

Partition coefficients of polystyrene in liquid and supercritical 1,1,1-chlorodifluoroethane

M. Hamedi*, Ph. Desmarest, F. Cansell and R. Tufeu

Laboratoire d'Ingénierie des Matériaux et des Hautes Pressions, C.N.R.S.,
 Institut Galilée, Université Paris Nord, 93430 Villetaneuse, France
 (Revised 1 April 1997)

The phase equilibrium of the system consisting of polydisperse polystyrene in liquid 1,1,1-chlorodifluoroethane (R142b) was investigated in the temperature range 395–454 K and pressure range 6.8–30 MPa. Partition coefficients were determined from the overall polystyrene concentration in the solvent-rich phase measured by u.v. absorption spectroscopy and from the polymer distributions in the two coexisting phases of the two-phase system at equilibrium. The partition coefficient of a polymeric pseudocomponent (corresponding to a slice of the polymer chromatogram) is defined as the ratio of its mass concentration in the solvent-rich phase to its weight fraction in the polymer-rich phase on a solvent-free basis. At constant temperature and pressure, the partition coefficient of a pseudocomponent is shown experimentally to be independent of the polymer distribution in the polymer-rich phase. Therefore the mass-based partition coefficient, as defined, of a pseudocomponent can be identified with the mass concentration of this pseudocomponent in the solvent-rich phase for an equilibrium in which only a pseudocomponent and the solvent are involved. For given experimental conditions, the partition coefficients are found to have a log-linear dependence on the chain molar mass. From the temperature and pressure effects on the partition coefficients, the potential of R142b for fractionation is discussed. © 1997 Elsevier Science Ltd.

(Keywords: polystyrene; partition coefficient; 1,1,1-chlorodifluoroethane)

INTRODUCTION

Supercritical fluids (SCF) are increasingly used as solvents in separation processes¹. The main advantage of the use of solvents in supercritical conditions lies in the continuous adjustability of solvent power through changes in the operating conditions^{2,3}. This property makes them very attractive for polymer processing. Many studies report methods used to purify, fractionate and synthesize polymers using SCF^{4–10}. The engineering design of such processes requires a knowledge of the polymer–solvent system phase behaviour.

Most of the investigations reported in the literature concerning the phase behaviour of polymer solutions were carried out with polymer standards having a polymolecularity index ($I = M_w/M_n$) of <1.1 ^{11–16}. Phase diagrams were obtained by measurement of the dew or bubble points of solutions of known composition. Saraf and Kiran¹¹ obtained the coexistence curves (P, x) of polystyrene (PS) with different degrees of polymerization (DP) in several alkanes. These phase diagrams were found to be very sensitive to the molar mass of the polymer and to the solvent. An increase in polymer DP or the use of a poor solvent significantly increases the demixing pressures. Using a similar experimental procedure, Chen and Radosz¹³ obtained pressure–temperature constant-composition phase diagrams for poly(ethylene–propylene) (with different DP) in supercritical olefins. As the polymer molar mass was increased, the lower critical solution temperature (LCST) curve was shifted to lower temperatures until the UCST and LCST curves merged into a single curve. These diagrams

have been of great interest as a practical means of characterizing polymer solutions and of elucidating thermodynamic and configurational properties of macromolecules, but they would not provide sufficient information for studies of mass transfer from a bulk polydisperse polymer to a solvent.

In fact, a polymer is in most cases a mixture of chains having different molar masses and must be considered as a multicomponent mixture. Therefore a knowledge of polymer average mass and distribution would not be sufficient to determine the distribution and/or the polymer concentration in the solvent-rich phase at equilibrium. The pertinent parameter characterizing each component of a multicomponent two-phase system is in fact the mass-based partition coefficient k_i , defined for each component i as the ratio of its weight fraction in the solvent-rich phase, ω_i^y , to its weight fraction in the polymer-rich phase, ω_i^s :

$$k_i = \omega_i^y / \omega_i^s \quad (1)$$

For polymers, various other formulations of the partition coefficient were adopted by Shultz and Jirgensons¹⁷, Flory^{18,19} and Breitenback and Wolf²⁰

Experimentally, it is easier to obtain a partition coefficient k_i' :

$$k_i' = \frac{W_i^y}{W_i^s}$$

where W_i^y is expressed in kg of i -mer per kg of solvent and W_i^s is the weight fraction of the i -mer expressed on a solvent-free basis (g of i -mer per g of PS in the polymer-rich phase). Experimental k_i' determinations using a continuous flow extraction have been performed by Kumar *et al.*²¹. These experiments showed that this partition coefficient was

* To whom correspondence should be addressed

independent of the polymer-rich phase composition for polystyrene of low DP in butane. As a consequence, the as-determined partition coefficient can be identified with the *i*-mer concentration at equilibrium in the solvent-rich phase when a solvent-*i*-mer binary is considered under the same operating conditions.

