

Surface Molecular Mobility and Functionality for Amphiphilic Copolymers Having Hydrophilic and/or Hydrophobic Side-Chains

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Some comb-like copolymers composed of methyl methacrylate (MMA), methoxypolyethyleneglycol methacrylate (MPEGMA) as a hydrophilic component, and methoxypolypropyleneglycol methacrylate (MPPGMA) or Poly (dimethylsiloxane) methacrylate (PDMSMA) as a hydrophobic component were synthesized by both living radical photo-polymerization and ordinary radical polymerization. Surface molecular mobility for these copolymers was discussed via dynamic contact angle (DCA), adhesion tension relaxation (ATR) and XPS and so on. We have also studied on the application of these copolymers as functional polymer such as the blood compatible material, adhesive, PSA and polymeric surface-active agent. Since these copolymers 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 copolymers had almost the same emulsification capability as commercially available low molecular weight emulsifiers. Conversely, a difference in surface and interfacial tension behavior of aqueous solution of these copolymers could be observed. We think that it was due to the chain arrangements (random or block sequence) of the copolymers. For this paper, we present the emulsion polymerization of the copolymers via the polymeric emulsifier having hydrophobic and hydrophilic side-chains.

Key words: comb-like polymer, dynamic contact angle (DCA), adhesion tension relaxation (ATR), emulsion polymerization, emulsifier

1. INTRODUCTION

We [1-6] have studied on surface properties for comb-like polymers having hydrophilic and/or hydrophobic side chains and their applications to the functional polymeric materials via X-ray photoelectron spectroscopy (XPS), dynamic contact angle (DCA) and so on. Copolymers mainly composed of methyl methacrylate (MMA), methoxypolyethyleneglycol methacrylate (MPEGMA) as a hydrophilic component and methoxypolypropyleneglycol methacrylate (MPPGMA) as a hydrophobic component were synthesized by radical polymerization in an organic solvent. From these studies, it was shown that the various functionalities were originated from the molecular mobility of their side chains based on each surface free energy, and the coexistence of hydrophilic and hydrophobic side chains results in the high environmental responsibility.

Recently, since an organic solvent used for the polymeric material is harmful to a human body and pollute environment, the usage is restricted. Accordingly, polymerization manner and usage style for the polymeric material should be necessary to convert from an organic solvent into a waterborne system. Thus, we have synthesized these polymeric materials via emulsion polymerization and tried to apply them as an adhesive. 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 co-monomer butyl acrylate (BA). Results of this

modification have previously been reported on [7]. Another improvement was emulsion polymerization using synthesized polymeric emulsifiers. We are in agreement that using the polymeric emulsifiers may reduce some problems related to a low molecular weight emulsifier. Our prospect on this improvement has also been achieved [8]. Summarizing our findings, the synthesized polymeric emulsifiers composed of the same components as the synthesized polymeric emulsions had very high surface activity and the high capabilities of the polymeric emulsions via synthesized emulsifier also led to the improvement of two mechanical properties as an adhesive. However, since the polymeric emulsifiers were exhibited a high capability in only one kind of emulsion, it was necessary to enable a versatility over many objects.

In this study, polymeric surfactants were synthesized by both living radical photo-polymerization and ordinary radical polymerization corresponding to the previous report [7]. Component of these polymeric surfactants were not necessarily the same as those of a target emulsion. In addition, we also polymerised emulsions containing our synthesized polymeric surfactants and measured several characteristics as well as tensile adhesion strength and 90-degree peel strength for their adhesive properties. Furthermore, in order to analyze surface dynamics of the synthesized polymeric surfactants, we measured the film surface casted from an organic solution of the surfactant via DCA, adhesion tension relaxation (ATR), and XPS.

2. EXPERIMENTAL

2.1 Materials

Monomers used for the polymeric surfactant were methyl methacrylate (MMA), methoxypolyethylene-glycol methacrylate (MPEGMA), 2-acrylamido 2-methyl 1-propane sulfonic acid (AMPS), lauryl methacrylate (LMA) and stearyl methacrylate (SMA). The chemical structures of these monomers are shown in Fig.1. The molecular weight (Mn) and the number of repeating unit (n) in side chains of MPEGMA were 1100~1160 and 22.8~24.2, respectively. MPEGMA, AMPS, LMA and SMA were used as received from Aldrich Co.

Monomers used for the emulsion polymerization were MMA, MPEGMA and methoxypolypropyleneglycol methacrylate (MPPGMA). In this case, acrylic acid (AA) as a co-monomer was added in order to increase cohesion. Co-monomer butyl acrylate (BA) and ethylhexyl acrylate (EHA) were also used for modifying the emulsions. 1-dodecanethiol and ammonium peroxydisulfate (APS) were added as a chain transfer agent and initiator, respectively. These monomers and reagents were of commercially available grade and were purified via normal methods.

