

Controlled Particle Size of Miniemulsion Polymerization in Presence of Different Hydrophobic Agents

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Abstract : Polystyrene (PS) within a size range of 82–132 nm was successfully synthesized by miniemulsion polymerization, where the particle size responded to the nature and amount of the added hydrophobes. Three different types of hydrophobes (hexadecane, polycarbonate and Jaffamine M-600) were chosen in this study and each resulted in a different emulsification behavior than PS alone. The hydrophobic agents were mainly chosen due to their limited water solubility. The chosen sonication time for emulsion and hydrophobes were sufficient to mini-emulsify droplets and to polymerize them to PS. Scanning electron and transmission electron microscopy were used to study the morphology of the produced PSS. Thermogravimetric analysis revealed polymer stability was improved as a result of incorporation of hexadecane, polycarbonate and Jaffamine M-600 as hydrophobes. Unimodal particles of PS were prepared as resins, which would be convenient products for many industrials especially as packaging materials.

Keywords: nanoparticle size; miniemulsion; hydrophobe agent.

1- Introduction

PS is a plastic material used in thousands of remarkably tough, flexible, and lightweight products and applications, including food containers, packaging materials, cars, boats and computer parts¹. PS is inert and has no smell of styrene; therefore, PS is usually used in applications where hygiene is important, such as health care and food packaging products.

Miniemulsion is an important class of emulsions that are stabilized against coalescence using surface active agents and the effect of Ostwald ripening. Miniemulsion polymerization has recently grown from its initial reporting to being the focus of much industrial and academic research². This technique of polymerization is usually produced by high-power homogenization and yields stable droplets with a narrow size distribution range of 50 to 500 nm.

The polymerization system for the preparation of polymer latex is usually consists of five principle components including, monomer, initiator, a hydrophobic agent, aqueous phase and surfactant. The miniemulsion polymerization conserves many advantages of traditional emulsion polymerization, where it allows us to use the same monomer and reactor systems, while overcoming some of its limitations and opening the door to novel applications^{3,4,5}. The main difference between traditional emulsion and miniemulsion polymerization is the particle creation mechanism.

Through miniemulsion polymerization processes the droplets are formed by imposing high energy (stirring, homogenized or sonification) on a mixture of all reactants before the start of reaction⁴. When

miniemulsion process is done correctly, the droplets will be small enough to successfully capture free radicals generated in the aqueous phase and will behave as small individual reactors; ideally becoming particles. The first essential step in miniemulsion Polymerization is therefore the emulsification of the monomer and aqueous phases using some type of high sonifier amplitude in order to break up the monomer phase in to nano-droplets, and reach average droplet diameters on the order of 50–150 nm.

What is more, Homogenization of the emulsions to miniemulsions is an important step which performed using different methods. In many articles stirring was employed by an ultra-turrax and homogenizer. However, the shear attained by these techniques is not sufficient in order to get small and homogeneously distributed droplet^{6,7,8}. Meanwhile, homogenization process was recently performed using sonication for the in miniemulsions and it achieved an outstanding stability of the prepared miniemulsion^{9,10}.

It was found that hydrophobe is very important for stabilization of mini-droplets which decrease Ostwald ripening³. By using a sufficient amount of hydrophobe and applying an efficient homogenization process, it is possible to prepare to a miniemulsion of extra stability^{11,12,13}. Additionally, an important factor to prepare stable miniemulsions is the choice of the appropriate surfactant and co-surfactant. These additives are further lowering the interfacial energy, but cannot form micelles aggregates itself^{14,15}.

After that, stabilized of nano-size droplet during polymerization is a vital role to reach narrow distribution index for prepared polymer latex. Hydrophobic agents (hexadecane, polycarbonate and Jaffamine M-600) were played this role to established stable nano-reactor through miniemulsion polymerization technique. Synthesis of nano-size polystyrene particles is successfully working up as one of the most abundant polymer in packaging materials manufacture and applications. Uni-model particle sizes of polymer enhanced manufacture processing with narrow melting range and avoid migration of low molecular weight from plastic packaging materials to packed items. Economic and healthy advantage can be clearly reflected from control of defined polymers as modified packaging materials.

