Conversion of expanded polystyrene waste to nanoparticles via nanoprecipitation

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ABSTRACT: The conversion of polymeric waste into useful, value added material is considered as an efficient method for polymeric waste management because of the environmental issues caused by such materials. This work proposes a simple, cost-effective strategy for the conversion of expanded polystyrene waste into polystyrene nanoparticles via nanoprecipitation. In this method, expanded polystyrene is dissolved in a suitable solvent for example, tetrahydrofuran and added to a nonsolvent, such as water, to precipitate polystyrene nanoparticles of diameter less than 500 nm. The study also investigates the influence of various process parameters such as, initial concentration of expanded polystyrene, the speed of stirring, the solvent to water volume ratio and the solvent type used for nanoprecipitation, on the size and polydispersity of the precipitated PS nanoparticles. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 42904.

INTRODUCTION

The expanded polystyrene (EPS) obtained from polystyrene (PS) of molecular weight between 160,000 and 260,000 is extensively used as packing and insulating material. EPS is essentially light-weight foam containing about 2% PS and 98% air. It is typically obtained from solid beads of PS by using small amounts of blowing agent such as butane or pentane during processing.[1,2] The large volume to weight ratio of the order of 30–50 makes EPS waste economically nonviable for recycling and it usually ends up in landfill or incineration.[2,3] The conversion of EPS waste has become an attractive strategy in the recent years to reduce the environmental issues caused by such materials. A number of useful materials have been produced by the conversion of waste EPS into such as, PS nanofibers, effective polyelectrolytes, and ion exchange membranes via chemical modification for the treatment of industrial waste water etc.[2,4,5]

In the present work, we show that EPS waste can be used for the synthesis of PS nanoparticles via nanoprecipitation. In this technique, EPS is dissolved in a suitable solvent, such as tetrahydrofuran (THF) and added to water (a nonsolvent for PS) with continuous stirring, to precipitate PS nanoparticles. This will cause supersaturation of PS macromolecules and thereby, nucleation and further growth of PS nanoparticles occurred.[6–9] The precipitated nanoparticles were then characterized extensively to measure the thermal and physico-chemical properties of the nanoparticles. The important process parameters influencing the size and polydispersity of the precipitated nanoparticles were studied by means of scanning electron microscopy (SEM) and dynamic light scattering (DLS). The production of polymeric nanoparticles, with no residual contaminants, finds immense application for targeted drug delivery, fluorescence imaging etc., where a proper control of size and morphology of the polymer nanoparticle is important.[10–13]

MATERIALS AND METHODS

Materials

EPS waste for the nanoprecipitation was obtained from a packing material and the solvents—THF (AR grade, Rankem), 1, 4-dioxane (AR grade, Fisher Scientific) and acetone (AR grade, Rankem) were used for nanoprecipitation process. Also deionized (Milli-Q) water (18.2 MΩ.cm) was used for all experiments as the aqueous medium.

Synthesis of PS Particles from EPS Waste

EPS sample used for nanoprecipitation was annealed at 150°C for 12 hours in a hot air oven to remove volatile matters, if any.

Supporting Information Figure S1(a,b) show respectively, the EPS sample before annealing and the dense mass formed after annealing. These images clearly demonstrate the shrinking of the EPS sample because of the removal of air and other volatile matter. Then the annealed EPS sample was dissolved in THF using a magnetic stirrer at room temperature to get a clear solution as shown in Supporting Information Figure S1(c). The solvents used for dissolving EPS were completely miscible with water, under experimental conditions. Supporting Information Figure S1(d) represents a schematic of the experimental setup of the nanoprecipitation process for the precipitation of PS nanoparticles. In a typical experiment, 0.5 mL of the solution of EPS sample in THF, having a concentration of 2 mg/mL was added from a burette gradually (at a flow rate of approximately 1 mL/min) into a glass vial containing 10 mL of Milli-Q water which was continuously stirred using a magnetic stirrer at 500 rpm. As shown in Supporting Information Figure S1(e), water in the glass vial instantaneously turned turbid, indicating the formation of PS nanoparticles. The stirring was continued for about 15 minutes to ensure the completion of the process. The suspension containing THF, water, and the precipitated PS nanoparticles was kept at 50°C for about 12 hours to evaporate THF. The particles were separated by repeated centrifugation and re-dispersion in Milli-Q water.