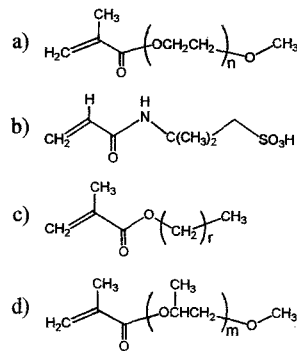


Fig.1 Chemical structures of monomers a)MPEGMA, b)AMPS, c)LMA(r=11) or SMA(r=17) and d)MPPGMA.

2.2 Preparation of Polymeric Surfactant and Polymeric Emulsion

The polymeric surfactants were prepared by means of the following two techniques. Terpolymer P(MMA-co-MPEGMA)-b-PLMA was synthesized by living radical photo- polymerization under irradiation of

a UV light source. Photo-polymerization was carried out in MEK at room temperature for 6~8 hours with a sealed bottle of argon atmosphere using benzyl N, N-diethyldithiocarbamate (BDC) or p-xylylene bis(N, N-diethyldithiocarbamate) (XDC) as a photo-iniferter [9]. This sample was found to be block co-polymer. The block co-polymer was polymerized via two-step method. The second monomer, LMA, was co-polymerized successively after co-polymer P(MMA-co-MPEGMA) was prepared first. However, since it proved to be difficult to produce complete isolation of a pure block co-polymer, this terpolymer could subsequently not be sufficiently purified. Other co-polymers except for the block co-polymerized terpolymer were synthesized by ordinary radical polymerization in methyl ethyl ketone (MEK)/p-xylene solution (1:1 vol. ratio). This solution polymerization was carried out at 70 °C for 6~8 hours using 2,2-azo bis (isobutyronitrile) (AIBN) as an initiator. These samples were found to be random co-polymers. Nomenclature and the characteristics of all of the synthesized polymeric surfactants are listed in Table I.

Polymeric emulsions used in this study were prepared by emulsion polymerization using the synthesized polymeric surfactants as mentioned above. The emulsion polymerization was carried out via the dropping method. Feed composition of the monomers was set at 70wt% of MMA, 15wt% of MPEGMA, 15wt% of MPPGMA, 3wt% of AA, and 5wt% of BA, or EHA. These compositions have been reported on previously and their emulsions exhibited the best emulsion properties [7].

2.3 Estimation of Polymeric Surfactant and Polymeric Emulsion

The characteristics of the synthesized polymeric surfactants were determined by gel permeation chromatography (GPC, TOSOH-8020) via the polystyrene standard and proton-NMR (Varian 400MHz NMR) using chloroform-d₁ as a solvent.

Surfactant 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. Surface chemical properties were estimated via experimental entries as follows. The surface tensions of the aqueous solution of the synthesized polymeric

Table 1 Nomenclature and characteristics of synthesized polymeric surfactants.

Co-polymer	Feed (wt%)	Sample Name	Composition ^{*1} (wt%)	Mw ^{*2} (x10 ⁻⁴)	Mw/Mn
p(MMA-co-MPEGMA-co-LMA)	10/45/45	L-1	22 /52 /26	2.5	1.5
p(MMA-co-MPEGMA-co-LMA)	10/60/30	L-2	18 /77 / 5	2.6	1.5
p(MMA-co-MPEGMA)-b-p-LMA [#]	10/40/50	L-3b	37 /49 /14	4.6	1.4
p(MMA-co-MPEGMA-co-SMA)	10/60/30	S-4	30 /48 /22	N/D	N/D
p(MMA-co-AMPS-co-LMA)	10/45/45	L-A1	N/D	N/D	N/D
p(MMA-co-AMPS-co-SMA)	30/50/20	S-A2	N/D	N/D	N/D
p(MMA-co- AMPS-co-MPEGMA-co-LMA)	30/35/5/30	L-AM1	N/D	N/D	N/D
p(MMA-co-AMPS-co-MPEGMA-co-LMA)	30/30/10/31	L-AM2	N/D	N/D	N/D
p(MMA-co-AMPS-co-MPEGMA-co-LMA)	30/20/20/32	L-AM3	N/D	N/D	N/D
p(MMA-co-AMPS-co-MPEGMA-co-SMA)	30/30/10/30	S-AM4	N/D	N/D	N/D

^{*1} Determined by¹H-NMR, ^{*2} Relative molecular weight determined by GPC
[#] Mw of first product [p(MMA-co-MPEGMA)] showed 3.8 x 10, N/D Not determined due to poor solvency in chloroform

surfactants were determined by Du-Noy (Pt-ring) method. The interfacial tensions of the aqueous solution of polymeric surfactant in contact with lipophilic n-hexane were also determined by the same methods as above. The value of Hydrophile-Lipophile-Balance (HLB) and the cloud point (cp) were calculated from the cloudy number. The cloudy number was determined by the titrating method [10].

