Study on polystyrene conformational changes in supercritical fluid anti-solvent process by small angle X-ray scattering

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A preliminary study of the polymer conformation in supercritical fluid anti-solvent process was carried out by the method of grazing-incidence small angle X-ray scattering at the station of Beijing Synchrotron Radiation Facility (BSRF). The experiments showed that in the continuous process of adding an anti-solvent, polymer chain stretching occurred from random coil to a curled sphere.

INTRODUCTION

In recent years, more and more emphasis is put on supercritical fluid technology. There are two main reasons: first, supercritical fluids have many unique properties; second, this technique causes little or no pollution [1-3]. Supercritical fluids (SCFs) have many unique properties near the critical point; the fluid physical and chemical properties such as viscosity, density, diffusion coefficient, solvation capability, dielectric constant are sensitive to changes in temperature and pressure. Viscosity and diffusion coefficients are close to those of gases, the density and the solvation ability are close to those of liquids. So far, supercritical fluid technology has been applied in many areas such as extraction and separation technology [4], petrochemistry [5], analytical techniques [6], chemical reaction engineering, materials science, biotechnology, etc. [7, 8], and has broad prospect.

Preparation of particles is an important part of the chemical industry. Particles which have different properties can be used as stationary phases, adsorbents, catalyst carriers, etc., supercritical fluid anti-solvent process technology applications have attracted attention in this regard [9, 10]. The principle of the anti-solvent process (SAS) is: Many substances are soluble in organic solvents, but insoluble in a certain gas or a supercritical fluid. Meanwhile, under high pressure, the solubility of CO_2 and other gases in many organic solvents is high, resulting in volume expansion of the solvent, therefore, when the gas or supercritical fluid is dissolved in the solvent, the solvent capacity for dissolving the solute decreases,

and under appropriate conditions part or all of the solute can be precipitated which is called anti-solvent process (SAS). In the anti-solvent process, the nature of the precipitate (particle size, crystal type, etc.) can be adjusted by pressure, temperature and speed of the gas dissolution. SAS techniques have applications in many areas such as natural products isolation, explosive fragmentation [11], preparation of drug particles [12], recrystallization of inorganic substances [11], etc.

Small angle X-ray scattering (SAXS) originates from spatial fluctuations of the electronic density within a material. It is ideally suitable for investigating the geometric structure of inhomogeneous materials containing regions in which fluctuation or variation in electron density extends over distances of about 0.4 nm to 200 nm (e. g., nanomaterials or porous materials). The X-ray intensity emitted from a common X-ray source is always very low, so that the application of SAXS is limited. By using synchrotron radiation with high intensity as X-ray source, SAXS measurement can be well improved [13, 14].

Our work is to make use of small angle x-ray scattering (SAXS) study of polystyrene conformational changes in the supercritical fluid anti-solvent process. X-ray scattering like other light scattering is caused by the unevenness of the system. For example, there are particles of dust and water vapor in the atmosphere, the electron densities of the atmospheric dust and water vapor are different. When the light illuminates the subject, they produce scattered light. If the size of the particles (as the polymer solution) dispersed in uniform media is a few microns, because the X-ray waves are much smaller than visible light, only a small range of angles ($\theta < 2°$) of the scattered light can be observed [15]. The intensity of the scattered

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light, intensity angular dependence are concerned with the particle size, morphology and distribution. So you can use small angle x-ray scattering to study the size and morphology of the polymer in a supercritical fluid anti-solvent process [16].

Small-angle x-ray scattering (SAXS) experimental station equipped with an SAXS camera was used for the on-line control and data acquisition. SAXS has an accuracy of 1 μm slit system, ionization chamber for monitoring the light intensity, it has a plane perpendicular to the beam which can be both horizontally and vertically adjusted to the direction of the sample, low vacuum pipe which can adjust length, sealed with 25 μm thick Kapton film at both ends, detector is a scintillation counter. Angular resolution of the device is better than 016 m rad. Synchrotron light source has a small source size, collimation, high brightness advantage (higher than ordinary light by at least 2 to 3 orders of magnitude), which can greatly improve the resolution and sensitivity, shorten the time of the experiment, simplify complicated data rectification work, carry out studies on the structure which cannot be carried out with a conventional X-ray source [17].

30 years ago, using Flory's mean-field theory, Stockmayer first proposed that if the solvent becomes poor solvent from a good solvent, flexible polymer chain can curl into uniform density sphere from random coil stretch. Theory and practice of this prophecy have fostered extensive research. Research on the polymer chains transition in supercritical fluid anti-solvent process, not only has important theoretical significance, but it is relevant to many biological processes; it also makes sense for promoting the development of supercritical fluid technology.

