Chinese Chemical Letters Vol. 11, No. 12, pp. 1093–1094, 2000

Small Angle X-ray Scattering Study of PS Conformation in Tetrahydrofuran Solvent with Gas Anti-solvent

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Abstract: Small angle X-ray scattering (SAXS) was used to study the effect of dissolved CO_2 on the conformation of polystyrene (PS) in PS/tetrahydrofuran(THF) solution at 308.15 K and at pressures up to 3 MPa. The cloud pressure and the expansion curve of the solution were also determined. The dependence of the conformation on pressure was discussed.

Keywords: Small angle X-ray scattering, polystyrene, THF, CO_2, conformation.

Compressed gases or supercritical fluids (SCFs) are highly soluble in some liquid solvents, and thus reduces the solvent strength of the liquids[1]. As a result, precipitation of the dissolved solutes occurs, which is called as gas anti-solvent (GAS) process. Recently, this new technique has been used to produce fine particles of different compounds, such as polymers[2]. Effect of the dissolved gases on the conformation of polymer molecules is a very interesting topic. In this work, we report the first application of small angle X-ray scattering (SAXS) to study the conformation of a polymer in the solution with a GAS.

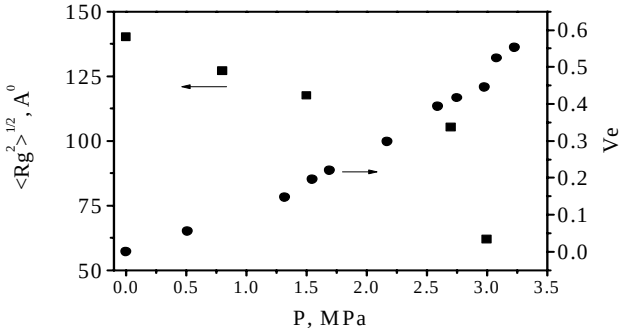
The average molecular weight of the PS was 7.8×10^4 with a narrow molecular weight distribution (Mw/Mn=1.1), which was kindly supplied by Polymer Laboratory of Institute of Chemistry, Chinese Academy of Sciences. The concentration of PS in CO_2-free PS/THF solution was in the range from 6.74×10^{-4} to 8.36×10^{-3}g/cm^3. SAXS experiments were carried out at Beamline 4B9A at Beijing Synchrotron Radiation Facility. A high pressure, temperature-controlled sample cell with two diamond windows was used. Its structure was similar to that of our UV sample cell[3].

The temperature of the cell was controlled at 308.15 K. A known amount of PS/THF solution was introduced into the sample cell. CO_2 was then charged and mixed with the liquid solution under controlled pressure. Scattering measurement was performed. The scattering curve of the CO_2/THF solution without PS was also determined at the same condition, which was used as background in the data treatment.

Using the procedure reported[4], the radii of gyration $\langle Rg^2\rangle^{1/2}$ were obtained from the SAXS data, which reflect the conformation of polymer chains. **Figure 1** shows the dependence of $\langle Rg^2\rangle^{1/2}$ on pressure and the volume expansion (Ve= Δ V/V, V is the

volume of gas-free solution, ΔV is the volume change caused by the dissolved CO_2) of the solution caused by anti-solvent.

Figure 1 Dependence of $<Rg^2>^{1/2}$ on pressure and volume expansion



It is well known that the larger the $<Rg^2>^{1/2}$, the more expanded the polymer is in the solution. It can be seen from **Figure 1** that $<Rg^2>^{1/2}$ decreases with increasing pressure, or volume expansion. It indicates that the PS chain experience shrinking in the course of adding anti-solvent CO_2. THF is a good solvent for PS and the coil expanded due to prevailing intersegmental repulsion. After adding CO_2, the solvent power of THF is reduced and PS chain shrunk due to prevailing intersegmental attraction. In addition, $<Rg^2>^{1/2}$ is more sensitive to pressure at the higher pressure.

Acknowledgments

This work was supported by the National Basic Research Project-Macromolecular Condensed State and the National Natural Science Foundation of China (29633020, 29725308)

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Received 15 May 2000