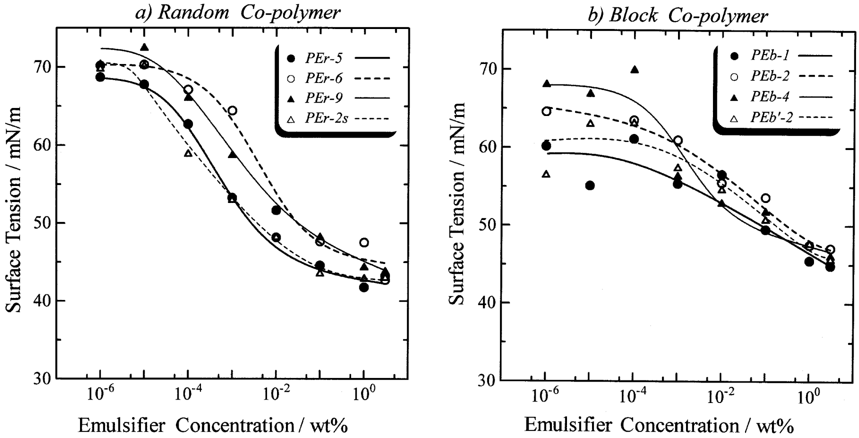


FIGURE 4 Surface tensions of aqueous solutions of synthesized (a) random and (b) block copolymerized emulsifiers plotted against emulsifier concentration.

micelle concentration (c.m.c.) estimated from the breaking point of the curves was close to 0.01%.

On the other hand, when the two figures were compared with each other, the dependencies of the surface tensions on concentration were found to be different. The surface tensions of the random copolymers (Figure 4a) decreased monotonously from approximately 70 mN/m to nearly 40 mN/m. Contrarily, although the surface tensions of the block copolymers (Figure 4b) maintained constancy in a region of concentration lower than 0.001%, after that it apparently decreased from approximately 60 mN/m to nearly 45 mN/m. It is suggested that the difference in this behavior is due to the conformation of the polymeric emulsifier. In the next figure, speculation regarding this behavior is explained using a graft chain model of the comblike polymer. Figure 5 shows the conformations of polymeric emulsifier having different chain arrangements in an aqueous solution. Here, the decrease in surface tension should correspond to the adsorption of the hydrophobic segment to the surface of the solution and micelle formation. In the case of a random copolymer, a micelle could be made of one molecule by means of the association of the hydrophobic PPG segment *via* the intramolecular hydrophobic interaction. On the surface (micelle/water interface) of this micelle, a hydrophilic PEG segment could be arranged so as to minimize water/micelle interfacial free energy. This molecule also could be adsorbed as shown in this

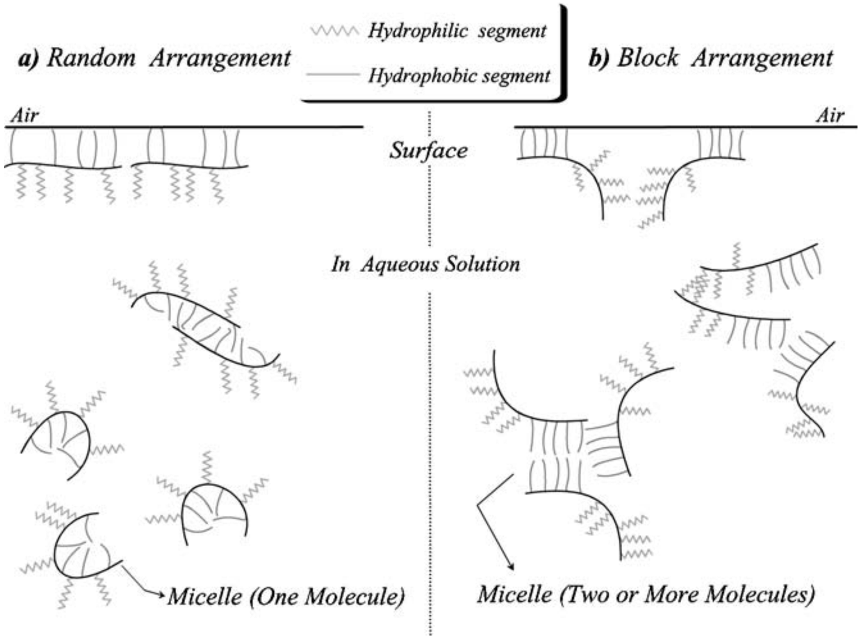


FIGURE 5 Adsorption of hydrophobic segments at the surface of aqueous solution and micelle formation for comblike polymeric emulsifier having (a) random or (b) block arrangement.

