Structural effects of a novel polymeric emulsifier – SSIPM modified tetracarboxylic acid terminated polyester on the emulsion polymerization of butyl methacrylate

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Abstract

A novel polymeric emulsifier, SMTAPE, was prepared by end-capping sulfopolyester polyol with TMA in this study. This polymeric emulsifier is applied for BMA emulsion polymerization. Also investigated herein is how SMTAPE's chemical structures, e.g. SSIPM contents and molecular weights, influence the behavior of emulsion polymerization and subsequent PBMA lattices. Experimental results indicate that SMTAPE emulsifiers with a shorter average hydrophobic length stabilize the PBMA latex by the depletion mechanism. Although possessing good mechanical stability, using those emulsifiers has a higher coagulum during the synthesis stage. However, the SMTAPE emulsifiers with a longer average hydrophobic length anchor strongly on the PBMA latex particles and stabilize them by an electrostatic force with a negligible amount of steric stabilization. Although possessing better synthesis stability, using these emulsifiers has a poor mechanical stability. In addition, according to these experimental results, formation of the subsequent PBMA latex is attributed to a coagulation process of particle precursors, micellar particles as well as existing PBMA latex particles. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Latex; Polymeric emulsifier; Polyester

1. Introduction

Latex can be directly used without causing pollution from organic solvents, accounting for its diverse applications such as in coating, adhesives, paper and textile finishes. Conventional latex is prepared from emulsion polymerization in the presence of low molecular weight emulsifiers, possibly causing a reduction in adhesion and durability of the final product [1]. Resolving these problems makes emulsifier-free emulsion polymerization an interesting research topic.

Previous investigations have used polymeric emulsifiers, polyelectrolytes and polysoaps to replace conventional emulsifiers in emulsion polymerization [2–6]. Among the various polymeric emulsifiers, polyester-based emulsifier is of paramount concern. Other investigations have reported on the role of carboxylic acid-terminated saturated polyesters as an emulsifier at pH $\approx$ 8.5 [7,8]. Stability of the subsequent latex, as prepared from emulsion polymerization in the presence of tetracarboxylic acid terminated polyester emulsifiers, heavily relies on the molecular weight of

polymeric emulsifiers [9]. An insufficient molecular weight would complicate the ability of these main chains in a loop form to anchor themselves on the latex surface. Consequently, the latex stability would decrease.

In addition, sulfopolyester has also been reported to be a polymeric emulsifier for emulsion polymerization [10,11]. Those investigations noted high emulsion latex stability when the ratio of sulfopolyester emulsifier to monomer exceeds 20%. Moreover, depleting stabilization was proposed for this sulfopolyester emulsifiers [11].

In this study, we synthesized a novel polymeric emulsifier, tetracarboxylic acid terminated sulfopolyester by bulk condensation of diethylene glycol (DEG), isophthalic acid (IPA) and 5-sulfoisophthalic acid dimethyl ester sodium salt (SSIPM) [12,13]; following the end-capping reaction with trimellitic anhydride (Scheme 1). This polyester is used as emulsifier for butyl methacrylate (BMA) emulsion polymerization. Also investigated herein is how the polymeric emulsifiers' chemical structures, e.g. SSIPM contents and molecular weights, influence the behaviors of emulsion polymerization and the stability of the subsequent polybutyl methacrylate latices. Various experiments are also performed to