2- Experimental

2.1. Materials and Chemicals

Styrene (98 %, Aldrich) was purified twice with sodium hydroxide treatment and distilled over CaH₂ freshly before used. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Aldrich), methanol, sodium hydroxide, calcium hydride and sodium n-dodecyl sulfate (SDS) were used without further purification. Hydroquinone (HQ, Fluka), methanol (99.99%, Aldrich), hexane ($\geq 99\%$, MERCK), hexadecane (HD, >98%, Fluka) and O-(2-Aminopropyl)-O'-(2-methoxyethyl) polypropylene glycol (Jaffamine M-600, Aldrich) were used as received.

2.2. Synthesis of polystyrene through miniemulsion polymerization

In three necks double jacket reactor (250 ml) 14.3 g of styrene and 757 mg hydrophobe (hexadecane (HD), polycarbonate (PC) and Jaffamine) were mixed and added to a solution of 142.6 mg Jaffamine M-600 in 67.28 g of water. The mixture was degassed (vac/N₂, followed by stirring 30 min under N₂ at 100 min⁻¹). The mixture was stirred for 1 h at 800 min⁻¹. After that, miniemulsion was prepared by ultra-sonication for 11 minute (Amp. 90%) with an ultrasonic disintegrator Branson 450W. A slight stream of nitrogen was applied and the emulsion was cooled with ice water. The formed miniemulsion was transferred to the reaction vessel. After short degassing, the temperature was raised to 72 °C. After reaching T, an aqueous solution of initiator (460 mg AIBN in 7.1 g water, degassed under N₂ for 30 min) was added. The polymerization reaction was performed at 800 rpm for 4 h. Then the reaction mixture was cooled up to 25 °C. The reaction vessel immersed in ice bath to decrease the temperature until room temperature. 5 ml of product uptake for particle size measurements. 40 g of the dispersion were precipitated in 300 mL MeOH (1 wt% HQ).

Table 1. Experimental recipes of miniemulsion polymerization of styrene in presence and absence of different hydrophobe agents.

Exp.	Hydrophobe	Temp., °C	Time, hrs	M/I, mole	Hydrophobe, Mole % *	Sonication %/time, min.
RM-2	-----	72	2	50.45	-----	-----
RM-22	Hexadecane	72	2	50.45	4.46	90/11
RM-24	Hexadecane	72	4	43.15	8.71	90/11
RM-25	Hexadecane	72	6	35.22	13.22	90/11
RM-32	polycarbonate	72	2	50.45	4.46	90/11
RM-33	polycarbonate	72	4	43.15	8.71	90/11
RM-34	polycarbonate	72	6	35.22	13.22	90/11
RM-46	Jaffamine M-600	72	2	50.45	4.46	90/11
RM-47	Jaffamine M-600	72	4	43.15	8.71	90/11
RM-48	Jaffamine M-600	72	6	35.22	13.22	90/11

*Mole percentage was calculated related to surfactant concentration.

2.3. Sample Preparation for DLS:

250 mg of latex was added to 20g Millipore water (containing 0.1 wt% SDS and 0.1 wt% HQ) the mixture is stirred for 30 minutes at room temperature.

2.4. Measurements and Analysis

2.4.1. Dynamic Light Scattering (DLS):

Nano-ZS(Malvern Co., UK) with measurement range 0.3 nm – 10.0 microns (diameter), Light source He-Ne laser 633nm, Max 5mW and minimum sample volume 12 µL was used to measure the particle size of prepared latex.

