

Glass Transition Temperature of High Molecular Weight Polystyrene: Effect of Particle Size, Bulk to Micron to Nano

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ABSTRACT

High molecular weight nano/micron sized polystyrene ($M_v=1 \times 10^6$) was prepared from styrene and hydrogen peroxide over a range of temperature, shear rate and concentration of catalysts. Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and atomic force microscopy (AFM) measurements indicated that the size of particles matched with that of the single polymer chain. The same chemical structure of both nano/micron and bulk polystyrene was confirmed by means of FTIR spectroscopy studies. Thermal analysis indicated that nano/micron sized particles exhibited a significantly higher glass transition temperature ($\sim 106^\circ\text{C}$) than micron size particle ($\sim 102^\circ\text{C}$) and bulk ($T_g = 89^\circ\text{C}$) polystyrene. The effect of particle size on T_g is explained by the existing models of Keddie et al [1], Forrest et al. [2] and Youngli et al. [3]

Keywords: Polystyrene, Nanoparticles, Glass transition temperature, Differential scanning calorimeter.

INTRODUCTION

Micron and nano-sized polymer particles have wide field of interest including industrial to biomedical applications. Heterogeneous polymer blends of submicrometer scale containing nanoparticles of two different polymers exhibit better mechanical, optical and electro-optical properties. Among them T_g is a key parameter to characterize a polymer in engineering applications. It affects all aspect of material properties. As for example the elastic modulus can decrease by as much as three to five orders of magnitude on heating/cooling through T_g . Despite much theoretical (thermodynamic approach to purely kinetics) and experimental effort, the nature of T_g remains an unsolved problem and a still challenging subject of interest from a scientific and technological point of view. However considerable progress has been achieved to understand the effect of film thickness on T_g of polymer using Brillouin light scattering, transmission ellipsometry, X-ray reflectivity, etc. Various explanations for the phenomena i.e., the increased glass transition temperature with a decrease of film thickness have been proposed including a decrease in film

density, decrease in the entanglement, an enrichment of chain ends on the surface, the enhanced mobility of surface layers, the sliding-loop dynamics of De Gennes, etc. All these studies are related to thin films [1-3] and micro particles of polystyrene [4]. In this study, we present a case where the polymer chains are in nanoscale without losing its high molecular weight. The nanosized particles were characterized through FTIR, TEM, AFM, SEM and differential scanning calorimeter.

EXPERIMENTAL

Materials Preparation

The synthesis of high molecular weight nano/micron sized polystyrene using styrene and hydrogen peroxide over a range of temperature, shear rate, solvent and concentration of catalyst is reported elsewhere [4,5].

Infrared Spectroscopy (IR)

The IR spectra of commercially available PS and PS particles were recorded using a BRUKER VECTOR22 FTIR spectrometer at 25°C . For all samples, the scanned wave number range was $4000\text{-}500\text{ cm}^{-1}$.

Atomic Force Microscopy (AFM)

AFM was performed with a nanoscope equipment (Molecular Imaging, USA) using AAC (Acoustic AC) mode. The instrument was equipped with data point 512×512 , E-Scanner with a scan speed of 1.5-2.2 lines/sec and commercial silicon tips cantilever (NSC 12 (c) from MikroMasch, force constant of 0.6 N/m, resonance frequency of 150KHz, and the tip diameter of 10 nm). Atomic force microscope images were recorded in ambient atmosphere on the mica substrate, providing a set of photographic images of the process as it spans the nanometer to micrometer-length scales.

Transmission Electron Microscopy (TEM)

Particle size of the PS particles were determined with a JEOL JEM-100CX transmission microscope. After proper dispersion through ultrasonication, a drop of this mixture was placed on a carbon coated copper grid of 400 mesh size.

Scanning Electron Microscopy (SEM)

The particle size and morphology of nanopolymer were also determined by using a FEI QUANTA 200 Scanning Electron Microscope (SEM). Prior to SEM studies, the samples were sputter coated with Au-Pd without touching the surface.

Differential Scanning Calorimetry (DSC)

Thermal analyses of spherical PS micro and nano particles, and bulk PS were done with Perkinelmer Diamo DSC instrument to calculate the glass transition temperature (T_g). The scanning rate was $10^\circ\text{C}/\text{min}$ from 30°C to 200°C . N_2 gas was used as an inert atmosphere to avoid degradation of PS. Before, DSC run, instrument was calibrated from 30°C to 250°C using indium ($T_m^0=156.6^\circ\text{C}$ and $\Delta H_f^0=28.5\text{J/g}$) and zinc ($T_m^0=419.47^\circ\text{C}$ and $\Delta H_f^0=23.01\text{J/g}$). All the samples were encapsulated inside the Al pan and lid with mass of $\sim 5\pm 0.1$ mg for each experiment.

