

Effect of Gas Antisolvent on Conformation of Polystyrene in Toluene: Viscosity and Small-Angle X-ray Scattering Study

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ABSTRACT: Synchrotron radiation small-angle X-ray scattering (SAXS) and the viscosity technique were used to investigate the effect of dissolved CO₂ in toluene on the conformation of polystyrene (PS) in the solution. The viscosity of PS solution decreases faster with increasing antisolvent CO₂ pressure than that of the solvent in the absence of the polymer. The intrinsic viscosity $[\eta]$ calculated using the well-known Huggins equation decreases with antisolvent pressure. It was found that the second virial coefficient A_2 and the apparent mean-square radius of gyration $\langle R_g^2 \rangle^{1/2}$ decreases with pressure of antisolvent CO₂. All these phenomena can be attributed to the shrink of PS chain in the course of adding the gas antisolvent because the interaction between the polymer and solvent becomes weaker. The values $\langle R_g^2 \rangle^{1/2}$ at different pressures obtained from SAXS data agree reasonably with those calculated from Flory theory using the viscosity data determined in this work. This implies that Flory theory, which has been used widely for the solutions of polymers in liquid solvents, is also applicable to the polymer solution with gas antisolvent.

Introduction

Compressed fluids, including supercritical fluids, have been used in polymer separation and purification processes such as extraction and fractionation,¹ impregnation of polymers with additives, and conditioning polymer films.^{2,3} Recently, several innovative processes have been developed which utilize compressed fluids in the production of advanced polymeric materials such as microcellular foams, gels, fibers, and particles.^{4,5} CO₂ is a desirable solvent for polymer processing since it is nontoxic, nonflammable, and inexpensive. After processing, CO₂ can be removed from the polymers completely simply by decreasing the pressure.

The use of compressed CO₂ for fine particle formation is a rapidly developing field of research.¹ The gaseous antisolvent (GAS) process is one of the most important ones.⁶ The possibility of obtaining solvent free micro-particles with narrow size distribution makes this technology especially attractive. The basis of GAS technique⁷ is that a dense gas is generally soluble in organic solvents and in solutions with the solutes. Dissolution of gas causes a volume expansion of the solvent and lowers solvent power, which forces the solute to precipitate. Because of the high and uniform degree of supersaturation, small particles with a narrow size distribution can be obtained. Moreover, it is possible to extract all the solvent in the products, and to obtain solvent-free product. To date, GAS processes have been successfully used in the recrystallization of organic solids,^{8,9} the fractionation of natural products,^{10,11} the preparation of ultrafine particles et al.^{7,12–22} Since only a few kinds of polymers have been found to be soluble in compressed CO₂,²³ compressed CO₂ can also be used as an environmentally benign antisolvent for processing

most polymers. Some related papers have been published,^{15–22} and they were mainly focused on how the operating parameters affect the properties of the products. We are very interested in the polymer conformation in GAS process, since the solubility of a gas in an organic solvent can be tuned by pressure and temperature, accordingly, the polymer morphology be tailored. The investigation to this problem has both practical and theoretical importance.

It is well-known that small-angle X-ray scattering (SAXS) and viscosity measurement are useful techniques for studying polymer solutions. In one hand, SAXS can provide information about apparent mean-square radius of gyration $\langle R_g^2 \rangle^{1/2}$ and the second virial coefficient (A_2), which are related to the conformation of the polymer and intermolecular interaction in the solution, respectively.²⁴ Some papers have been published for studying polymer solutions by SAXS in the absence of gas antisolvent.^{25–30} On the other hand, evaluation of intrinsic viscosity, $[\eta]$, can provide valuable information on the changes in the solvent–polymer interactions as the system conditions are changed. An important quantification of this relationship is given by the dilute solution theory of Flory,³¹ which shows that $[\eta]$ at a given molecular weight is dependent on $\langle R_g^2 \rangle^{1/2}$. The effects of temperature, pressure, solvent quality, concentration, chain architecture, and molecular weight upon both $\langle R_g^2 \rangle^{1/2}$ and $[\eta]$ have been explored by extensive theoretical efforts and many experimental studies.^{32–36} There have also been a number of previous high-pressure studies on polymer solutions in the absence of gas antisolvent, which involve $[\eta]$, $\langle R_g^2 \rangle^{1/2}$, (A_2), and hydrodynamic radius (R_h).^{37–41} Generally, viscosity of a polymer solution increases with hydrostatic pressure (typically $\approx 20\%$ per kbar).^{37–40} The radius of gyration, however, shows no consistence trend with pressure,⁴¹ and it may either increase or decrease

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with increasing pressure in good solvent. One of the most important and straightforward relationship was between $\langle R_g^2 \rangle^{1/2}$ and $[\eta]$ as given by the theory of Flory:³¹

$$[\eta] = \phi' \langle R_g^2 \rangle^{3/2} M^{-1} \quad (1)$$

Here $\phi' = 6^{3/2} \phi \approx 3.7 \times 10^{22} \text{ dL/mol} \cdot \text{cm}^3$, ϕ is the Flory constant, $\langle R_g^2 \rangle^{1/2}$ is the radius of gyration, and M is the molecular weight.