The general properties of the polymeric emulsion were estimated via its viscosity, non-volatile content and particle size distribution. The viscosity was determined by rotational viscometer (Brookfield RVT) according to Japan Industrial Standard (JIS) K6828. The non-volatile content was also determined according to the same standard as above. The particle distribution of the pre-emulsified monomer emulsion and its polymeric emulsion was estimated via median and mode size, and distribution pattern. These measurements were performed using a Laser Diffraction Particle Size Analyzer SALAD-2000 (Shimadzu Co.). 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 tensile adhesion strength was measured at 1mm/min in tensile speed using a TENSILON testing machine (Orientec Co.). The 90-degree peel strength was measured at 200mm/min in peel speed using a AGS-1000A type peel testing machine (Shimadzu Co.).

2.4 Evaluation regarding Surface Dynamics

Surface dynamics for the films of the synthesized polymeric surfactants were evaluated from experimental results of DCA, ATR and XPS. MEK was used as a casting solvent and the film surface was casted from a solution of 2wt% of each surfactant onto the predefined aluminum plate (l: 50mm, w: 20mm, d: 0.5mm). The aluminum plates were dried for 24 hours or more in vacuum at R.T.. DCA and ATR were measured by means of Wilhelmy technique using DCA20 (Orientec Co.) and identifications of surface composition were determined by measurement of XPS using ESCA850 (Shimadzu Co.).

3. RESULT AND DISCUSSION

3.1 Properties of Polymeric Surfactant

The surface tensions of the aqueous solution of the synthesized polymeric surfactants plotted against surfactant concentration are shown in Fig.2. The surface tensions decreased with an increase in surfactant concentration. Consequently, it is clear that these surfactants could be used as a surface-active agent. In addition, critical micelle concentration (c.m.c.) estimated from the breaking point of the curves was close to 0.01%. Next, the interfacial tensions of the aqueous solution of the synthesized polymeric surfactants in contact with lipophilic n-hexane plotted against surfactant concentration are shown in Fig.3. The interfacial tensions also decreased greatly from approximately 45 mN/m to nearly 10 mN/m in correspondence to the experimental results for surface tension. Therefore, this fact suggests clearly that these polymeric surfactants have a high emulsification capability to lipophilic or hydrophobic materials. In this report, although the detailed result of the emulsification test was not able to be shown

regrettably, its result was good in all samples. Thus, it is thought that the experimental results for interfacial tension support the result of emulsification test in terms of surface chemistry.

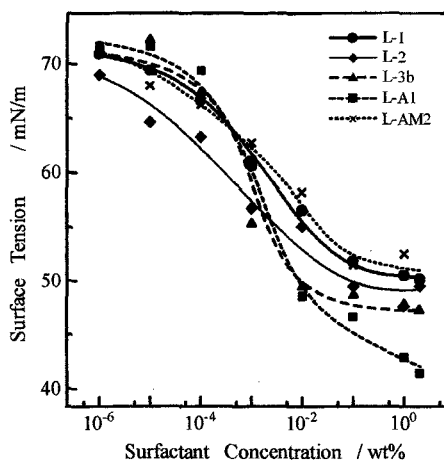


Fig.2 Surface tensions of aqueous solution of synthesized polymeric surfactants plotted against surfactant concentration.

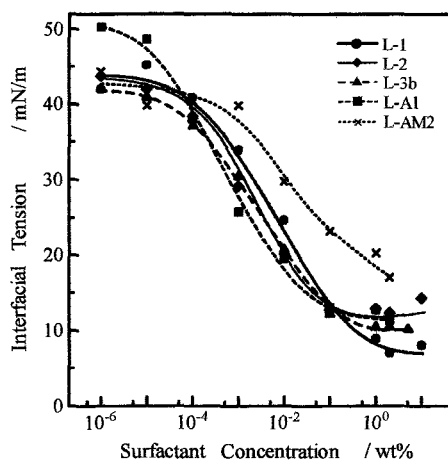


Fig.3 Interfacial tensions of aqueous solution of synthesized polymeric surfactants in contact with lipophilic n-hexane plotted against surfactant concentration.