2.4.2. Size Exclusion Chromatography (SEC)

Molar masses were measured by SEC Agilent Series 1100, CHCl₃; 1 mL/min, RI detector, columns PL-MIXED-B-LS (300x7.5 mm) and 10mm PS-gel (Agilent Co., USA).

2.4.4. TGA

Pyris 1 TGA PerkinElmer Instruments, USA is a vertical design with a high sensitivity balance and quick response furnace. Measurements were performed at a heating rate of ± 5 °C/minute under nitrogen with temperature range from room temperature to 800 °C. The instrument was calibrated with Curie-point-standard (nickel and iron alloy).

2.4.5. SEM

SEM Ultra 55 plus (Zeiss Co., Germany) was used. the thinned dispersions from the DLS measurements were used to prepare the samples on C-pads, air dried and sputtered with 3 nm Pt. Alternatively, the powder of dried precipitated samples was applied on C-pads and sputtered with 3 nm Pt was used.

2.4.6. TEM measurement

The inspection of polymer matrix particles (polystyrene) was carried out using transmission electron microscope. The examination was carried out for very dilute suspension of the corresponding polymer latex in distilled water using TEM photographs of Jeol JEM- 1230 Type and an acceleration voltage of 80 Kv. The microscopy probes of the polymer particle samples were prepared by adding a small drop of the distilled water dispersions onto a Lacey carbon film-coated copper grid and allowed to dry in air.

3. Results And Discussion

Table 2. Molar ratios and particle size of polystyrene prepared in presence and absence of different hydrophobe agents.

Exp.	Hydrophobe Agent	Mn g/mol	Mw g/mol	PDI	M/I, mole	hydrophobe Mole % *	Particles size, nm
RM-2	-----	25000	205500	8.22	50.45	-----	150
RM-22	Hexadecane	30600	295400	6.35	50.45	4.46	119
RM-24	Hexadecane	38000	216600	5.70	43.15	8.71	112
RM-25	Hexadecane	44100	206400	4.68	35.22	13.22	110
RM-32	Polycarbonate	21800	213600	4.80	50.45	4.46	89
RM-33	Polycarbonate	22700	232400	3.24	43.42	8.71	85
RM-34	Polycarbonate	31500	257700	2.99	35.14	13.22	82
RM-46	Jaffamine M-600	23600	54300	2.32	50.45	4.46	132
RM-47	Jaffamine M-600	32400	68000	2.11	42.87	8.71	127
RM-48	Jaffamine M-600	37300	67200	1.84	35.01	13.22	118

Number average molecular weight, Mn & weight average molecular weight, Mw & polydispersity index, PDI & monomer/initiator ratio, M/I.

Table 2 shows the particle size distributions of PS latex in presence and absence of nominated different hydrophobe agents (polycarbonate, hexadecane and Jaffamine M-600). Narrow distributions of prepared polymer are exhibited in this table which reflects the uni-modal distribution of the particles. As previously mentioned, the importance of hydrophobe is the stabilization of mini-droplets. Moreover, as it is shown in Table 2 the polydispersity of the prepared miniemulsion was decreased by increasing the amount of hydrophobe.

Furthermore, Table 2 summarizes the results of size exclusion chromatography. Mn, Mw and PDI results were determined for characterization of polystyrene in presence and absence of (hexadecane, polycarbonate and Jaffamine M-600) as hydrophobes. These results revels that the increase in monomer to initiator ratio (M/I) results in a decrease in Mn and increase in Mw and consequently PDI was increased.

Furthermore as size exclusion chromatography, it was expected and previously mentioned, for all of the chosen hydrophobes, as the hydrophobe percentage increased the size of polystyrene particle decreased. It is a result of the low water solubility of the three types of the hydrophobes which are able to prevent any monomer from diffusing through the aqueous phase. Moreover, the average particle size of miniemulsion prepared by HD was 113 nm, 85 nm for that prepared by PC and 126 nm for what prepared by JFM-600. This reflects that the most stabilized polystyrene particles were performed in presence of polycarbonate.

