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SYNTHESIS OF AMPHIPHILIC COPOLYMERS BASED ON ACRYLATES BY FREE-RADICAL POLYMERIZATION AND THEIR APPLICATION IN ALKYD EMULSIONS

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Key Words: Amphiphilic Copolymers, Poly(ethylene glycol), Stearyl Acrylate, Surface Tension, Alkyd Emulsions

ABSTRACT

Novel amphiphilic copolymers which contained poly(ethylene glycol) side-chain, long-chain alkyl pendant groups, and carboxyl groups have been synthesized by the conventional free-radical copolymerization of special monomers. The products were characterized by analysis of Fourier transform infrared spectroscopy (FT-IR), Gel Permeation Chromatography (GPC), and ^{1}H NMR. Based on the measurement of surface tension of aqueous copolymer solutions with various concentrations at an air/water interface, the critical micelle concentrations (CMC) was found to be lower along with the increase of copolymer concentration.

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Experimental results showed that CMC of this kind of amphiphilic polymer appeared in the range of 0.01~0.1 g/L. The amphiphilic polymer was mixed with an anionic surfactant (SDBS) in different proportions at aqueous solution and then successfully used in the preparation of alkyd emulsions. The results were compared with those of alkyd emulsions without polymeric surfactant. Steric stabilization of amphiphilic polymer was investigated by the observation of the stability of alkyd emulsions. The emulsions were stable after resting at ambient temperature for four months.

INTRODUCTION

Amphiphilic copolymers containing poly(ethylene glycol) (PEG) have attracted much attention for their preparation strategies and physicochemical properties. In addition due to PEG's unique hydrophilic properties, there has been growing interest in their applications, especially in the design of drug-delivery systems and for the modification of biomedical polymer surfaces [1-4]. Extensive reports are seen regarding preparation of amphiphilic PEG-grafted copolymers by either copolymerization of vinyl monomers with PEG macromonomers or syntheses of polymeric precursors followed by PEG conjugation *via* polymeric analogous reactions. In spite of the great versatility of biological applications offered by the various structures of amphiphilic copolymers contained PEG, relatively few reports have appeared dealing with copolymer surfactants contained PEG chains, alkyl chains and carboxyl groups in the same macromolecule prepared via free-radical copolymerization and their application in coatings.

In formulating products such as paints, inks, cosmetics, and pharmaceuticals, it is often necessary to emulsify liquid components and to stabilize dispersions of solid particles in a single aqueous formulation. Stabilization may be successfully accomplished using mixtures of conventional and/or polymeric emulsifiers and dispersion stabilizers. However, as complex formulations age, one component may interact with increasing levels of emulsifier or stabilizer, depriving other components, and thus causing instability. Henk and Creutz *et al.* recently described some examples of this kind of problem regarding pigmented paints, in which the binder was an emulsified alkyd [5-9]. They suggested a potential solution to such problems, namely to use emulsifier/dispersion stabilizers with multiple functionalities. There was also a description of the successful use of a polymeric emulsifier/stabilizer in which polyethylene glycol (hydrophilic), long-chain alkyl (oleophilic), and carboxyl groups (pigmentphilic) existed in the same macromolecule, but the composition of this kind of material was described only in general terms [5, 7]. Li *et al.* investigated the effect of a hydrophobically modified anionic polymer (a maleic anhydride α-olefin copolymer), which has a comb-like structure, on the stability of alumina suspension [10]. They indicated that the stability of the suspension enhanced by both steric and electrostatic repulsion.

In this study, we investigated the synthesis of a triple-affinity copolymer by conventional free-radical copolymerization. It formed from poly(ethylene glycol) methacrylate (a nonionic hydrophilic monomer) , stearyl methacrylate (a hydrophobic monomer), several anionic hydrophilic monomers, including acrylic acid, methacrylic acid and itaconic acid. This method was adopted because it enables incorporation of a wide variety of monomers into the polymers and it is readily implemented. We evaluated their micelle solution, surface-active properties and utilities in emulsified alkyd.

