

# Solubility of Polystyrene in Liquid Sulfur Dioxide

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## Synopsis

The two-phase equilibrium in the system polystyrene (PS)–liquid sulfur dioxide [ $\text{SO}_2(l)$ ] was investigated, mainly at room temperature. The system consisted of an upper PS-rich phase, concentration (30–50)% depending on the way of preparation, and a lower phase containing less than 1% PS. The range of molecular weights of the PS samples used was 22,000–350,000 ( $\bar{M}_w$ ). PS with an  $\bar{M}_w$  value of 22,000 dissolved homogeneously in  $\text{SO}_2(l)$ . In systems forming two phases a fractionation of PS with respect to molecular weight was observed. The  $\bar{M}_w$  value of the PS fraction dissolved in the lower PS lean phase was always substantially lower than that of the upper phase. When increasing the temperature to 90–95°C, the two phases disappeared and the PS component formed a jellylike mass with a very low solubility in  $\text{SO}_2(l)$ . Also in the supercritical dense  $\text{SO}_2$  gas, the solubility of PS was a few tenths of a percent only. Experiments with Soxhlet extraction indicated an extractability of a few percent.

## INTRODUCTION

Even though it is known that certain polymers, e.g., polystyrene, poly(methyl methacrylate) (PMMA) and poly(vinyl acetate) (PVAC), can be dissolved in liquid sulfur dioxide,<sup>1–4</sup> very little attention has been paid to the properties of the corresponding solutions. The system polystyrene–liquid sulfur dioxide [PS- $\text{SO}_2(l)$ ] appears to possess some especially interesting features, as it consists of two phases.<sup>5</sup> Also, from the technical point of view, the low cost of liquid sulfur dioxide seems to motivate a closer study of this system.

The use of  $\text{SO}_2(l)$  as solvent for polymers has been discussed by Hata et al. It was found, for instance, that polystyrene, poly(methyl methacrylate), and poly(vinyl acetate), are easily dissolved in  $\text{SO}_2(l)$  at  $-15^\circ\text{C}$  to give homogeneous clear solutions.<sup>1–3</sup> A number of other polymers, too, can be dissolved in  $\text{SO}_2$ , provided certain solubilizing agents are added. Methacrylates, styrene, and modacrylic polymers, i.e., copolymers of not more than 85% poly(acrylonitrile) with vinyl acetate, can be dissolved substantially without solubilizing agents. Certain phenols and halogenaliphatic acids promote the solubilization of polyamides, poly(ethylene terephthalate), polyacrylics, and acrylonitrile copolymers.

Cellulose can be dissolved in  $\text{SO}_2(l)$  containing, e.g., secondary or tertiary amines.<sup>6–9</sup> Blake and Shore<sup>10</sup> found certain piperazine based polyamides and polyurethanes to be soluble in  $\text{SO}_2(l)$ , the solution being used for fibre spinning.

Sherr and Carlin<sup>11</sup> utilized the solubility and swelling of a number of polymers in  $\text{SO}_2(l)$  to produce foamed materials by release of pressure or simple evaporation. They found that poly(methyl methacrylate), polycarbonate (bisphenol-A-based), poly(methyl acrylate), and poly(vinyl acetate) formed solutions

in  $\text{SO}_2(l)$ . Polystyrene formed a gel mass under these conditions. A number of acrylonitrile-based copolymers were brought into solution, some of them forming gels.

Several of the numerous papers dealing with the polymerization of styrene in  $\text{SO}_2(l)$  mention that the PS- $\text{SO}_2(l)$  system separates into two liquid phases. The upper phase contains almost all the polystyrene as a concentrated [(30–50)%] viscous solution, while the lower phase consists of practically pure  $\text{SO}_2(l)$ .<sup>5</sup>

The present paper describes some preliminary experiments concerning two-phase PS- $\text{SO}_2(l)$  equilibrium and its dependence on molecular weight and temperature, including supercritical states. Some experiments concerning the extractability of PS and some other polymers with  $\text{SO}_2(l)$  are also described.

