

Study the effect of surfactants on Emulsion Co-polymerization rate of P-Methyl Styrene with Methyl Methacrylate

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Abstract

Two different types of surfactants one ionic surfactant and the non-ionic surfactant were used in this stage. The surfactants were dodecyl sulfate (SDS) and Sorbitan monooleate (Span 80) respectively. The kinetic study was carried out in PMMA seeded growth with the two different surfactants and it found that the conversion time of monomer into the polymer with span 80 was longer than the conversion time with SDS. Emulsion Co-polymerization of P-Methyl Styrene with Methyl Methacrylate takes place in a two stage seeded emulsion polymerization. The synthesis of the polymer was done in the presence of surfactants. The initial stage involves the synthesis of PMMA particles through the use of emulsion polymerization reaction using dodecyl sulfate (SDS). The second stage involves the synthesis of PMMA –PPMS composite polymer particles. The PMMA particles will act as the seeds in the second stage.

Keywords: (emulsion, Co-polymerization m, polymer, kinetic, monomer, Particle)

1. Introduction.

Polymerization seeks to react with monomer molecules to form chains or structures. This polymerization can be achieved in two ways: step growth and chain growth and these two mechanisms involve the self-organization of the materials [1].

Emulsion polymerization is a complicated heterogonous process of a lot ingredients Water, surfactant, a water-insoluble monomer such as styrene and a water soluble initiator such as potassium persulfate. The emulsion polymerization includes the reaction of free radicals with stabilized hydrophobic monomer molecules by surfactant (e.g. dodecyl sulfate) in a

continues aqueous phase. When the level of surfactant is larger than its micelles concentration, micelles are generated. The hold of radicals by micelles leads to form nucleated particle hence the chain length achieve via the absorb monomer [2].

The process of Emulsion Polymerization is described by the use of three distinct intervals called I, II and III. The intervals are classified based on the compositions and behaviour of the different emulsions. This takes place in respect to the number of particles and the presence or absence of the monomer micelles and droplets.

Particle formation takes place at interval I under very specific conditions like the presence of monomer droplets, surfactants, monomer swollen micelles and precursor particles. As particles are being formed, the number of particles, concentration of particles per unit volume also increases throughout this interval. The reaction rate of the electrosterically stabilized emulsion polymerization systems also increases as the particles will be formed at the end of this interval.

Interval II takes place with the conclusion of particle formation period. The number of particles will remain constant at this interval. All the aqueous phase oligomers are capable of entering the latex particle. The interior particle in this interval is saturated with a monomer at some specific concentration with the excess monomer acting like monomer droplets. Constant concentration is attained through diffusion of the monomer.

Interval III is characterized by the depletion of all the monomers in the solution. The only monomers present in the emulsion are the unreacted monomers. The concentrations of monomers in this interval are no longer saturated as before. It leads to a decrease in the rate of polymerization [1]. Co-polymerization seeks to bring together different monomers with differing active centers. The co-polymerization process can also be viewed as a systematic method of effect changes in polymer properties and provides for the introduction of several different functional groups to the polymer (Reddy *et al.*, 2008; Heuts *et al.*, 1998). There are many different solvents and surfactants which have differing dielectric

constants, solubility parameters and dipole moments that can be selected to facilitate an increase in the rate of polymerization (Reddy *et al.* 2008). The process of co-polymerization is also highly regulated by the effects of temperature on the average radical reactivity indicating an enthalpic component to any penultimate unit effect (Coote *et al.*, 1997).

Motokawa *et al.* (2012) noted that the formation of polymerization 'droplets' and their dispersal during the co-polymerization process of conventional monomers styrene (St) and methyl methacrylate. The interfractal structure of these droplets has an important regulatory role in the behavior of the surfactants that may be used to mediate the reaction [3]. The process of emulsion polymerization involves the use of a surfactant to disperse the monomer and avoid the issues of droplet formation (Gilbert, 1995)[4], Mekki *et al.* (2010) [5] noted that the use of surfactants can lead to a more stable solution resulting in a narrow range of resultant particles and that the concentration of the surfactant was a major determinant of the final particular size.

