

STUDY ON THE POLYMERIZATION KINETICS AND STABILITY OF P(UA)/MMA MICROEMULSION*

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Abstract Urethane acrylate anionomer (APUA) as a kind of new type polymerizable emulsifier was synthesized using 2,4-toluene diisocyanate (TDI), polypropylene glycol (PPG), 2-hydroxyethyl methacrylate (HEMA) and dimethylolpropionic acid (DMPA). The critical micelle concentration (CMC) of APUA was measured by the methods of conductance and surface tension. The comparative studies between polymerizable emulsifier APUA and conventional emulsifier sodium dodecyl sulfate (SDS) were carried out in the emulsion polymerization of methyl methacrylate (MMA). Polymerization kinetics, stability, size and morphology of the latex particles were investigated. It was found that in APUA both water soluble initiator potassium persulfate (KPS) and oil soluble initiator 2,2'-azobisisobutyronitrile (AIBN) can start the reaction of MMA, and the polymerization rate and yield were very high. On using AIBN as an initiator, the conversion-time behavior of MMA with APUA as emulsifier was different to that of SDS as emulsifier, signifying a different nucleation mechanism of the polymer latex particle. The average size of the two kinds of particles is about 50 nm. The particle size decreases with increasing emulsifier concentration. On using KPS as the initiator, APUA as emulsifier, cross-linking hydrogel of PMMA would be formed, but SDS was used as emulsifier and the hydrogel of PMMA was not present.

Keywords Polymerizable emulsifiers, Urethane acrylate, Polymerization kinetics, Stability, Nucleation mechanism

INTRODUCTION

A polymerisable emulsifier's molecule consists of three parts: hydrophilic part, hydrophobic part and polymerizable group. They present all the typical properties of conventional surfactants, such as formation of micelles and reduction of interfacial tension of the water. In addition, due to the existence of a polymerizable group, they can overcome some of the shortcomings encountered with conventional emulsifiers, e.g. they would not be desorbed from the particle surface or exuded from the latex film, and can improve some properties of the latex and film^[1, 2]. Moreover, as polymerisable emulsifiers are comonomers, through studies in this field, emulsion polymerization theory may be further perfected. Up to now only a few papers have been published concerning the field of polymerizable emulsifiers.

Urquiola *et al.*^[3] compared the behavior of both polymerizable emulsifier in sodium dodecyl allylsulfosuccinate (TREMLF-40) and its hydrogenated equivalent non-polymerizable emulsifier in the emulsion polymerization of vinyl acetate (VAc). They found that the conversion-time behavior was different for the two emulsifiers. The TREMLF-40 reduced the polymerization rate with increasing emulsifier concentration, while its hydrogenated derivative showed the opposite behavior, i.e., the polymerization rate increased with increasing emulsifier concentration. Then for two series of emulsifiers the particle size revealed a decrease with increasing surfactant concentration. An explanation for the seemingly ambiguous results obtained for the polymerizable surfactant was sought by examining the reactivity of the vinyl group in copolymerization of vinyl acetate and its allyl group in a chain transfer reaction. Urquiola's paper also pointed out that the reactivity of monomer and

* This work was supported by the National Natural Science Foundation of China (Contract Grant No. 29974007).

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Received April 12, 2000

polymerizable emulsifier is an important factor for the polymerization kinetics. Cochin *et al.*^[4] investigated the emulsion polymerization of styrene (St) using similar polymerizable and conventional emulsifiers, and the polymeric cationic emulsifiers. Their experiments showed that the polymerization rate and the properties of the latex depended sensitively on the emulsifier type and on the charge properties of the initiator. In the case of polymerizable emulsifier, the most important differences were the usage of different kinds of initiators. In the case of using KPS as initiator, the polymerization rate and yield were very low and aggregated polymer was separated out from the latex (> 80 min). When using cationic initiator instead of KPS, the results were completely different. However with conventional emulsifier, the emulsion polymerization processes were very similar to each other when initiated by the two kinds of initiators.