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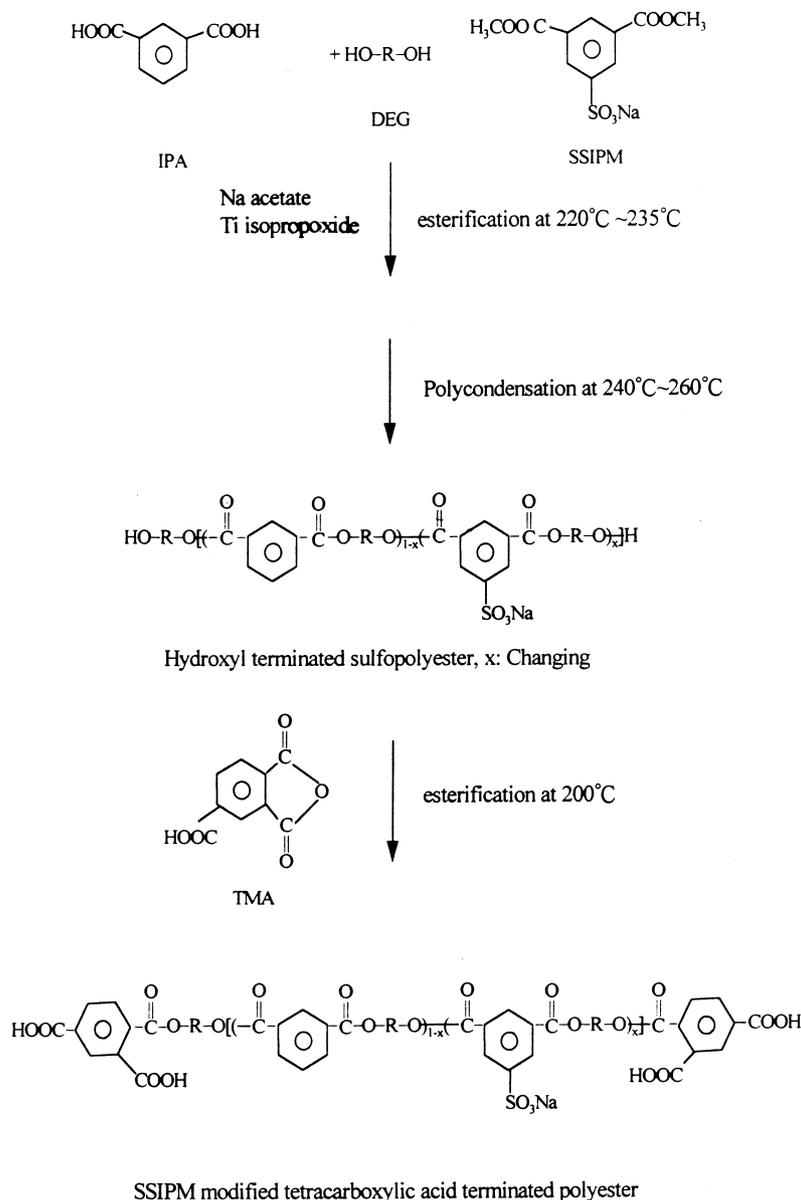
Scheme 1.

understand thoroughly the stabilization mechanism and the latex formation process of this system.

2. Experimental

2.1. Materials

Materials used in this study were butyl methacrylate (BMA) (Acros), potassium persulfate (KPS) (Janssen), sodium lauryl sulfate (SLS) (Acros), and potassium hydroxide (KOH) (TEDIA). All the chemicals were of reagent grade and used as received. Water was deionized.

2.2. Synthesis of SSIPM modified tetracarboxylic acid terminated polyester (SMTAPE) emulsifier

SMTAPE emulsifiers were synthesized by two-step bulk condensation polymerization, as illustrated in Scheme 1. Sulfopolyester polyol was synthesized during the first step and, then, the hydroxyl terminated sulfopolyester was reacted with stochiometric amounts of trimellitic anhydride. The procedures are as follows: one and half mole diethylene glycol (DEG) (TEDIA, reagent grade), one mole diacid, and a mixture of isophthalic acid (IPA) (Lancaster, reagent grade) and designed amounts of 5-sulfoisophthalic acid dimethyl ester sodium salt (SSIPM) (TIC, reagent grade) with catalyst, titanium isopropoxide and sodium acetate, were poured into a stainless steel reactor, purged with

Table 1
Emulsion polymerization recipes

Ingredients	Amount (g)
Water	212.50
Emulsifier (SMTAPE)	Variable (10%, 20%, 30% wt based on monomer)
$K_2S_2O_8$	0.31 (1% wt based on monomer)
Butyl methacrylate	31.25

nitrogen and heated to 220°C–235°C to proceed with the esterification reaction. The extent of reaction was monitored by the methanol and water removed during the synthesis step. Beyond 95% extent of esterification, a vacuum was applied to the system. The temperature was then raised to 240°C–260°C for melt condensation polymerization to form a sulfopolyester polyol. When the molecular weight of sulfopolyester polyol monitored by hydroxyl value reached the desired value, the temperature was cooled to 200°C and the vacuum was broken by purging N_2. A stochiometeric amount of trimellitic anhydride was immediately added. After 70 min, SMTAPE emulsifier was obtained.