Due to nucleate the practical in the Intervals I which means increase the number concentration or density of practical. Therefore the instabilities and sensitivities are inherent in this stage resulting from the nucleation kinetic, they are unavoidable directly. Thereby, it is advantage if the interval I separate and this can be attained by using seeded growth polymerization. The seeded growth polymerization starts from interval II or III, it is based on the carrying out the interval I and forming the seed latex then purifies it by dialysis or ultra-filtration to take off soluble initiator decomposition products and excess surfactant. After that, the seeded growth carries out by adding the monomer, surfactant and initiator where the interval II and III occur. The seeded growth polymerization guarantees that the unavoidable instabilities and sensitivities occur only during the production of the seed not in the second stage where the most polymers grow, in this stage there will be no new particles [4].

This study is aimed to prepare p (methyl methacrylate) - poly (p- methyl styrene) by p(methyl methacrylate) seeded emulsion polymerization of p-methyl styrene using different surfactants SDS and Span 80. In the seeded

emulsion polymerization the two stages emulsion polymerization carry out to synthesize polymer-polymer composite practicals. In the first stage PMMA latex was prepared with emulsion polymerization and then PMMA latex was used in the second stage of the reaction with PMS and two different surfactants. In addition, study seeks to explore the effect of the surfactants on the polymerization reaction by the kinetic analysis of the reaction. The effect of the different surfactant has not been studied before for the emulsion Co- polymerization of P-methyl styrene with methyl methacrylate. The kinetic analysis that employed in this study requires following the mass change of the formed polymer with time through the volume change of polymer during the copolymerization.

The PMMA seed latex was prepared at 60° C using the potassium persulphate (K₂S₂O₈) as initiator and SDS as surfactant. Then amount of p-methyl styrene and one surfactant were mixed with PMMA seed latex and stirred in oil bath at 50° C. When the temperature was stabilized the K₂S₂O₈ was added. This step was repeated with the another surfactant using the same quantity of monomer and at same temperature (50° C).

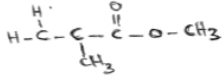
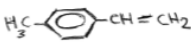

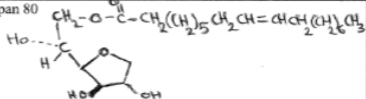
Compound	Symbol	Chemical structure
Methyl methacrylate	MMA	
p-methyl styrene	PMS	
Dodecyl sulfate	SDS	
Sorbitan Monooleat	Span 80	

Table (1): the chemical structure of the used monomers and surfactants

2. Experimental Work.

2.1 Synthesis of PMMA seed latex:

Equipment used: 500 ml round-bottomed flask, 1L beaker, 30 cm dry column, turrax dispersion device, oil bath, quick fit connector for bubbling nitrogen through reaction and dialysis tubing.

Chemical used: 0.1574 g of potassium per sulfate (KPS), 0.1533 g of dodecyl sulfate (SDS), 32.2270 g of methyl methacrylate, aluminium oxide, and 300 ml of distilled water.

2.1.1 Experimental procedure:

Methyl methacrylate was passed through the filled column by 4 - 6 cm dry aluminium oxide to remove any quinone inhibitor. The ingredients were placed in beaker, the turrax dispersion device was used to mix the ingredient for 60 seconds and a homogeneous milky mixture was obtained. The homogeneous milky mixture was transferred to 500ml round-bottomed flask where nitrogen was continued to flow over the top of the mixture and the mixture was heated for 4 hours at about 60 C°. After the 4 hours were run out, the mixture was cooled and transferred to dialysis tubing for clean the latex and remove unreacted Material as well as the polyelectrolytes that absorbed by the latex partials on their surfaces [6]. The dialysis tubing was tied in the other end. The mixture of latex in dialysis tubing “sausage” was placed in a large beaker full in water, the rubber tubing was set up to deliver additional water to the beaker at about 1 ml per minute, and the beaker was arranged to overflow down the sink. The tap was left running for one week. After one week, the contents of dialysis sausage “ latex “ was kept to next step (the latex represents the poly methyl methacrylate (PMMA) which will use for the next step as seed).