For a two-phase system composed of a polydisperse polystyrene and a solvent, the concentration of each *i*-mer in the solvent-rich phase would depend only on its partition coefficient and weight fraction in the polymer-rich phase at equilibrium. Hence the overall polymer concentration in the solvent-rich phase is a linear combination of k_i' values and the weight fractions of the components *i* in the polymer-rich phase.

It will be shown that the experimental results of Pradhan *et al.*²² on supercritical propane and polystyrene can be explained using the above consideration, which simplifies the study of multicomponent phase equilibria. We have therefore developed an experimental procedure for the determination of $k' = f(M)$. The influence of pressure, temperature and parent polymer composition on the partition coefficient have been investigated. The method is based on on-line u.v. measurements of polymer concentration in the solvent-rich phase with 1,1,1-chlorodifluoroethane (R142b) as the solvent and polystyrene as the

solute. The system studied is a liquid-fluid phase equilibrium since the investigated temperature range is above the glass transition temperature (T_g) of polystyrene (373 K), which is expected to be lowered by a compressed solvent that would behave as a plasticizer²³.

EXPERIMENTAL

Materials and equipment

The solvent R142b (99.8% purity) was supplied by Dehon Industrie. Its critical temperature and critical pressure are respectively 410.3 K and 4.04 MPa²⁴.

Solvent density data are necessary for the calculation of the partition coefficients. R142b densities have been measured by Sousa *et al.*²⁵ at temperatures < 404 K. For higher temperatures only a few data were found, for pressures < 10 MPa²⁶.

We supplemented these available data by measuring the density of R142b at 392.2 and 423.4 K up to 30 MPa with a variable-volume sapphire cell used previously for the determination of phase equilibria of solutions²⁷. Walsh and Dee²⁸ found that the Sanchez-Lacombe²⁹ equation of state (EOS) gives good PVT fits for halocarbons in supercritical conditions. This equation was used. Its fit to our measurements and to the data in the literature is shown in Figure 1, using the following parameters: $\rho^* = 1417 \text{ kg m}^{-3}$, $P^* = 2.99 \times 10^8 \text{ Pa}$, $T^* = 427.9 \text{ K}$. The densities at 453 K were obtained by using this EOS, the predictions of which should be good, as long as these points are away from the critical point of R142b. Moreover, the predicted densities are in the range for which the fit was made.

The polystyrene samples used were a mixture of different standards supplied by Aldrich (2500, 4000 and 13 000 g mol^{-1}) and Thouzard et Matignon (7000 and 9600 g mol^{-1}).

The experimental setup used for partition coefficient measurements is shown in Figure 2. Its main component was a closed loop consisting of a circulating pump (operating up to 493 K and 32 MPa), a cylindrical fixed bed of a mixture of PS and Raschig rings, and a u.v.-visible optical cell equipped with a sapphire window (Figure 3).

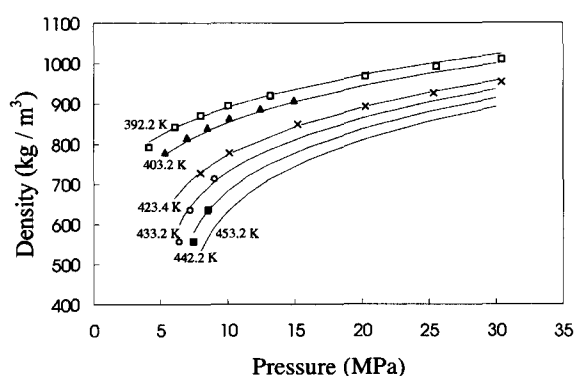


Figure 1 PVT of R142b measurements: \blacktriangle , Sousa *et al.*²⁵; \circ , \blacksquare , Yada *et al.*²⁶; \square , \times , our measurements. The lines are the predictions of the Sanchez-Lacombe equation of state