In preparing water-borne alkyd emulsion, the study utilized the synergetic effect of polymeric surfactant and anionic surfactant. We assumed that a random copolymer consisting of comb-like PEG and alkyl chain would play the role of steric stabilizer in emulsion as long as it would be composed of proper unit structure. The molecules of the polymeric emulsifier in surface-active interface presumably are oriented in such a way that their polar hydrophilic groups are directed towards the dispersive medium (water) while their non-polar hydrophobic hydrocarbon chains are directed towards the dispersed phase.

EXPERIMENTAL

Materials

Stearyl methacrylate (SMA) with *ca*. 35% cetyl methacrylate, obtained from Aldrich Chemical Co., was recrystallized from methanol before use. Acrylic acid (AA), methacrylic acid (MAA), and butyl methacrylate (BMA) from Aldrich were treated respectively with active acidic or neutral aluminum oxides and then vacuum distilled under nitrogen prior to use to remove inhibitors. Other chemicals obtained from Aldrich were used as received, which were included poly(ethylene glycol) methacrylate (PEGMA, M_n~360) as co-monomer, t-butyl peracetate (t-BPA, 50 wt%) as initiator, 1-dodecanethiol (1-DDT, 98 wt%) as transfer, 2-propanol as solvent, and itaconic acid (IA) as co-monomer. The soya modified linear polyester, LV-803, with 100% solid content, was kindly provided by Lawter International Inc. Sodium dodecylbenzene sulfonate (SDBS) as anionic surfactant, was supplied by Rhone-Poulenc Co. Deionized water was used for all experiments.

Synthesis of the Copolymers

The free-radical copolymerization was carried out in a 500-mL 4-neck round-bottom flask equipped with a glass stirring rod with a Teflon paddle, an addition funnel, a nitrogen inlet, a thermometer and a reflux condenser with a gas outlet. A heating mantle and a temperature controller were used in the equipment. A typical procedure for copolymer **C5** and **C6** is described as follows: To the flask a solution of t-BPA 0.66 g and 2-propanol 30 mL was added, stirred, and subsequently heated to 82°C under nitrogen for 20 minutes. The co-monomer was slowly added into the flask in 2 hours, which was composed of PEGMA 18 g, SMA 6.79 g, MAA 0.43 g, AA 1.80 g, 50 wt% t-BPA 1.50 g, 1-DDT 1.08 g and 2-propanol 50 mL. After the addition was complete, stirring was continued for 2 hours at 82°C. The solvent in the reactant were removed using a rotary evaporator at 100°C under water aspirator pressure. The product was redissolved into a small amount of tetrahydrofuran (THF) and purified by repeated precipitation from n-hexane, followed by filtration and drying under vacuum.

TABLE 1. Monomer, Initiator, and Transfer Agent Compositions in Copolymers Synthesized[a]

Polymer No.	PEGMA	SMA	AA	IA	BMA	MAA	t-BPA[b]	1-DDT[b]
C1	10	10	30	5	45	_	4.6	3.8
C2	9	9	27	5	50	_	4.6	1.8
C3	45	20	8.5	5.3	_	_	3.8	2.5
C4	50	20	25	5	_	_	8.0	5.0
C5	**50**	**20**	**25**	_	_	**5**	**8.0**	**5.0**
C6	**50**	**20**	**25**	_	_	**5**	**8.0**	**2.5**
C7	34	_	13	_	_	53	4.6	2.5

[a] Composition, mol %;

[b] Mole fraction based on the total amount of monomers.

Copolymers **C1 –C4** and **C7** were synthesized by similar procedures with the compositions as shown in Table 1. The products were transparent, viscous semi-solids.

Characterization of the Copolymers

Molecular weight and molecular weight distribution (MW & MWD) were measured by Gel Permeation Chromatography (GPC) apparatus equipped with Hewlett Parkard (HP) Series 1050 Quad Pump and HP 1047A Differential Refractometer. THF was used as eluant at a flow rate of 0.9 mL/min, and polystyrene standards were used for calibration. The infrared spectra were recorded on a Nicolet Magna 510P FT-IR spectrometer at 4 cm^{-1} resolution with 16 scans per spectrum. ^1H NMR spectra were obtained from a Bruker MSL-300 spectrometer using $CDCl_3$ as solvent.