In this work, SAXS and the viscosity technique were used to study the conformation of polystyrene (PS) chain in PS-toluene solution in the presence of antisolvent CO_2 . No quantitative study for the effect of a gas antisolvent pressure on the conformation of polymers in solutions was found in a literature survey.

Experimental Section

Materials. The polystyrene (PS) ($M_w = 7.8 \times 10^4$) with narrow molecular weight distribution of 1.1 was kindly supplied by State Key Laboratory of Polymer Science, Institute of Chemistry, Chinese Academy of Sciences. Toluene (AR grade) was produced by Beijing Chemical Factory. The PS/toluene solutions were prepared by the gravimetric method. The original concentrations C_0 (CO_2 -free) in our study were 4.6×10^{-4} , 6.9×10^{-4} , 1.07×10^{-3} , 3.2×10^{-3} , and $9.2 \times 10^{-3} \text{ g/cm}^3$.

Apparatus and Procedures for Volume Expansion and Cloud Point Pressures. The apparatus consisted mainly of a 30-mL optical stainless steel cell, a magnetic stirrer, a constant temperature water bath, a pressure gauge, a gas cylinder, and a high-pressure pump. The accuracy of the pressure gauge, which was composed of a transducer (FOX-BORO/ICT) and an indicator, was $\pm 0.025 \text{ MPa}$ in the pressure range 0–20 MPa. The temperature of the water bath was controlled by a HAAKE F3 controller. The temperature was determined using a platinum resistance thermometer (Beijing Chaoyang Automatic Instrument Factory, XMT) with an accuracy of $\pm 0.1 \text{ K}$.

In a typical experiment, a suitable amount of PS/toluene solution was loaded into the optical cell, and the cell was stabilized at the desired temperature. CO_2 was charged into the cell using the high-pressure pump until suitable pressure was reached. The stirrer was started. At the beginning, the pressure decreased and the volume of the liquid increased with time because of the dissolution of CO_2 . The pressure remained constant with time when equilibrium was reached. The volume at equilibrium condition was known by reading the graduations on the cell. Some polymer molecules precipitated when the equilibrium pressure was high enough, which could be seen clearly through the windows of the optical cell. The cloud pressure, which was defined as the pressure at which polymer begins to precipitate, was determined.

Viscosity and Density Measurements. The high-pressure apparatus for determining the viscosity and density of the solution saturated with CO_2 is shown in Figure 1, which was similar to that used previously.⁴² The main difference was that there was a falling slug viscometer⁴³ between the view cell and the liquid sample bomb, so the viscosity of the solution could be determined at any antisolvent pressures. The viscosity was calculated using the following well-known equation:

$$\eta = k(\rho_s - \rho)t \quad (2)$$

η is the viscosity of the solution; t denotes the falling time of slug; ρ_s and ρ stand for the densities of the slug and solution; k is the instrument constant. The viscometer was calibrated using 60, 40, and 20 wt % glycol in water and ethanol at 35 °C. k was determined from the slope of the plot of η vs $(\rho_s - \rho)t$.

In a typical experiment, a suitable amount of PS/toluene solution was charged into the optical cell and the viscometer

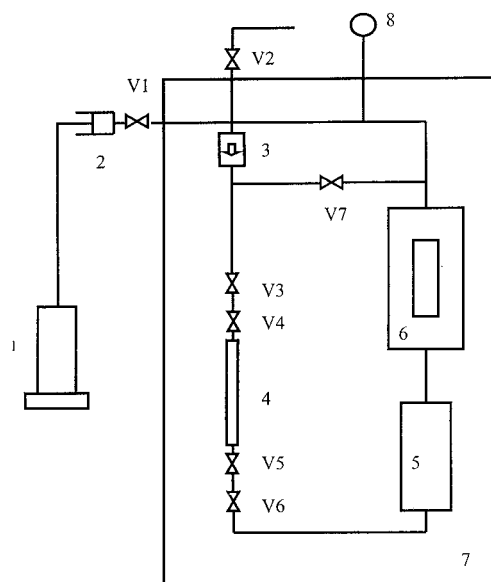


Figure 1. Schematic diagram of the experimental apparatus for measuring solubility of CO_2 in toluene, and viscosity and density of the liquid phase. Key: (1) gas cylinder; (2) high-pressure pump; (3) solenoid circulation pump; (4) liquid sample bomb; (5) falling slug viscometer; (6) optical cell; (7) constant-temperature bath; (8) pressure gauge, V1–V7 valves.