The gravimetric technique was employed to determine the conversion /time of the monomer into the polymer which represents in yield percentage. The 1ml seed latex was dried and weighted.



Figure (1) Photograph of emulsion of methyl methacrylate in operation.

2.2 The kinetic study of the Seeded emulsion Polymerization

Equipment used: 250 ml round-bottomed flask, oil bath, thermometer and 66 cm tube.

Chemical used: 50 ml of seed latex (PMMA), 150 ml of water, 25 ml MMA, 25ml p-methyl styrene, 0.1524 g of dodecyl sulfate (SDS) and 0.1502 g of potassium persulfate(KPS).

2.2.1 Experimental procedure:

The equipment was set as shown in figure (2). The seed, MMA, p-methyl styrene, SDS and water were placed in the around-bottom flask and put in the oil bath. When the temperature was controlled at 50 C° the solution of KPS was added and 28.5 cm of the tube was filled with water. The video recording was used to track the progress of the reaction and indicated the decrease of water level with the passage of time. The level of water versus the time was recorded. The steps above were repeated with 0.1567g of KPS and 0.1567 g of span 80 as surfactant instead SDS. The readings were recorded. Using the gravimetric technique the monomer conversion for formed polymer with SDS and span 80 as surfactants .



Figure(2): Photograph of watching the seeded emulsion polymerization of P(methyl methacrylate) with P-methyl styrene and two different surfactant.

3. Results and dissection

3.1 Determination of percentage of yield:

$$\text{The percentage of yield \%} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100$$

The experimental yield of the latex “methyl methacrylate” was 0.0784 g.

Methyl methacrylate (monomer) in 1ml = initial mass of methyl methacrylate $\times \frac{1\text{ml}}{\text{total volume of the solution} + \text{volume of methyl methacrylate}}$

$$\text{Hence, the mass of methyl methacrylate in 1ml} = 32.2270 \text{ g} \times \frac{1\text{ml}}{300\text{ml} + \frac{32.2270\text{g}}{1.178 \text{ g/ml}}} = 0.0985 \text{ g}$$

The theoretical yield of methyl methacrylate = 0.0985 g.

$$\text{Therefore, the percentage of yield} = \frac{0.0784}{0.0985} \times 100 = 79.6 \%$$

3.2 ^1H NMR analysis:

^1H NMR was employed in this study to characterize the copolymer and determine the solubility of p-methyl styrene.

The solubility of p-methyl styrene in water was obtained by mixing 1.013 g of PMS with 500 ml of water in separation funnel then the aqueous layer separated. 200 ml of the aqueous layer was mixed with 10 ml dichloromethane then the ^1H NMR sample was taken from extracted aqueous layer. The ^1H NMR samples for the characterize copolymerization and the solubility of PMS were made using deuterated chloroform. The calculation of solubility of PMS using HNMR spectrum The PMS has 4 protons that shown in NMR between (7.25 - 7.75 ppm) so the ratio between integral and the number of protons = $1/4 = 0.25$. Whereas, the ^1H NMR spectra show that the peak between (5.00 - 5.75 ppm) belongs to the 2 protons of dichloromethane.

Hence the ratio between the integral and the number of protons = $\frac{103.8755}{2} = 51.93775$

Therefore 0.25 PSM: 51.93775 DCM

The number of moles of DCM = mass of DCM/ M. Wt.

The moles of DCM = (density \times volume)/M. Wt
 $= (1.325 \text{ g/ml} \times 10 \text{ ml})/83.92 \text{ g/mol} = 0.157888$
mole

The moles of PMS = $0.157888 \times \left(\frac{0.25}{51.093775}\right) = 0.00076$ mole

Hence the solubility of PMS in 500 ml water = $0.000531 \text{ mole}/0.5 \text{ L} = 1.062 \times 10^{-3} \text{ mole/L}$.