RESULTS AND DISCUSSION

The nano and micron sized polystyrene (PS) is synthesized over a range of temperature, shear rate and catalyst [4-5]. After ultrasonication of 5 mins, a stable mixture is formed and evaporation of alcohol resulted a mixture of stable suspension of PS nanoparticles. Moreover, the PS nanoparticles are spherical in shape, which are confirmed from AFM, TEM and SEM. The graphs (Figs 1 to 4) show that the particles are spheroid of 25 nm.

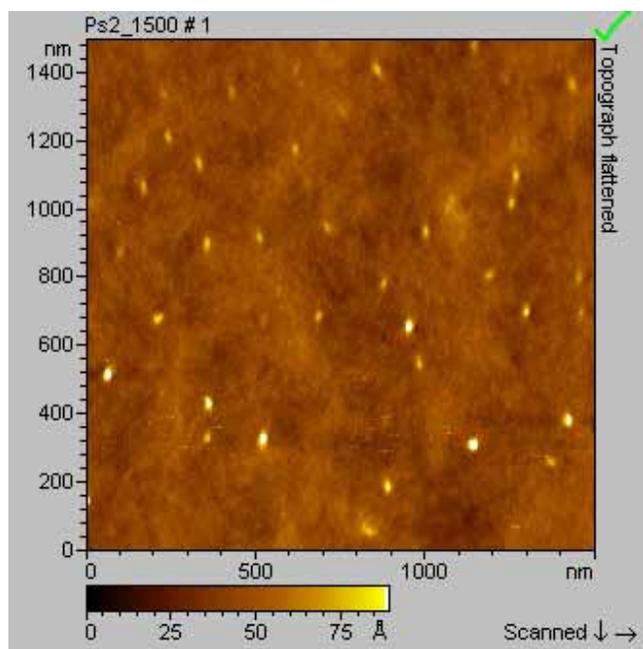


Fig 1: AFM image of PS nano particles (2D image)

A supplementary craze to be noted, there is always a distribution of PS nanoparticles and these distributions are shown in the histogram (Fig 5). From this figure it is clear that the novel technique [4-5] produces nanopolymer within a range of 20 to 37 nm. This suggests that 18% particles have a

diameter of less than 20 nm and 55% nanopolymer are less than 25 nm. It is also worth to mention here this technique produces nanoparticles with a yield of 100%.

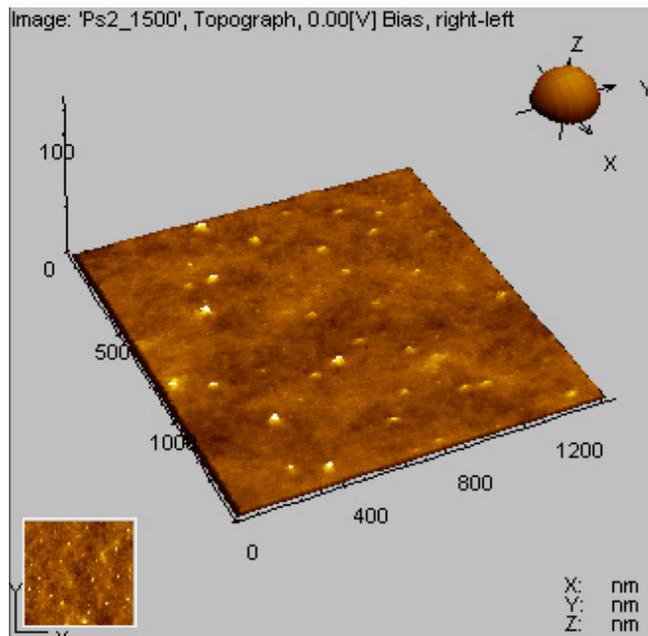


Fig 2: AFM image of PS nano particles (3D image)