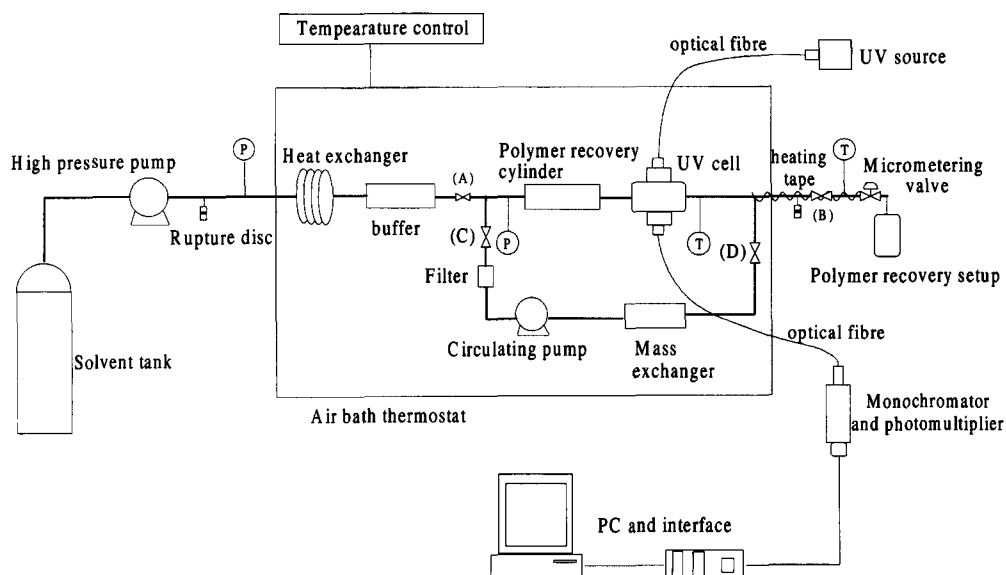


Figure 2 Experimental setup for the measurement of partition coefficients

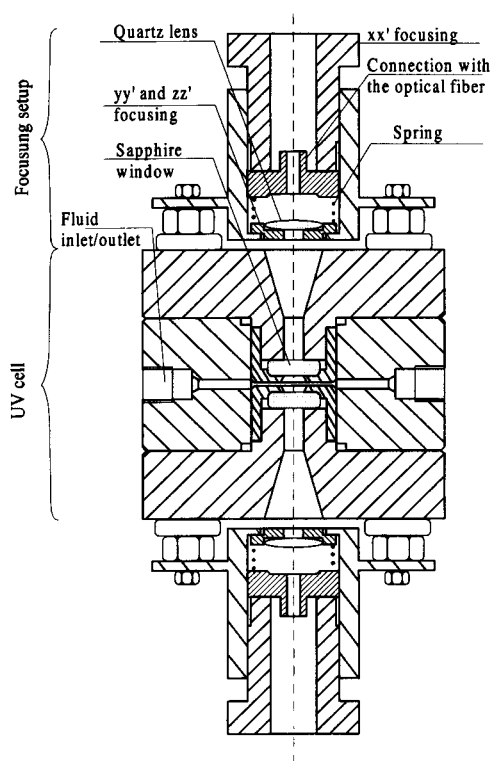


Figure 3 u.v. cell and focusing setup

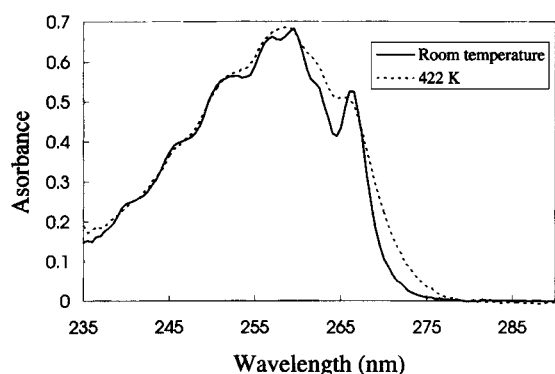


Figure 4 Influence of temperature on absorption spectra of polystyrene in tetrahydrofuran and dichloromethane

The latter was used for measurements of PS concentration in the solvent-rich phase and could be operated up to 673 K and 40 MPa. The whole system was maintained at a constant temperature within ± 0.5 K in two air-bath thermostats. A separate thermostat was used to preheat the pure fluid. Pressure was measured with 0.05 MPa accuracy using a calibrated strain-gauge transducer. An Autoclave Engineers micrometering valve at the outlet allowed pressure control when the solubilized polystyrene was recovered. The light source was a xenon lamp. Fibre optics and an adapted u.v.-grade focusing optical setup ensured

light transmission. The transmitted light was analysed with a Jobin-Yvon monochromator model H20, then recorded by a personal computer via a Jobin-Yvon interface (model Spectralink).

Absorption coefficient measurements

The use of u.v. absorption for measuring concentration requires a knowledge of the polystyrene absorption coefficient in R142b, and the influence of pressure and temperature on this parameter. No data were found in the literature for this system. R142b is gaseous at ambient pressure and temperature, and the preparation of calibrated polystyrene solutions was difficult. We therefore studied the effects of temperature and pressure on the polystyrene absorption coefficient using two solvents of different nature: tetrahydrofuran and dichloromethane (u.v. grade from Aldrich).