2.3. Emulsion polymerization

Table 1 presents a typical emulsion polymerization recipe. Emulsion polymerization was performed in a 500 ml four-neck glass reactor equipped with a mechanical stirrer (Teflon baffle stirrer), a reflux-cooler, a thermometer and a nitrogen flushing. A thermostated water bath was employed to control the reaction temperature. The polymerization was performed as follows: 200 g of deionized water,

appropriate amounts of polyester emulsifier and potassium hydroxide for neutralization degree (α) 1.1 were poured in the reactor, purged with nitrogen, while the speed of the stirrer was controlled at 250 rpm. Next, the temperature was raised to 70°C, after the emulsifier completely dissolved, the pH value was adjusted to 8.5 by adding 1.2 M potassium hydroxide aqueous solution. Next, about 1 ml sample was taken to measure the particle size after cooling to room temperature. Stirrer speed was then reduced to 160 rpm, and 31.25 g of butyl methacrylate was added. After 8 min, 0.31 g of potassium persulfate dissolved in 12.5 g of deionized water was filled through a sampling hole, and the time was set as $t = 0$. Samples with known volume were taken at given time intervals of the polymerization by a hypodermic syringe. The samples were discharged in a flask containing 0.1 wt% hydroquinone aqueous solution of the same volume to inhibit further polymerization. The total reaction was completed after 2 h.

2.4. Characterization

The average particle size of the micellar particle in the polymeric emulsifier aqueous solution and the subsequent latices were determined by Malvern 4700 Dynamic Light Scattering spectrophotometer. High resolution [1]H-nmr spectra of SMTAPE emulsifier were recorded in CF_3COOH on a 400 MHZ Bruker nmr by using tetramethylsilane as the internal standard.

Mechanical stabilities were determined by maron test at room temperature with 1000 rpm, 20 kg load for 5 min. The aggregates were then filtered with 200 mesh filter and dried at 110°C for 4 h.

Table 2
Compositions of SMTAPE emulsifiers

Sample	Sulfopolyester X_{SSIPM}[a]%	$\bar{M}_{n_{sp}}$[b]	SMTAPE $\bar{M}_{n_e}$[c]	Acid value	Y_{SSIPM}[d] contents (unit/chain)	Average hydrophobic length[e]	Notes[h]
A_1	0	3500	3800	59.0	0	15	0%
A_2	4.5	4400	4700	48.3	0.8	9[f] and 18[g]	85%
A_3	7	5100	5400	41.1	1.5	8.5	100%
A_4	10	4400	4700	47.3	1.8	6.5	100%
A_5	20	5200	5500	42.4	4	4	100%
A_7	7	11 400	11 500	24.3	3.3	11	100%
A_6	7	6900	7100	31.3	2	9	100%
A_8	7	2500	2800	63.8	0.7	5[f] and 10[g]	70%
A_9	7	1500	1800	110.6	0.4	3[f] and 6[g]	40%

[a] Mol% based on the total diacid.

[b] From OH titration.

[c] $\bar{M}_{n_e} = \bar{M}_{n_{sp}} + \bar{M}_n$ (TMA of chain ends).

[d] Y_{SSIPM} content $= X_{SSIPM} \times ((\bar{M}_{n_{sp}} - 105)/\bar{M}_w$ of repeat unit); per repeat unit represents the segment of

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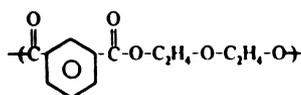
[e] Average hydrophobic length = number of repeat units between any two hydrophilic groups (sulfonic or carboxylic).

[f] SMTAPE has SSIPM units in the backbone and carboxylic group at the chain ends.

[g] SMTAPE has carboxylic groups at the chain ends without SSIPM in the backbones.