Characterization of PS Nanoparticles

The thermal and physico-chemical properties of the precipitated PS nanoparticles were characterized by means of various techniques like Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and solution densitometry. FTIR spectrum of the synthesized nanoparticles was recorded in the solid form as a KBr pellet, in the standard wavenumber range of 400–4000 cm^{-1} using JASCO FTIR-4100 instrument. The ^{1}H NMR spectrum was recorded on Bruker 400 spectrometer at 400 MHz using deuterated chloroform (CDCl$_3$) as solvent. The thermal properties of the synthesized PS nanoparticles were characterized using DSC and TGA. DSC (Q 2000, TA Instruments) measurements of the nanoparticles were carried out in a temperature range of 25–250°C with a heating rate of 10°C/min. Thermogravimetric analysis (TGA) of the PS nanoparticles was carried out (SDT Q600, TA instruments) in the temperature range of 25–800°C at a ramp heating rate of 10°C/min in a nitrogen atmosphere.

To confirm the formation of PS particles upon nanoprecipitation, about 10 μL of the final suspension was taken on a glass substrate, and the sample upon the evaporation of water was imaged by scanning electron microscopy (S-4800 FE-SEM, Hitachi, Japan) at an accelerating voltage of 5 kV. The sample was sputter coated with gold for 60 seconds prior to SEM imaging.

The size and polydispersity of the PS nanoparticles were obtained using the dynamic light scattering (SZ – 100, Horiba, Japan) at a scattering angle of 90°. The measurements were performed at 25°C, after adequate dilution of each sample with Milli-Q water to avoid multiple scattering from the sample. The field autocorrelation function, $g^{(1)}(t)$ was recorded for a duration of 60 s for each sample. For a monodispersed sample, the correlation function decays exponentially as a single exponential function:

$$g^{(1)}(t) = \exp(-\Gamma t) \tag{1}$$

where $\Gamma = Dq^2$.[14,15] In this relationship, q is the scattering vector

$$q = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \tag{2}$$

where n is the refractive index of the medium, λ is the wavelength of laser, and θ is the scattering angle.[14,15]

In the equation for Γ, D represents the translational diffusion coefficient, which can be used to determine the hydrodynamic radius, R_h of the particles from Stokes–Einstein relationship,

$$D = \frac{k_B T}{6\pi \eta R_h} \tag{3}$$

where k_B is Boltzmann's constant, T is the temperature, and η is the viscosity of the suspending medium.[16]

Because of inherent polydispersity of the particles obtained through nanoprecipitation technique, the decay of $g^{(1)}(t)$ represented as an integral over a distribution of decay rates as[14–17]

$$g^{(1)}(t) = \int_0^\infty G(\Gamma)\exp(-\Gamma t)d\Gamma \tag{4}$$

This eq. (4), when expanded around a mean value, $\overline{\Gamma}$ and after neglecting the higher order terms can be expressed as a quadratic equation in time, t as

$$\ln(g^{(1)}(t)) = \ln B - \overline{\Gamma} t + \frac{\mu_2 t^2}{2} \tag{5}$$

where B represents the baseline, $\overline{\Gamma}$ is the mean and μ_2 is the variance.[15] The ratio, $\mu_2/\overline{\Gamma}^2$ is a measure of the polydispersity of the sample and it is usually denoted as polydispersity index (PDI).[15] According to eq. (5), by using a quadratic fit for $\ln[g^{(1)}(t)]$ vs. delay time data, the mean and variance can be obtained. Since $\overline{\Gamma} = \overline{D}q^2$, the average diffusion coefficient, $\overline{D}$ can be determined, this can in turn be used to find the mean hydraulic radius of the particles, $\overline{R_h}$ using the Stokes–Einstein relationship.[15]

RESULTS AND DISCUSSION

As discussed earlier, because of the complete miscibility of THF–water system under experimental condition, phase separation occurs, causing instantaneous generation of polymer nuclei beyond a critical nucleation concentration.[6] These nuclei grow further either by the diffusion of PS molecules from the bulk to the nuclei already formed or by the aggregation of nuclei, in case of diffusion limited system.[7–9] Thus the process of nanoprecipitation leads to the formation of polymer nanoparticles without the aid of any other additives.