by vacuum. After the system had reached thermal equilibrium, CO_2 was compressed into the system until desired pressure was reached. The solenoid-operated circulation pump was started to circulate the vapor phase through the viscometer, the cell, and the liquid sample bomb. We measured the fall time of the slug about every 30 min, and the circulation pump was stopped during the measurements. The equilibrium was reached when the fall time of the slug did not change with time. The fall time was measured 10–15 times for each equilibrium conditions, and the reproducibility was better than $\pm 0.5\%$. The density of the solution at each condition was easily known by the volume and mass of liquid sample bomb. The amount of CO_2 in the liquid sample bomb was determined by the PVT method.⁴⁴ The liquid composition was calculated on the basis of total weight of the liquid sample and the weight of CO_2 in the sample.

SAXS Experiments. The experimental apparatus for the SAXS study was similar to that used for on-line FT-IR measurement that was described in detail previously.⁴⁵ Briefly, the apparatus was consisted mainly of a gas cylinder, a high-pressure pump, a digital pressure gauge, a high-pressure SAXS cell, a thermometer, a temperature controller, and valves and fittings of different kinds. The pressure gauge as described above, consisted of a transducer (FOX-BORO/ICT) and an indicator. The schematic diagram of the temperature-controlled SAXS cell is shown in Figure 2. It was composed mainly of a stainless steel body and two diamond windows of 8 mm in diameter and 0.4 mm in thickness. Diamond is an excellent window material for SAXS studies because it has low absorbance and low scattering power. The cell body was coiled with an electric heater and heat-insulate ribbon outside, which is not shown in Figure 2. The X-ray path length of the cell was 1.5 mm, and the internal volume of the cell was 2.7 cm^3 . There was a small magnetic stirrer in the cell to stir the fluids before the SAXS measurements, so that the equilibrium could be reached in a shorter period of time. The insulated cell was electrically heated to $\pm 0.1 \text{ K}$ of the desired temperature by using a temperature controller with a platinum resistance temperature probe (model XMT, produced by Beijing Chaoyang Automatic Instrument Factory).

SAXS experiments were carried out at Beamline 4B9A at the Beijing Synchrotron Radiation Facility, using a SAXS apparatus constructed at the station. A detailed description of the spectrometer was given elsewhere.⁴⁶ The detector can

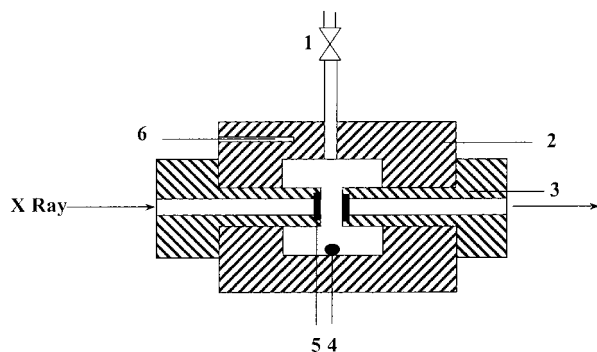


Figure 2. Schematic diagram of the SAXS cell. Key: (1) ball valve; (2) stainless steel body; (3) nut; (4) stirrer; (5) diamond window; (6) thermometer probe.

be translated along the vertical and horizontal axes in a range of 30 mm with a precision of 10 μm . The experiments had an angular resolution of better than 0.5 mrad with this setting. The data accumulation time was 3 min. The angular range was chosen so as to provide data from $h = 0.005 \text{ \AA}^{-1}$ to $h = 0.15 \text{ \AA}^{-1}$, where the magnitude of scattering vector $h = 2\pi(\sin \theta)/\lambda$, with θ and λ being respectively the scattering angle and incident X-ray wavelength of 1.54 \AA . The distance between the sample chamber and the detector was 1.52 m. Background scattering from the slit collimator, the solvent, and the residual air path between the vacuum chamber and the detector was measured and subtracted. It should be mentioned that, for each measurement, the solvent with antisolvent CO_2 at the same temperature and pressure was used as the background solvent, so that we could obtain the information on polymer chain. Excess SAXS scattering from the PS solute was also corrected for incident beam decay and transmission.

Before the experiment, SAXS cell was flushed with CO_2 , and then suitable amount of PS/toluene solution was filled into the cell. CO_2 was charged into the cell with stirring at the temperature of interesting. The cell was connected to the SAXS apparatus after the equilibrium was reached and the X-ray scattering was recorded. Moreover, the pressures investigated were the same as those for viscosity study.

SAXS Data Processing. We are interested in the conformation of polymer chain in solution in the presence of the antisolvent. Its scattering curve is obtained by subtracting the scattering of the solvent + antisolvent (background scattering) from the scattering of the polymer + solvent + antisolvent solution.