## EXPERIMENTAL

### Materials

Most of the experiments were performed using four different grades of polystyrene, one commercial quality (BASF Polystrol 158K) and three laboratory products with varying molecular weights. In addition, a low molecular telomer type PS kindly provided by BASF, Ludwigshafen/Rhein, was used. The molecular weight values of the PS-samples are given in Table I. In the extraction experiments commercial plastic grades were used.

The  $\text{SO}_2(l)$ , obtained from AGA, Special Gases Div., Stockholm, Sweden, had a purity better than 99.98%. Before being used, it was redistilled. Its boiling point (b.p.) at 0.1013 MPa is  $-10^\circ\text{C}$ , its density at this point being  $1.46\text{ g/cm}^3$ . At  $20^\circ\text{C}$  its equilibrium pressure is 0.326 MPa and its density  $1.38\text{ g/cm}^3$ . Its critical point is at  $157.8^\circ\text{C}$  and 7.88 MPa, solubility parameter  $10.1\text{ cal}^{1/2}/\text{ml}^{1/2}$  at room temperature (RT) ( $20 \pm 0.5^\circ\text{C}$ ).

### Methods

#### Pressure Vessels

Two types of pressure vessels were used: a cylindrical jacketed glass vessel with a volume of  $75\text{ cm}^3$  (Ingenieur bureau SFS, Zürich, Switzerland) and a conventional stainless-steel vessel with a volume of  $750\text{ cm}^3$  (Forschungsinstitut Berghof GmbH, Tübingen-Lustnau, BRD). The glass vessel, Figure 1, was designed for a maximum pressure of 10 MPa, the steel vessel for 20 MPa. Both types could be heated to  $200^\circ\text{C}$ .

TABLE I  
Molecular Weight of the PS Samples

PS sample	$\bar{M}_w$
BASF Polystyrol 158K	350,000
Polysciences	280,000
BDH Chemicals, A	400,000
BDH Chemicals, B	200,000
BASF (telomer type)	22,000

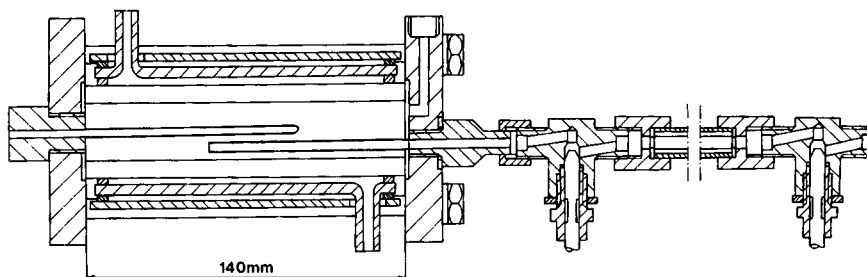


Fig. 1. Glass vessel with sampling container; nominal pressure 10 MPa.

The volumes of the two phases in the PS- $\text{SO}_2(l)$  system were measured optically using the glass vessel. In certain experiments the concentration of PS was determined gravimetrically by weighing the glass vessel. The errors in the volume and concentration were less than 1%. The pressure was determined using an electronic pressure gauge (Phillips PR 9370) with an accuracy of  $\pm 0.005$  MPa. Temperature readings were obtained using a platinum resistance thermometer giving an accuracy of  $\pm 0.05^\circ\text{C}$ . Both instruments were connected to a recorder. The other types of measurements used in this investigation are described in the text (sampling techniques, etc.).

### Extraction Apparatus

The extraction device was a Soxhlet-extractor provided with a cooling jacket ( $-15^\circ\text{C}$ ) enclosing its middle section.<sup>12</sup> The maximum volume of liquid  $\text{SO}_2$  in the extraction part of the device was  $25\text{ cm}^3$ , the liquid being drawn down to the reservoir on average 5 times/hr. The amount of polymer in the cellulosic extraction tube was 4–6 g.

## RESULTS

### Phase Equilibria in the System PS- $\text{SO}_2(l)$

As reported in ref. 5, PS dissolved in  $\text{SO}_2(l)$  forms two phases. The upper phase, which is highly viscous at room temperature and even more so at  $-10^\circ\text{C}$ , i.e., the boiling point of  $\text{SO}_2(l)$ , contains practically all the polymer, while the lower phase consists of almost pure  $\text{SO}_2$  with less than 1% of solute. The experiment described in the following two sections relate to RT ( $20 \pm 0.5^\circ\text{C}$ ).