The precipitated PS particles were extensively characterized using various techniques like FTIR, NMR, DSC, TGA, and solution densitometry. The spectra obtained from FTIR and NMR shows the characteristic peaks of PS (Supporting Information, Figures S2 and S3) with no residual contaminants. The DSC
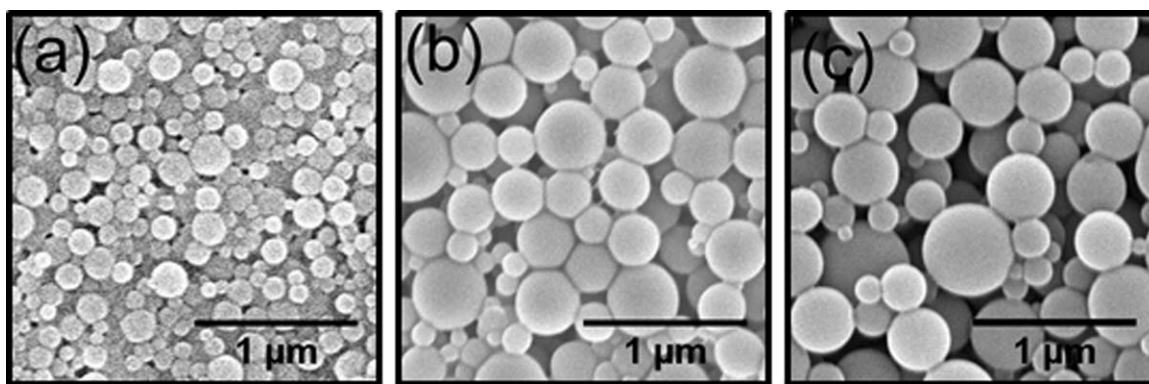
Figure 1. Representative SEM images of PS nanoparticles prepared from EPS concentrations of (a) 0.5 mg/mL, (b) 4 mg/mL, and (c) 8 mg/mL, keeping a constant stirring speed of 500 rpm and by adding 0.5 mL of the solutions into 10 mL Milli-Q water. The corresponding polydispersity index and size of the particles were presented in Table I.

Table I. Effect of Process Parameters on the Size and Polydispersity of the PS Nanoparticles

Solvent used	Initial concentration of EPS (mg/mL)	RPM	Solvent : water	Dia_{mean} (nm)	Mean PDI
THF	0.5	500	0.5 : 10	218	0.18
THF	4	500	0.5 : 10	389	0.25
THF	8	500	0.5 : 10	456	0.35
THF	2	100	0.5 : 10	451	0.45
THF	2	500	0.5 : 10	265	0.25
THF	2	1000	0.5 : 10	206	0.2
THF	8	500	0.5 : 5	Multiple peaks[a]	
THF	8	500	0.5 : 2.5	Multiple peaks[a]	
Acetone	0.5	500	0.5 : 10	117	0.095
1, 4- Dioxane	0.5	500	0.5 : 10	205	0.24

The mean size and polydispersity are calculated based on the method of cumulants analysis. Further details of the analysis and the autocorrelation functions are provided in the supporting information.
[a] The corresponding SEM images and size distribution curves obtained from DLS measurement are shown in Figure 2.

and TGA thermograms and solution densitometry also confirm the characteristic glass transition temperature, degradation temperature and density of PS (Supporting information, Figures S4 and S5).

Effect of Process Parameters on the Size and Polydispersity of PS Nanoparticles

The dependency of size and polydispersity of the PS nanoparticles on the process parameters such as, initial concentration of EPS,
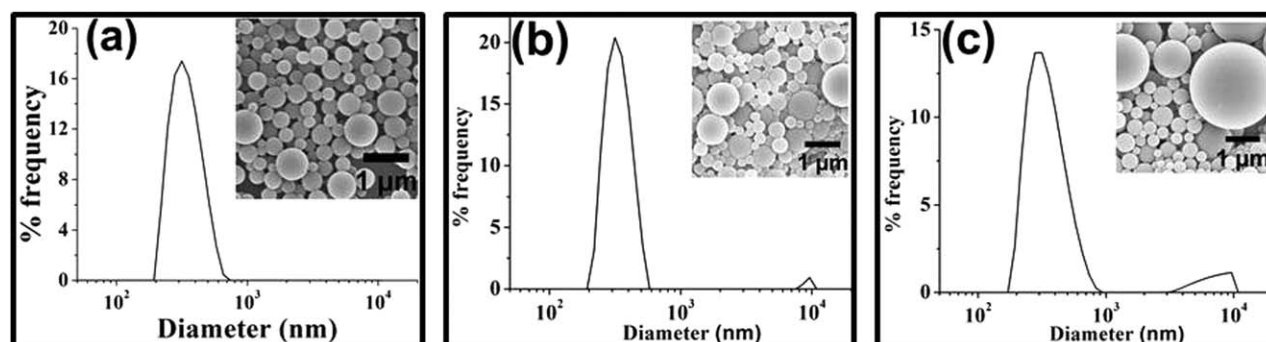