In this paper, using small-angle X-ray scattering (SAXS), preliminary studies on the polymer conformational changes within supercritical fluid anti-solvent (SAS) process were performed. These changes are characterized by sharing radius of gyration Rg, which verify the feasibility study using SAXS. In the future, we will carry out more in-depth and meticulous research in this area.

EXPERIMENTAL

Materials

CO_2, purity 99.995% (Beijing Analytical Instrument Factory), polystyrene (PS), Mw = 7.8×10^6, Mw / Mn = 1.1 (Institute of Chemistry), toluene (Beijing Chemical Plant), in SAXS experiments, the concentration of PS/toluene solution was 3.2×10^{-3} g/mL.

Methods

Small-angle x-ray scattering (SAXS) experiment was carried out in the Beijing synchrotron radiation beam line within 4B9A small angle X-ray scattering experimental station. Put the sample cell which contains PS solution into the scattering chamber, add anti-solvent to the solution and measure the parameters Pc under continued pressure until the cloud point pressure in the scattering device. Fluid pressure was controlled by gauges (IC Sensor Co., Model 193), pressure measurement error is less than ±0105MPa, the temperature of scattering pool was controlled by a platinum resistance thermometer, the temperature measurement error is less than ±0.1K.

RESULTS AND DISCUSSION

Scattered light intensity changes with pressure

Synchrotron radiation SAXS experiment was performed at 35℃ and concentration of 3.2×10^{-3} g/mL of the polystyrene/toluene solution. The latter was continuously pressurized, after equilibrium, the scattering intensity I (h) measured under each pressure value with an angle (h) changed. In this experiment, six different pressures were used: 1, 21.6, 32.8, 41.6, 49.6, 55.2 ($\times 10^5$Pa), shown in Fig.1. From the scatter diagram can be seen that at a lower pressure, the scattering intensity I (h) is monotonously decreasing, which indicates that the PS chain stretching presented random coil conformation. At 49.66×10^5Pa pressure, the scatter graph shows oscillations, which indicate that PS random coil curling happens and becomes spherical. Our equilibrium experiments also proved that the solution cloud point pressure was Pc 48.3×10^5Pa, when the pressure is greater than Pc, phase separation and precipitation occurs
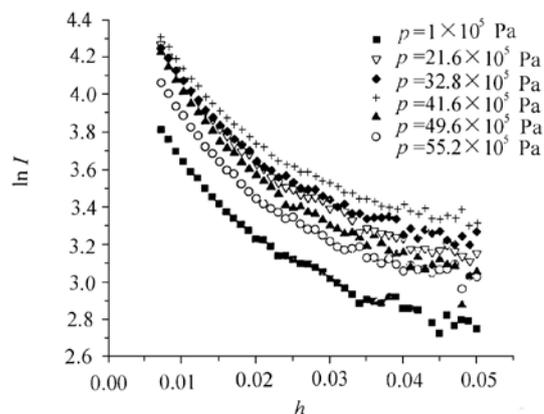
Fig.1. Scattering intensity I (h) with an angle (h) changes when PS/toluene solution is continuously pressurized.

In the scatter plot we also see that when P < Pc, the scatter plot of the six different pressures substantially coincides which indicates that I (h) is independent of pressure. From the theory, for the same molecular weight and concentration conditions, the scattering intensity should be a constant; when P > Pc, the scattering intensity decreases with increasing pressure. For this light intensity decrease there may be two reasons: one reason may be due to the curled sphere when PS chain density is increased, so that the center of the sphere segment of the scattered light may be blocked on the surface of the segment and second scattering occurs, so that the scattered light intensity decreases; another factor may be due to the curling process, causing a change in the long chain of solvated polymer, resulting in a decrease in scattered light.

Sharing radius of gyration (Rg) changes with pressure

With In(h) as the vertical axis and h^2 as the horizontal axis, the slope of the line is $-R_g^2 / 3$, a function of chain size (Rg) which describes PS can be obtained. Scattering vector $h = (4\pi / \lambda) \sin \theta$, scattering intensity I (h) according to the following formula, deducing absorption of substrate and scattering of the substrate, the parameters of sample thickness and light intensity Po derived normalize [18].

$$I(h) = \frac{[I_m(h) - I_d(h)] - [I_s(h) - I_d(h)] \exp(-\mu_f t_f)}{p_o \mu_f t_f \exp(-\mu_f t_f - \mu_s t_s)}$$