[h] Percentage of SMTAPE having SSIPM groups.
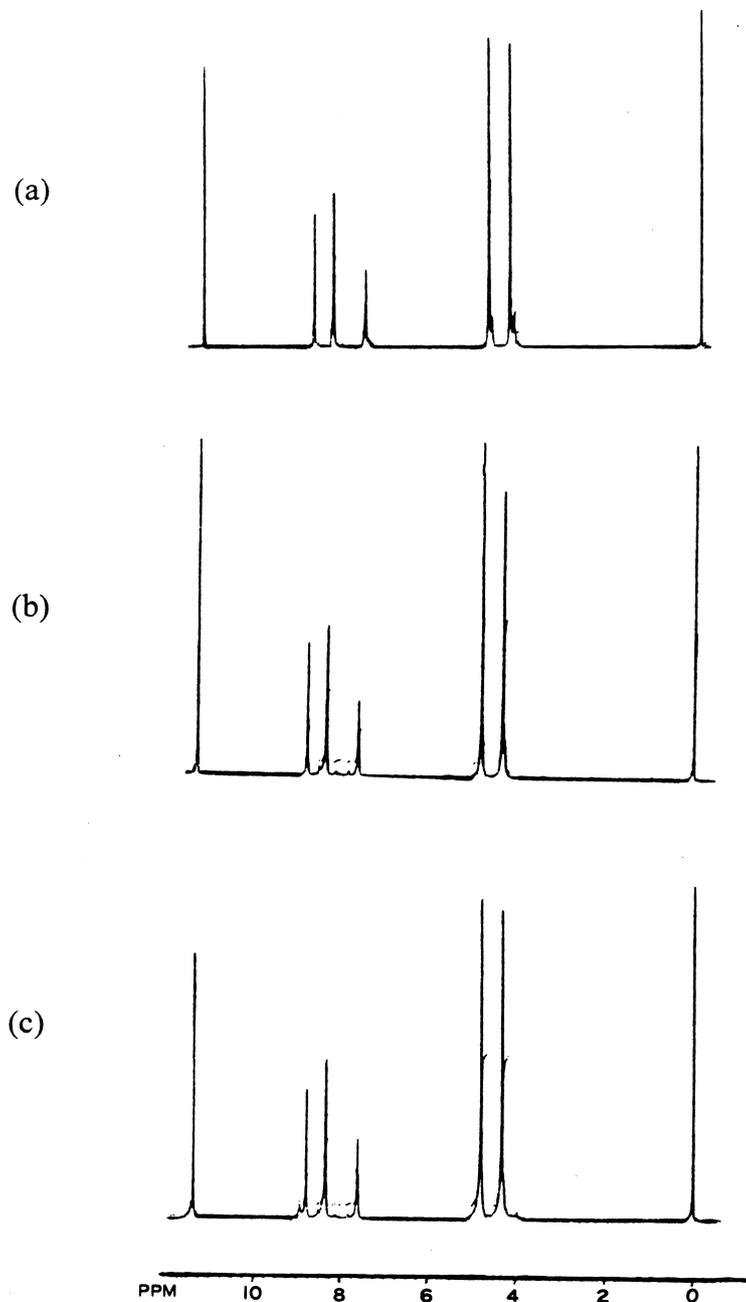
Fig. 1. ^{1}H-NMR results of (a) polyester polyol, (b) TMA-terminated polyester polyol, (c) SMTAPE.

Freeze–thaw stabilities were determined by subjecting the latices to a number of cycles where the sample were frozen below $-15°C$ for 12 h and then allowed to thaw to room temperature for 12 h.

Next, the pH stabilities were determined by adding 5 ml of the latices to 40 ml of 0.05 N HCl aqueous solution. The final pH was about pH $\approx$ 1, and unstable latex would precipitate out. GPC (SP Thermo separation product) was used to determine the number average molecular weight ($\bar{M}_n$) and weight average molecular weight ($\bar{M}_w$) of SMTAPE emulsifier, sulfopolyester polyol and subsequent PBMA latices. The GPC samples were dissolved in a mixture of fifteen

parts of DMF and eighty five parts of THF, using THF as the elution solvent.

3. Results and discussion

3.1. SMTAPE polymeric emulsifiers

SMTAPE polymeric emulsifiers were prepared by bulk condensation of EG, IPA and SSIPM to form sulfopolyester polyol initially, then followed by end-capping the hydroxyl group with TMA. Table 2 lists the various compositions and

Table 3
Dispersivities of SMTAPE emulsifier

Sample	A_1	A_2	A_3	A_4	A_5	A_7	A_6	A_8	A_9
$\bar{M}_n$	3800	4700	5400	4700	5500	11 500	7100	2800	1800
SSIPM mol%[a]	0	4.5	7	10	20	7	7	7	7
14.5% in aq [b]	(×)[c]	(×)[c]	(×)[c]	37.5	8.0	(×)[c]	(×)[c]	47.6	45.2
7.5% in aq [b]	(×)[c]	(×)[c]	12.8	10.4	8.0	(×)[c]	(×)[c]	10.6	9.1
3.5% in aq [b]	(×)[c]	(×)[c]	12.8	10	7.9	20.1	20.0	11.0	9.0
3.5% in aq [b]	(×)[c]	(×)[c]	13.8	11.1	7.3	33.1	19.7	33.3	466.7

[a] Based on total diacid.

[b] Samples were dispersed at 70°C, mechanical stirring was replaced by shaking with hand; wt%, units: nm.

[c] (×) Does not dissolve completely.

molecular weights of these emulsifiers. The molecular weights of sulfopolyester polyol were determined by chain-end-OH titration. The molecular weights of SMTAPE were obtained by adding the TMA molecular weight to the sulfopolyester polyol molecular weights. To ensure no side reaction occurred during the end-capping reaction, the GPC results of the subsequent SMTAPE were compared with those of the prepolymer sulfopolyester polyol. It was found that both polymers do not differ significantly in terms of GPC curves. Fig. 1(a), (b) and (c) display the [1]H-nmr spectra of polyester polyol, TMA-terminated polyester and SMTAPE, respectively.