figure. On the other hand, in the case of a block copolymer, some molecules could be associated by the strong hydrophobic interaction of the PPG block to make the micelle. Therefore, since many molecules are required to make micelles, the surface tension of the solution shows relatively high values in the region of low emulsifier concentration and clearly decreased according to the concentration. This speculation refers to the structural model of a polymeric emulsifier as reported by Jones, et al. [11].

The interfacial tensions of the aqueous solution of the synthesized polymeric emulsifiers in contact with lipophilic n-hexane plotted against emulsifier concentration are shown in Figure 6. Figures 6a and 6b show the interfacial tension of random (PEr and PEr-s series) and block (PEb and PEb′ series) copolymerized emulsifiers, respectively. In both Figures 6a and 6b, the interfacial tensions also decreased with an increase in emulsifier concentration in correspondence to the experimental results for surface tension. This fact suggests clearly that these polymeric emulsifiers have a high emulsification capability to lipophilic or hydrophobic materials and

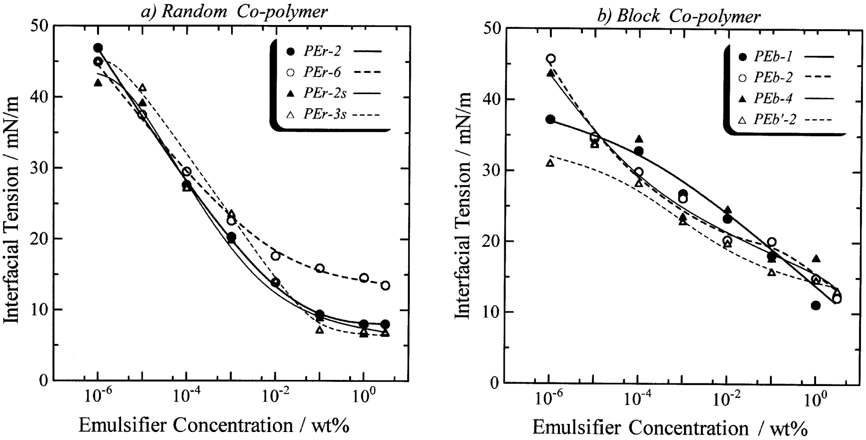


FIGURE 6 Interfacial tensions of aqueous solutions of synthesized (a) random and (b) block copolymerized emulsifiers in contact with lipophilic n-hexane plotted against emulsifier concentration.

supports the result of the emulsification test in terms of surface chemistry, as described in Table 4. On the other hand, although the interfacial tensions of random copolymers (Figure 6a) showed the same dependencies as in Figure 4a, the dependencies of block copolymers (Figure 6b) were different from those in Figure 4b. The interfacial tensions of block copolymers decreased gradually in the region of high emulsifier concentration (~ 1%). This behavior means that in the n-hexane/water interface of an aqueous solution of a block copolymer, the number of molecules required for adsorption was higher than that of a random copolymer. Therefore, it has been shown that the surface activity of random copolymerized emulsifiers is higher than that of block copolymerized emulsifiers in terms of surface chemistry.