^1H NMR spectrum of copolymerization shows that the chemical shift of methyl protons is in the region between (0.60 - 1.06 ppm), methylene and methine protons in the region between (1.13 - 2.25 ppm), methoxy protons in the region between (3.25 - 3.63 ppm) and the phenyl protons between (6.12 - 7.25 ppm). The mole fraction of monomer PMS (x_{PMS}) can be calculated from the NMR spectrum using the following equation:

$$x_{\text{PMS}} = \text{area of aromatic} / \text{total area}$$

$$x_{\text{PMS}} = \text{APMS} / (\text{APMS} + \text{AMMA})$$

$$x_{\text{PMS}} = 1 / (1 + 0.6980 + 3.2627)$$

Hence the mole fraction of PMS is 0.202. figure (3) and figure (4) show the ¹HNMR spectrum for analysing the solubility of PMS and the characterizing of the copolymerization respectively.

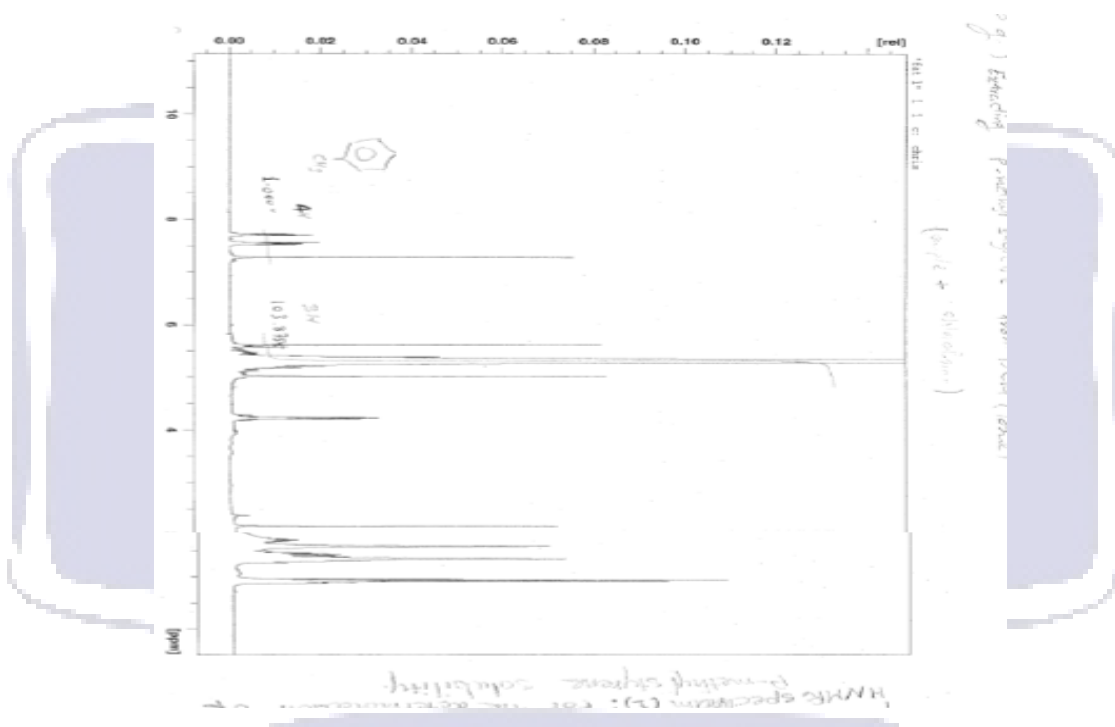


Figure (3): ¹HNMR spectrum of the analysing the solubility of PMS

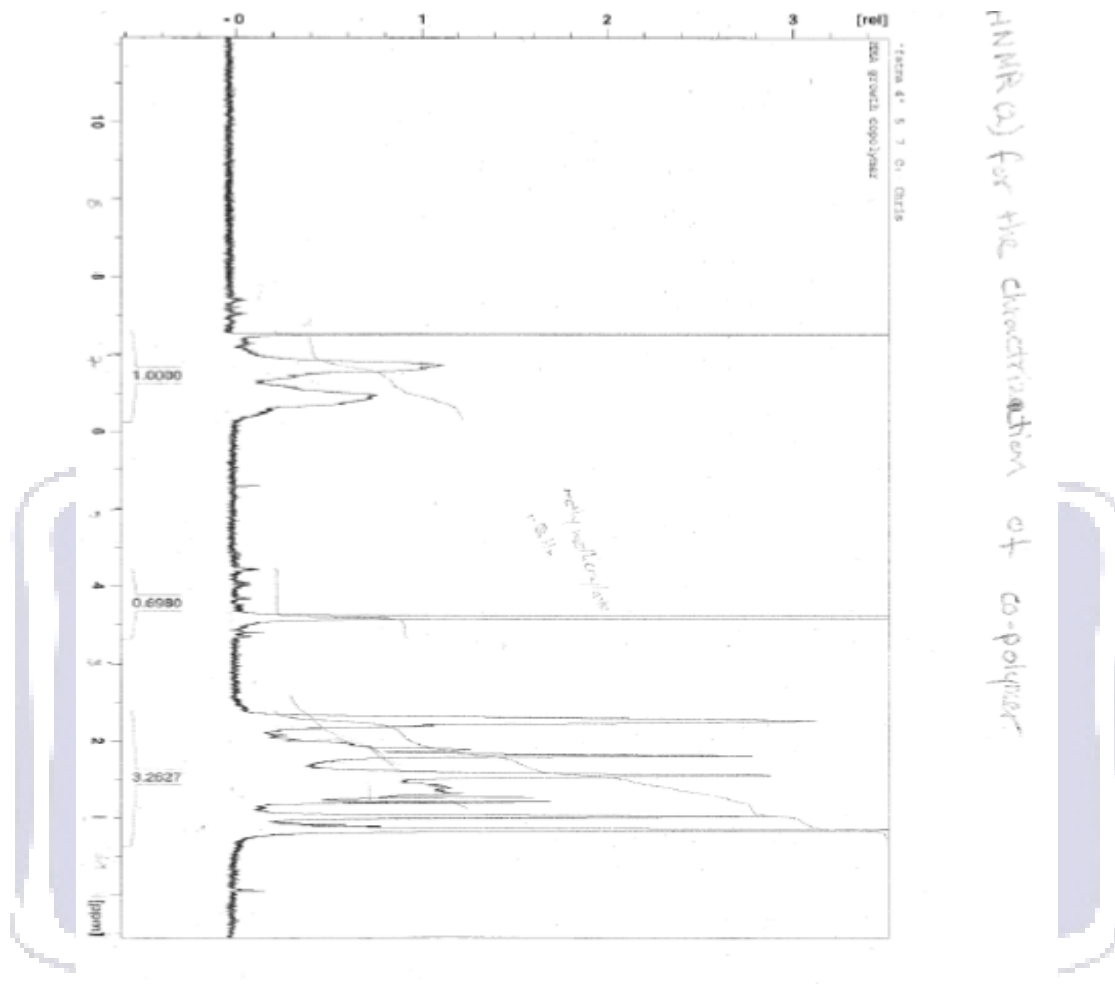


Figure (4): ¹H NMR spectrum of the characterizing of the copolymerization

3.3 The results of kinetic study:

From the kinetic results the kinetic analysis was obtained by plotting the change mass (Δx) of the polymer against time change (Δt). The mass change was calculated by using the following equation:

$$\Delta x = \frac{(\Delta V \times \Delta d)}{\text{total mass of monoer} \times \left(\frac{dP(PMS)}{\Delta d} \right)} \dots\dots\dots (1)$$

(Δd) is density change of PMMA and MMA

$$\begin{aligned} (\Delta d) &= \text{density of PMMA} - \text{density of MMA} \\ &= 1.178 - 0.909 \end{aligned}$$

$$(\text{Total mass of monomers}) = (V \times d) \text{ MMA} + (V \times d) \text{ PMS}$$

The density of PMMA is 1.178 g/cm^3 , density of MMA is 0.909 g/cm^3
density of PMS is 0.897 g/cm^3

$d_p(\text{PMS})$ is the density of PMS and it is 1.04 g/cm^3 . ΔV is volume change in polymer which calculated from the high change and ΔV is volume change of the reaction mixture during the reaction ΔV was calculated from the tube area and the high change of the mixture reaction (Δh).

$$\Delta V = \Delta h \times \text{area}$$

The area of tube was determined by filling the tube with known volume of water and using the tube length.

$$V_{\text{water}} = 32 \text{ g/cm}^3, \text{ tube length} = 66 \text{ cm. Hence the area} = V_{\text{water}} \times (1/\text{tube length})$$

$$\text{Area} = 32 \text{ g/cm}^3 \times (1/66 \text{ cm}) = 0.485 \text{ cm}^2.$$

Figure (5) and (6) show the plot of Δx against Δt of the co-polymerization of p- methyl styrene (PMS) with methyl methacrylate (MMA) with SDS and Span respectively.