Five calibrated solutions of polystyrene in the two solvents were prepared. The absorption coefficients were measured in the u.v. cell. Experiments were carried out with tetrahydrofuran at ambient temperature and pressures ranging from 0.1 to 30 MPa and no significant change in the absorption coefficients was found. The temperature effect was determined by making measurements at ambient temperature and 422 K at respectively 0.1 and 17.8 MPa. Figure 4 shows the polystyrene spectra at ambient temperature and at 422 K. As expected, spectral broadening is observed at the higher temperature. The absorption coefficients were measured at the peaks located at 259 ± 1 and 266 ± 1 nm. The data obtained are given in Table 1. For both solvents, the increase in temperature is accompanied by a decrease in absorption coefficient (due to the spectral broadening). At 422 K, the values obtained for both solvents agree within experimental error. Therefore we assume that PS absorption behaves in the same way in R142b at 259 and 266 nm. Considering the precision of the measurements, we assume that the absorption coefficients remain constant in the temperature range 120–180°C, i.e. 205×10^3 and $154 \times 10^3 \text{ cm}^2 \text{ mol}^{-1}$ at 259 and 266 nm respectively.

Procedure

The system was heated to the working temperature and filled with the solvent using the high-pressure pump. The loop was then isolated (by closing valve A) and the circulating pump was activated. When the transmitted light at 259 nm showed no variation of for at least 6 h, indicating that equilibrium had been reached, the solubilized polymer could be recovered. The whole run lasted ~ 15 h. By closing the valves C and D, the polymer recovery cylinder and the u.v. cell were then isolated from the rest of the loop and the solvent inlet (valve A) was opened to sweep the solution at constant pressure. Polymer was recovered by expanding the solution at atmospheric pressure. The polymer recovery cylinder was large enough for at least 5 mg of solubilized polymer to be recovered. This quantity was necessary for polymer composition analysis. A u.v. spectrum was taken before and after recovery, to measure the overall solubility

Table 1 Absorption coefficient of polystyrene in dichloromethane and tetrahydrofuran: influence of temperature at 259 and 266 nm

Wavelength (nm)	Absorption coefficient at 293 K ($10^{-3} \text{ cm}^2 \text{ mol}^{-1}$)		Absorption coefficient at 422 K ($10^{-3} \text{ cm}^2 \text{ mol}^{-1}$)	
	Dichloromethane	THF	Dichloromethane	THF
259	208.8	208.0	205.2	205.5
266	162.3	166.4	153.7	154.9

at equilibrium. The solubilized polymer, the initial polymer and the polymer remaining in the mass exchanger were analysed using size exclusion chromatography in tetrahydrofuran, with a Waters apparatus (Ultrasyl columns of pore sizes 10, 50 and 100 nm) calibrated with standard polystyrene samples.

Partition coefficient calculation

The resolution of s.e.c. cannot yield the weight fraction of each chain length contained in a polymer mixture. The chromatograms were therefore divided into slices δt , referred to as pseudocomponents corresponding to the average elution time t_i .

The partition coefficients can be calculated from a knowledge of the total polymer concentration (from u.v. measurement), the volume of the loop, the mass distribution of the extracted and initial polymers and the total amount of polystyrene initially introduced into the contactor.

The distribution of the polymer-rich phase at equilibrium was obtained by subtracting the mass of each solubilized pseudocomponent from its mass in the initially introduced polymer. The distributions obtained by calculation and by analysis should be close to each other. In addition to the s.e.c. accuracy, the differences may be attributed to two factors induced by the experimental procedure: on one hand by the precipitation of the solubilized polymer remaining in the mass exchanger at the end of the experiment, and on the other hand by polymer dragging during loop depressurization at the end of the experiment. In fact the polymer precipitation was negligible, considering the small volume of the mass exchanger and the low polymer solubility. Moreover, we believe that polymer dragging was negligible, because depressurization was operated at room temperature.

Figure 5 shows the pseudocomponent weight fractions in the solvent-rich phase of the calculated polymer at equilibrium and of the polymer remaining in the mass exchanger at 424 K and 24.6 MPa. Here the initial charge was 1.190 g of parent polymer and the solubilized polymer mass in the loop was 0.064 g. Figure 5 shows two main features: (1) the weight fractions of the cuts below 2300 g mol^{-1} and above $11\,100 \text{ g mol}^{-1}$ are too small for accurate measurement of the partition coefficient; (2) the solubilized polymer comprises the fractions of relatively low molar masses.