3.1. Dynamic Light Scattering (DLS):

Miniemulsion is an excellent appropriate technique to prepare polymer nanoparticles. It can be stabilized through the addition of a hydrophobe which increase dispersion stability by inhibiting Ostwald ripening³. This is can be clarified by results that obtained by dynamic light scattering as shown in figure 1.

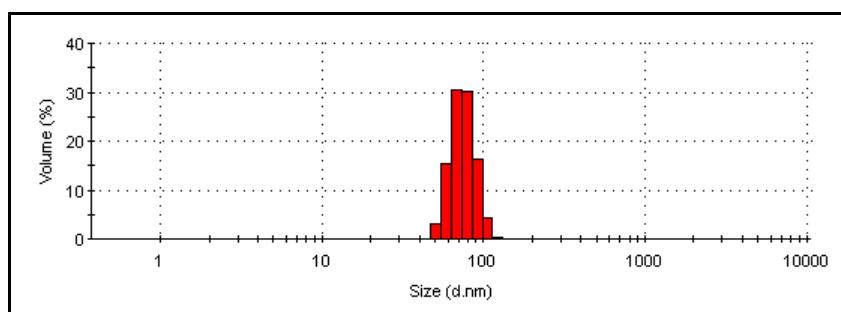


Figure1. Dynamic light scattering of particle size distribution of polystyrene using polycarbonate as a hydrophobe.

Low water solubility of the used types of hydrophobes was able to prevent it from diffusing through the aqueous phase. Therefore, it was minimized the system's free energy by keeping the hydrophobe around the droplet with save distance depending on chain length of hydrophobes. As a subsequently, particles distribution of PS latex obtained by polycarbonate as a hydrophobe was the lowest size and consequently it is of the highest stability (as illustrated in table 2), so the DLS study was performed by polycarbonate. It mainly related to the decrease in system's free energy and its power which counteracts the Laplace pressure of the emulsion droplets that maintain a narrow particles distribution. Furthermore, the particles narrow distribution in polymer layer enhances their applications in complete coating of packaging and biomedical applications. These results are coincident with the fact that the hydrophobe effectiveness increases as water solubility decreases in the continuous phase³¹.

3.2. Thermogravimetric analysis (TGA):

The thermogravimetric analysis curves of polystyrene in absence and presence of different hydrophobic agents are shown in Figure 2. The polymer stability was fairly improved as a result of incorporation of hexadecane, polycarbonate and Jaffamine M-600 as hydrophobes. The order of this improvement was the best for polycarbonate then Jaffamine M-600 and finally was by hexadecane. Therefore, it is clear that the preparation of polystyrene in presence of all types of hydrophobes strengthen the PS chain to avoid heat degradation especially using polycarbonate as a hydrophobe.

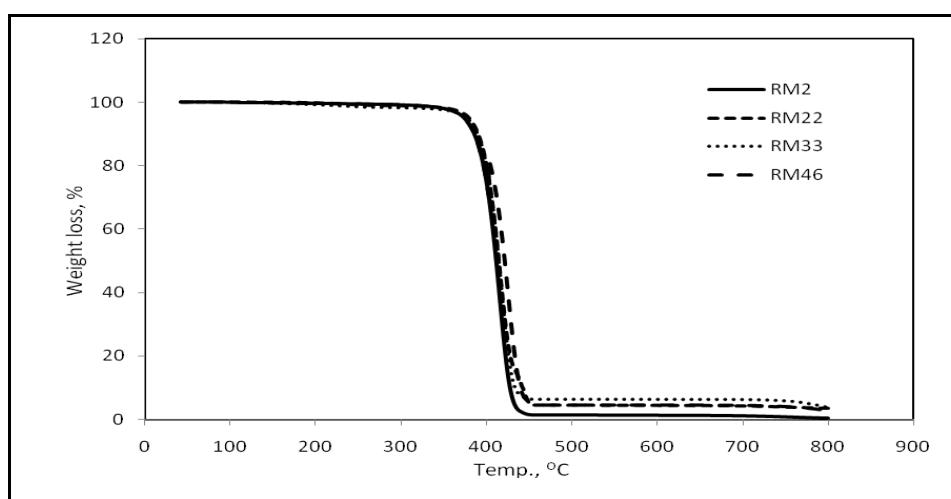


Figure 2. Thermograph of PS in absence and presence of different types of hydrophobe agents.

