

# Role of Emulsifiers in Preparation of Core-shell Particles Via Step-wise Emulsion Polymerization

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## ABSTRACT

Polyoxyethylene (POE) ( $n= 6, 15$  and  $30$ ) nonylphenols and sodium lauryl sulphate (SLS) are common emulsifiers with specific structural characteristics. SLS is an ionic emulsifier, but POE nonylphenols are non-ionic with homologous structures. They are different in hydrophilic-lipophilic balance, which affects the properties of corresponding latex. Therefore, polystyrene-poly(*N,N*-diethylaminoethyl methacrylate) particles were prepared by seeded emulsion polymerization in order to produce particles with core-shell morphology. Potassium persulphate was chosen as the water-soluble initiator and the obtained polymers were analyzed by differential scanning calorimetry and gel permeation chromatography. Also the morphology of particles were assigned by using scanning electron microscopy and transmission electron microscopy.

**Key Words:** styrene, *N,N*-diethylaminoethyl methacrylate, emulsifiers, emulsion polymerization, core-shell particles

## INTRODUCTION

Emulsions are disperse systems, which in general terms contain two insoluble or slightly soluble phases. The phase with larger amount is called external or continuous phase and the smaller amount phase is called internal or dispersed phase [1]. Emulsions are also divided to four categories according to the size of dispersed phase: (i) macroemulsion, (ii) microemulsion, (iii) colloid and (iv) latex [2]. The latexes that are discussed here are polymeric emulsions in which polymer particles are dispersed in aqueous phase.

One of the main components in emulsions is the emulsifier. Selection of emulsifier has an important role in preparation of a suitable and stable emulsion. One of the conventional ways in selection of an emulsifier is considering hydrophilic-lipophilic balance (HLB) of the desired emulsifier, which was firstly introduced by Griffin [3]. He anticipated a dimensionless number (0-20) to each emulsifier which displays its solubility in water or oil. The importance of knowing HLB of emulsifiers is that in order to have stable emulsions, we should select our system in a manner that the HLB of the emulsifier and

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the dispersed phase (monomer, polymer or any other component) would be more or less the same.

According to structural characteristics, emulsifiers could be non-ionic or ionic. A non-ionic emulsifier should produce stable micelles and emulsions in high concentrations. This concentration could be decreased if we use mixture of non-ionic emulsifiers with different HLB amounts. However, ionic emulsifiers should not be used alone in preparation of spherical particles. Because the repulsion of same charges would result in disordered spherical micelles. This repulsion also exists in hydrated form of ionic groups [1]. If a mixture of ionic and non-ionic emulsifiers is applied, the problems owing to high-concentration consumption of non-ionic emulsifiers and amorphous micelles and particles of ionic-emulsifiers would be eliminated.

It is noteworthy that, in order to have emulsions with monodisperse particles, we should know the critical micelle concentration (CMC) of the corresponding emulsifier [4].

In this paper, our aim is to investigate the effect of emulsifier type and its quantity on the two-step emulsion polymerization of styrene and *N,N*-diethylaminoethylmethacrylate (DEAEMA). This type of emulsion polymerization has been applied in several industries such as paint and coatings [5–7]. Also it has been used in preparation of opacifiers [8], void particles and impact modifiers [9–11], water absorbents [12], tacky films [13], binders [14], and styrene-butadiene rubber [15]. There are also several reports on kinetics and characterization studies of core-shell particles [16, 17]. The morphology of the obtained particles and the effect of mixture of emulsifiers on the morphology are discussed in this paper.

## EXPERIMENTAL

### Materials

Styrene was purchased from Merck Chemical Co. and DEAEMA was supplied by Polysciences, Inc. They were purified by vacuum distillation and stored in dark at  $-20\text{ }^{\circ}\text{C}$ . Potassium persulphate (KPS), sodium lauryl sulphate (SLS) and osmium tetroxide were

purchased from Polysciences, Inc. The epoxide resin (EPON 812) used for moulding of samples in transmission electron microscopy (TEM) analysis was obtained from Shell Chemical Co. Polyoxyethylene (POE) ( $n=6, 15$  and  $30$ ) nonylphenols were also obtained from BASF and used without further purification. Double-distilled water was used in all experiments.

### Equipment

The samples were characterized by scanning electron microscopy (a STEREOSCAN 360 SEM, Cambridge Instrument), transmission electron microscopy (a Zeiss 10C TEM) and differential scanning calorimetry (a PL DSC). The samples were microtomed using an ultramicrotome (V 2088 LKB, Pharmacia). GPC analyses were performed by using Waters 150 C HPLC/GPC.

### Sample Preparation and Procedure

Reaction conditions are given in Table 1. The details of experimental procedure has been reported before [18]. Samples were prepared for SEM and TEM according to the methods reported previously by the authors [18].