Polymerisable emulsifier also can be used in many important fields, such as in the preparation of functional polymer latex, hydrogel and microemulsion^[5, 6].

In this paper, a new type of polymerizable emulsifier, urethane acrylate anionomer (APUA), was synthesized and applied to the emulsion polymerization of MMA. Because APUA is used as both polymerizable emulsifier and copolymerization monomer, the toughness and water-resistance of PMMA could be improved. The polymerization kinetics, stability, and morphology of latex particles, was studied and compared for different initiators, AIBN and KPS.

EXPERIMENTAL

Material

In the synthesis of APUA, 2,4-toluene diisocyanate (TDI), polypropylene glycol (PPG, $M_w = 1000$), 2-hydroxyethyl methacrylate (HEMA), dimethylolpropionic acid (DMPA), triethylamine (TEA), dibutyltin dilaurate were used. *N,N*-Dimethylacetamide (DMAc) was used as a solvent for DMPA and a viscosity reducer.

TDI was vacuum-distilled before use. The inhibitor in HEMA was removed by passing HEMA through a special column. Methyl methacrylate monomer was distilled under reduced pressure. 2,2'-Azobisisobutyronitrile (AIBN) and potassium persulfate (KPS) were recrystallized and dried at 30°C under reduced pressure. Sodium dodecyl sulfate (SDS) was used as received.

Synthesis of APUA

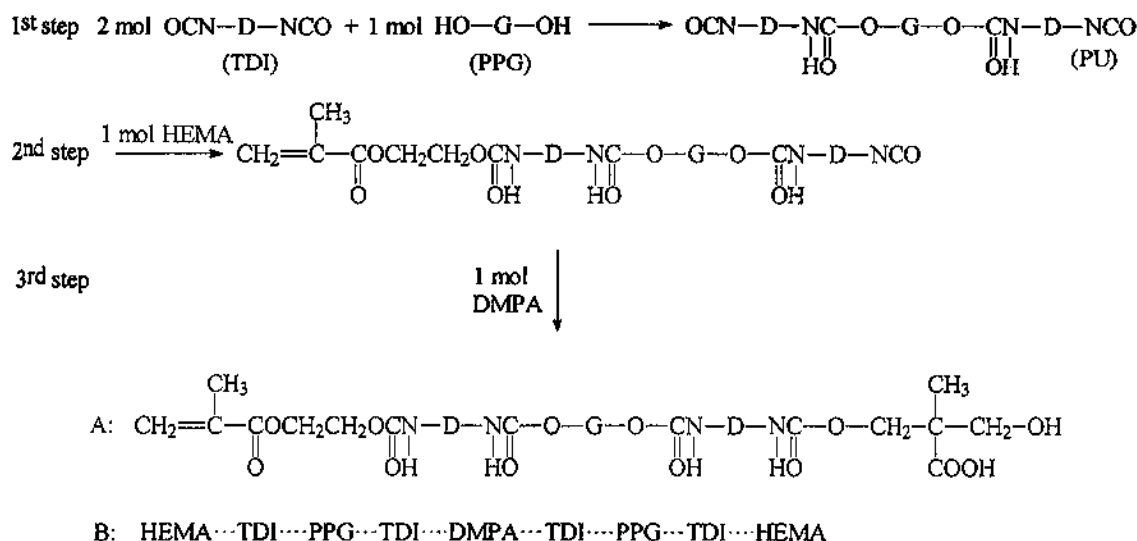
Polymerisable emulsifier APUA was synthesized by a three-step process. The reaction procedure and molecular structure of APUA are shown in Scheme 1. The reaction was carried out in a four-necked glass reactor equipped with a stirrer, thermometer, reflux condenser, and inlet system for nitrogen gas. In the first step, TDI and PPG were poured into the glass reactor and nitrogen gas was passed in to eliminate the residual moisture at low temperature. A proper amount of dibutyltin dilaurate was added under stirring. The reaction temperature was raised to 50°C so that 2 mol of TDI was reacted with 1 mol of PPG, introducing a NCO group to each end of the molecule. In this stage, care must be taken to control the molar ratio of the reaction and temperature, so as not to increase the molecular weight. The temperature was maintained at 50°C for 6 h, then increased to 75°C to maintain an acceptable rate of reaction. To determining the completion of reaction, the change of the NCO value during the reaction was measured using a dibutylamine back-titration method.