The scattering intensities $I_{\text{exp}}(h, C)$ measured as a function of momentum transfer h and polymer concentration C of the polymer, usually expressed in g/cm^3 , may be treated according to Zimm and Flory and Bouche²⁴

$$\frac{KC}{I_{\text{exp}}(h, C)} = \frac{1}{M_w I_n(h)} + 2A_2 Q(h)C + \dots \quad (3)$$

where K is the optical constant, A_2 is the second virial coefficient, M_w is molecular weight of the dissolved polymer, and $I_n(h)$ is the single particle scattering function. $Q(h)$ and $I_n(h)$ are normalized in such a way that $I_n(0) = 1$ and $Q(0) = 1$. The first term in right side of eq 3 is merely due to intramolecular interference, whereas the higher term reflect the influence of the intermolecular interference.

From eq 3, if $h \rightarrow 0$, we can also obtain the equation²⁴

$$\lim_{h \rightarrow 0} \frac{KC}{I_{\text{exp}}(h, C)} = \frac{1}{M_w} (1 + 2A_2 M_w C + \dots) \quad (4)$$

from which the thermodynamic analysis of the dilute system can be performed. If $C \rightarrow 0$, we can obtain the equation²⁴

$$\lim_{C \rightarrow 0} \frac{KC}{I_{\text{exp}}(h, C)} = \frac{1}{M_w I_n(h)} = \frac{1}{M_w} \left(1 + \frac{\langle R_g^2 \rangle}{3} h^2 \dots \right) \quad (5)$$

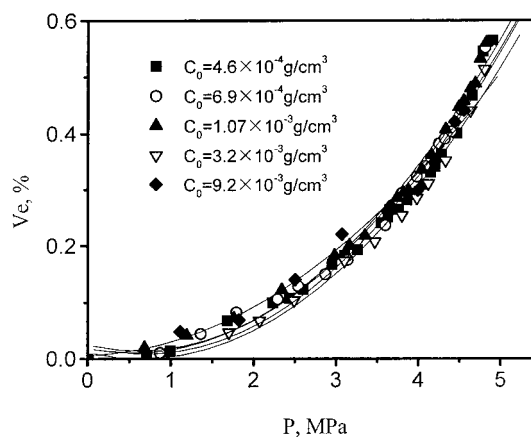


Figure 3. Dependence of volume expansion of the solutions with different original PS concentrations (C_0) on antisolvent CO_2 pressure.

which contains all information on the shape and the conformation of the isolated macromolecules in solution. The initial slopes of eq 4 vs C and eq 5 vs h^2 yield the second virial constant A_2 and mean square radius of gyration $\langle R_g^2 \rangle^{1/2}$, respectively. The K is required to use eqs 4 and 5. To a first approximation, we only consider the first two terms of the right side in eq 3. At the angle of $h = 0$, from eq 3, we have

$$\frac{KC}{I_{\text{exp}}(0, C)} = \frac{1}{M_w} + 2A_2 C \quad (6)$$

or

$$\frac{1}{M_w C} = -2A_2 + \frac{K}{I_{\text{exp}}(0, C)} \quad (7)$$

Thus, K and A_2 can be obtained from the slope and intercept of the $1/M_w C$ vs $1/I_{\text{exp}}(0, C)$ plot.

Results and Discussion

1. Phase Behavior. The volume expansion V_e and cloud pressure of the solutions were determined at different antisolvent pressures in the temperature range from 298.15 to 328.15 K. In this work, V_e is defined as $(V - V_0)/V_0$, where V and V_0 are the volumes of the solution after and before dissolving CO_2 . As examples, Figure 3 shows the V_e data of the solutions of different original concentrations at 308.15 K and different pressures. The C_0 in the figure is the original concentration of PS (CO_2 -free). The V_e experiments were repeated at least three times for each equilibrium condition and the reproducibility was better than $\pm 1\%$. It was estimated that the accuracy of the measurements was better than $\pm 2\%$. Figure 3 shows that the effect of PS concentration on the V_e is very limited. Figure 4 shows the cloud point pressures of the solutions of various original concentrations at different temperatures. As expected, the cloud pressure decreases with the original concentration of PS. Obviously, the concentration of a solution decreases with V_e or pressure. The V_e and cloud point pressure data in Figures 3 and 4 allowed us to determine how much CO_2 -free solution should be charged into the SAXS cell at different temperatures and pressures and what conditions we should choose for the viscosity and SAXS investigations.