The surface activity of the copolymer surfactant in water was measured at an air/water interface [11] at 20 to 45°C and ambient pressure using a tensiometer, a “Dynometer” from BYK Chimie Co. The tensiometer was calibrated with deionized water before use. The platinum ring and glassware were cleaned with a strong base solution and rinsed with tap water and deionized water. A 25 g/L mixture of aqueous polymeric surfactant was freshly prepared and then diluted to the desired concentration for each measurement. Surface tension was measured three times at each concentration, and the values were averaged.

The measurement of pH in a series of aqueous copolymers was made using ORION model 201A pH meter. The measurement of viscosity was run on LVDV-II viscometer from Brookfield Engineering Laboratory Inc. The -COOH content in the polymer was determined by conventional titration using standard KOH solution and subsequently calculated the molar fraction of carboxyl group.

Preparation of Emulsions and their Stability

The post-emulsification of alkyd LV-803 was carried out in a 3-neck round-bottom flask equipped with a high-speed stirrer, an addition funnel, a condenser and a water bath. Under high-speed stirring at 40-45°C, the aqueous mixtures (pH-8), which contained 1-4 wt% polymeric emulsifier and 2 wt% SDBS, were fed dropwise into the flask with LV-803 (10 g) at 40°C for 20 minutes. At first, the mixture in the flask became a high viscosity white opaque liquid. As addition of the surfactant-water mixtures approached completion, the viscosity of the mixture decreased. After the addition was complete, the stirring was kept at 40-45°C for 1 hour. The product was a low viscosity, milky alkyd emulsion with solids around 56-60 wt% without any organic solvent. The stabilization of emulsions was evaluated by observation of particle sizes at intervals.

Particle size and particle size distribution (PS & PSD) were determined by dynamic laser light scattering on L&N Microtrac Particle Analyzer 9200 series from Leeds & Northrup Co. Emulsion samples were diluted with deionized water to the concentration with about 0.1 wt% of resin. The number-average (D_n), volume-average (D_v) diameters were calculated by the instrument. The polydispersity is expressed as D_v/D_n (D_v equals to weight-average diameter, D_w, when particles are assumed to have the identical density regardless of their particle sizes).

RESULTS AND DISCUSSION

Synthesis of Amphiphilic Copolymers

Syntheses of PEG-contained amphiphilic copolymers have been reported elsewhere. For example, Chiu *et al.* synthesized amphiphilic copolymers comprising monomeric units of SMA, methyl acrylate, acrylic acid and PEG acrylate by the cooplymers of SMA and acryloyl chloride reacted subsequently with methoxy PEG, methanol and water, respectively [4]. Lee *et al.* prepared graft copolymers of alkyl methacrylates with monomethoxy poly(ethylene glycol) (mPEG) methacrylate macromonomers by free-radical polymerization [12]. In this study, the preparation of amphiphilic copolymers was performed by copolymerization of the various monomers under starved monomer conditions (Figure 1).

Copolymerization compositions are shown in Table 1. PEGMA, SMA and AA were used as the basic monomers to prepare copolymers. The PEGMA molecule has a relatively long pendent of PEG that is hydrophilic. SMA pos-

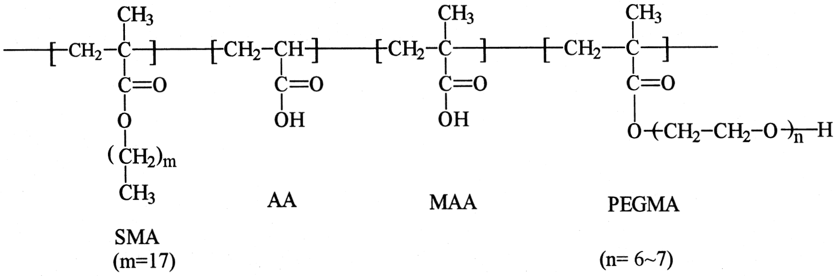

Figure 1. Idealized structure of copolymers synthesized.