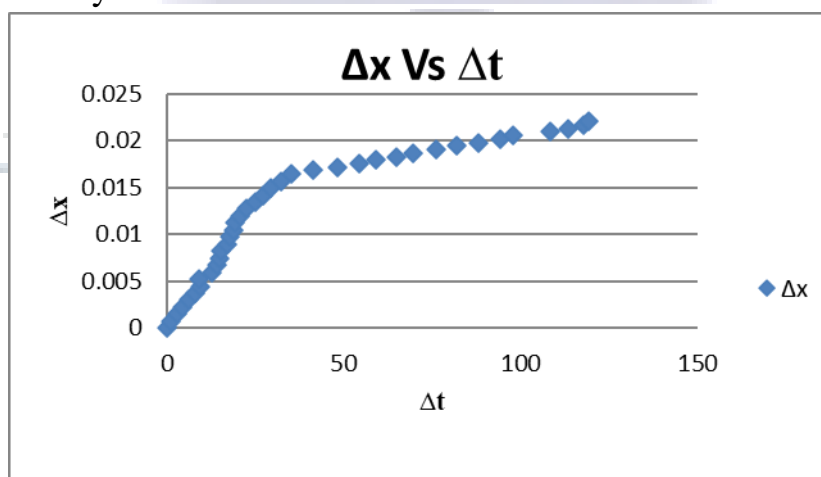


Figure (5): The mass change of the monomer converted into the polymer against time for a MMA seeded emulsion polymerization with PMS and SDS as surfactant.

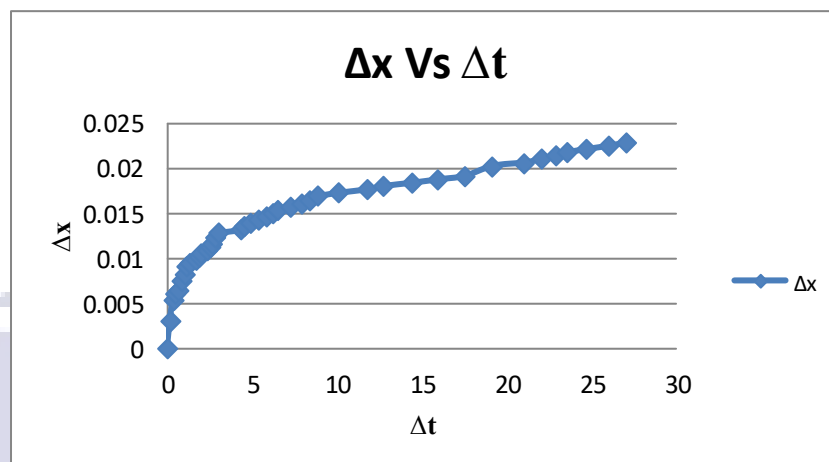


Figure (6): The mass change of the monomer converted into the polymer against time for a MMA seeded emulsion polymerization with PMS and span 80 as surfactant.

3.4 The calculation of percentage of polymer yield that resulted from co-polymerization:

This calculation is obtained from carrying out the gravimetric technique. This technique used to know the conversion /time of the monomer into the polymer. One of the polymers was dried and weighted.

$$\text{Weight of polymer in 1ml} = \frac{\text{mass of MMA} + \text{mass of PMS}}{\text{total volume of the solution}} \times 1\text{ml}$$

Where $V_{\text{MMA}} = 25 \text{ ml}$, $d = 0.909 \text{ g/ml}$ hence $m_{\text{MMA}} = 25 \times 0.909 = 22.43 \text{ g}$
 $V_{\text{PMS}} = 25\text{ml}$, $d = 0.897 \text{ g/ml}$ hence mass = 22.73 g.

