

## **Emulsion Stability with PLA as Co-Surfactant**

**Yenny Meliana and Melati Septiyanti**

*Pusat Penelitian Kimia – LIPI, Kawasan Puspiptek Serpong, 15314*

*E-mail: yenn001@lipi.go.id*

*Received: 10-Feb-2016    Revised: 25-Mar-2016    Accepted: 17-Mei-2016*

### **ABSTRACT**

**Emulsion Stability with PLA as Co-Surfactant.** Polystyrene emulsion based plastic raw material requires emulsion surfactant stabilizer to control its stability. Sometimes, single surfactant is not enough to reduce surface tension to the required value, hence co-surfactant is added into the system to reduce the particle size and narrow the size distribution. However, surfactant and co-surfactant concentration affect stability of the droplets by preventing Ostwald ripening. This study investigated styrene emulsion stability using Poly Lactic Acid (PLA) as hydrophobic co-surfactant and Sodium Dodecyl Sulfate (SDS) as the surfactant. PLA concentration was ranged from 1 to 5wt%, while SDS concentrations were 5 and 10 wt%. Emulsion stability was monitored by droplet size which was analyzed for 2 h and the data were recorded for every 10 min. The best condition resulted from this research is emulsion system with concentration PLA 5 wt% and SDS 10 wt%, with the particle size range 59-97.5 nm.

**Keywords:** miniemulsion polymerization, co-surfactant, biopolymer, nanomaterial, poly lactic acid (PLA)

### **ABSTRAK**

**Stabilitas Emulsi Menggunakan PLA sebagai Ko-Surfaktan.** Bahan baku plastik berupa emulsi polistirena memerlukan stabilizer berupa surfaktan untuk mengontrol stabilitas emulsinya. Terkadang, satu surfaktan belum cukup untuk mereduksi tegangan permukaan sampai ke nilai yang dibutuhkan, sehingga ko-surfaktan ditambahkan ke dalam sistem untuk mereduksi ukuran partikel dan mempersempit distribusi ukuran. Namun demikian, konsentrasi surfaktan dan ko-surfaktan mempengaruhi stabilitas suatu droplet dengan mencegah terjadinya Ostwald ripening. Penelitian ini menyelidiki stabilitas emulsi stirena menggunakan Poly Lactic Acid (PLA) sebagai ko-surfaktan hidrofobik dan Sodium Dodecyl Sulfate (SDS) sebagai surfaktan. Konsentrasi PLA berkisar dari 1 sampai 5% wt, sedangkan konsentrasi SDS adalah 5 dan 10% wt. Stabilitas emulsi dimonitor melalui ukuran droplet yang dianalisis selama dua jam, dan data dicatat setiap sepuluh menit. Kondisi terbaik dari penelitian ini adalah sistem emulsi dengan

*konsentrasi PLA 5% wt dan SDS 10% wt, yang menghasilkan ukuran partikel berkisar 59-97,5 nm.*

**Kata Kunci:** *polimerisasi miniemulsi, ko-surfaktan, biopolimer, nanomaterial, poli asam laktat*

## INTRODUCTION

The success of monomer droplet nucleation in miniemulsion polymerization lies in its stability during reaction. Stability control of emulsion is highly important in emulsion system because it might be break down in a span of certain time. To prevent the defect of the emulsion, it is studied the miniemulsion system which has a good kinetics stability. Miniemulsions is a system which covering size range 50-200 nm. This system is kinetically stable due to very small droplet size that makes this system do not undergo creaming, flocculation, coalescence, and sedimentation [1].

The most common way to prepare miniemulsion is through direct emulsification method. The dispersed phase is added to the continuous phase with high energy agitation. The form of the emulsion is either oil in water (O/W) or water in oil (W/O) [2]. Miniemulsion contain oil, water and emulsifier which is an important factor to determine small sized droplets because its effect to decrease the interfacial tension between oil and water phase of the emulsion. The emulsifier commonly used is surfactant [3]. Surfactant also play an important role to stabilized emulsion against coalescence [4]. The concentration of surfactant used to form miniemulsion system is ranged between 5-10% [5]. Sometimes, single surfactant is not enough to reduce surface tension to the required value because of its properties. Thus, second surfactant or co-surfactant is added into the system to alter the physicochemical properties of the miniemulsion, such as reducing the particle size and narrowing the size distribution [6]. Concentration of co-surfactant also affect stability of the droplets through prevention Ostwald ripening [7]. Co-surfactant should be extremely insoluble in aqueous phase and extremely soluble in the monomer droplet. Common materials which are used as co-surfactant are cetyl alcohol or hexadecane. Other studies also used polymer as co-surfactant [8]. The addition of 1-5 wt% co-surfactant into the emulsion system can effectively prevent the small monomer to diffuse to a larger ones caused by the osmotic pressure effect [9].