In the second step, the temperature was decreased to room temperature. 1 mol of HEMA was introduced slowly into the reactor and reacted for 4 h at 45°C. Then the temperature was raised to 65°C for 1.5 h, in order to introduce a reactive vinyl group onto the molecular ends as polymerizable part of the emulsifier.

In the third step, after dissolving 1 wt% of dibutyltin dilaurate, 1 mol of DMPA dissolved in DMAc was placed in the reactor at room temperature. The reaction temperature was maintained for 5 h at 45°C and 1.5 h at 65°C, resulting in introduction of a carboxylic acid group on the end side of molecule as hydrophilic part. The completion of reaction was determined by the disappearance of the NCO stretching peak (2270 cm^{-1}) in the IR spectrum.

To purify DMAc, unreacted HEMA and DMPA, the reaction mixture was precipitated from the water and filtered several times to give a crude product. The crude product was dried in vacuum. The carboxylic acid group

of the product was ionized with an appropriate amount of triethylamine at room temperature for 1 h. The reaction procedure and molecular structure of APUA are shown in Scheme 1^[7].



Scheme 1 The reaction procedure and molecular structure of APUA

Preparation of P(UA)/MMA Composite Miniemulsions and Polymerization

APUA was charged into a four-necked flask equipped with stirrer, thermometer, reflux condenser and inlet system for nitrogen gas. Distilled deionized water (DDI water) was slowly added to the reactor at room temperature with low speed stirring at first, then high speed stirring. AIBN dissolved in MMA was added dropwise to the flask slowly under stirring (when using KPS as initiator, KPS was dissolved in water and then added to the flask after MMA had been added). The polymerization was carried out at 75°C for 2 h under a nitrogen atmosphere with mechanical agitation. The basic recipe for the preparation of UV-curable PMUA emulsion is shown in Table 1.

Table 1. Basic recipe for the preparation of UV-curable PMUA emulsions

Chemical	Weight (g)
MMA	15
APUA	2.25
H ₂ O	80
AIBN	0.075–0.15
KPS	0.075–0.15

Determination of Conversion

A latex sample withdrawn from the reactor was added to a hydroquinone solution to stop the polymerization. The latex sample was dried in an oven to constant weight. Conversion of this sample can be determined from the original monomer content and the dried polymer sample weight.

Transmission Electron Microscopy

The morphology of latex particle were determined by transmission electron microscopy (TEM) using a 100-SX TEM with a magnification of 4.8×10^4 . TEM specimens were stained with RuO₄ vapor for one week.

Polymerization Stability

The final latex product was filtered through a sieve of 100 mesh in series in order to collect the coagulum formed during polymerization. Scraps adhering to the agitator, thermometer, and reactor wall were also collected. Total solid content was determined gravimetrically.

RESULTS AND DISCUSSION

CMC Determination

The molecular structure of the polymerizable emulsifier (APUA) is shown in Scheme 1. APUA is a mixture of A and B, but the content of B is very little in the mixture (about 5%). The emulsion efficiency of A is better than B. The property of APUA as a surface-active agent was determined by using conductance measurement. Figure 1 shows the conductance-concentration curve obtained from the conductance concentration. The turning area on the conductance curve is identified as CMC (3%~4%) of APUA (A) in the water solution. The inflection area is not a point, but a range. The reason is that the molecular weight of APUA is very large and poly-dispersed, and it is not a typical emulsifier. So APUA could not form classical micelles, but just a kind of assemblage.