The solubility of CO_2 in the solution is directly related with pressure. The solubility of CO_2 and the densities of the solutions of different PS concentrations were determined at 308.15 K and different antisolvent pres-

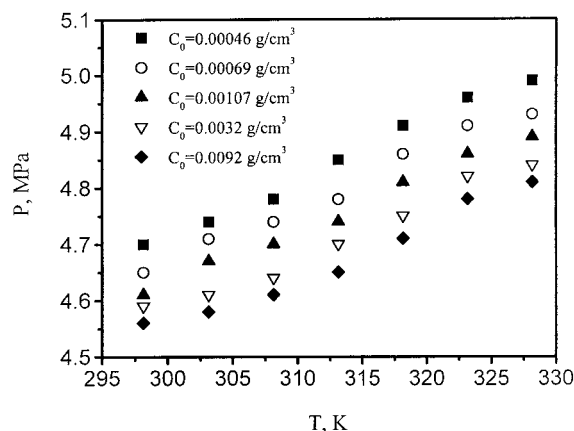


Figure 4. Cloud point pressures of solutions with different original PS concentrations (C_0) at different temperatures.

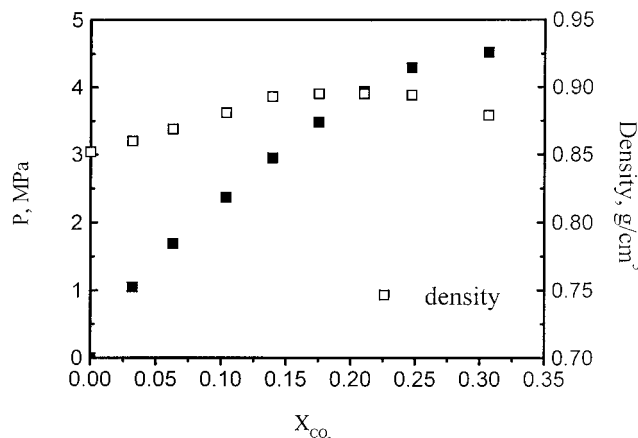


Figure 5. Effect of pressure on the solubility of CO_2 in toluene X_{CO_2} (weight fraction) and the density of the liquid phase at 308.15 K ($C_0 = 0.00046 \text{ g/cm}^3$).

tures. As an example, Figure 5 shows the solubility of CO_2 , X_{CO_2} (weight fraction), in an PS/toluene solution ($C_0 = 0.00046 \text{ g/cm}^3$) as a function of its partial pressure at 308.15 K. As expected, the solubility increases with its partial pressure. The corresponding density of the liquid phases is also shown in the figure, which was required in the viscosity calculation as can be known from eq 2. It should be mentioned that the effect of C_0 on the solubility and density is not noticeable at our experimental conditions. By combination of the results in Figures 3 and 5, the pressure–volume expansion–composition relation can be known.

2. Viscosity. In this work, we determined the viscosity η of PS/toluene solutions with original concentrations of 4.6×10^{-4} , 6.9×10^{-4} , 1.07×10^{-3} , 3.2×10^{-3} , and $9.2 \times 10^{-3} \text{ g/cm}^3$. The pressure of antisolvent CO_2 was up to 4.2 MPa. The results at 308.15 K are shown in Figure 6. It should be emphasized that all the experiments were conducted under equilibrium conditions.

The results in Figure 6 show that η decreases linearly with pressure of CO_2 at fixed temperature. The main reason is because the dissolved CO_2 can reduce viscosity of a liquid. It is also interesting to notice that the decrease in viscosity with pressure is greater for the concentrated solutions than in dilute solutions; i.e., η is more sensitive to pressure for concentrated solutions. This must be related with conformation change of the polymer in solvent, which results from weaker interaction between the polymer and the solvent with adding antisolvent CO_2 .

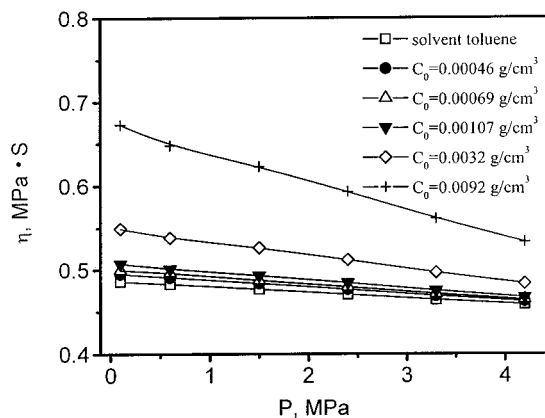


Figure 6. Dependence of the viscosity of the solutions η on antisolvent CO_2 pressure at 308.15 K for different original concentrations (C_0).