### Composition of the Upper PS-Rich Phase

The concentration of PS in the upper PS-rich phase was determined from the weight of the glass vessel containing the PS- $\text{SO}_2(l)$  system and from the volumes of the lower and upper phases. This calculation was made with the simplifying assumption, that the PS concentration in the lower phase can be neglected. As shown below, this assumption was justified. For all the PS grades used, with the exception of the homogeneously dissolving low  $\bar{M}_w$  grade ( $\bar{M}_w = 22,000$ ), the PS concentration of the upper phase was found to be close to 50% by weight at  $20^\circ\text{C}$ . However, this was only true of measurements for which the PS component

was allowed to dissolve in the SO<sub>2</sub> liquid without mechanical agitation. After the formation of the upper phase was complete, a process taking a few hours at RT, the height of the upper layer remained constant, even when the observation time was extended over weeks. Unless stated all experiments relate to systems not subjected to any mechanical agitation, i.e., systems apparently in equilibrium.

When the system was subjected to mechanical agitation, for instance by boiling off SO<sub>2</sub> through a valve in the top plate of the glass vessel, a peculiar phenomenon was observed, in that the volume of the upper layer increased significantly as the volume of the SO<sub>2</sub> liquid in the lower layer was reduced. The linearity of the volume change was remarkable, as was also the magnitude of the effect. In a typical experiment, using 69.6 g SO(*l*), and 15.0 g PS with  $\bar{M}_w = 400,000$ , the PS concentration in the upper phase decreased from 50.5% to ca. 35% when the volume of the lower phase was reduced from 40.9 to 1.1 cm<sup>3</sup>. This reduction in concentration of PS in the upper layer was accompanied by a corresponding increase in its thickness (volume). The PS concentration in the lower phase remained constant and, in the present context, negligible.

It may thus be concluded that the PS concentration in the upper PS-rich phase is strongly dependent on mechanical agitation of the system. This could be verified by experiments where the contents of the vessel was agitated in a shaking device. In this case too, the limiting concentration of PS in the upper phase was found to be approximately 33% for all the PS grades investigated. It is to be noted that neither an increase in temperature (up to ca. 80°C) nor prolonged standing of the system (weeks) could bring about similar effects.

### Composition of the Lower Phase

In contrast to the high concentration of PS in the upper phase, i.e., (35–50)%, depending on the conditions during preparation, the concentration in lower phase was small. This was so for all the PS grades used, with the exception of the 22,000  $\bar{M}_w$  grade, which dissolved without forming two separate phases.

In a typical experiment, 15.0 g of PS ( $\bar{M}_w = 400,000$ ) was dissolved in 75 g SO<sub>2</sub>(*l*) in the glass vessel, which was provided with a small sampling container (2 cm<sup>3</sup>) connected by a tube to the central part of the lower phase, see Figure 1. After filling the container, the SO<sub>2</sub> sample was allowed to boil off and the solids content was determined gravimetrically. The procedure was repeated several times in order to collect easily measurable quantities of PS.

In the above experiment, the weight concentration of the solid dissolved in the lower phase was 0.15%, i.e., 0.75% of the total amount of PS. Similar results were obtained in experiments with the other PS grades. The solid recovered from the lower phase was relatively soft. Its molecular weight was substantially lower than that of the original sample (see below).

With regard to the phase separation effect it should be noted that, rather naturally, two phases are observed only in PS-SO<sub>2</sub>(*l*) systems, where the total PS concentration is lower than that of the upper PS-rich phase, i.e., ca. 50% and 33% before and after mechanical agitation, respectively. When the total PS concentration is higher, only one phase is formed.

### Viscosity of the PS-Rich Phase

The viscosity of the PS-rich phase was determined at various temperatures using the falling sphere method.<sup>13</sup> Due to space limitations, a length of fall of only 10 cm could be used. A solution of 37.4 g PS (BHD,  $\bar{M}_w = 400,000$ ) in SO<sub>2</sub>(l), giving a volume ratio of 14.35:1.13 of the upper and lower phases, respectively, was prepared in the glass vessel. The system was allowed to equilibrate for 2 days. The sphere of polished stainless steel had a diameter of 6.35 mm and weight of 1.041 g. It was released by an electromagnetic device and its movement was followed with a traveling microscope.