The obtained latex was dried at  $60\text{ }^{\circ}\text{C}$  under vacuum and used for GPC analysis. The mobile phase dimethylformamide (DMF) with flow rate of  $1\text{ mL}\cdot\text{min}^{-1}$  in the period of 40 min. GPC data were recorded at  $70\text{ }^{\circ}\text{C}$  on an Ultrastrogel column equipped with a RI detector. Also polystyrene was used as standard for calibration.

The reactor type was similar to that described by Poehlein et al. [19].

## RESULTS AND DISCUSSION

Experiment 1 (Table 1) shows a typical emulsion polymerization using an ionic emulsifier, SLS. The first step of polymerization proceeds well but by addition of DEAEMA in the second step, the coagulation suddenly occurs in large amounts.

At first we thought that the instability of emulsion was due to small amounts of emulsifier.

**Table 1.** Experimental conditions.

Experiment No.	DEAEMA (mol)	Styrene (mol)	Water (g)	SLS (mol)	POE (n=6) (mol)	POE (n=15) (mol)	POE (n=30) (mol)	KPS (mol)	Reaction time (h)	
									Step 1	Step 2
1	$5.56 \times 10^{-2}$	0.41	450	0.01	–	–	–	$3.0 \times 10^{-3}$	2.5	–
2	$5.56 \times 10^{-2}$	0.41	450	0.02	–	–	–	$3.0 \times 10^{-3}$	2.5	–
3	$1.73 \times 10^{-2}$	0.45	280	–	–	$6.05 \times 10^{-3}$	–	$2.1 \times 10^{-3}$	3.0	4.0
4	$3.23 \times 10^{-2}$	0.42	280	–	$1.24 \times 10^{-3}$	–	$2.72 \times 10^{-3}$	$2.8 \times 10^{-3}$	5.0	5.0
5	$3.23 \times 10^{-2}$	0.45	280	–	–	–	$1.95 \times 10^{-3}$	$2.7 \times 10^{-3}$	5.0	6.0
6	$3.23 \times 10^{-2}$	0.45	280	–	–	–	$1.57 \times 10^{-3}$	$2.7 \times 10^{-3}$	6.0	8.0

Therefore, in experiment 2 the emulsifier concentration was raised up to about two-fold in comparison to experiment 1. Unfortunately, after addition of DEAEMA in experiment 2, the coagulation was observed as well. So we were notified to the sensitivity of ionic emulsifiers to pH variations. The second monomer (DEAEMA) is a tertiary amine and correspondingly is a strong base. After addition of this monomer to the primary formed latex, pH of the latex severely changed and coagulation occurred.

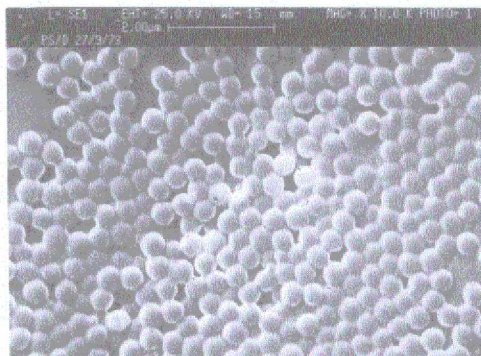
In order to prevent pH variations, buffers could be used. Hence, buffers with pH 6 and 7 from Merck Chemical Co. were applied. To control pH variations we were obliged to spend a large amount of the buffer which, resulted in dilution of the emulsion. This was not desirable. As a consequence, we concluded that the ionic emulsifiers were not suitable for such systems with basic monomer and we were notified to non-ionic emulsifiers. It should be noted that we have some restrictions in using ionic emulsifiers even with longer alkyl chain or higher hydrophobicity. It comes from the ionic character of this compound that limits its application in systems with pH changes.

In experiment 3, polyoxyethylene (n=15) nonylphenol with HLB= 14.4 was used as a non-ionic emulsifier [20]. The sudden coagulation, observed in experiment 2, was suppressed here. But the emulsifier was unable to stabilize the final emulsion and phase separation occurred after few hours and sedimentation, which is a reversible process, was observed. DSC analysis of the final product shows that the two monomers have been copolymerized. Tg of the product is 51.2 °C, whereas, in the case of polystyrene and

polyDEAEMA they are 100 °C and 14–24 °C respectively [21]. This confirms that the copolymerization reaction has been carried out in this experiment. SEM micrographs, before addition of DEAEMA (Figure 1) and after that (Figure 2), show the presence of primary particles of PS with 430 nm diameter (Figure 1). At the end of second step, either primary particles' diameter would increase or secondary smaller particles (190 nm) would appear (Figure 2).