To understand the effect of antisolvent pressure upon the configuration of the dissolved polymer, we calculate the specific viscosity as a function of pressure

$$\eta_{\text{sp}} = \eta(p)/\eta_0(p) - 1 \quad (8)$$

where $\eta_{\text{sp}}(p)$ is specific viscosity at constant pressure, $\eta(p)$ and $\eta_0(p)$ are viscosity of the solution and solvent at the same pressure, respectively. This ratio effectively removes the solvent-dominated viscosity and allows for a direct examination of polymer behavior. This is also the first step to obtain the intrinsic viscosity⁴⁷ from which dilute solution polymer theory can be applied

$$[\eta] = \lim_{C \rightarrow 0} (\eta_{\text{sp}}/C(p)) \quad (9)$$

where $[\eta]$ is intrinsic viscosity, and $C(p)$ is the concentration of the solution at different antisolvent pressure which can be easily calculated from original PS concentration and the volume expansion shown in Figure 3.

$[\eta]$ is calculated from η_{sp} by the familiar Huggins equation⁴⁷

$$\frac{\eta_{\text{sp}}(p)}{C(p)} = [\eta] + k_H[\eta]^2 C(p) + \dots \quad (10)$$

where K_H is the Huggins interaction parameter which is related to the shape of the polymer molecules and its degree of association.

$\eta_{\text{sp}}(p)/C(p)$ is plotted against the concentration at different pressures $C(p)$ in Figure 7. Intrinsic viscosity $[\eta]$ and Huggins constants can be obtained from the intercepts and the slopes of the curves, respectively. The results are listed in Table 1. As shown in Table 1, the intrinsic viscosity $[\eta]$ decreases with pressure. The intrinsic viscosity is directly related with the conformation of the polymer in the solution and it is higher when the polymer is extended. It is also well-known that a polymer chain is more extend in good solvent. In our experimental system, toluene is a good solvent for PS, while CO_2 is a very poor and used as an antisolvent. The solvent power of toluene is reduced in the course of adding antisolvent CO_2 , since the solubility of CO_2 in the solvent increases with pressure; i.e., the solvent strength decreases with pressure. Thus, it is not surprised that the intrinsic viscosity is highest in toluene, and decreases with the partial pressure of CO_2 .

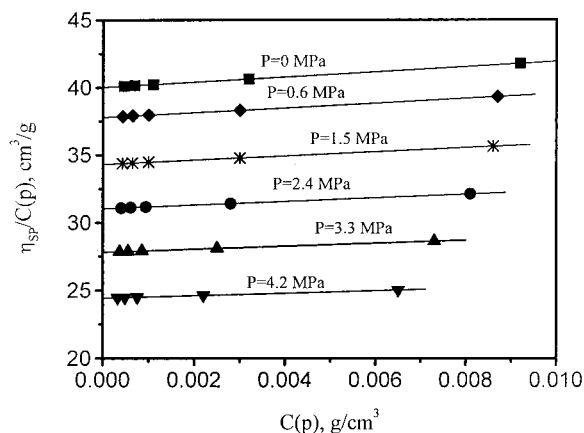


Figure 7. Huggins plots for PS in toluene at different antisolvent CO₂ pressures.

Table 1. Intrinsic Viscosity and Huggins Constant under Different Pressures of Antisolvent CO₂ for Polystyrene in Toluene at 35 °C

pressure, MPa	[η], cm ³ /g	Huggins const	overlap concn C*, g/cm ³
0	40.02	0.120	0.154
0.6	37.79	0.125	0.163
1.5	34.32	0.132	0.179
2.4	31.04	0.140	0.198
3.3	27.79	0.148	0.221
4.2	24.42	0.155	0.252

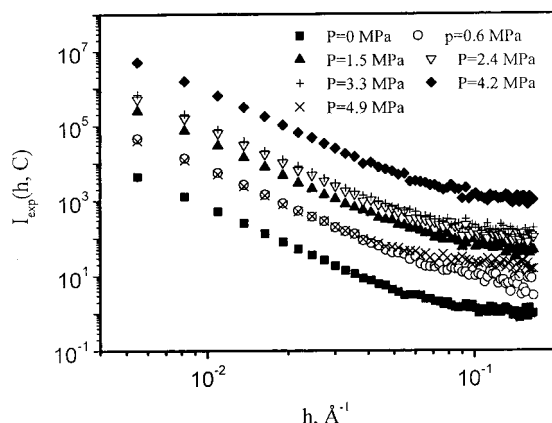


Figure 8. Effect of antisolvent CO₂ pressure on SAXS spectra of the solution ($C_0 = 0.00046$ g/cm³).

The overlap concentration C^* at which polymer coils begin to overlap and entangle can be calculated from^{48,49}

$$C^* = M/(N_A R_g^3) \quad (11)$$

where M and R_g are molecular weight and gyration radius of a polymer chain respectively, and N_A is Avogadro's number. The radius of gyration was calculated from intrinsic viscosity data in Table 1 and Flory solution theory³¹ as described in eq 1. The results showed that the concentrations of the solutions studied in this work were much lower than overlap concentration, i.e., the polymers in the solutions were not overlapped.