The polymer that is used as co-surfactant is Poly Lactic Acid (PLA). PLA is an environmental friendly polymer which has biodegradable and biocompatible properties [10]. It is sustainable since it is derived from renewable resources such as corn or rice. PLA is a non-toxic material and has

no carcinogenic effect that make PLA biocompatible with the living organism [11].

This study investigates styrene emulsion stability using PLA as hydrophobic co-surfactant. PLA concentration was varying from 1-5wt%, while as the surfactant; SDS concentrations were 5 and 10 wt%. Emulsion stability was monitored by droplet size and polydispersity index.

## **MATERIALS AND METHOD**

### *Materials*

The emulsion consists of two phases, oil phase and water phase. Oil phase consists of Styrene (stabilised) for synthesis Merck as monomer of the emulsion, Poly Lactic Acid (PLA) Ingeo 7001D, with molecular weight  $110.1 \times 10^3$  g/mol as co-surfactant and Chloroform for analysis Emsure Merck as PLA solvent. Water phase consists of Aquademineralization, Sodium Dodecyl Sulfate (SDS) Ph Eur Merck as surfactant, Natrium Bicarbonate as solution buffer.

### *Preparation of Miniemulsion*

PLA was dissolved in 5 ml of chloroform and then mixed with styrene to form oil phase. Deionized water, SDS and Natrium Bicarbonate were stirred in a low speed using magnetic stirrer. Oil phase and water phase were mixed by magnetic stirrer for 10 min for pre-emulsion stage. Then, the emulsion was sonicated by Qsonica Sonicators, amplitude 40% for 30 min, with sequence 30 s on and 2 s off to form miniemulsion. The sonication was done with an ice bath to prevent polimerization process. The PLA and SDS were varied from 1-5% wt and 5 & 10% wt, respectively. The variation of the emulsion composition is shown in Table.1

**Table 1.** Variation of emulsion composition

Experiment	Oil Phase ( 20% )		Water Phase ( 80% )	
	PLA (% wt)	Styrene (% wt)	SDS (% wt)	Water (% wt)
I	1	99	5	95
	2.5	97.5	5	95
	5	95	5	95
II	1	99	10	90
	2.5	97.5	10	90
	5	95	10	90

### *Characterization*

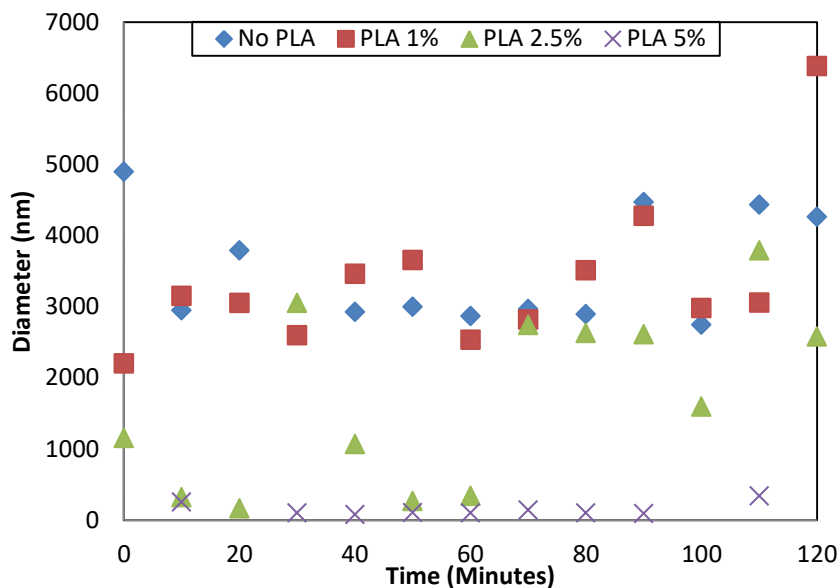
The characterization for the emulsion stability is monitored by droplet size and polydispersity index, using Particle Size Analyzer (PSA) Horiba Nano Partica SZ-100. The droplet size was investigated in 2 h and the data were recorded for every 10 min. The sample was dispersed into solution dilution. The composition of the solution dilution is 2.365 g/L SDS and 0.2 g/L styrene in 1 L deionized water and then it was stirred at low speed for 24 h.