The average hydrophobic length is calculated according to the number of repeated units between any two hydrophilic groups, either sulfonic (in the chain) or carboxylic group (at the chain end). Some samples, e.g. samples A_2, A_8 and A_9, have two average hydrophobic lengths because only partial SMTAPE chains incoperate with SSIPM. Therefore, SMTAPE with SSIPM unit has a shorter average hydrophobic length than those without SSIPM.

3.2. Dispersivities and micellar conformation of SMTAPE emulsifiers

In this study, the sizes of micellar particles in an aqueous solution were found to decrease with an increase of their dispersivities. Table 3 lists the micellar sizes of SMTAPE with similar molecular weights (about 5000 g/mol), but different SSIPM contents, and the micellar sizes of SMTAPE with same SSIPM contents (7 mol% based on total diacid) but different molecular weights. From Table 3, we can infer that the dispersivities of SMTAPE increase with an increase of the hydrophilic group (SSIPM) contents. Moreover, Table 3 also reveals that the dispersivities of SMTPAE increase with a decrease of their molecular weights. However, the long-term dispersivities of SMTPAE relate to an optimum molecular weight ($\bar{M}_n$) of around 5000–7000 g/mol. The micellar sizes of samples A_8 and A_9 increase as measured after dispersion for 7 days. The long-term dispersivities of high molecular weight SMTAPE also decrease as exhibited by sample A_7.

Based on the compositions described in Table 2, SMTAPE emulsifier has two types of molecules: (a) low molecular weight of tetracarboxylic acid terminated polyester emulsifier, as studied by Cuirassier [9] and (b) SSIPM containing polyester emulsifier considered as polyelectrolyte-type water dispersible polymers [14–16]. Fig. 2 depicts the micellar conformation.

For the low molecular weight of SMTAPE, partial molecules do not contain a SSIPM unit in their polymer chain because only 7 mol% of SSIPM is added. Under this circumstance, there is only 40% of polymer chains in

~ : hydrophobic segments

o: sulfonate salt hydrophilic groups

× : Neutralized Diacid hydrophilic groups

(m)   (n)
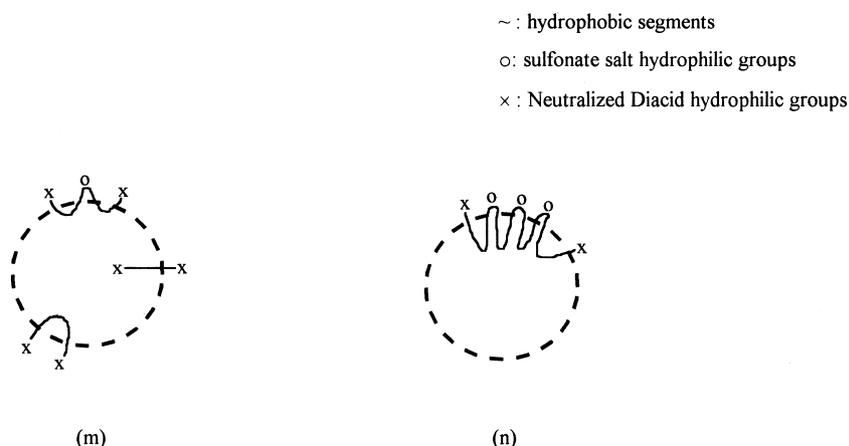
Fig. 2. Schematic representation of chain conformation for neutralized SMTAPE micelles.

Table 4
The structural effect of SMTAPE emulsifier on BMA emulsion polymerization

Sample	Emulsifiers used[a]	Micellar particle size (Dz, nm)	Latex particle size (Dz, nm)	no. of micellar particle/no. of latex particle	Coagulum (wt%)	R_p (mol/liter s) $\times^{-3b}$	$\bar{M}_w \times 10^{5c}$	$\bar{M}_w/\bar{M}_n$	MS[d]	CS[e]
a3	A3(20)	12.5	45.1	8	0.16	5.46	9.6	3.5	8.1	(×)
a4	A4(20)	9.8	49.2	22	0.14	7.19	9.7	4.2	<0.01	(○)
a5	A5(20)	7.1	51.9	64	1.68	12.11	12.3	4.2	<0.01	(○)
a0	SLS(1)	—	65.2	—	<0.1	—	2.8	5.5	21.0	—
a7	A7(20)	15.8	45.0	5	0.21	4.17	9.5	4.9	12.5	(○)
a6	A6(20)	14.6	48.0	6	0.23	6.24	9.5	4.3	10.0	(○)
a8	A8(20)	9.1	52.6	32	0.08	10.19	10.9	4.5	<0.01	(×)
a9	A9(20)	6.1	56.5	129	0.47	11.83	11.2	5.2	<0.01	(×)
a4-0	A4(10)	9.9	63.0	22	0.96	7.67	9.6	4.7	8.6	—
a4-1	A4(30)	9.1	47.3	36	0.11	12.58	13.8	3.8	<0.01	—