1. with SDS, the weight of polymer in 1ml = $(22.43 + 22.73) \times \frac{1ml}{233} = 0.194$

g

The experimental yield = 0.0171 g

$$\text{Therefore, \% yield} = \frac{0.0171}{0.194} \times 100 = 8.81 \%$$

2. with span, the weight of polymer in 1ml = $(22.43 + 22.73) \times \frac{1ml}{253} = 0.178$

g

The experimental yield = 0.039

$$\text{Hence, \% yield} = \frac{0.039}{0.178} \times 100 = 21.91$$

%

It is clear from the graphs (dilatometer study) that the conversion time of monomer into the polymer for a MMA seeded growth with PMS and SDS surfactant is longer than the conversion time of monomer into the polymer for a MMA with PMS and span 80 surfactant. By comparing the dilatometer study and the gravimetric study we found that yield of the polymer formed using span 80 as surfactant is much more than the yield of the polymer formed with SDS, it is very agreed with the Δx against time whereas, the yield with the SDS is not agreed with the Δx against time which is acceptable according to the inaccuracy gravimetric.

The differences between the ionic surfactant and non-ionic surfactant that during the particles nucleation the ionic surfactant especially SDS are more efficient than non-ionic surfactant and more better colloidal stabilizer in the first stage of particles growth

The suggestion mechanism of the MMA seed growth in emulsion polymerization (Greenwood & Luckham, 1998)[7]. According to some studies which indicated that the first stage and the nucleation step based on the interactions between the monomers and the surfactants (Ozdeger & Sudol, 1997)[8]. in the non ionic surfactants which are soluble in the

monomer droplet or in the particles the interactions between the monomers and surfactant are more remarkable. Therefore, the concentration of surfactant will decrease in water at the early stage of polymerization and in case the concentration above CMC (critical micelle Concentrations), the micellization will avoid.

4. Conclusion

This study sought to investigate the two stage of the seeded emulsion polymerization. This involved the use of the process to synthesize PMMA – PPMS polymer composite particles plus the presence of surfactants. The kinetic study was conducted in the seeded growth polymerization using SDS and span 80 as surfactants.

It is hoped that the results obtained for the kinetic study of PMMA seeded emulsion with PMS using SDS and span 80 as surfactants will consider and continue in the future studies to find out the mechanism of this polymerization with ionic and non ionic surfactants.

4. References

1. Liu, K. Nie, Z., Zhao, N., Li., W., Rubinstein, M. and Kumacheva, E. (2010). Step-growth polymerisation of inorganic nonoparticles. *Science*, 329 (5988), pp. 197-200.
2. Chern, C.-S. (2008). Principles and applications of emulsion polymerization. Chicester: John Wiley & Sons, Inc.
3. Motokawa, R., Taniguchi, T., Sasaki, Y., Enomoto, Y., Murakami, F., Kasuya, M., Kohri, M. and Nakahira, T. (2012). Small-angle neutron scattering study on specific polymerisation loci induced by copolymerisation of polymerizable surfactant and styrene during miniemulsion polymerisation. *Macromolecules*, 45(23), 9435-9444.
4. Gilbert, R.G. (1995). *Emulsion Polymerisation*. Academic Press, Sydney.

5. Mekki, S., Saidi-Besbes, Elaissari, A., Valour, J.P. And Derdour, A. (2010). Synthesis of new anionic and cationic polymerizable surfactants for emulsion polymerisation of styrene. Macromolecular Symposia, 296(1), 100-106.
6. Litt, M., Patsiga, R., & Stannett, V. (1970). Emulsion polymerization of vinyl acetate. II. Journal of Polymer Science Part A-1: Polymer Chemistry, 8(12), 3607-3649. doi: 10.1002/pol.1970.150081221
7. Greenwood, R.; Luckham, P.F.; Gregory, T. colloid surf, A: physicochem Eng A spectr 1998, 144,139.
8. Ozdeger, E.; Sudol, E. D.; El-Aasser, M.S.; Klein, A. J Polym Sci, Part A: Polym Chem 1997, 35, 3827.