The measurements gave the following values of kinematic viscosity: 545 St (20°C), 222 St (40°C), 105 St (60°C), and 69 St (80°C). These values relate to a PS concentration of 40%; they are only approximate as the variation of the density with temperature was not determined.

### Molecular Weight of PS Dissolved in the Two Phases

From the waxy appearance of the residue obtained after evaporation of SO<sub>2</sub> from samples taken from the lower phase, it was concluded that a fractionation with regard to molecular weight occurs between the two phases. This conclusion was verified experimentally using gel permeation chromatography (GPC), and measurements of intrinsic viscosity.

We dissolved 10 g PS in 60 g SO<sub>2</sub>(l) and allowed it to equilibrate for 48 hr. Samples taken from the two phases were evaporated, the residues were weighed, dissolved in benzene, and the intrinsic viscosity of the solutions determined in the usual manner. The result of these measurements together with GPC data are summarized in Table II for two PS grades with  $\bar{M}_w = 215,000$  and 240,000, respectively. There was a significant difference in the average molecular weight of the PS in the two phases. The results presented in Table II also indicate that a slight degradation of the polystyrene might have occurred. This effect will be investigated in a forthcoming publication.

### Influence of Temperature on the Volume of the Two Phases

The influence of temperature on the volumes of the two phases was measured optically in the glass vessel. The lower phase expanded somewhat faster than the PS-rich phase. The volume changes were, however, moderate only and significantly smaller than those observed when mechanically agitating the system

TABLE II  
Molecular Weights of Polystyrene in the Two Layers of the PS-SO<sub>2</sub>(l) System

Material		$\bar{M}_v$ ( $\eta_{intr.}$ )	$\bar{M}_n$ (GPC)	$\bar{M}_w$ (GPC)
PS Polysciences	upper layer	210,000	82,000	280,000
PS Polysciences	lower layer	14,000	11,000	16,000
PS Polysciences	original material	215,000	87,000	280,000
PS Polystyrol 158K BASF	upper layer	240,000	117,000	330,000
PS Polystyrol 158K BASF	lower layer	7,000	10,500	16,000
PS Polystyrol 158K BASF	original material	240,000	135,000	350,000

by boiling off the lower phase or by shaking. For example 15 g PS,  $\bar{M}_w = 280,000$ , dissolved in 45.4 cm<sup>3</sup> SO<sub>2</sub>(*l*) formed two phases with volumes of upper and lower 26 and 34 cm<sup>3</sup>, respectively. When increasing the temperature from 20 to 88°C the volumes of the upper and lower phases increased linearly by 9.2% and 8.0%, respectively. Experiments with the other  $\bar{M}_w$  grades produced similar results.

### Supercritical Region

The experiments designed to estimate the concentration of polystyrene dissolved in the supercritical phase were performed using two pressure vessels. A quantity of 100 g PS,  $\bar{M}_w = 200,000$ , was dissolved in 200 g SO<sub>2</sub> in the steel vessel. After heating the system to 165°C, i.e., ca. 10°C above the critical temperature, for 0.1 hr, a part of the supercritical phase was transferred through a valve to the glass vessel in which an open sampling tube, volume 8.60 cm<sup>3</sup>, was placed so that it was filled with the condensing phase. The solids concentration was determined gravimetrically using this sampling tube after boiling off the SO<sub>2</sub> liquid. Five consecutive samples were taken from the steel vessel during each experiment. The pressure in this vessel did not at any time fall below the critical value during the sampling procedure. The results of the experiment are given in Table III.

Even though, for natural reasons, the accuracy of experiments of this type is relatively low, it could be shown that supercritical SO<sub>2</sub> under the conditions used dissolves less than 1% of an oily residue containing varying amounts of sulfur. This residue probably consisted of degradation products and sulfur-modified styrene-based compounds. The sulfur content increased with temperature and the time in the supercritical state.

By observing the behaviour of the PS-SO<sub>2</sub>(*l*) system in the glass vessel it was noted that the upper phase disappeared at 90–100°C. As could be expected, due to the lowering of density of SO<sub>2</sub>(*l*) when temperature was increased, the PS sank as a jellylike mass to the bottom of the vessel leaving only one liquid phase.