## **RESULTS AND DISCUSSION**

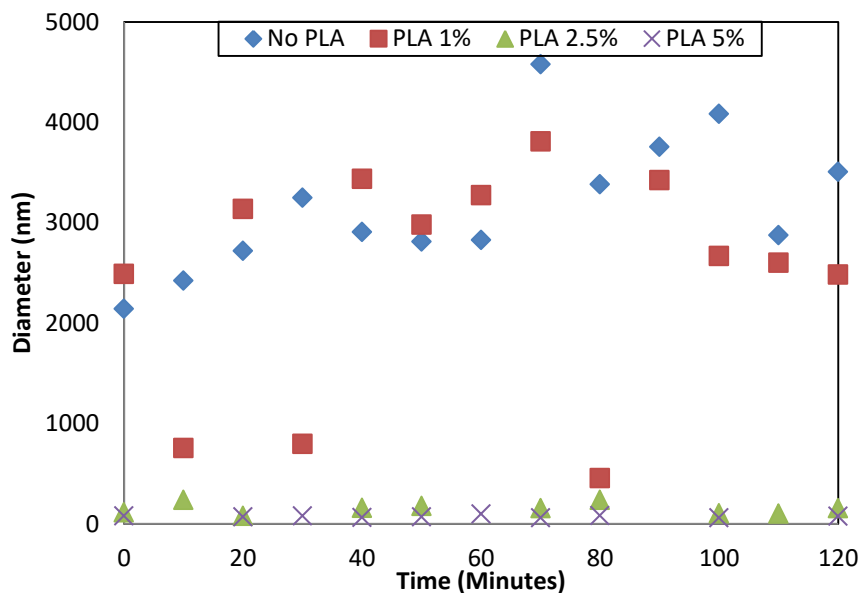
### *Effect of PLA concentration on droplet size*

Average monomer droplet diameter (nm) as a function of time for styrene emulsion with PLA as the co-surfactant is shown in Figure 1. It can be seen that the droplet size is in the range between 2700-5000 nm with no addition of PLA. Similar result was recorded for addition of 1% PLA that resulting droplet size between 2000 and 6400 nm. However, lower droplet size was obtained for 5% PLA, which was in between 90-350 nm. The emulsion system with no PLA has unstable system. It separated into two phase within 10 min. Incorporating PLA as the co-surfactant into the system affected the droplet size; the higher PLA concentration, the lower droplet size. It can be explained that hydrophilic polymeric co-surfactant caused less effective effect in retarding Ostwald ripening phenomena. The hydrophobicity along with the escalation of PLA concentration can reduce the droplet size of the emulsion system. The high molecular weight of the co-surfactant can conduct particle formation via homogeneous nucleation mechanism which is lead to rapid reduction of the droplet size diameter [12]. Moreover, the strong hydrophobic interactions create molecular cluster in the dispersed phase which slow down the ostwald ripening rate [13]. This is shown with the reduction tendency on droplet size by increasing the concentration of PLA as co-surfactant.

In the case of using 10% SDS (experiment II), the addition of PLA decreased the droplet size as can be seen in Figure 2. For the same PLA concentration, lower droplet sizes were obtained for 10% SDS compared to those that using 5% SDS. It can be explained that the surface area per molecule of SDS increases with increasing particle size, which means the smaller particle size require more surfactant concentration to obtain the stable system [14]. This is shown in the result of the experiment II with concentration SDS 10%, produce the smaller and homogenous emulsion system as shown on the figure above.



**Figure 1.** Average monomer droplet size upon aging at 25 °C as a function of time for styrene emulsion stabilized by 5% SDS



**Figure 2.** Average monomer droplet size upon aging at 25 °C as a function of time for styrene emulsion stabilized by 10% SDS

*Effect of PLA concentration on Polydispersity Index (PI)*

The homogeneity of the emulsion is shown by the polydispersity index (PI) which describes the distribution range of the particle droplet size. Polydispersity value which is less than 0.1 describes that the emulsion is

monodisperse. It means that the emulsion has a homogenous droplet size distribution [15]. The polydispersity (PI) of the emulsion system is shown in Table 2 and Table 3, for 5% SDS and 10% SDS, respectively. It is shown that the PI is decreasing with the increase of PLA concentration which is correlated to the homogeneity of the emulsion.