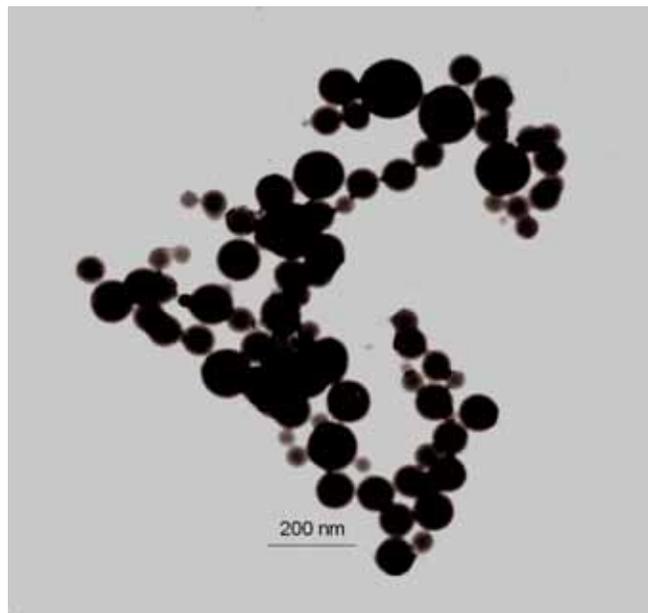


Fig 3: TEM image of PS particles

Infrared (IR) spectra (Fig 6) were used to find out the difference in chemical structure between the nano/micron sized PS and commercial PS. The peak positions at 3027 , 2885 , 1492 , 1370 and 757 cm^{-1} are assigned to the stretching of -C-H bond in phenyl ring, asymmetric stretching of -C-H bond, asymmetric stretching of -C-H bond, symmetric stretching of -C-H bond and rocking of -C-H bond in phenyl

ring respectively. The other two peaks 901 and 851 cm^{-1} are associated to the α crystal form of PS. Another two peaks at 911 and 855 cm^{-1} are assigned to the β crystal form of PS. It is very interesting to report that there is no difference in chemical structure between the commercial PS and nano/micron sized high molecular weight PS. The high molecular weight of nano/micron sized polymer is confirmed through the measurement of viscosity average molecular weight ($M_v=1 \times 10^6$).

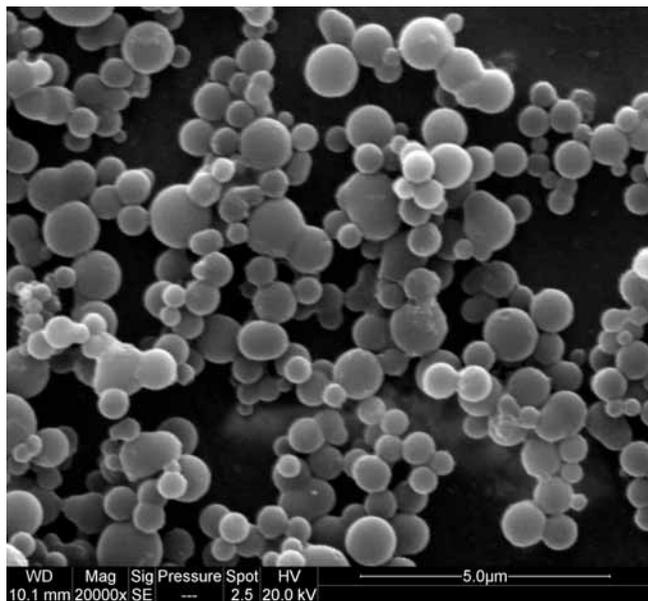


Fig 4: SEM image of PS particles.

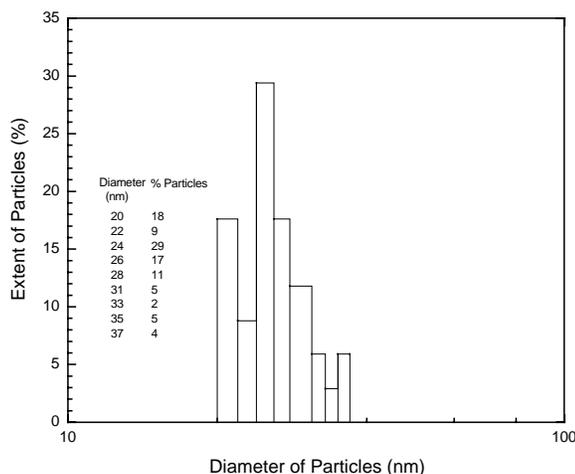


Fig 5: Particle size distributions of PS particles, calculated from AFM image.

Fig 7 shows the heat flow curve of commercial and nano/micron sized PS. It is observed that the T_g of PS nano particles have higher value than that of its bulk and micron sized particles. As the particle size decreases to nano size, the T_g gradually increases from 89°C (bulk PS) to 106°C

(nanosized PS, particle size ~ 25 nm). The variation of T_g with particle size can be explained as follows: It is reported that the increase in T_g of polymer particles or thin film with respect to the bulk polymer is due to the higher chemical interaction between the substrate and film than the Van der Waals force or hydrogen bonding between the polymer chains and substrate [1-2]. Whereas the reduction in T_g values for thin polymer film on the substrate is a result of the existence of a “liquid-like” layer near the free surface of the film. But when polymer chains are in spheroid form it is to be expected that the chains will remain in more compressed and restricted form. Furthermore, the authors did not expect in this study that the enhancement of T_g of PS macro/nano particles is due the secondary interactions (Van der Waals force or hydrogen bonding) between the Al (sample pan and lid) and PS particles.