[a] Concentration of emulsifiers, wt%, based on BAM monomer.
[b] Based on 20%–70% conversion.
[c] The parts of PBMA, data obtained from GPC, based on PS standard.
[d] MS: mechanical stability; coagulation, wt%.
[e] CS: chemical stability; (×) represent precipitation; (○) represent stable.
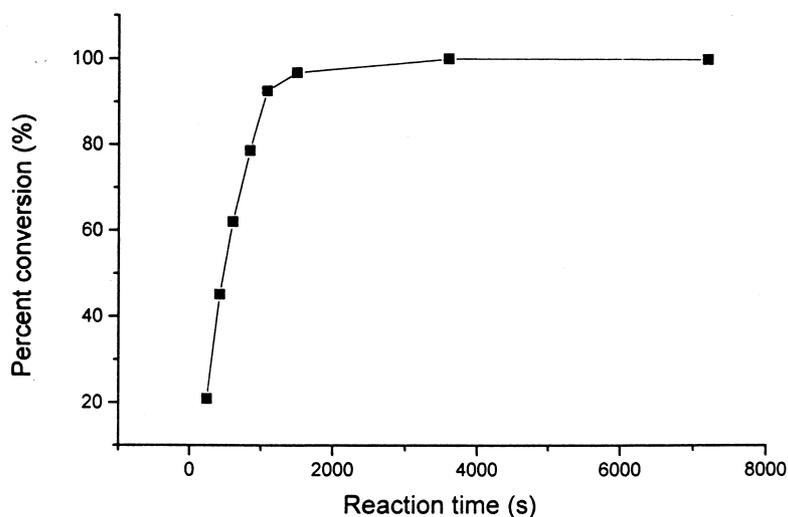
Fig. 3. Time-conversion curve of the BMA emulsion polymerization at 70°C using SMTAPE A_4 as emulsifier. A typical time–conversion curve in the emulsion polymerization of this system.

sample A_9 have SSIPM structures, as shown in conformation (m) of Fig. 2. The micellar particles of these low molecular weight emulsifiers prefer to aggregate together as the short hydrophobic length of tetracarboxylic acid terminated polyester cannot remain stable in micellar particles. In long-term testing, the micellar particle size increases with time. In addition, the conformation of A_8 in an aqueous solution can be considered as the conformation (m) in Fig. 2. The micellar particle size increases slightly, indicating that small parts of lower molecular weight emulsifiers are incorporated into this sample A_8. If the molecular weight of SMTAPE is sufficiently high, SSIPM is allowed to incoperate into each polymer chain to enhance SMTAPE's long-term stabilities, as conformation (n) in Fig. 2. When the molecular weight ($\bar{M}_n$) reaches 11500 g/mol (sample A_7), the long chain entanglement as well as its low hydrophilicity causes a decrease of dispersivity and long-term stability. However, in the SMTAPE system studied herein, the average hydrophobic length (or the hydrophilicity) of SMTAPE emulsifier determines the micellar particle size in an aqueous solution at dispersing stage (or short-term stage). Moreover, a longer average hydrophobic length causes large micellar particle sizes.

3.3. Emulsion polymerization using SMTAPE emulsifier

In addition to the conformation and stability studies of SMTAPE micelle, the BMA emulsion polymerization using these polymeric emulsifiers is also performed herein. Table 4 demonstrates how the SMTAPE molecular weights, the SSIPM contents in SMTAPE, and the various amounts of SMTAPE emulsifiers (using SMTAPE A_4) affect the emulsion polymerization, while Fig. 3 shows a typical time–conversion curve of this emulsion polymerization system. According to these results, the emulsion polymerization rates increase with the number of micellar particles as well as with a decrease of micellar particle sizes. The reaction rates calculated in these systems are extremely high at the early stage of the reaction, which differ from the conventional emulsion polymerization which shows a low reaction rate in the nucleation period [19,20]. It indicates that the nucleation period seems to be short in our system. This phenomenon is the same for using polystyrene–polyethylene oxide block copolymer as the emulsifier [6]. Based on theoretical calculations, the number of micellar particles are several to decades time higher than the number of subsequent PBMA latex particles. This finding suggests that several to decades micellar particles lead to one PBMA latex particle. It reveals a coagulation nucleation mechanism which resembles the emulsion polymerization with polymeric emulsifiers [6,17,18].