CMC of POE (n=15) nonylphenol is  $7.9 \times 10^{-4}$  mol. L<sup>-1</sup> [22] and we used excess amount of this emulsifier up to 24-fold. This excess amount may form secondary micelles in which secondary particles would appear.

In order to confirm the above results, GPC analysis of PS in the first step (Figure 3) and the product of the second step (Figure 4) were recorded. Number average molecular weight ( $\bar{M}_n$ ) of PS in Figure 3 was 10914 and its weight average molecular

**Figure 1.** SEM Micrograph of PS from experiment 3.

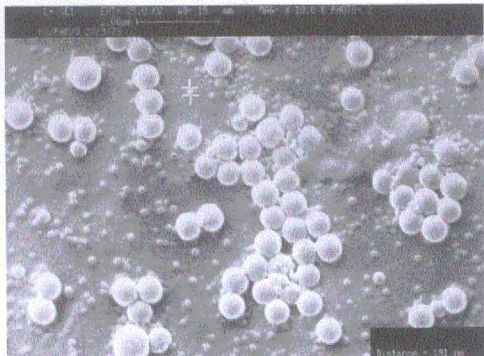


Figure 2. SEM Micrograph of PS-PDEAEMA from experiment 3.

weight ( $\bar{M}_w$ ) was 29932 with polydispersity ( $P_d$ ) of 2.74. Those of the product of second step polymerization (PS-PDEAEMA) were 42,522, 1,804,414 and 42.44, respectively (Figure 4). They would be related to copolymerization of DEAEEMA with remaining styrene, which has caused to increase the above average molecular weights.

Our purpose was to prepare structural particles with two different polymeric layers via a two-step emulsion polymerization by changing the emulsifier type and concentration.

Hence, we used a mixture of non-ionic emulsifiers with different HLB values: POE ( $n=6$ ) nonylphenol (HLB=10.9) and POE ( $n=30$ ) nonylphenol (HLB=17.1) [20] in experiment 4. Due to the weights

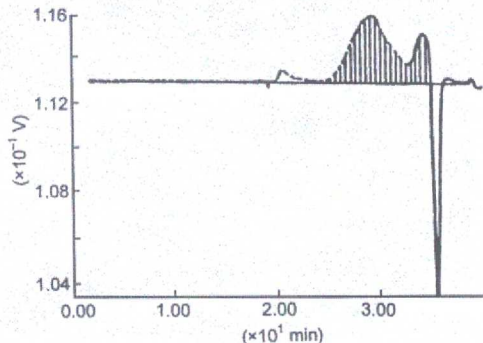


Figure 3. GPC Analysis of PS from experiment 3.

used, the HLB of the mixture is calculated as below:

$$(\text{HLB})_{\text{mix}} = W_1(\text{HLB})_1 + W_2(\text{HLB})_2 / W_1 + W_2 =$$

$$(0.6 \times 10.9) + (4.2 \times 17.1) / 0.6 + 4.2 = 16.3$$

where,  $(\text{HLB})_{\text{mix}}$ : HLB of the mixture of emulsifiers and  $W_1$  and  $W_2$ : weights (g) of each emulsifier.

This mixture of emulsifiers excluded the problem of sedimentation, which was observed in experiment 3. But the amount of coagulation during the polymerization reaction became more than before. This was anticipated to the high concentration of corresponding latex. It should be noted that the reason for increasing the amount of initiator was to accelerate the polymerization rate.

In another effort, we used only POE ( $n=30$ ) nonylphenol as emulsifier (experiment 5). The amount of emulsifier in experiment 3 (POE ( $n=15$ ) nonylphenol) was 24-fold of its CMC and in experiment 5 it was 30-fold (for POE ( $n=30$ ) nonylphenol). Here, no sedimentation was observed. As shown in SEM micrograph (Figure 5), particles with 315 nm diameter have been produced. It is noteworthy that DSC analysis shows two distinct glass transition temperatures at 105 °C and 29–30 °C which correspond to the homopolymers of PS and PDEAEMA, respectively and one at 56 °C, related to the copolymer of styrene and DEAEEMA [18].

Experiment 6 was set in order to optimize reaction conditions with increasing particles' diameter. Therefore, the reaction time for the first step

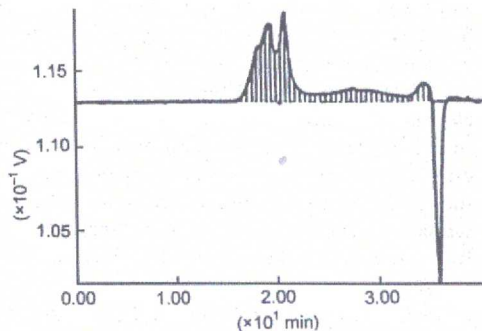
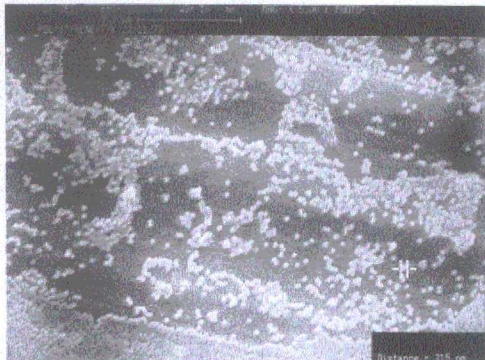


Figure 4. GPC Analysis of PS from experiment 3.