3.3. Scanning Electron Microscope (SEM):

The Scanning Electron Microscopic micrograph of the prepared polystyrene (using polycarbonate as a hydrophobe, as it was the best hydrophobe) miniemulsion particles is given in figure 3.

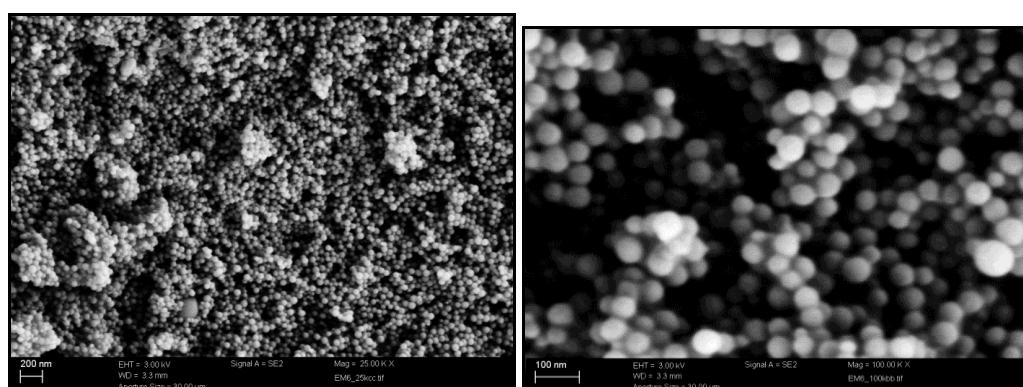


Figure 3. Electron scanning micrographs of polystyrene using polycarbonate as a hydrophobe.

It was in two different magnifications with a very dense layer of polystyrene chains. The figure illustrates that the particles are uni-modal dispersed and particles' surface is smooth. The average diameter of polystyrene particles is less than 100 nm which support our claim of the extra stability of polystyrene using polycarbonate as a hydrophobe agent.

3.4. Transmission electron (TEM):

Transmission electron microscopy was used for further morphological investigation of the prepared polystyrene (using polycarbonate as a hydrophobe) miniemulsion particles. As it is shown on figure 4, the calculated average diameter of polystyrene particles is less than 53 nm as shown on the figure. Moreover, the figure illustrates that the nature of the prepared polystyrene particles is spherical.

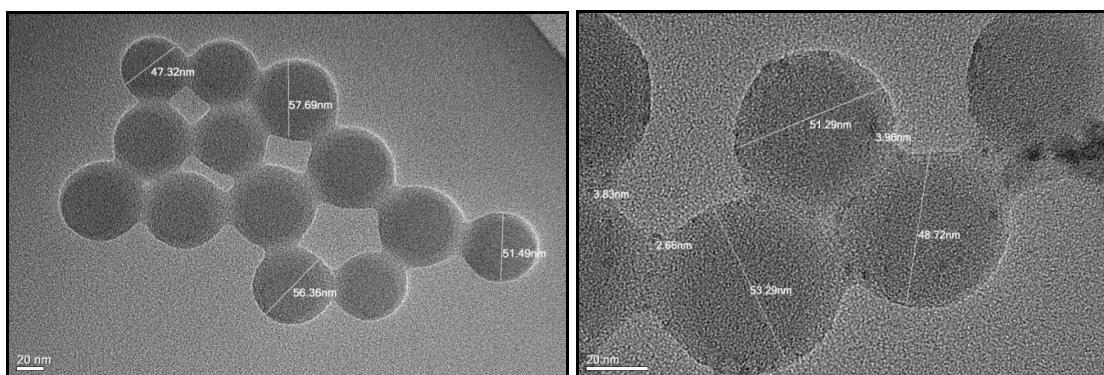


Figure 4. Transmission electron micrographs (TEM) of polystyrene using polycarbonate as a hydrophobe.