Figure 2. Particle size distribution curves obtained from DLS for the PS particles prepared via nanoprecipitation by adding 1 mL of EPS solution having concentration 8 mg/mL in THF added to (a) 10 mL Milli-Q water, (b) 5 mL Milli-Q water, and (c) 2.5 mL Milli-Q water, at a stirring speed of 500 rpm, showing the formation of microparticles along with nanoparticles with the decrease in the volume of aqueous phase. The insets are the respective SEM images of the particles.

Table II. The Hansen Total Solubility Parameter and Solvent–Water Interaction Parameter Values of Water, PS and the Solvents Used for the Nanoprecipitation of PS Nanoparticles

Parameter	Acetone	1,4-dioxane	THF	water	PS
δ_t, (MPa$^{1/2}$)	19.9	20.5	19.4	47.8	19.07
$\chi_{solvent-water} = \frac{V_{solvent}}{RT}(\delta_{solvent} - \delta_{water})^2$	23.23	25.77	26.58	-	-

δ_t is the Hansen total solubility parameter. $\chi_{solvent-water}$ is the solvent–water interaction parameter calculated using the total solubility parameter values of solvent($\delta_{solvent}$) and water (δ_{water}), molar volume of solvent ($V_{solvent}$), universal gas constant (R) and temperature (T).[19]

stirring speed, solvent to water volume ratio, and nature of solvent were investigated. The effect of concentration of EPS on the nanoprecipitation process was investigated by varying the concentrations from 0.5 to 10 mg/mL. Figure 1(a–c) show representative SEM images of PS nanoparticles precipitated with EPS of 0.5, 4, and 8 mg/mL concentration at a constant stirring speed of 500 rpm. Because of the polydispersity of the particles, the mean size and polydispersity were calculated by the method of cumulants[14–17] of the autocorrelation data obtained from DLS measurement (Supporting information, Figure S6) and the corresponding values are enlisted in Table I. These values, in agreement with the SEM images, exhibited an increase in size and polydispersity with increase in initial concentration of EPS. At a higher polymer concentration, the large number of nuclei generated can grow by aggregation of polymer nuclei. The increased viscosity of the liquid medium and enhanced mass transfer resistance will lead to the formation of the larger nanoparticles by the mechanism of diffusion limited aggregation.[8,9,18–20] Hence these results show the possibility of generation of fairly monodispersed particles when a lower concentration of polymeric precursor is used for the nanoprecipitation process.

The influence of stirring speed on the size of the PS nanoparticles was examined by conducting the nanoprecipitation process at various stirring speeds—100, 500, and 1000 rpm, using an EPS concentration of 2 mg/mL. From the SEM images and DLS data of these samples (Figures S7 and S8, respectively, in the supporting information), it was observed that, as the stirring speed (rpm) increases, the mean size and polydispersity of the precipitated particles, as enlisted in Table I, decreases. This feature can be attributed to the rapid mixing of the organic phase into aqueous phase, allowing better distribution of polymer chains. This leads to the formation of large number of smaller nuclei and hence smaller nanoparticles.[10,19]

The influence of ratio of volume of solvent phase to that of aqueous phase for the nanoprecipitation process on the size and polydispersity of the nanoparticles was also evaluated by varying the ratio of solvent phase to aqueous phase volume. From the SEM and DLS analyses of PS particles prepared by adding 1 mL of EPS solution having concentration of 8 mg/mL into vials containing 2.5 mL and 5 mL of water, it was observed that as this ratio increases, along with the nanoparticles, PS microparticles were formed due to the spinodal decomposition. The SEM images and particle size distribution curves are shown in Figure 2. This indicated the nanoprecipitation outside the "ouzo region" or the metastable region between the spinodal and binodal curves, where a mixture of nano and micro particles is expected to precipitate.[7,8,21]