In the above formula, I_d (h) is the background noise, I_m (h) and I_s (h), respectively the actual measured scattering intensity and the substrate measured scattering intensity, μ_f, t_f, and μ_s, t_s are the absorption coefficient and the thickness respectively film (f) and the substrate (t). We summarize the sharing rotation radius (Rg) changes with pressure in Fig. 2.
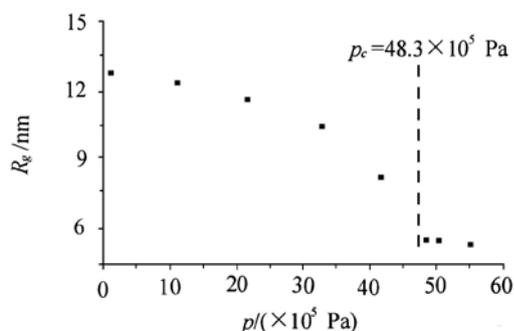

Fig.2. Effect of pressure on PS chain size (Rg)

As the pressure increases, the central portion of each polymer chain shrinks, Rg makes steep drop, in the areaI, $p < p_c$, Rg becomes small with increasing pressure, which shows that strong contraction occurred in the molecular chain. In the areaII, $p > p_c$, Rg is linearly decreasing, which shows only a slight molecular chain of PS shrinkage.

According to PS chain size (Rg) dependence on the pressure, we propose a mechanism: in the continuous process of adding an anti-solvent, polymer chain stretching occurred from random coil to a curled sphere, and this process can be divided into two sub-processes: rapid contraction of non-entangled chains and entanglement and slow contraction of the chain.

CONCLUSION

Using small angle X-ray scattering, we studied the polymer conformational changes in the supercritical fluid anti-solvent process. From the analysis of the experimental parameters it can be concluded that: the more CO_2 is added to the polymer solution, the more easily molecules are separated, and the conformational change with which the polymer chain stretches from random coil to curl the ball is also easily found.

REFERENCES

1.S.F. Li, X.W. Wu, C.X. Hou, Y. Zhang, *Modern Chemical Industry*, **27**, 1 (2007).
2.J. Jung, M. Pemut, *Journal of Supercritical Fluids*, **20**, 179 (2001).
3.C. Quan, S.F. Li, S.J. Tian, *Journal of supercritical fluids,* **31**, 149 (2004).
4.Y.Y. Gao, H. You, C. Chen, X.L. He, C.S. Chen, *Food Sci.* **23**, 154 (2002).
5.T.J. Liu, Z.G. Du, Y. Guo, X.H. Yang, Y.G. Zhang, *Chem. Ind. & Eng. Pro.(China)*, **30**, 1676 (2011).
6.Y.P. Wang, *Chinese Traditional Patent Medicine*, **33**, 1070 (2011).
7.J.M Levy. *J. Chromatographic Science*, **27**, 341 (1989).
8.M.J. Burk, S. Feng, M.F. Gross, W. Tumas, *Am. Chem. Soc.*, **117**, 8277(1995).
9.L.Y. Lee, L.K. Lim, J. Hua, C.H. Wang, *Chem. Eng. Sci.*, **63**, 3366 (2008).
10.K. Byrappa, S. Ohara, T. Adschiri, *Adv. Drug Deliv. Rev.*, **60**, 299 (2008).

11. M.A. McHug, V.J. Krukonis, *Supercritical Fluid Extraction, Principles and Practice,* 2nd ed., Boston, Butterworth-Heinemann, 1994.

12. W.J. Schmitt, M.C. Salada, G.G. Shook, S.M. Speaker*, AIChE J.*, **41**, 2476 (1995).

13. W.H. Wang, H.Y. Han, Y.C. Yu, L. Li, X.H. Guo, *Journal of East China University of Science and Technology (Natural Science Edition),* **41**, 277 (2015).

14. C.Z. Yang, J. M. Newsarn, *Progress in Physics*, **12**, 130 (1992).

15. W.H. Wang, L. Li, X. J. Yu, H. Han, X. Guo, *Journal of Polymer Science: Part B. Polymer Physics,* **52**, 1681(2014).

16. Q. De Robillard, X. Guo, M. Ballauff, T. Narayanan, *Macromolecules*, **33**, 9109 (2000).

17. B.Z. Dong, W.J. Sheng, *High Energy Physics and Nuclear Physics,* **19,** 284 (1995).

18. X.X. Guo, M.F. Guo, *Beijing Synchrotron Radiation Facility Annual Report,* **1**, 70 (1997).