**Table 2.** Polydispersity for Styrene emulsion stabilized by 5% SDS

Time (Minutes)	Experiment I			
	No PLA	PLA 1%	PLA 2.5%	PLA 5%
0	0.461	0.867	0.483	1.755
10	0.283	0.313	0.494	0.61
20	0.449	0.336	0.496	0.671
30	--	1.007	0.794	0.206
40	1.075	0.446	1.447	0.129
50	0.97	0.190	0.708	0.351
60	1.16	1.049	0.481	0.242
70	1.107	1.145	1.430	0.295
80	1.426	0.355	1.345	0.147
90	0.783	0.369	1.056	0.234
100	1.176	1.369	1.782	--
110	0.386	1.237	0.553	0.753
120	0.217	0.569	0.986	0.999

**Table 3.** Polydispersity for Styrene emulsion stabilized by 10% SDS

Time (Minutes)	Experiment II			
	No PLA	PLA 1%	PLA 2.5%	PLA 5%
0	0.060	0.827	0.742	0.340
10	0.792	0.810	0.597	0.797
20	0.502	2.153	0.439	0.635
30	0.018	1.026	--	0.111
40	0.756	0.243	0.455	0.612
50	0.847	0.912	0.513	0.451
60	0.924	0.473	3.177	0.711
70	0.266	0.216	0.774	0.329
80	0.465	1.056	0.468	0.256
90	0.080	0.396	0.522	0.549
100	0.083	0.967	0.505	0.484
110	0.979	1.060	0.608	0.786
120	0.642	1.034	0.477	0.523

## CONCLUSION

Emulsion stability with addition of PLA as the co-surfactant into the styrene emulsion system has been studied by monitoring the droplet size. The smallest droplet size and stable system obtained from system with SDS concentration of 10 wt% and PLA concentration of 5 wt%. The particle size range for this condition is between 59-97.5 nm.

## ACKNOWLEDGEMENT

The authors would like to thank Indonesian Institute of Sciences for supporting this research.

## REFERENCES

- [1]. Rajalakshmi R, Mahesh K, Kumar CA. A critical review on nano emulsions. *Int J Innov Drug Discov* 2011;1(1):1-8.
- [2]. Sevcokova P, Vltavska P, Kasparkova V, Krejci J. Formation, characterization and stability of nanoemulsions prepared by phase inversion. *Math Methods Tech Eng Environ Sci* 2011:132-7.
- [3]. Gupta A, Eral HB, Hatton TA, Doyle PS. Nanoemulsions: Formation, properties and applications. *Soft Matter* 2016;12:2826-41.
- [4]. Crespy D, Landfester K. Miniemulsion polymerization as a versatile tool for the synthesis of functionalized polymers. *Beilstein J Org Chem* 2010;6:132-48.
- [5]. Tadros T, Izquierdo P, Esquena J, Solans C. Formation and stability of nano-emulsions. *Adv Colloid Interface Sci* 2004;109:303–18.
- [6]. Sharma N, Madan P, Lin S. Effect of process and formulation variables on the preparation of parenteral paclitaxel-loaded biodegradable polymeric nanoparticles: A co-surfactant study. *Asian J Pharm Sci* 2016;11( 3):404–16.
- [7]. Guo J, Pan Q, Huang C, Zhao Y, Ovyang X, Huo Y, Duan S. The role of surfactant and costabilizer in controlling size of manocapsules containing TEGDMA in miniemulsion. *J Wuhan Univ Technol Mater Sci Ed* 2009;24(6):1004–6.
- [8]. Schork FJ, Guo J. Continuous miniemulsion polymerization. *Macromol React Eng* 2008;2:287–303.
- [9]. Chern C, *Principles And Applications Of Emulsion*. Hoboken, NJ, USA: John Wiley & Sons, Inc., 2008.
- [10]. Zhang W, Wang Y. Synthesis and properties of high molecular weight

- poly (lactic acid) and its resultant fibers. *Chinese J Polym Sci* 2008;26(4):425–32.
- [11]. Rasal RM, Janorkar AV, Hirt DE. Progress in polymer science poly (lactic acid ) modifications. *Prog Polym Sci* 2010;35(3):338–56.
- [12]. Lei Y, Luo Y, Chen F, Mei L. Sulfonation process and desalination effect of polystyrene/PVDF semi-interpenetrating polymer network cation exchange membrane. *Polymers (Basel)* 2014;6:1914–28.
- [13]. Meliana Y, Chern CS. Effect of the molecular weight of n-alkane costabilizers on the ostwald ripening of styrene miniemulsions. *J Dispers Sci Technol* 2013;34(5):632–8.
- [14]. Landfester K. Recent development in miniemulsions-formation and stability mechanisms. *Macromol Symp* 2000;150:171–8.
- [15]. Nanocomposix. Nanocomposix's guide to dynamic light scattering measurement and analysis. *Guidel Dyn Light Scatt Meas Anal* 2012;1(3):1–7.