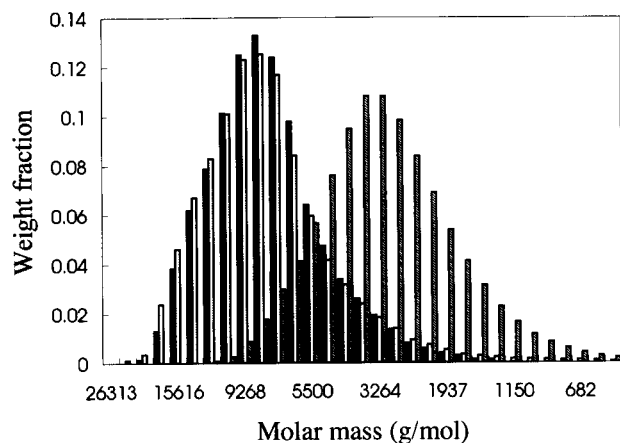


Figure 5 Mass distributions of polymer remaining in mass exchanger at equilibrium, obtained by calculation (shaded squares) and s.e.c. analysis (■), and mass distribution of solubilized polymer (hatched squares). $T = 424 \text{ K}$, $P = 24.6 \text{ MPa}$

RESULTS AND DISCUSSION

The first part of the work consisted in verifying whether the distribution of the parent polymer had an influence on the partition coefficient. The latter was measured for two different distributions of the parent polymer (Figure 6) under the same operating conditions. These experiments were performed at 426 K and $23.6 \pm 0.2 \text{ MPa}$. The results are presented in Figure 7. For both samples, the partition coefficients have a log-linear dependence on the chain molar mass, and fall on the same line, within experimental error. The partition coefficient may therefore be considered as independent of the parent polymer distribution, which is in agreement with the work of Kumar *et al.*²¹ on supercritical ethane and polystyrene with molar masses $< 3000 \text{ g mol}^{-1}$.

Pradhan *et al.*²² have measured the solubility of a 3250 g mol^{-1} weight-average molar mass (M_w) sample of polystyrene ($I = 1.06$) in supercritical propane. It was found to be 0.176 kg of PS per kg of propane (0.15 in weight fraction). The solubility of a 30:70 (w/w) mixture of this sample and a $M_w 47\,950 \text{ g mol}^{-1}$ ($I = 1.05$) sample measured under the same experimental conditions was found to be 0.053 kg of PS per kg of propane (0.05 in weight fraction). Assume that the 3250 g mol^{-1} sample is a mixture of n pseudocomponents each having a weight fraction W_i^{s1} in the polymer-rich phase (on a solvent-free basis). If k_i' is the partition coefficient of each pseudocomponent, then the

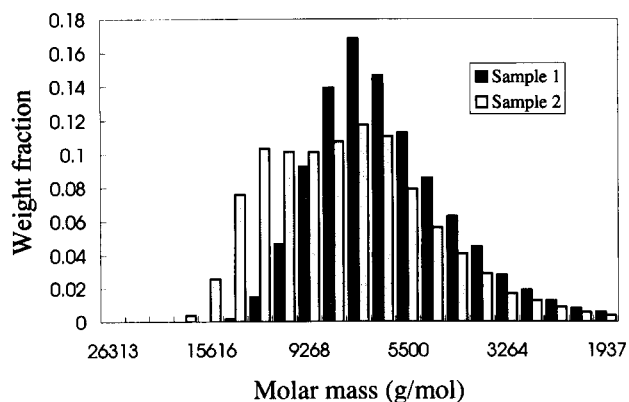


Figure 6 Composition of samples remaining in mass exchanger used to study effect of polymer composition on partition coefficient. $T = 426 \text{ K}$, $P = 23.6 \text{ MPa}$

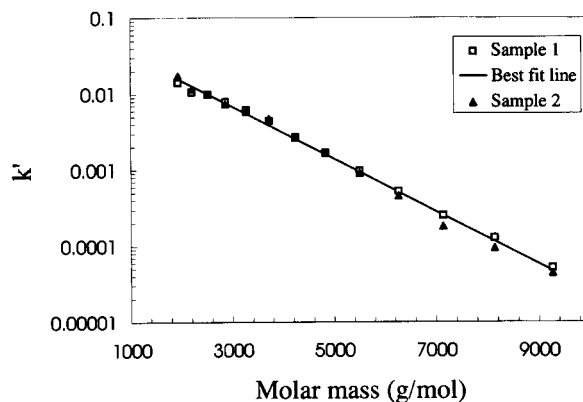
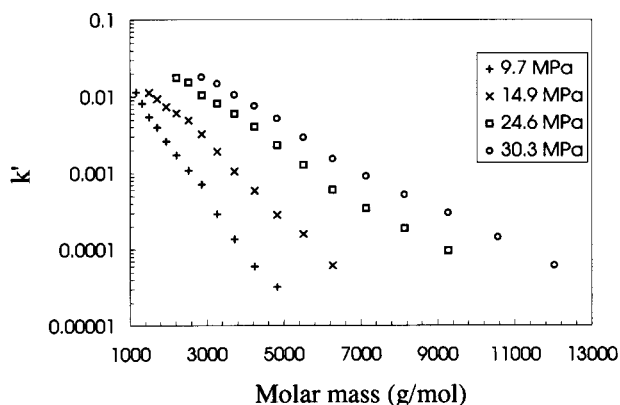