According to this study, the growth rate of latex particle is proportional to the conversion rate, i.e. high conversion rates correspond to high latex growth rates. The weight average molecular weight ($\bar{M}_w$) of PBMA synthesized using SMTAPE emulsifier exceeds that of the conventional emulsion polymer using SLS emulsifier under the same initiator concentration. The reaction rate and weight average molecular weights ($\bar{M}_w$) in Table 4 increase with the increase of the number of SMTAPE emulsifier micellar particle. Based on the Smith–Ewart theory, the higher the particles number, the longer the lifetime of the polymeric radical in particle is observed, so the reaction rate and weight average molecular weights increases. As in conventional emulsion polymerization, Table 4 shows the higher concentration of SMTAPE emulsifier (wt% emulsifier/ monomer) results in a higher polymerization rate, smaller particle size and higher molecular weight of the subsequent latex polymer. Such a phenomenon is attributed to that a high concentration of emulsifiers can stabilize a substantial amount of latex particles. Fig. 4 displays a SEM micrograph of the subsequent latex (sample a_4). This micrograph reveals
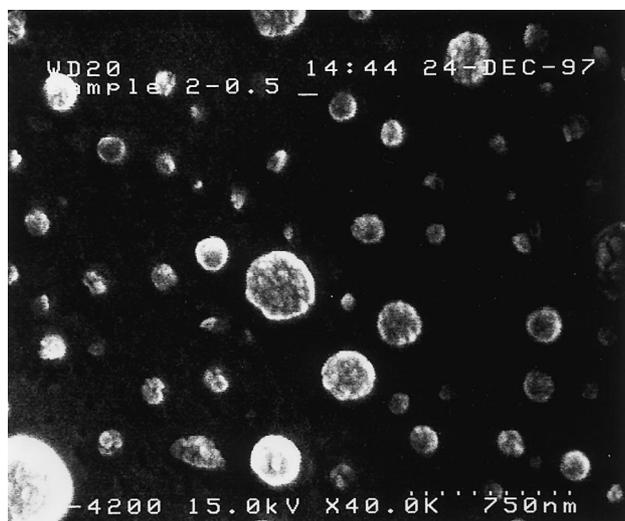
Fig. 4. The SEM micrograph of the subsequent latex (sample a_4).

that some of the PBMA latex particles consist of several smaller particles.

Based on the experimental results, a model for latex particle growth using SMTAPE emulsifier is proposed as follows. Once dispersed in an aqueous solution, SMTAPE can form micellar particles with a diameter of 6–17 nm (Table 3). The fact that these micelles are sufficiently large accounts for why the nucleation period is short during the early stage of emulsion polymerization. As long as polymeric precursors are formed, they assimilate with SMTAPE micellar particles and the existing particles to form a PBMA latex. This assimilation causes a decrease in the number of particles and the particle size growth rate is as rapidly as the reaction rate. Owing to the instability of the growing latex particle, the growing latex continues to assimilate with micellar particle or existing particle until all monomers are exhausted.

3.4. Stability of PBMA emulsion using SMTAPE emulsifier

The stability of emulsion polymerization generally depends on the hydrophilic–hydrophobic ratio of the polymeric emulsifier [17]. For emulsifiers with a lower hydrophilicity, they prefer to participate in the oil phase, resulting in leaving small hydrophilic groups for aqueous phase stabilization (a negligible amount of steric stabilization). However, polymeric emulsifiers with high hydrophilicity are likely in the water phase, resulting in weak adsorption and low surface coverage. The most effective polymeric emulsifier implies that it stabilizes the highest number of particles or the smallest particle sizes [17].