3. SAXS Study. In this work, we determined scattering intensity at original PS concentrations of 4.6×10^{-4} , 6.9×10^{-4} , 1.07×10^{-3} , 3.2×10^{-3} , and 9.2×10^{-3} g/cm³ at the same antisolvent pressures as those for viscosity measurements. As examples, Figure 8 shows double logarithm plot of scattering intensity $I_{\text{exp}}(h, C)$

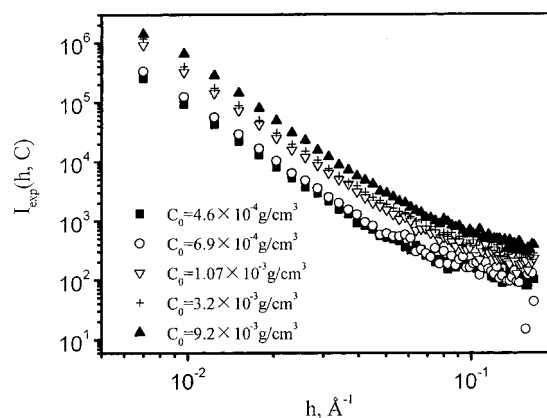


Figure 9. Effect of original solution concentration (C_0) on SAXS spectra of the solutions at antisolvent CO₂ pressure of 2.40 MPa.

vs scattering angle h at $C_0 = 4.6 \times 10^{-4}$ g/cm³ and different antisolvent CO₂ pressures, with $I_{\text{exp}}(h, C)$ being the scattered intensity due to the PS solute.

The scattering intensity increases with pressure at pressures lower than cloud pressure. We have known that the X-ray scattering is due to the contrast provided by the difference in electron densities in the solute and solvent. In the system investigated here, the electron density of the solute PS is 0.343 e/Å³ and that of the solvent toluene is 0.282 e/Å³.⁵⁰ The increasing of the scattering intensity may result from the aggregation of the polymer chain. Another feature of SAXS profiles is that the scattering intensity at the pressure higher than cloud pressure decreases considerably. It may result from the precipitation of some PS in the solution because the pressure is higher than the cloud pressure. The precipitated PS dropped below the irradiated volume.

Figure 9 shows double logarithm plot of $I_{\text{exp}}(h, C)$ vs h for PS/toluene solutions of different original concentrations at 2.4 MPa. The magnitude of the polymer concentration effect depends on the shape and charge of the particle and the solvent. No general function exists which would allow prediction of the magnitude of the concentration effect. From Figure 9, we can say that the concentration has a large effect on the scattering of the polymer solution.

To use eq 7 to obtain A_2 and K at different antisolvent pressures, the double logarithm scattering intensity plots of $I_{\text{exp}}(h, C)$ vs h at different concentrations were obtained using the experimental data. The concentration C has been corrected for the volume expansion using the results in Figure 3. The data were extrapolated to $h = 0$, and the values of $I_{\text{exp}}(0, C)$ were obtained. Figure 10 shows the $1/M_w C$ vs $I_{\text{exp}}(0, C)$ curves which are linear in the concentration range studied in this work. This verifies that we can get reliable results although we only considered the first two terms in the right side of eq 3. Thus, K and A_2 at different antisolvent pressures were easily obtained from slope and intercept of $1/M_w C$ vs $I_{\text{exp}}(0, C)$ curves, and the results are listed in Table 2.

We could not find the A_2 data in the presence of gas antisolvent in the literature. However, the A_2 of the PS-toluene binary solution reported by Berry et al.⁵¹ was 0.00055, which was close to that obtained in this work.

The second virial constant A_2 is related with the solvent power of the solvent for the polymer. As expected, A_2 depends on the partial pressure of antisolvent

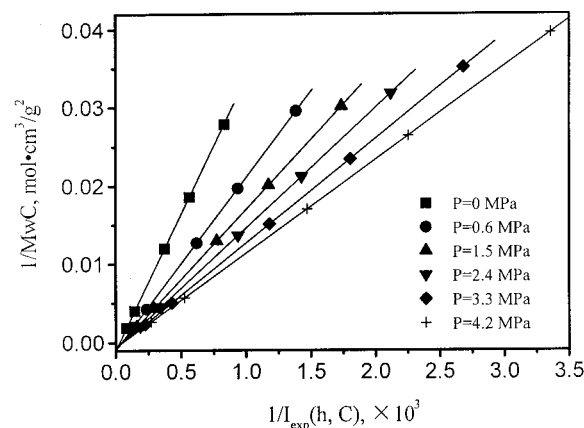


Figure 10. Plots of $1/M_w C$ against $1/I_{\text{exp}}(0, C)$ at different antisolvent pressures.