Figure 7 Influence of polymer composition on partition coefficient at $T = 426 \text{ K}$, $P = 23.6 \text{ MPa}$. Total polystyrene mass concentration for samples 1 and 2 respectively 1.1 and 0.7 g polystyrene per kg solvent

Table 2 Molar mass and polydispersity index of samples used for experiments at 424 K

Pressure (MPa)	9.7	14.9	24.6	30.3
M_w (g mol ⁻¹)	4260	4510	8420	8800
I	1.48	1.37	1.22	1.33
C^* (kg kg ⁻¹) ^a	7.9×10^{-4}	2.1×10^{-3}	1.4×10^{-3}	1.9×10^{-3}

^aTotal overall mass concentration for these experiments at equilibrium.


Figure 8 Partition coefficient at 424 K as a function of molar mass at different pressures. Overall polystyrene solubility and parent polymer molar mass are given in Table 2

overall concentration of polystyrene W_t^{v1} is given by:

$$W_t^{v1} = \sum_1^n W_i^{v1} = \sum_1^n k_i' W_i^{s1} \quad (2)$$

where W_i^{v1} is the concentration of the pseudocomponent i at equilibrium in the solvent-rich phase for the first experiment. For the second experiment equation (2) becomes:

$$W_t^{v2} = \sum_1^{n+m} k_i' W_i^{s2} = \sum_1^n k_i' W_i^{s2} + \sum_{n+1}^{n+m} k_i' W_i^{s2} \quad (3)$$

where subscript m stands for the pseudocomponents of the 47950 g mol⁻¹ sample. The partition coefficient k' has a log-linear dependence on polymer molar mass. Therefore it takes negligible values for the pseudocomponents of the 47950 g mol⁻¹ sample, which is also the case for the second term of equation (3). Considering the 30:70 polymer mixture composition, equation (3) becomes:

$$W_t^{v2} = \sum_1^n k_i' (0.3 W_i^{s1}) = 0.3 W_t^{s1} \quad (4)$$

The overall polystyrene concentration in the solvent-rich phase is therefore expected to be 0.053 kg kg⁻¹, which is equal to the experimental value. The results of these experiments are therefore consistent with the independence of the partition coefficient on the polymer distribution in the polymer-rich phase.

Daneshvar and Gulari³⁰ have measured the partition coefficient defined by equation (1) of poly(ethylene glycol) forming a two-phase system with supercritical CO₂. It was found to have a log-linear dependence on polymer molar mass for sufficiently high degrees of polymerization, i.e. when end-group effects become negligible. Such a partition coefficient differs by a constant factor from k' for a given experiment. References 22 and 30 therefore corroborate the log-linear dependence of the partition coefficient on polymer molar mass.

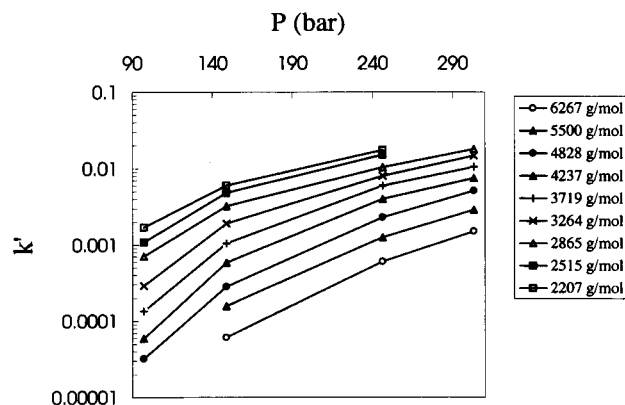

Figure 9 Partition coefficient as a function of pressure for pseudocomponent molar masses ranging from 2200 to 6300 g mol⁻¹. $T = 424$ K

Figure 8 shows the influence of pressure on the partition coefficient at 424 K. An increase in pressure has two effects: an increase in the partition coefficient for all i -mers, and a decrease in the slope of the $k' = f(M)$ curve. The partition coefficient increases by three orders of magnitude for PS chains having a difference in molar mass of 4000 g mol⁻¹ at 9.7 MPa, whereas at 30.3 MPa the increase is only one order of magnitude for the same molar mass difference. Consequently, increasing the pressure leads to a higher rate of extraction but a lower selectivity. Such a property is specific to supercritical fluids, making them very attractive for selective extraction processes.