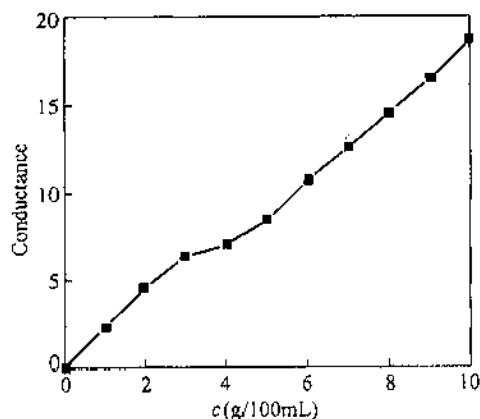


Fig. 1 Conductance curve as a function of APUA concentration in water at room temperature (A and B)

Polymerization Kinetics of MMA

Using APUA as emulsifier, the polymerization kinetics of MMA at different concentrations of AIBN and KPS was investigated. Curves of conversion versus time are shown in Fig. 2. It can be seen that the polymerization occurs rapidly and reaches a high degree for both KPS and AIBN initiators. Monomer conversion is almost complete after about 20 min. The kinetic curves are similar to the conventional emulsion polymerization, and the nucleation of latex particle take place in a short time period.

Figures 2(a) and 2(b) indicate that the polymerization rate of MMA increases with increasing initiator content of AIBN and KPS, respectively. The rate of polymerization, R_p (mol/L · min), is calculated from the slope of the linear portion of the monomer conversion versus time plots in Fig. 2(a), and we obtained a result of $R_p \propto [AIBN]^{0.25}$.

When using AIBN and KPS, respectively as initiator, the polymerization rate with SDS (CMC, 0.24%) or APUA as emulsifier was compared (Fig. 3). When AIBN was used, the polymerization rate was much faster for APUA than SDS (Fig. 3a). The main reason might be the different properties of APUA and SDS. Because APUA is a prepolymer with a molecular weight about 4,000, the emulsion formed by using emulsifier APUA contains a greater number of micro droplets of MMA, and the size of the droplets is very small, similar to micelles. This can also be proved from its good emulsifying property^[8]. When AIBN was used, its polymerization mechanism was quite similar to micro-suspension (or microemulsion) polymerization because the radicals from AIBN and the polymerization site occur mainly in the micro-droplets of monomer. The faster polymerization rate is due to the greater number of micro droplets and the nucleated particles^[9]. Since SDS is a conventional low molecular emulsifier and the emulsion prepared with SDS contains a large number of micelles and many large-size monomer droplets, therefore the polymerization rate is low. When AIBN is used, the polymerization mechanism is close to suspension polymerization.