sesses a long, hydrophobic alkyl chain with affinity to resin. AA, of course, is a water-soluble monomer with charged carboxyl group. In addition to these three monomers, MAA, BMA and IA were used to form copolymers. The reactivity of all monomers used should be considered because of the potential for unusual behavior by large monomers with PEGMA and SMA. There are two main effects that influence the ability of macromonomers to copolymerize [13, 14]: (1) the effect of side groups associated with the terminal double bond and (2) the length of the pendant chain. It appears that the first parameter plays the major role. Both the conventional monomers and the large monomers used in this study are methacrylates with different ester units. As polar effects of ester parts do not differ substantially and the lengths of the large monomer side-chains should not have a pronounced effect on the macromonomer's reactivity [13], the copolymerization parameters were similar for all combinations used.

IA was selected as a monomer to be attempted to co-polymerize with other monomers because it has double carboxyl group. IA was also miscible with other monomers in 2-propanol. Considering the slight difference of monomer reactivity ratios, the dropwise addition of mixed monomers was adopted in the synthetic procedure so that polymerization would occur under monomer starved conditions. It was found that a spot of solids of IA remained in the resulted copolymers **C1** and **C2**, which could not dissolve completely in water. Thus, it apparently indicates that the reactivity ratio of IA does not match with other monomers. On the other hand, more quantity of BMA in copolymers resulted in

TABLE 2. Characteristics of Copolymer Surfactants

Polymer No.	[M]/[I]/[S] (mole ratio)	M_n	M_w/M_n	Micelle size[α] D_n (nm)	-COOH content[β] (mol %)
C5	100 :8.0 :5.0	1.4×104	4.55	13	22.3
C6	100 :8.0 :2.5	1.9×104	4.75	15	22.5

[α] Measured concentrations were 25.28 g/L for **C5** and 24.40 g/L for **C6**, respectively.

[β] Measured by conventional titration using 0.0956N/mL of standard KOH aqueous solution, and subsequently calculated -COOH content based on the total amount of co-monomers.

the poor solubility in water. Copolymers of **C3** and **C4** were synthesized by increasing PEGMA and SMA amounts without BMA. The problem of non-polymerized IA particles still existed.

The optimal copolymers were **C5** and **C6**, which had monomer molar ratio of PEGMA/SMA/AA/MAA=50/20/25/5. Two kinds of initial feed molar ratio of monomer/initiator/transfer agent were adopted (**C5:** [M]/[I]/[S]= 100**:**8.0**:**5.0 and **C6:** [M]/[I]/[S]=100**:**8.0**:**2.5) in order to obtain different molecular weights as shown in Table 2. It is well known that M_n of copolymers decreases with the increase of the amount of chain transfer agent. The experimental results of the -COOH content confirmed that there are carboxyl groups in the polymer.

For **C5** and **C6**, the micelle solutions were translucent with light blue color when the concentration was respectively high up to ca. 25.28 g/L and 24.40 g/L, while the copolymer surfactant solution formed transparent, colorless solution at lower concentration with 0.506 g/L and 0.488 g/L, respectively. The micelle sizes were measured by dynamic laser light scattering on L&N Microtrac Particle Analyzer 9200 series from Leeds & Northrup Co., giving the particle sizes between 13-15 nm with the concentration about 25 g/L.

We tried to prepare a copolymer named **C7** without SMA. It dissolved or formed micelles in water at concentrations up to 25 g/L. It did not contain any long-chain alkyl in the molecule, and its surfactant properties would be proved inefficient in later tests.