TABLE III  
Experiments at Supercritical Conditions. PS Concentration in Supercritical SO<sub>2</sub>

Quantity PS BDH $\bar{M}_w =$ $2 \times 10^5$ (g)	Quantity SO <sub>2</sub> (g)	Total concentration of PS (%)	Pressure interval during sampling (MPa)	Sampling temperature (°C)	Time in supercritical state (hr)	Solid content in super- critical SO <sub>2</sub> (%)
100	200	33.0	9.5–8.7	165	0.1	0.12
100	500	17.0	9.5–8.7	165	0.1	0.11
100	300	25.0	9.3–8.7	162	0.1	0.16
100	950	9.5	12.5–8.5	178	0.1	1.10
100	200	33.0	10.0–9.0	170	0.1	0.41
100	600	14.5	9.5–8.7	165	1.2	0.12

### Soxhlet Extraction of PS and Plastic Mixtures with $\text{SO}_2(l)$

Soxhlet-extraction experiments with a number of polymers showed that polymers reported to be completely soluble in liquid  $\text{SO}_2$  exhibited a widely differing extractability. This was, for instance, the case with PMMA, PVAC, and PC (polycarbonate, Makrolon 3100, Bayer), which were completely extractable, while PS could be extracted to a few percent only [(2–3)%] under the conditions used ( $-15^\circ\text{C}$  for 24 hr). Due to the occurrence of two phases and the high viscosity of the PS- $\text{SO}_2(l)$  system the extraction results were difficult to interpret. The molecular weight ( $\bar{M}_w$ ) of the PS samples varied between 200,000 and 400,000. Both granulated and pulverized samples were used. Polysulfone behaved similarly to PS in that only a few percent could be brought into solution by extraction, despite prolonged treatment (several days). The extractability of ABS (Marbon Chemicals type Cycolac DA 10000) corresponded roughly to its styrene content. Similar results were obtained in experiments on the extraction of plastic mixtures simulating the composition of municipal and other plastic-containing waste.

### FINAL REMARKS

This paper describes the first part of a larger investigation of various polymer- $\text{SO}_2$  systems and their possible applications. Due to its importance, the PS- $\text{SO}_2(l)$  system provides a natural first step in such a study. The experiments described relate to the feasibility of extracting PS and certain other polymers from plastic mixtures and waste with  $\text{SO}_2(l)$  as solvent. The low cost of this liquid as compared to conventional PS solvents is an especially important factor when considering separation and recovery from plastic-containing waste using solvent based methods.<sup>14–16</sup> Despite the low extractability in a conventional Soxhlet device, there appears to be no difficulties in developing an  $\text{SO}_2(l)$ -based extraction process for the recovery of primarily PS. Furthermore, the occurrence of two phases in the PS- $\text{SO}_2(l)$  system could be an advantage when properly utilized. Results obtained with a pilot plant built in our laboratory show recovery figures in the region of 95% of the PS component contained in mixtures of various types.<sup>17</sup>

$\text{SO}_2(l)$  is a solvent for a comparatively large number of polymers. Among those not listed earlier in the literature, we found the following to be soluble: various grades of acrylonitrile-butadiene-styrene (ABS) and styrene-acrylonitrile copolymers (SAN) (Montecatini Edison Kostil type AN), polysulfone (Union Carbide type 1700), polyethersulfone (ICI, 200 P), poly(vinyl pyrrolidone) (GAF K-90), and cellulose acetate butyrate (Bayer Cellidor BspM). Partial solubility or swelling was recorded for SBR-rubbers and ethylene-vinyl acetate copolymers of varying composition. Unplasticized PVC softened substantially, becoming rubbery and highly extensible. In certain cases, e.g., PMMA, the polymer was dissolved in mixtures of  $\text{SO}_2(l)$  with nonsolvents. Special mention should be made of the possibility of fractionating, with respect to molecular weight, polymers that form two phases in  $\text{SO}_2(l)$ . As well as PS, polysulfone was found to behave in this way.

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Received January 10, 1978

Revised June 15, 1978