3.2 Properties of Polymeric Emulsion

Viscosity, non-volatile content and features of the polymeric emulsions, which were synthesized using polymeric surfactants, are shown in Table 2. The viscosities of all the samples were relatively high and it was shown that an effect of thickening for co-monomer EHA was larger than that of co-monomer BA, except the case of Em1. The non-volatile contents were nearly consistent with their theoretical values. In addition, the non-volatile contents of some kinds of samples were higher than theoretical values. It is expected that the water content of the particular polymeric emulsions is confined to the intra-molecular graft chains by hydrated and/or ionized segments. From the properties of these polymeric emulsions, it was shown that polymerization proceeded easier than that of a series containing two commercially available surfactants in the previous study [7]. Furthermore, it was also shown that these properties

Table 2 Viscosities, non-volatile contents and features of polymeric emulsions, which were synthesized using polymeric surfactant.

Emulsion No. ^{*1} (surfactant Used)	Emulsifier (wt%/Mo ^{*2}) Modifier (wt%/Mo ^{*2})	Viscosity (10 ⁻³ mPa·s)	Non Volatile Content [calc.] (wt%)	Feature
Em1 (L-1)	2.5	29.2	51.3	Creamy
	BA 5.0		[47.8]	
	2.5	5.09	50.4	
Em2 (L-2)	EHA 5.0		[47.8]	Creamy
	2.5	6.70	49.1	
	BA 5.0		[47.8]	
Em3 (L-3b)	2.5	85.8	45.9	Creamy
	EHA 5.0		[47.9]	
	2.5	2.21	48.4	
Em4 (L-AM1)	BA 5.0		[47.8]	Creamy
	2.5	31.8	44.5	
	EHA 5.0		[47.8]	
Em5 (L-AM2)	2.5	14.5	48.1	Creamy
	BA 5.0		[48.3]	
	2.5	47.2	48.9	
	EHA 5.0		[48.3]	Creamy
	2.5	27.0	50.6	
	BA 5.0		[48.8]	
	2.5	140	48.9	Creamy
	EHA 5.0		[48.7]	

*1 Common feed of polymeric emulsions (Em1-5) was regulated to 70% of MMA, 15% of MPEGMA and 15% of MPPGMA, *2 Monomer gross weight (g)

were affected by the conditions of polymerization such as the stability of temperature rather than the kind of the polymeric surfactants and the constituent components of the polymerized emulsion.

3.3 Surface Dynamics of Film Formed from Polymeric Surfactant

As described in the introduction, some multicomponent polymeric systems such as amphiphilic co-polymers show the high environmental responsibility. The contributing factor is explained as follows: these polymeric systems adsorb and orient selectively to the surface of their systems so as to minimize interfacial free energy in response to a polarity of an environmental medium. An experimental result of the DCA for L-3b is shown in Fig.4. The DCA curves of 1st and 2nd run, and advancing and receding contact angles (θ_a and θ_r) in each cycle are represented in the figure. θ_a and θ_r in the 1st cycle were 91.5 and 31.6 deg, respectively, and consequently showed a large contact angle hysteresis ($\Delta\theta = \theta_a - \theta_r$). This is due to a high segmental mobility of co-polymer L-3b having the comparatively long hydrophilic and hydrophobic side chains. Contrarily, $\Delta\theta$

for the 2nd cycle displayed a small value because of the decrease in θ_a . Such a characteristic behaviour could not usually be observed on the generic polymer surface. Furthermore, the DCA curve in advancing process for the 2nd cycle did not maintain a constant slope and shifted to the direction of that for the 1st cycle within the measurement time of 2nd cycle run. Therefore, as shown in the figure, θ_a in the tail-end part of this curve was almost recovered to that for the 1st cycle. This fact denotes that the hydrophobic segments reorient gradually during the measurement to the surface, which changed in hydrophile at once by dipping.

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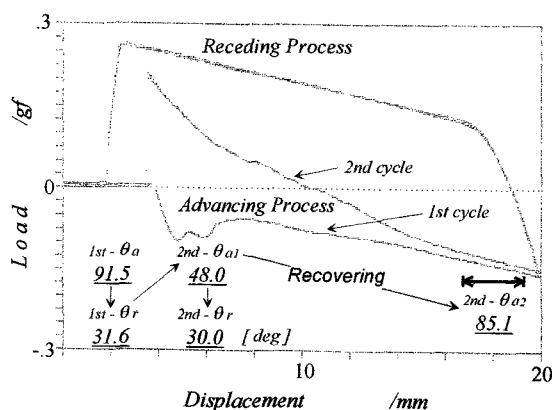


Fig.4 DCA curves for solvent-casted film of synthesized polymeric surfactant (L-3b).