FT-IR and ^{1}H NMR Spectra of the Copolymer

The structure of copolymer **C5** was characterized firstly by FT-IR as shown in Figure 2. A strong band at 1724 cm^{-1} can be attributed to the ester group of acrylate and the presence of carboxylic group from acrylic acid. The strong absorption in the region of 2922 cm^{-1} to 2855 cm^{-1} is due to C–H stretching of CH_3– and CH_2– .A broad band at 3491 cm^{-1} may be due to free O–H group of PEG and carboxylic groups. The presence of C–O–C of ester is proved by the strong absorption band at 1133 cm^{-1}. The peak attributed to C=C about 1610-1640 cm^{-1} disappeared, suggesting that all monomers have polymerized to form copolymers. ^{1}H NMR spectrum of the obtained polymer **C5** is shown in Figure 3. Referring to PEO and SMA monomer, the assignments were carried out and give in the figure. From these assignments, it is confirmed that the products obtained were formed *via* copolymerization of the monomers.

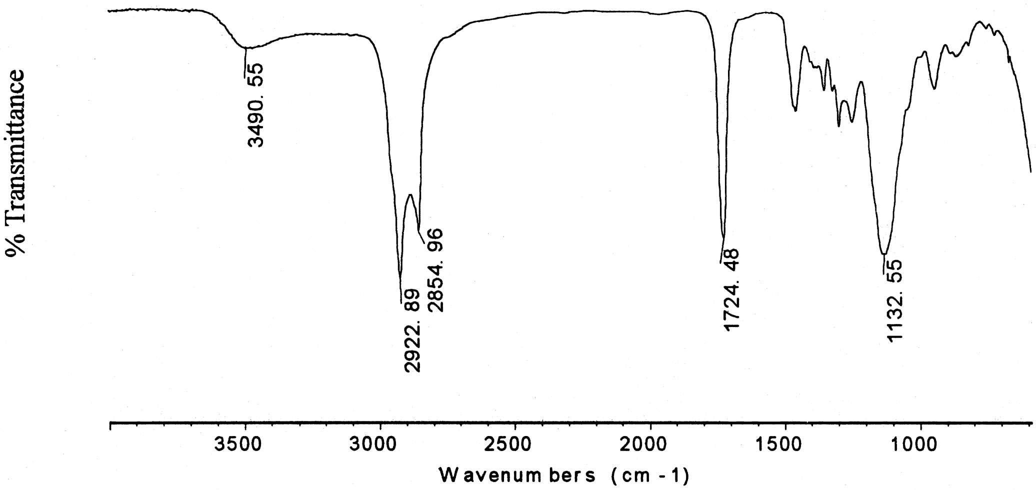

Figure 2. FT-IR spectrum of copolymer **C5**.

Surface Active Properties

Surface active properties of the copolymers **C5** and **C6** at the air/water interfaces were determined by surface tension measurement at various temperatures. Critical micelle concentrations (CMC) of these amphiphilic copolymers were evaluated by the measurement of distinct slope change in the plot of surface tension *versus* concentration of copolymers. Surface tensions plotted against the logarithm of concentration of polymer **C5** and **C6** are shown in Figure 4. The surface tensions of other copolymers are not presented here because of their poor solubility in water or less efficient emulsification. As expected, both **C5** and **C6** gave similar curves for surface tension *vs*. concentration and exhibited significant surface-active behavior, as indicated by the substantial decrease in surface tension with increasing copolymer concentration in water. Critical micelle concentrations (CMC) of polymeric surfactant appeared in the range of 0.01-0.1 g/L. The lowest surface tension achieved were 42 dyn/cm and 38 dyn/cm at 25°C, respectively, a decrease of at least 30 dyn/cm compared with pure water. Under the same measurement condition, molecular weight did not obviously contribute to a similar decrease tendency of the surface tension regardless of **C5** (M_n: 1.4×10^4) or **C6** (M_n: 1.9×10^4).