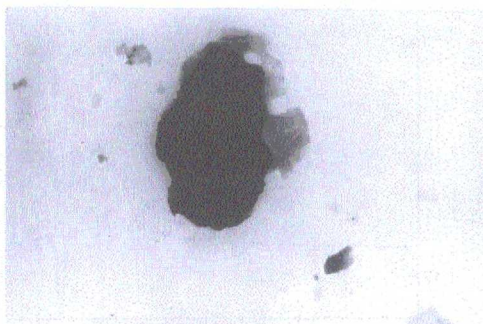
**Figure 5.** SEM Micrograph of PS-PDEAEMA from experiment 5.

polymerization was raised to eliminate the probability of undesired copolymerization. Also the emulsifier concentration was decreased to 24-fold of CMC (as experiment 3) to control the particle size. SEM Micrograph of the obtained product (Figure 6) reveals the spherical particles.

TEM Micrograph of the obtained particles (Figure 7) shows where DEAEAMA monomers are polymerized and deposited. It is obvious that the stained PS by  $\text{OsO}_4$  exists in the core and the unstained PDEAEMA is in the shell of each particle in two distinct domains. This reveals that polymer



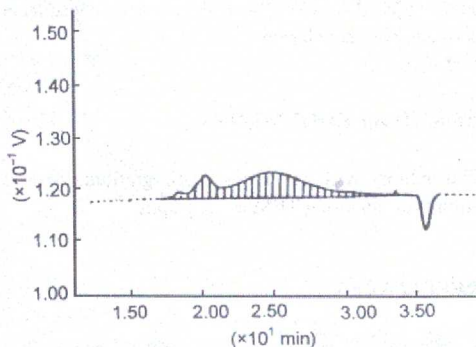
**Figure 6.** SEM Micrograph of PS-PDEAEMA from experiment 6.



**Figure 7.** TEM Micrograph of PS-PDEAEMA from experiment 6. The lighter (gray) is PDEAEMA and the darker (black) region reveals the PS domain.

particles with core-shell structure have been prepared via emulsion polymerization, in addition to the formation of the latex without any coagulation and sedimentation. It should be noted that the shapeless particles in the TEM micrograph result from the procedure used for sample preparation. The spherical shape of the particles is confirmed by SEM micrograph (Figure 6).

The GPC data show an increase in molecular weights from the first ( $\overline{M}_n = 112,011$ ,  $\overline{M}_w = 560,969$  and  $P_d = 5.01$ ) (Figure 8) to the second step of polymerization ( $\overline{M}_n = 198,450$ ,  $\overline{M}_w = 1,430,681$  and  $P_d = 7.21$ ) (Figure 9). This may be the result of small degree of grafting the shell polymers to the PS core.



**Figure 8.** GPC Analysis of PS from experiment 6.

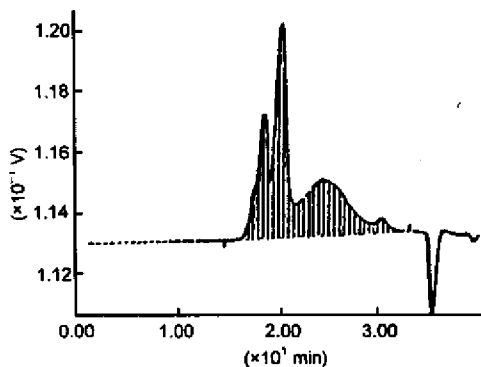


Figure 9. GPC Analysis of PS from experiment 6.

## CONCLUSION

The procedure presented here, resulted in preparation of polymer particles of styrene and *N,N*-diethyl-aminoethyl methacrylate having core-shell morphology via emulsion polymerization. The external domain of these particles consists of PDEAEMA and the internal domain includes PS. The above particles were produced by emulsion polymerization using nonionic emulsifier (POE with  $n=30$ ) and potassium persulphate. There were several emulsifiers examined and their effects on the polymeric particle structure were also investigated.

Spherical shapes of the particles were detected by SEM and the core-shell morphology was investigated by TEM. However, DSC and GPC data helped us in perfecting our conclusion.

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