The characteristics of the parent polymers used for the experiments at 424 K are given in Table 2. Although the molar weights differ from one experiment to another, k' is a smooth function of pressure for given pseudocomponent, as shown in Figure 9. This behaviour reinforces the previous conclusion about the independence of the partition coefficient on the parent polymer composition.

The influence of temperature at constant solvent density was investigated. For liquids far from the critical point, a change in temperature at constant pressure is followed by a very small change in density. Therefore solubility studies in liquids at different temperatures account mainly for temperature effects. At supercritical and near-supercritical conditions, no such approximation can be made: a change in temperature at constant pressure is followed by a considerable change in density (see Figure 1). Therefore, operating at the same density and at different temperatures requires, at mean time, a pressure change. Figures 10 and 11 show k_i' as a function of PS molar mass at two constant densities (920 and 850 kg m⁻³). Considering the very low polymer concentrations, the solution densities have been assumed to be equal to the pure solvent densities. As expected, the partition coefficients are higher at higher temperatures. An increase of more than one order of magnitude for a 60 K increase is observed for $M_i = 3000$ g mol⁻¹ at a solvent

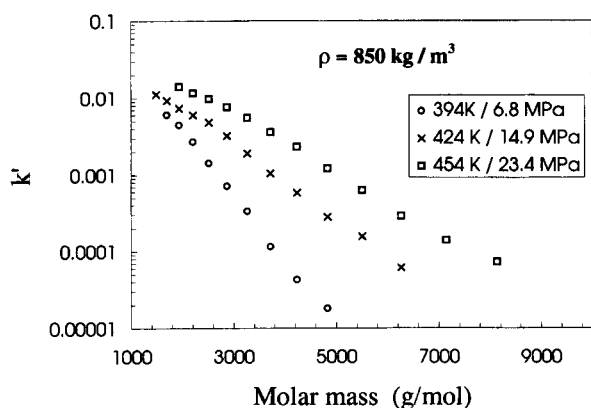


Figure 10 Partition coefficient as a function of molar mass at constant solvent density for different temperatures. $\rho = 850 \text{ kg m}^{-3}$

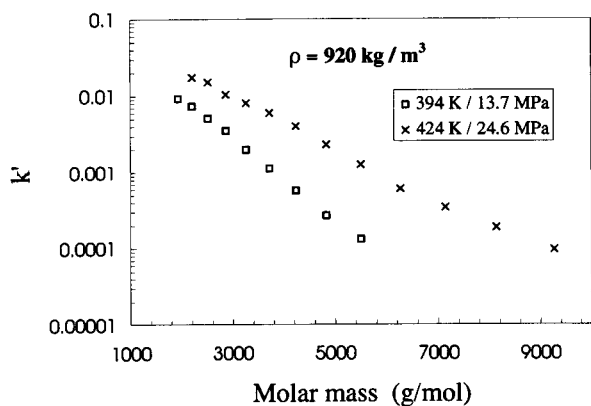


Figure 11 Pseudopartition coefficient as a function of molar mass at constant solvent density for different temperatures. $\rho = 920 \text{ kg m}^{-3}$

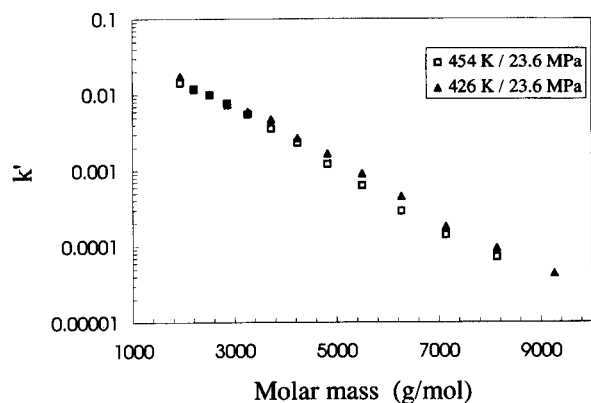


Figure 12 Isobaric (23.6 MPa) plot of $\log k'$ as a function of molar mass for two temperatures

density of 850 kg m^{-3} . It should be noticed that the curve slope changes with temperature.

Isobaric plots (23.6 MPa) of $\log k'$ versus M_i at two different temperatures (454 and 426 K) are shown in Figure 12. Both curves are very close to each other. At this pressure, the effect of the density change of the solvent due to the temperature variation at constant pressure compensates the effect of temperature change on solvent power. Studies of the solubility of low-molar-mass compounds in supercritical fluids show similar behaviour, and two solubility regions are observed. In the first region,

the effect on solubility due to the decrease in solvent density with temperature rise at constant pressure is larger than the temperature change effect (retrograde condensation), whereas in the second region (which concerns higher pressures) the relative effects of the temperature change and of the induced solvent density change are reversed. The (P, x) diagram of PS in pentane obtained by Saraf and Kiran¹¹ is an illustration of this behaviour.