The results indicate that there is no significant affect of the molecular weight on the surface active properties, even though the copolymers differed by about 5000 in the number-average molecular weight. Although the critical

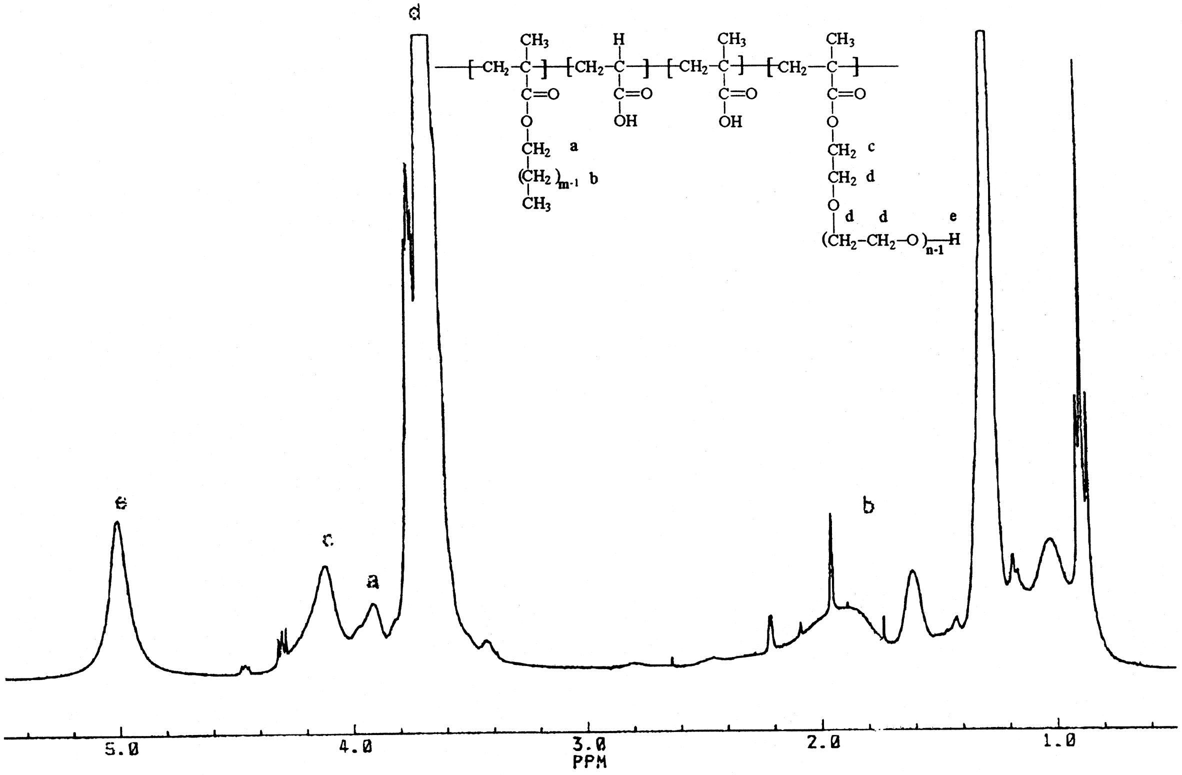

Figure 3. ^{1}H NMR spectrum for amphiphili copolymer **C5** in CD_3Cl.

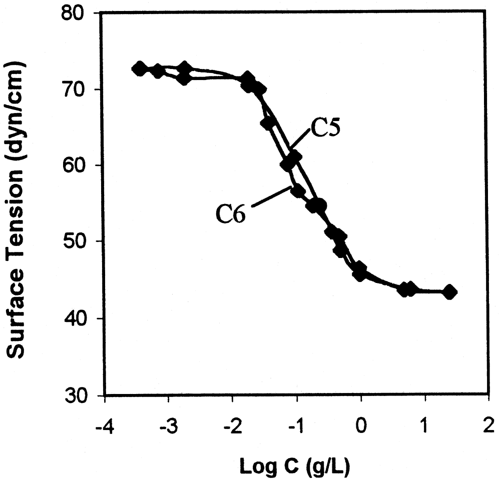

Figure 4. Plot of surface tension *vs.* logarithm of the concentration of aqueous copolymer surfactant solutions (**C5** and **C6**) at 20°C.

micelle phenomena appeared within a wide range of the concentration, the results show that the amphiphilic copolymers contribute significantly to the active properties.