HLB and Cloud Point

The cloudy number determined by titration, the HLB value and the cloud point (cp,°C) calculated from the cloudy number of the synthesized polymeric emulsifiers are shown in Table 5. The HLB value and the cp of all series ranged from 9 ~ 12 and 54 ~ 82°C, respectively. In addition, both the HLB value and the cp of block copolymerized emulsifiers were higher than those of random copolymerized emulsifiers. Here, the HLB value of commercially available hydrophilic (O/W type) and lipophilic (W/O type) surfactants ranges from 8 ~ 18 and 3.5 ~ 6, respectively. Therefore, it was found that all of the synthesized

TABLE 5 Cloudy Number, Cloud Point (cp), and HLB of Synthesized Polymeric Emulsifiers

Polymeric Emulsifier (Std. Emulsifiers*)	Cloudy Number, $A_{av.}$ (Average Value, ml) (8.91–38.0)	Cloud Point, $cp^{\#}$ (°C) (40.6–143)	$HLB^{\#}$ (8–18)
PEr-1	12.5	63.1±1	10.2±0.1
PEr-2	11.0	54.3±3	9.34±0.3
PEr-3	13.2	67.2±1	10.6±0.1
PEr-4	13.5	68.7±2	10.8±0.1
PEr-5	12.6	63.9±2	10.2±0.3
PEr-6	13.1	66.6±2	10.5±0.3
PEr-7	13.8	70.4±2	10.9±0.2
PEr-9	11.9	59.7±1	9.88±0.1
PEb-2	15.9	80.5±3	11.9±0.2
PEb-3	16.2	81.6±4	12.0±0.4
PEb-5	15.5	78.5±3	11.7±0.3
PEb′-1	15.4	78.1±3	11.7±0.3
PEb′-2	15.4	77.9±3	11.7±0.3
PEb′-3	15.8	79.8±2	11.8±0.2
PEr-1s	12.9	65.4±2	10.4±0.3
PEr-2s	12.7	64.4±3	10.3±0.3
PEr-3s	13.6	69.5±1	10.8±0.1

*Ordinary hydrophilic nonionic emulsifiers (Functional Emulsifiers, CMC Publishing Co. LTD, (1998)).

#Calculated from cloudy number (A).

polymeric emulsifiers could be classified as hydrophilic surfactants for making an O/W type emulsion.

On the other hand, the relationship between HLB and hydrophilic MPEGMA content in Table 2 or the water solubility in Table 4 did not necessarily exhibit a positive correlation. It is concluded that since the actual applied structural model for HLB calculation was an oxyethylene/oxypropylene/oxyethylene triblock copolymer [10], a difference in the chain arrangements of block and graft (comblike) copolymers resulted in this relationship. Contrarily, the relationship between HLB and emulsification stability in Table 4 was reasonable. This suggests that HLB estimation is more practical than other indirect estimations.

Estimations of Polymeric Emulsion

Viscosity, Nonvolatile Content, and Features

Viscosity, nonvolatile content, and features of the polymeric emulsions which were synthesized using polymeric emulsifiers are shown

TABLE 6 Viscosities, Nonvolatile Contents, and Features of Polymeric Emulsions which were Synthesized Using Polymeric Emulsifiers

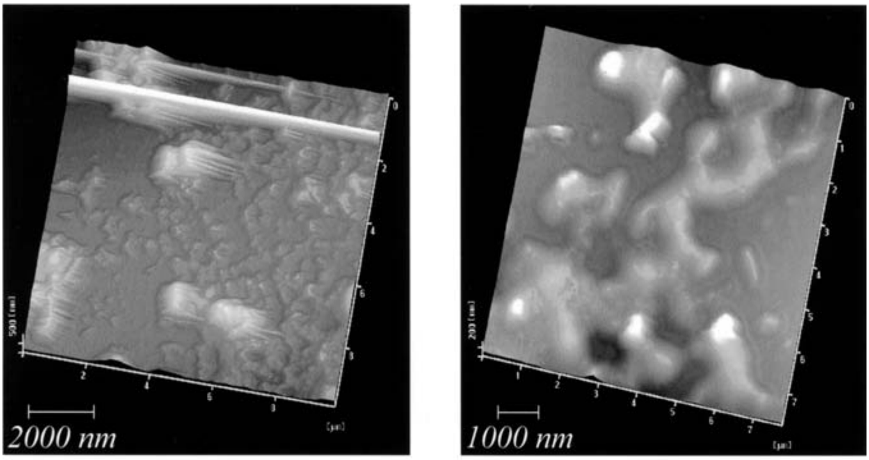
Polymeric emulsifier	Content (wt%/Mo.*)	Viscosity (10^{-3} mPa·s)	Nonvolatile content [calc.] (wt%)	Feature
L-PEr-2	3	–	48.4 [45.9]	Semisolid
L-PEr-3	3	145	34.0 [45.9]	Creamy
L-PEr-5	3	–	47.3 [45.7]	Semisolid
L-PEr-5B	3	–	45.7 [46.8]	Semisolid
L-PEr-8	3	1.38	46.3 [47.6]	Creamy
L-PEr-9	3	–	44.7 [45.7]	Semisolid
L-PEb-2	3	50.3	39.4 [45.5]	Creamy
L-PEb-3	3	98.6	50.2 [46.5]	Creamy
L-PEb-4	3	–	45.2 [45.5]	Semisolid
L-PEb′-2	3	21.5	47.1 [45.3]	Creamy
L-PEb′-3	3	–	44.5 [45.4]	Semisolid
L-PEr-1s	3	24.6	46.1 [45.4]	Creamy
L-PEr-2s	3	70.5	45.9 [45.2]	Creamy
L-PEr-3s	3	99.0	45.5 [45.6]	Creamy