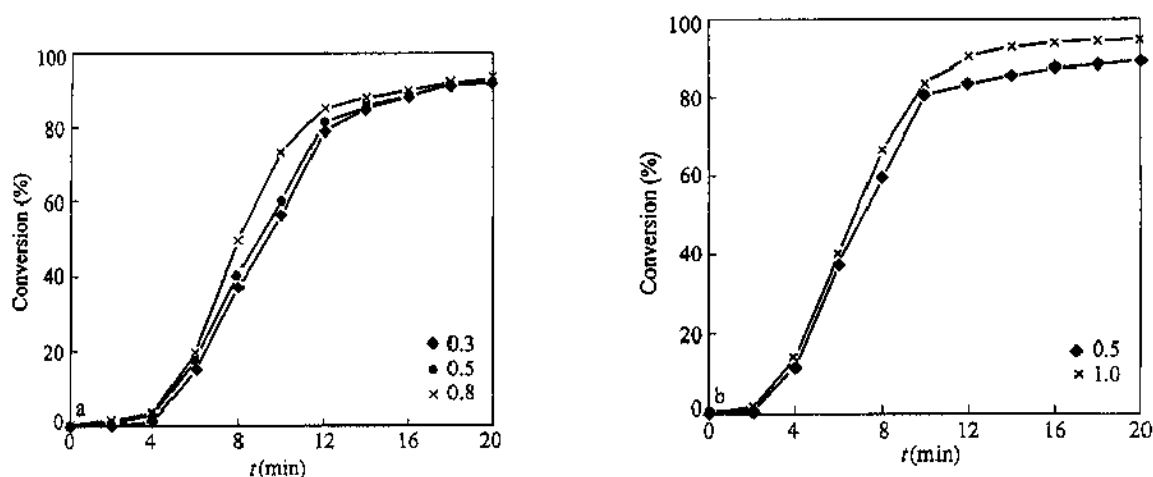


Fig. 2 Effect of initiator variety and concentration (% based on monomer) on the conversion-time behavior for the polymerization of MMA (a) AIBN; (b) KPS (APUA 2.8%, 75°C)

When water soluble KPS is used as an initiator, the polymerization rate of MMA is almost the same using either APUA or SDS as an emulsifier (Fig. 3b). The reason is that the nucleation reaction of latex particles takes place in micelles or micro droplets of MMA monomer as well as their similar polymerization mechanism of microemulsion (APUA) or emulsion (SDS). Because radicals of water-soluble initiator were formed in the aqueous phase, the effect between the two types of emulsifiers on the polymerization rate is smaller, so the R_p for SDS is slight higher than the R_p with APUA.

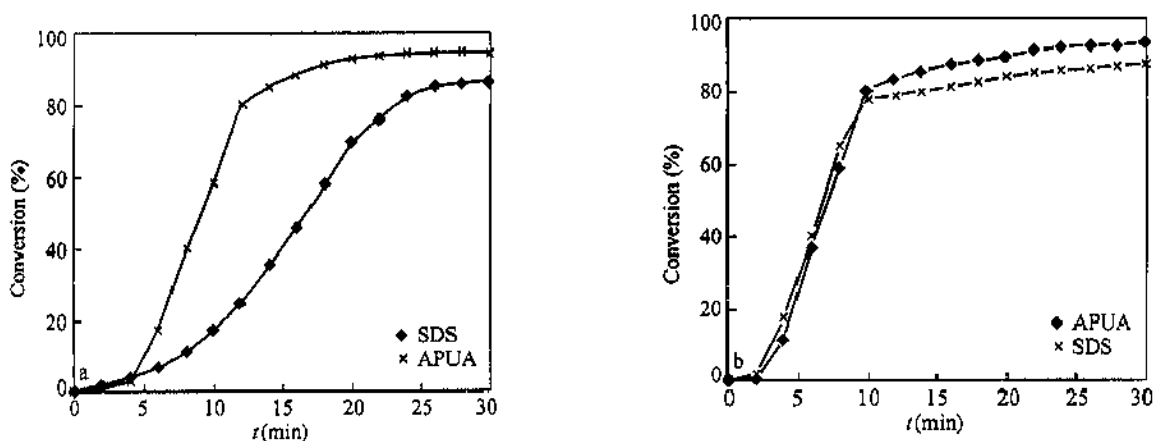


Fig. 3 Conversion versus time for different emulsifiers (SDS 0.38%; APUA 2.8%) and different initiators (a) AIBN (0.5%), (b) KPS (0.5%) (75°C)

Figure 4 is the TEM photomicrographs of latex particles prepared by two kinds of emulsifier. We also found that the size of particles prepared by APUA was smaller than by SDS. This is due to the microemulsion polymerization mechanism with a higher content of APUA as emulsifier.

Polymerization Stability

Table 2 shows the polymerization stability under different polymerization conditions. It can be seen that the polymerization stability becomes better with increasing amount of emulsifier. When the concentration of APUA emulsifier exceeded 2.8%, which corresponds to the CMC of emulsifier determined, the polymerization stability is good. Table 2 also shows that coagulum could be produced when using AIBN as initiator, but it does not

appear when using KPS as initiator. The possible reason is that the polymerization takes place mainly in the droplet of monomer when using APUA as emulsifier, and a few large-size particles produced is unstable under stirring which results in the formation of the coagulum^[10].