Table 4 depicts the trend of particle size, coagulum and mechanical stabilities in relation to the SSIPM contents and molecular weights of SMTAPE emulsifier. Consider a situation in which the SSIPM content is increased to 20 mol% and the hydrophobic length is reduced below 5 repeat units (Table 2). Under this circumstance, polymeric emulsifiers

with higher hydrophilicity would be likely to localize at the interface of water and PBMA particle, otherwise, it would dissolve into the water phase, resulting in weak adsorption and low surface coverage [17]. Consequently, PBMA latex is stabilized because of depletion [11], and has good mechanical stability. However, the amounts of latex coagulum and the size of subsequent latex particle increase with the use of SMTAPE emulsifier of high hydrophilicity (sample A_5), thereby forming a depleting stabilization mechanism. In contrast, the SMTAPE emulsifier containing 7 mol% SSIPM has a hydrophobic length higher than 9 repeat units, such as in samples A_7 and A_6. Those polymeric emulsifiers will either dissolve in PBMA phase or compact closely together, leaving a small hydrophilic segment into the water phase, which reveals electrostatic stabilization with negligible amount of steric stabilization. This phenomenon closely resembles the SLS emulsifier, which has poor mechanical stability in emulsion system and ultimately creates less coagulum in emulsion polymerization (Table 4). The SMTAPE containing 10 mol% SSIPM (hydrophobic length of around 6) has good synthesis and mechanical stabilities as shown in Table 4. When this hydrophobic length is in the range of an optimum hydrophobic and hydrophilic ratio, the hydrophobic segments can anchor themselves into the subsequent latex polymer. Moreover, hydrophilic segments can dissolve in water phase to perform steric stabilization. For samples a_8 and a_9, SMTAPE emulsifiers are a mixture of SMTAPE containing SSIPM and tetracarboxylic acid terminated polyester. The short hydrophobic length of SMTAPE containing SSIPM contributes to the latex depletion stabilization, the subsequent latices possess good mechanical stability. Notably, the tetracarboxylic acid terminated polyesters having hydrophobic length with 10 or 6 repeat units allow them to anchor the latex particle possessing low coagulum during polymerization. As the hydrophilicity of the A_9 SMTAPE emulsifier is higher than that of the A_8 SMTAPE emulsifier, both the coagulum during emulsion polymerization and the particle size of subsequent latex a_9 are larger than those of latex a_8.

Herein, a series of emulsion polymerization are performed using various concentration of A_4 SMTAPE emulsifier. Table 4 shows that the particle sizes of subsequent latex increase with the decrease of emulsifier concentration, in addition, both of the coagulum of the emulsion polymerization and coagulation of subsequent latex tested by maron tester increase.

Also investigated herein is how various SSIPM contents and molecular weights of SMTAPE emulsifier influence the freeze–thaw stability of the subsequent PBMA latex. Unfortunately, all of the latices synthesized in this study coagulate after one cycle freeze–thaw testing, indicating that the SMTAPE emulsifier cannot provide good freeze–thaw stabilities in the testing ranges of the study.

Investigations about the pH stabilities of the subsequent PBMA latices were performed using 0.05 N HCl aqueous solution. As soon as HCl is added, the terminated

tetracarboxylic acid group changes from potassium salt to carboxylic acid form, so the electrostatic repulsion force is lost and the latex particles are unstable. Table 4 presents the test results. Samples a_8 and a_9 latex can be precipitated at pH ≈ 1, indicating that SMTAPE with low molecular weight, the tetracarboxylic acid terminated group contributes to the major stabilizing force for PBMA latex particle. Interestingly, SMTAPE emulsifier with higher molecule weight has a smaller weight percentage of the tetracarboxylic acid terminated group in the total molecule. Therefore, the SSIPM moiety dominates the stabilization force in a latex particle and becomes stable even at pH ≈ 1. For SMTAPE with middle molecule weight ($\bar{M}_n \approx 5000$ g/mol) and low SSIPM contents (a_3), both hydrophilic group, carboxylic group and sulfonate salt group contribute stabilizing force towards PBMA latex particles.

4. Conclusion

This study report a novel polymeric emulsifier, SMTAPE, which is used for BMA emulsion polymerization, also as considered herein, the growth mechanism on BMA latices is a coagulation process. According to our results, the polymerization rate and polymer molecular weight heavily relies on the number of SMTAPE micellar particles. Interestingly, the average hydrophobic length (hydrophilicity) of SMTAPE influences the stability of the subsequent latex. In addition, decreasing the average hydrophobic length of SMTAPE (high hydrophilicity) increases the number of micellar particles, thereby accelerates the BMA polymerization rate. SMTAPE with a shorter average hydrophobic length tends to stabilize BMA latex by depleting stabilization mechanism. SMTAPEs show depletion stabilization when its average hydrophobic length is less than 5 repeat units. As the repeated unit exceeds 7, SMTAPEs likely stabilize latex by the electrostatic stabilization mechanism.

Between 5 and 7, the anchoring mechanism with steric stabilization plays an important role in stabilizing latex. Moreover, the hydrophobic repeat unit's flexibility, molecular weight and hydrophilicity might affect the influence of SMTAPE hydrophobic length on the latex's stability.

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