*Monomer gross weight (g).

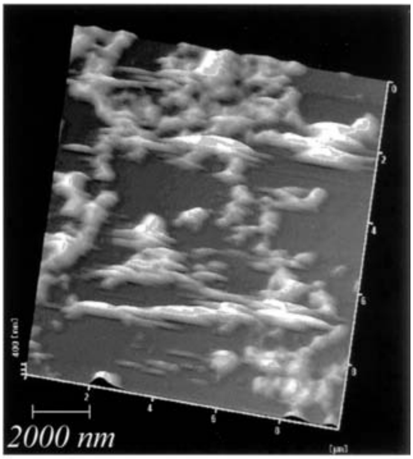
in Table 6. The viscosities of all the series, except for six types of coagulated emulsions, were relatively high, while those of the L-PEr-s series increased with an increase in hydrophobicity. The nonvolatile contents were nearly consistent with their theoretical values. In addition, the nonvolatile contents of some kinds of samples were higher than the theoretical values. It is expected that the water content of the particular polymeric emulsions is confined to the intramolecular graft chains by hydrated PEG segments. From the properties of these polymeric emulsions, excluding the coagulated emulsions, it was shown that polymerization proceeded more easily than that of a series containing Newcol-707SF and Pluronic-F68 as low molecular weight emulsifiers [7]. Furthermore, it was also shown that these properties were affected by the conditions of polymerization such as the stability of temperature rather than by the composition of the polymeric emulsifiers.

Surface Morphology

AFM topographic 3D images for delineating typical particles of polymeric emulsions, which were synthesized using polymeric emulsifiers, are shown in Figure 7. Figures 7a and 7b show the surface of coagulated emulsions, and Figure 7c shows the surface of a medium viscosity emulsion. The horizontal lines in the figures are the scratch marks traced by the AFM cantilever in contact mode. In



a) L-PEr-5 *b) L-PEr-5B*



c) L-PEr-2s

FIGURE 7 Surface topographic images of three types of polymeric emulsions observed by AFM.

Figure 7a, the diameters of the emulsion particles were found to be approximately 1 μm, and their shapes were close to spherical. In addition, flocculation of the particles could be observed locally. In Figure 7b, flocculation of particles was observed in the whole field, forming into cylindrical aggregates. This suggests a strong interaction such as tackiness, and it is clear that the interaction is due to comonomer BA. In Figure 7c, these emulsion particles were found to be the smallest in size, and their diameters were approximately 0.4 µm. In addition, flocculation of the particles could hardly be confirmed. As described in Table 6, it was expected that since this polymerization progressed smoothly, the interaction of the polymer particles would be weak.