Table 2. Effects of initiator and emulsifier on the polymerization stability

Symbol	APUA (wt%)	Initiator	[I] (wt%)	T (°C)	Coagulum (%)
H ₁	1.5	AIBN	0.5	75	4.9
H ₂	1.9	AIBN	0.5	75	4.2
H ₃	2.8	AIBN	0.5	75	0.7
H ₄	3.8	AIBN	0.5	75	0.69
G ₁	2.8	AIBN	0.3	75	0.75
G ₃	2.8	AIBN	0.8	75	0.87
G ₄	2.8	KPS	0.5	75	0
G ₅	2.8	KPS	1.0	75	0
T ₁	2.8	AIBN	0.5	65	0.69
T ₂	2.8	KPS	0.5	65	0
S ₁	SDS/0.38	AIBN	0.5	75	6.7
S ₂	SDS/0.38	KPS	0.5	75	0
S ₃	SDS/0.38	KPS	1.0	75	0

* Hydrogel appeared, APUA and SDS based on water; initiator based on monomer

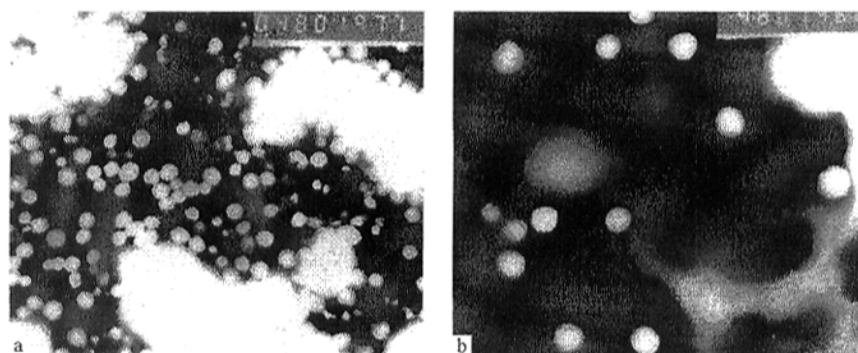


Fig. 5 TEM photomicrographs of latex particles using KPS as initiator
a) Before becoming hydrogel ($\times 48,000$)
b) After becoming hydrogel ($\times 48,000$)

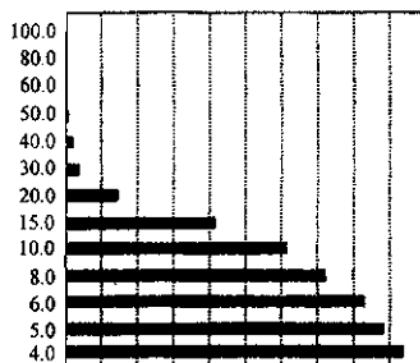


Fig. 6 Size distribution of latex particle after being hydrogel

It was found from experiments that when KPS was used as initiator, hydrogel was perhaps produced during

the reaction process or after the reaction, the emulsion system lost its fluidity and the size of latex particle increased from 40~80 nm to 4~20 μm ^[11]. Figures 5(a) and 5(b) show the morphology of latex particles before and after being turned into hydrogel. Furthermore, the size distribution of latex particle was still narrow. The formation of hydrogel was affected by reaction temperature, concentration of APUA, but the concentration of initiator was the most important factor. At 1.0% KPS concentration and 75°C, hydrogel appeared suddenly when the polymerization reaction was almost complete. Figure 6 shows the size distribution of latex particles after being turned into hydrogel. Under the same conditions, hydrogel did not appear on using SDS as emulsifier or AIBN as initiator. The properties of APUA, which contained a long chain and a polymerizable vinyl group, are responsible for producing the hydrogel.

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