Table 2. Values of K , A_2 , and $\langle R_g^2 \rangle^{1/2}$ of PS at Different Pressures

pressure, MPa	K , $\text{cm}^3\text{mol/g}^2$	A_2 , $\text{cm}^3\text{mol/g}^2$	$\langle R_g^2 \rangle^{1/2}$, Å
0	34.72	0.000 51	95.5
0.6	22.00	0.000 48	92.8
1.5	17.85	0.000 44	89.0
2.4	15.36	0.000 38	86.3
3.3	13.35	0.000 34	78.4
4.2	11.97	0.000 30	71.3

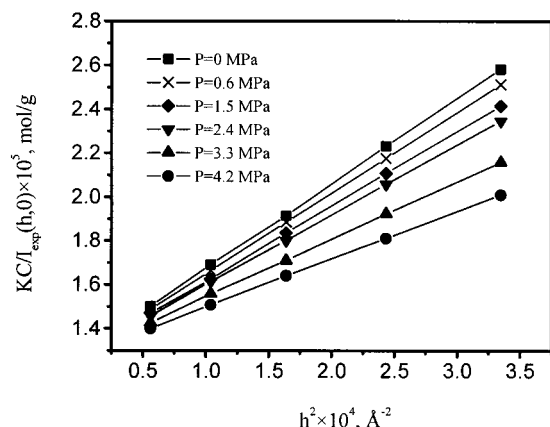


Figure 11. Plots of $KCI_{\text{exp}}(h, 0)$ against h^2 for PS in toluene at different antisolvent CO_2 pressures.

CO_2 . A_2 decreases with increasing antisolvent pressure, which indicates that the solvent power of toluene to PS decreases with adding of antisolvent CO_2 .

To calculate the mean square radius of gyration $\langle R_g^2 \rangle^{1/2}$ using eq 5, the data for $KCI_{\text{exp}}(h, C)_{C=0}$ are required. To do this, $KCI_{\text{exp}}(h, C)$ is plotted against C . The values of K in Table 2 were used in the calculation of $KCI_{\text{exp}}(h, C)$. $KCI_{\text{exp}}(h, C)$ vs C curves were extrapolated to zero concentration, and $(KCI_{\text{exp}}(h, C))_{C=0}$ was obtained. $(KCI_{\text{exp}}(h, C))_{C=0}$ vs h^2 curves are linear, as shown in Figure 11. Thus, $\langle R_g^2 \rangle^{1/2}$ can be evaluated from their slopes as can be known from eq 5. The results are given in Table 2 and Figure 12. The $\langle R_g^2 \rangle^{1/2}$ of PS in toluene (CO_2 -free) agrees with the literature value (97.7 Å).⁵¹

As shown in Figure 12, $\langle R_g^2 \rangle^{1/2}$ decreases with increasing pressure. It indicates that the PS chain experiences shrinking in the course of adding antisolvent CO_2 . Toluene is a good solvent for PS, and the coil expanded due to prevailing intersegmental repulsion; after addition of CO_2 , the solvent power of the solvent is reduced and PS chain is shrunk due to prevailing intersegmental

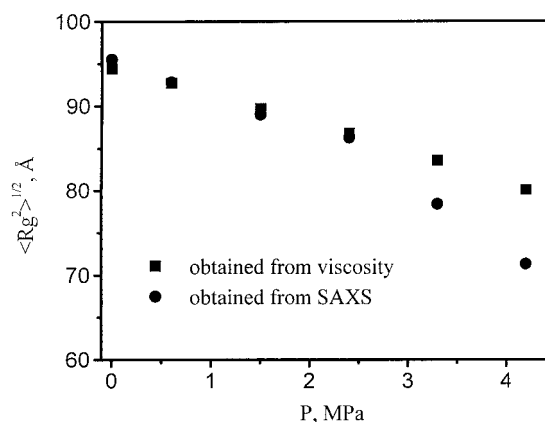


Figure 12. Effect of antisolvent CO_2 pressure on the $\langle R_g^2 \rangle^{1/2}$ at 308.15 K

attraction. This conclusion is the same as that obtained from the dependence of intrinsic viscosity on pressure.

As discussed above, $[\eta]$ is related with $\langle R_g^2 \rangle^{1/2}$ by eq 1.³¹ The $\langle R_g^2 \rangle^{1/2}$ values, calculated from eq 1 and $[\eta]$ obtained in this work, are also shown in Figure 12. We can see that the values of $\langle R_g^2 \rangle^{1/2}$ obtained from viscosity data agree reasonably with those from SAXS method, especially at the lower CO_2 pressures. This implies that Flory theory, which has been used widely for the solutions of polymers in liquid solvents, is also applicable to the polymer solution with gas antisolvent.

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