Particle Size Distribution

The particle diameters of the monomers in the aqueous solution of polymeric emulsifiers and their polymeric emulsions are shown in Table 7. The diameters of the monomer drops of all the series were smaller than 12 µm, and their distributions also exhibited a narrow Gaussian curve. Next, the particle diameters of the polymeric emulsions of all the series were 0.5 ∼ 110 µm, and their distributions were also found to be wide. Their distribution patterns represented a couple of peaks or a peak having some shoulders. The diameter of L-PEr-5B containing BA exhibited the largest size. This fact was consistent with the result of the AFM observation, as shown in Figure 7. In addition, when the diameters of the monomer drops were compared with the particle diameters of their polymeric emulsions, two tendencies could be observed. In the PEb series and PEb′-3, the monomer drops were

TABLE 7 Particle Size Distributions of Pre-emulsified Monomer Emulsions and Their Polymeric Emulsions

Monomer emulsion*	Particle diameter Median (µm)	Particle diameter Mode (µm)	Polymeric emulsion	Particle diameter Median (µm)	Particle diameter Mode (µm)
M-PEr-2	—	—	L-PEr-2	31	71
M-PEr-3	—	—	L-PEr-3	11	18
M-PEr-5	—	—	L-PEr-5	24	28
M-PEr-5B#	—	—	L-PEr-5B	70	11(× 10)
M-PEr-8	—	—	L-PEr-8	11	35
M-PEr-9	—	—	L-PEr-9	22	35
M-PEb-2	3.0	3.6	L-PEb-2	4.5	14
M-PEb-3	7.2	7.1	L-PEb-3	12	14
M-PEb-4	5.0	7.1	L-PEb-4	20	18
M-PEb′-2	6.3	7.1	L-PEb′-2	2.6	3.6
M-PEb′-3	6.9	11	L-PEb′-3	13	14
M-PEr-1s	4.0	4.5	L-PEr-1s	1.9	1.8
M-PEr-3s	4.9	5.6	L-PEr-3s	4.1	0.5

*Pre-emulsified monomer emulsions: monomers MMA, MPEGMA, MPPGMA, and AA.
#Pre-emulsified monomer emulsion, with added BA.

smaller than their polymer particles, while in the PEr-s series and PEb′-2, the monomer drops were larger than their polymer particles. Generally, if emulsion polymerization proceeds normally, the polymer particles should be smaller than their monomer drops. Therefore, it could be shown that the monomer emulsions of the PEr-s series and PEb′-2 resulted in normal polymeric emulsions. Contrarily, in the PEb series and PEb′-3, polymerization arose from an increase in the size of the polymer particles.

Mechanical Properties as an Adhesive

The tensile adhesion strength and 90-degree peel strength as a test of adhesion strength of the polymeric emulsions, which were synthesized using polymeric emulsifiers, are shown in Table 8. In Table 8,

TABLE 8 Tensile Adhesion Strength and 90-Degree Peel Strength, as Adhesives of Polymeric Emulsions that were Synthesized Using Polymeric Emulsifiers

Polymeric emulsion	Tensile adhesion strength		90-degree peel strength	
	(kgf/cm^2)	(N/mm^2)	(kgf/25 mm)	(N/25 mm)
P A A S*[1]	9.8	1.0	2.0	20
MP15-15*[2]	8.8	0.9	0.6	6.0
MP15-15B*[3]	11	1.1	1.7	17
L-PEr-3	2.4	0.2	0.9	9.5
L-PEr-5	5.3	0.5	1.0	10
L-PEr-5B	10	1.0	2.2	22
L-PEr-8	6.2	0.6	0.9	9.5
L-PEr-9	3.6	0.4	0.7	7.2
L-PEb-2	12	1.2	2.2	22
L-PEb-3	2.2	0.2	1.3	13
L-PEb-4	8.6	0.8	2.5	25
L-PEb′-2	11	1.1	2.6	26
L-PEb′-3	5.2	0.5	0.8	8.0
L-PEr-1s	4.2	0.4	0.7	7.2
L-PEr-2s	6.5	0.6	0.8	8.6
L-PEr-3s	2.6	0.3	0.5	4.8

*[1] Practical applicable adhesion strength.

*[2] Polymeric emulsion, which was polymerized via low molecular weight emulsifier (commercially available); Composition of MP15-15: MMA/MPEGMA/MPPGMA/AA = 70/15/15/3 (wt%).

*[3] Polymeric emulsion containing BA, which was polymerized via low molecular weight emulsifier (commercially available); Composition of MP15-15B: MMA/MPEGMA/MPPGMA/AA/BA = 70/15/15/3/5 (wt%).