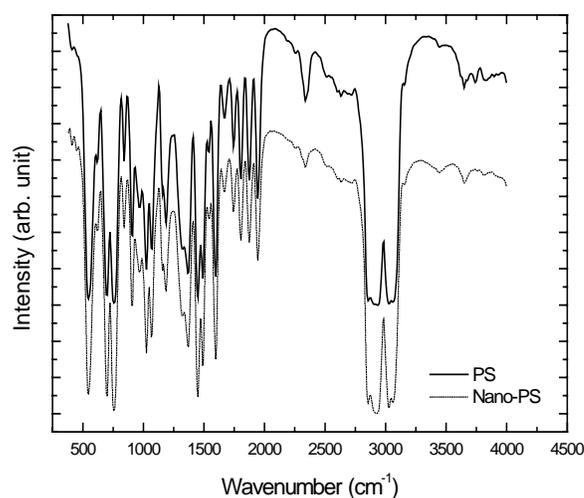


Fig 6: FT-IR spectra of commercial PS and PS particles

This spectacular elevation in T_g for PS particles are quite exciting from the finite size effect results reported by Keddie et al. [1] and Forrest et al. [2] for PS films. As the particle size decreases, the configuration entropy of PS particle decreases and become lower value which can be represent by the following equations [3],

$$\Delta S = \Delta C_p \ln \frac{T_{gp}}{T_{gb}} + (S_{gb} - S_{gp}) \quad \dots(1)$$

where, C_p stands for specific heat; subscript g, p and b stand for glassy state, particle and bulk respectively.

Another equation [3] shows the nano/micron particles have higher T_g value than that of bulk (N , k and x are degree of polymerization, Boltzmann const. and a constant of 5/3 respectively).

$$\ln \frac{T_{gp}}{T_{gb}} = \frac{kN}{\Delta C_p} (N^{\frac{x}{3}} + N^{-2} \ln 2) \quad \dots(2)$$

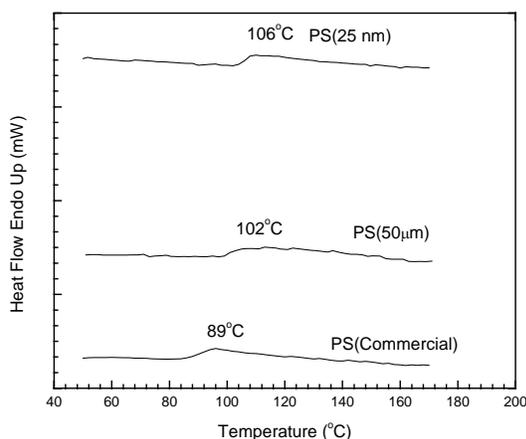


Fig 7: DSC plots for PS particles at the heating rate of 10°C/min

Thus, the theoretical justification agrees well with our experimental data. As the particle size decreases to micron and nano scale, the configuration entropy of PS particles decreases and become lower value with further reducing the particle size towards its single chain and T_g will be elevated. Again the elevation of T_g of PS nano particle than that of commercial PS is the resultant of the decrease in the configuration entropy of PS nano particles, as the free ends of the polymer molecules become restricted to move and make an order form in the crystal. For the larger particle (micron size PS) having the higher T_g than that of commercial PS means there is an increase in the probability of the molecule attached at the same side of the spherical particles or attached to opposite side of two or more distorted particles. All these reasons will make the PS micro/nano particles more rigid and elevate T_g .

CONCLUSIONS

The following conclusions have been drawn from the present investigation:

- Scanning electron microscopy, transmission electron microscopy and atomic force microscopy results show that the nano/micron sized polymers are spherical in shape.
- Particle size analyzer demonstrates that the novel technique produces nanoparticles, polystyrene within a range of 20 to 37 nm in diameter. 55% nanopolymer are less than 25 nm.
- Infrared spectroscopy studies of commercial and nanopolymer indicate that both polymers have same chemical structure and chemical bonding.
- The glass transition temperature increases from 89 (bulk sample) to 106°C nanoparticle of polystyrene

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REFERENCES

- [1] J.L. Keddie, R.A.L. Jones, and R.A. Cory; "Size dependent reduction of the glass transition temperature in polymer films". *Europhys. Lett.* **27**, 59-64 (1994).
- [2] J. A. Forrest, K. Dalnoki-Veress, J. R. Stevens, and J. R. Dutcher; "Effect of free surfaces on the glass transition temperature of thin polymer films". *Physical Review Letters* **77(10)**, 2002-2005 (1996).
- [3] Y. Mi, G. Xue, and X. Wang, "Glass transition of nano-sized single chain globules". *Polymer*, **42**, 6701-6705(2002).
- [4] K. K. Kar and P. Paik, "A Process for Preparation of micron sized High Molecular Weight Polymer" (Indian Patent No.2503/Del/2004)
- [5] K. K. Kar and P. Paik, "A Process for Preparation of nanoparticles of high molecular weight polyethylene, polypropylene and polystyrene" (Indian Patent No. 3161/Del/2005).