Conclusion

Polystyrene was successfully prepared by miniemulsion polymerization using three different hydrophobes (hexadecane, polycarbonate and Jaffamine M-600). All of the chosen hydrophobes were successfully decrease the polydispersity index of polystyrene. The polystyrene that prepared using Jaffamine M-600 has the lowest polydispersity index and increased the polystyrene chains heat resistance against degradation. The polystyrene that prepared in presence of polycarbonate has the lowest Ostwald ripening.

References

1. Ashby M., Shercliff H. and David C., Materials: engineering, science, processing and design, Oxford : Butterworth-Heinemann, 3rd Edition 2014.
2. Crespy D. And Landfester K., Miniemulsion polymerization as a versatile tool for the synthesis of functionalized polymers. Beilstein J Org Chem 2010, 6, 1132–48.
3. Landfester K., Polyreactions in miniemulsions, Macromol. Rapid Commun., 2001, 22 (12), 896-936.
4. AntoniettiM. and LandfesterK., Polyreactions in miniemulsions Prog. Polym. Sci., 2002, 27 (4), 689-757.
5. Landfester K., Montenegro R., Scherf U., GüNTNER R., Asawapirom U., Semiconducting polymer nanospheres in aqueous dispersion prepared by a miniemulsion process, Advanced Materials, 2002, 14 (9), 651-655 .
6. Abismail B., Canselier J. P., Wilhelm A. M., Delmas H., Gourdon C., Emulsification by ultrasound: drop size distribution and stability. Ultrason. Sonochem., 1999, 6, 75–83.
7. Walstra P., Chem. Eng. Sci. 1993, 48, 333–349.
8. Friberg S. E., Jones S., in: Kirk-Othmer Encyclopedia of Chemical Technology, 4 ed., Kroschwitz J. I., Ed., Wiley, New York 1994, Vol. 9, pp. 393–413.
9. Durbin D. P., El-Aasser M. S., Poehlein G. W., Vanderhoff J. W., Influence of Monomer Pre emulsification on Formation of Particles from Monomer Drop in Emulsion Polymerization, J. Appl. Polym. Sci. 1979, 24, 703–707.

10. Chou Y. J., El-Aasser M. S., Vanderhoff J. W., mechanism of emulsification of styrene using hexadecyltrimethylammonium bromide-cetyl alcohol mixtures, *j. Dispers. Sci. Technol.* 1980, 1, 129–150.
11. Landfester K., Bechthold N., Tiarks F., Antonietti M., Formulation and stability mechanisms of polymerizable miniemulsions, *Macromolecules*, 1999, 32 (16), 5222-5228.
12. Miller C. M., Sudol E. D., Silebi C. A., El-Aasser M. S. J., Miniemulsion polymerization of styrene: Evolution of the particle size distribution, *Polym. Sci., Polym. Chem. Ed.* 1995, 33, 1391.
13. Aizpurua I., Amalvy J., BarandiaranM.j., Influence of the polymeric hydrophobe on the kinetics of vinyl acetate miniemulsion polymerization, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2000, 166, 59–66.
14. Attwood D., Florence A. T., “Surfactant Systems - Their chemistry, pharmacy and biology”, Chapman and Hall, London 2012.
15. Ruckenstein E., Krishnan R., Effect of electrolytes and mixtures of surfactants on the oil-water interfacial tension and their role in formation of microemulsions, *J. Colloid Interface Sci.*, 1980, 76, 201–211.