Temperature also affected the surface tension reduction as shown in Figure 5. At the same concentration of copolymer, the surface tension of aqueous copolymer solution decreased with the increasing temperature. An interesting phenomenon for **C6** was that the surface tensions were 5 dyn/cm lower at 45°C than those at 20°C in the corresponding concentrations. The reason for this phenomenon can be explained as thus: the interactions between the water molecules are much stronger than that of interactions between the water molecules and the polymeric surfactants at higher temperature. The weak affinities between water molecule and polymeric surfactant resulted in a lower surface activity along with the high temperature.

pH Values of Aqueous Copolymer Surfactants

The pH values of copolymer aqueous solutions, whose concentrations were exactly equal to those of the solutions in above mentioned surface tension measurement, were determined at ambient temperature as shown in Figure 6. It was observed that pH slightly increased with the increase of concentration in extremely dilute conditions because the -COOH groups were too insignificant to change distinctly the pH value of water. However, when the concentration of

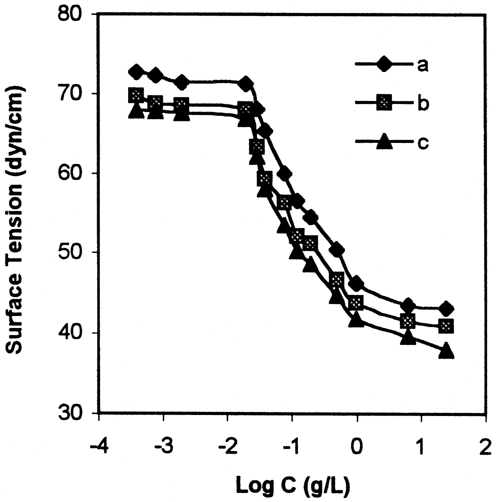

Figure 5. Effect of temperature on surface tension of copolymer surfactant (based on **C6**): (a) 20°C; (b) 35°C; (c) 45°C.

copolymer reached to 0.01g/L, pH decreased with the increase of concentrations. The concentration of turning point almost corresponded to that of turning point in the plot of surface tension vs. concentration, at which surface tension started to decrease substantially. The reduction of pH value resulted from the carboxyl

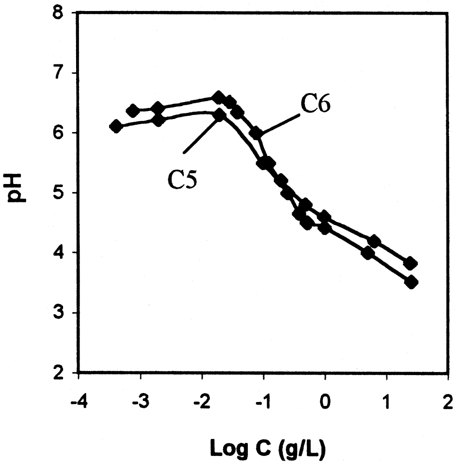

Figure 6. Effect of polymer concentration in aqueous solution on pH value at 25°C.

group increasing with the addition of copolymer in the solutions. It also gave an evidence that the carboxyl group (-COOH) existed in the copolymer.

Stability of the Emulsions

The purpose of further investigation was to determine the synergic effect of both amphiphilic copolymers and SDBS on the stability of water-borne alkyd varnish emulsions. The emulsification procedure was carried out at 40-45°C. To obtain stable water-borne alkyd emulsions, it is necessary to consider the synergic effect of anionic surfactant and polymeric surfactant [7, 8]. The composition of alkyd resin emulsion prepared by various quantities of copolymers in various proportion of the dispersing medium is presented in Table 3. The results showed that the optimum quantity of polymeric emulsifier for an alkyd emulsion in water was between 2-4 wt% , while SDBS amount maintained 2 wt% constantly (**E2**, **E3** and **E4**). The stable emulsions contained LV-803 resin in an amount of ca. 56-60% by weight without any organic solvent. SDBS was also used to emulsify alkyd alone with 2-4 wt% aqueous solution without any polymeric surfactant, but the emulsions yielded separated after two days (**E5** and **E6**).