Furthermore, the significance of various solvents on the morphology and size of the nanoparticles were analyzed by performing the nanoprecipitation experiments using two other solvents: acetone and 1, 4-dioxane. The observations made on the basis of DLS and SEM analyses are enlisted in Table I. From these observations, it is noticeable that, the use of acetone yielded smallest nanoparticles with least polydispersity. This can be explained based on the solvent–water interaction parameter, $\chi_{solvent-water}$ calculated using the total solubility parameter values of solvents and water (presented in Table II). From the solubility data, it is evident that, as $\chi_{solvent-water}$ decreases, the size of the nanoparticles also decreases. A lower value of $\chi_{solvent-water}$ indicates greater affinity of solvent for water, which promotes the diffusion of solvent and therefore, the polymer phase separates leading to the formation of smaller nanoparticles by nucleation and growth mechanism.[19]

CONCLUSION

In summary, the results presented in this article lead to the conclusion that PS nanoparticles can be prepared via the process of nanoprecipitation using EPS waste as the precursor. Using the methodology proposed in this article, nanoparticles with no residual contaminants can be prepared from polymeric waste and hence this encourages new methods for recycling the polymeric waste via the synthesis of particles. The method is simple and versatile, in principle; any polymeric waste can be converted into nanoparticles using a suitable solvent and nonsolvent combination. Moreover, the size and polydispersity of the nanoparticles prepared can be tuned by controlling the experimental conditions. The decrease in the concentration of polymer and an increase in the stirring speed (rpm) lead to a decrease in the size and polydispersity of the nanoparticles generated. When a lower volume of aqueous phase is used for nanoprecipitation, micron sized particles precipitated along with nanoparticles. Furthermore, the interaction between solvent used and water is found to have influence in the size of the nanoparticles. The size of the nanoparticles is found to decrease with decrease in the value of solvent water interaction parameter value of the solvent.

REFERENCES

1. Horvath, J. S. *Geotext. Geomembranes* **1994**, *13*, 263.
2. Shin, C.; Chase, G. G. *Polym. Bull.* **2005**, *55*, 209.
3. Murugan, D. In Chemical Engineering; I I T Madras: India, **2007**; p 157.

4. Bajdur, W.; Pajączkowska, J.; Makarucha, B.; Sułkowska, A.; Sułkowski, W. W. *Eur. Polym. J.* **2002**, *38*, 299.

5. Sułkowski Wieslaw, W.; Nowak, K.; Sułkowska, A.; Wolińska, A.; Bajdur Wioletta, M.; Pentak, D.; Mikuła, B. *Pure Appl. Chem.* **2009**, *81*, 2417.

6. LaMer, V. K.; Dinegar, R. H. *J. Am. Chem. Soc.* **1950**, *72*, 4847.

7. Vitale, S. A.; Katz, J. L. *Langmuir* **2003**, *19*, 4105.

8. Aubry, J.; Ganachaud, F.; Cohen Addad, J. P.; Cabane, B. *Langmuir* **2009**, *25*, 1970.

9. Lepeltier, E.; Bourgaux, C.; Couvreur, P. *Adv. Drug Deliv. Rev.* **2014**, *71*, 86.

10. Dong, Y.; Feng, S. S. *Biomaterials* **2004**, *25*, 2843.

11. Chorny, M.; Fishbein, I.; Danenberg, H. D.; Golomb, G. *J. Control. Release* **2002**, *83*, 389.

12. Mora-Huertas, C. E.; Fessi, H.; Elaissari, A. *Int. J. Pharm.* **2010**, *385*, 113.

13. Vollrath, A.; Schubert, S.; Schubert, U. S. *J. Mater. Chem. B* **2013**, *1*, 1994.

14. Frisken, B. *J. Appl. Opt.* **2001**, *40*, 4087.

15. Hassan, P. A.; Rana, S.; Verma, G. *Langmuir* **2015**, *31*, 3.

16. Hiemenz, P. C.; Rajagopalan, R. Principles of Colloid and Surface Chemistry, 3rd ed.; CRC Press: **1997**.

17. Pecora, R. *J. Nanopart. Res.* **2000**, *2*, 123.

18. Horn, D.; Rieger, J. *Angew. Chem. Int. Ed.* **2001**, *40*, 4330.

19. Galindo-Rodriguez, S.; Allemann, E.; Fessi, H.; Doelker, E. *Pharm. Res.* **2004**, *21*, 1428.

20. Zhang, C.; Pansare, V. J.; Prud'homme, R. K.; Priestley, R. D. *Soft Matter* **2012**, *8*, 86.

21. Ganachaud, F.; Katz, J. L. *ChemPhysChem* **2005**, *6*, 209.