PAAS is an abbreviation for Practical Applicable Adhesion Strength, which is required for use in building materials [12], and MP15-15 and MP15-15B represent the polymeric emulsions, which were synthesized *via* commercially available emulsifiers (Newcol-707SF and Pluronic-F68). MP15-15 and MP15-15B have the same compositions as other polymeric emulsions listed in the table. However, MP15-15B has the same composition as L-PEr-5B. Here, since the polymeric emulsions synthesized in this study correspond to the vinyl copolymerized resin emulsion (A:) or the acrylic resin emulsion (B:) prescribed by JIS A5536, the following estimations are obtained according to this prescription and PAAS. In addition, the adhesion strength required for these adhesives is $0.2\,\mathrm{N/mm^2}$ (A: and B:) as the tensile adhesion strength and 20.0 N/25 mm (A:) or 10.0 N/25 mm (B:) as the 90-degree peel strength.

Both the tensile adhesion strength and 90-degree peel strength of L-PEr-5, L-PEr-5B, L-PEb-2, L-PEb-4, and L-PEb′-2 exceeded the standard prescribed by JIS. In particular, the adhesion strength of L-PEr-5B, L-PEb-2, and L-PEb′-2 exceeded the PAAS. Accordingly, regarding adhesion properties it could be shown that the three above-mentioned polymeric emulsions could be used as practical applicable adhesives. Next, the adhesion strength of L-PEr-5B was higher than that of the other L-PEr series. It is clear that BA, as a comonomer, improves the adhesion strength of a polymeric emulsion as well as the relationship between MP15-15 and MP15-15B. Furthermore, both L-PEb-2 and L-PEb′-2 exhibited the best adhesion properties as described above, while these adhesion strengths also exceeded those of MP15-15B. In particular, the 90-degree peel strength exhibited a high value. Originally, in order to improve 90-degree peel strength by increasing toughness, BA has been used as a modifier in a previous study [7]. However, although both L-PEb-2 and L-PEb′-2 did not contain BA their adhesion strengths were found to be better than polymeric emulsions containing BA, such as MP15-15B and L-PEr-5B. Thus, it could be shown that the high adhesion strengths of both L-PEb-2 and L-PEb′-2 were due to the block copolymerized emulsifier.

On the other hand, the dependence of the adhesion properties on the compositions of the polymeric emulsifiers was inconclusive. It is suggested that the reason for this result is the conditions of polymerization, as described in Table 6. From the facts above, it could be shown that synthesized terpolymers, as emulsifiers, had capabilities similar to or higher than commercially available emulsifiers.

CONCLUSION

Some comblike terpolymers, composed of MMA, MPEGMA as a hydrophilic component, and MPPGMA as a hydrophobic component were synthesized by both living radical photopolymerization and ordinary radical polymerization. These terpolymers produced random or block chain arrangements. From experimental results of their characteristics, emulsification stability, and surface chemical properties, it was shown that these terpolymers could be used as emulsifiers. In particular, since both the surface tensions and interfacial tensions decreased with an increase in emulsifier concentration, it could be expected that these terpolymers would have strong surface activity. Furthermore, a difference in the behavior of the surface tensions of these terpolymers was observed. We suggest that it was due to the difference in the segmental mobility of the chain arrangements of the terpolymers.

On the other hand, the polymeric emulsions containing these terpolymers, also showed comparatively good emulsion as emulsifiers and mechanical properties as adhesives. In particular, although the polymeric emulsions that were synthesized using block copolymerized emulsifiers did not contain BA as the modifier, the adhesion strength of these polymeric emulsions exceeded that of BA-modified polymeric emulsions. As one reason for these results, we suggest that a polymeric emulsifier having the same components as the polymerized emulsions contributed to the improvement of the adhesion properties. In addition, the relationship between the emulsion properties and adhesion properties did not necessarily show a positive correlation. Summarizing our findings, we found that the synthesized terpolymers, as emulsifiers, had capabilities similar to or higher than commercially available emulsifiers.

In the future, we wish to synthesize more polymeric emulsifiers in order to apply them to various polymerization systems. These emulsifiers could be designed according to their surface chemical properties. Further examinations regarding this viewpoint will be required.

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