The stability of the emulsified particles in aqueous solution was evaluated by measuring the time evolution of the particle diameter in aqueous solution with

TABLE 3. Compositions of Alkyd Emulsions with Surfactant Solutions of SDBS and Copolymer **C5**.

Exp. No.	Surfactant solutions		Solid content in the emulsions (wt%)	Stability of emulsions after four months
	Copolymer (wt%)	SDBS (wt%)		
E1	1.0	1.0	56	Separated Partially (after 7 days)
E2	2.0	2.0	56	Stable
E3	3.0	2.0	60	Stable
E4	4.0	2.0	57	Stable
E5	0	2.0	50	Unstable (after 2 days)
E6	0	4.0	50	Unstable (after 2 days)

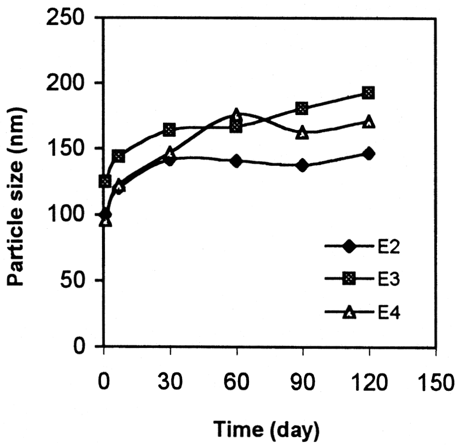

Figure 7. Variation of the diameters of the particle size from alkyd emulsion with time as measured by dynamic light scattering.

the dynamic laser light scattering techniques. As shown in Figure 7 and Table 4, they summarized the variation of droplet size and particle size distribution of latexes after different resting time. Although the results seemed not to have good regularity, little change of the droplet sizes showed that the emulsions of alkyd/water system, which was emulsified by the aqueous mixture of both SDBS and the polymeric emulsifier, were quite stable after four months. This means that the equilibrium in the emulsions is established between the emulsifiers forming micelles and the emulsifiers adsorbed on the surface of alkyd particles emulsified in the water. SDBS was used as anionic surfactant to reduce largely the interface tension of resin/water to obtain even emulsion. In the same system, the polymer are oriented in such a way that their poly(ethylene) glycol and carboxylic group are towards water phase, while their hydrocarbon backbones are adsorpted on the surface of particles, and their non-polar hydrophobic chain, stearyl group pendants, are directed towards the dispersed phase (latex particles), namely, anchoring of the surfactant on the latex particles . The protective colloid interface as a

TABLE 4. Particle Size Distribution of Emulsions after Resting Periods

Exp. No.	D_v/D_n (7 days)	D_v/D_n (30 days)	D_v/D_n (60 days)	D_v/D_n (90 days)	D_v/D_n (120 days)
E2	26.4	21.2	18.1	10.9	12.3
E3	7.0	11.4	16.3	9.9	10.8
E4	27.2	11.5	14.36	7.7	8.6

steric stabilizer is more compact than that of the case that SDBS exists separately [6, 15]. They have much more resistant and dense surface films because their polymeric chains are subjected to hydrogen bonds and Van der Waals forces. It is found that the anionic surfactant used for emulsification influence more the formation of the smaller size particles than the non-ionic polymeric surfactant used in the same quantity. We still have to solve a problem that the particle size distributions of emulsions are very wide through the post-emulsified processes.

CONCLUSION

Amphiphilic copolymers can be prepared by free-radical copolymerization. As a polymeric surfactant, this kind of copolymer can be mixed with anionic surfactant (SDBS) in aqueous solution and successfully used in the preparation of alkyd emulsions. There is a significant synergic effect between anionic surfactant and polymeric emulsifier. The distinct decrease of surface tension proved the surface activity of the polymeric surfactant at the air/water interface. The synthetic method in this report offered numerous possibilities for the manufacture of amphiphilc polymer. It also provides a potential application of alkyd emulsion for commercial purposes. FT-IR and ^{1}H NMR spectroscopy studies confirm that the various monomers used in this study are incorporated into the copolymer. The results of particle size of the alkyd emulsions demonstrate steric and electrostatic stability of the polymer surfactant.

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