CONCLUSIONS

By using a method in which the overall polystyrene concentration and composition in the solvent-rich phase are measured, the influence of pressure and temperature on the partition coefficient of polystyrene in R142b was investigated. Considering the experimental conditions, the partition coefficients were found to be independent of the polymer-rich composition in terms of polymer distribution. Consequently the partition coefficient is equal to the equilibrium mass concentration of pure *i*-mer in the solvent-rich phase as generally obtained with monodisperse samples. Conversely, from a knowledge of these partition coefficients, the overall solubility and solvent-rich composition can be calculated whatever the parent polymer's polymolecularity. Moreover, the solvent selectivity with respect to polymer molar mass can be assessed.

The selectivity is closely related to the slope of the linear curve which represents the logarithm of partition coefficient as a function of *i*-mer molecular weight. Generally, the selectivity is temperature- and pressure-dependent. Around 20 MPa, this selectivity is weakly temperature-dependent.

For temperatures not too far from the critical temperature of the solvent ($T/T_c < 1.1$), the solubility and the selectivity are strongly pressure-dependent (due to large solvent density variations).

The pressure dependence of the selectivity and of the solvent power of supercritical fluids makes them attractive for developing processes involving unreacted monomer removal, oligomer removal or fractionation of a broadly distributed polymer into narrow distributed fractions.

Preliminary experiments have shown that the solvent is well adapted for polystyrene fractionation³¹. From successive extractions with pressure profiling, we have obtained fractions of increasing average molecular weight M_n from 800 to 9500 g mol^{-1} , in agreement with the increase in partition coefficients with pressure.

ACKNOWLEDGEMENTS

We thank Dr Dominique Adès of the L.R.M. (Laboratoire de Recherche sur les Macromolécules de l'Université Paris 13, Avenue J. B. Clément, 93430 Villetaneuse, France) for the s.e.c. analysis.

REFERENCES

1. Radosz, M., Eur. Pat. Appl. 489 574, 1992; US Serial No. 892,462, now allowed, 1993.
2. Johansen, M. and Bruner, G., *Fluid Phase Equilib.*, 1994, **95**, 215.
3. Schmitt, W. J. and Reed, R. C., *J. Chem. Eng. Data*, 1986, **31**, 204.
4. Ylgor, I., McGrath, J. E. and Krukonic, V., *Polym. Bull.*, 1984, **12**, 491.
5. Ylgor, I., McGrath, J. E. and Krukonic, V., *Polym. Bull.*, 1984, **12**, 499.
6. Krukonic, V. J., *Polym. News*, 1985, **11**, 7.
7. Scholsky, K. M., O'Connor, V. M. and Weiss, C. S., *J. Appl. Polym. Sci.*, 1987, **33**, 2925.

8. Kiran, E. and Saraf, V., *J. Supercrit. Fluids*, 1990, **3**, 198.
9. Dhawan, J. C., Legendre, R. C., Bencsath, A. F. and Davis, R. M., *J. Supercrit. Fluids*, 1991, **4**, 160.
10. Romack, T. J., Maury, E. E. and DeSimon, J. M., *Macromolecules*, 1995, **28**, 912.
11. Saraf, V. P. and Kiran, E., *Polymer*, 1988, **29**, 2061.
12. Beckman, E. J., Koningsveld, R. and Porter, R. S., *Macromolecules*, 1990, **23**, 2321.
13. Chen, S. and Radosz, M., *Macromolecules*, 1992, **25**, 3089.
14. McClellan, A. K., Bauman, E. G. and McHugh, M. A., in *Supercritical Fluid Technology*, ed. J. M. L. Penninger, M. A. Radosz and V. J. Krukoni. Elsevier, Amsterdam, 1985, p. 161.
15. Kiran, E. and Zhuang, W., *Polymer*, 1992, **33**, 5259.
16. Meilchen, M. A., Hasch, B. M., Lee, S. H. and McHugh, M. A., *Polymer*, 1992, **33**, 1922.
17. Shultz, G. V. and Jirgensons, B., *Z. Phys. Chem. B*, 1940, **46**, 105.
18. Flory, P. J., *J. Chem. Phys.*, 1942, **10**, 41.
19. Flory, P. J., *J. Chem. Phys.*, 1942, **12**, 425.
20. Breitenback, J. W. and Wolf, B. A., *Makromol. Chem.*, 1967, **20**, 263.
21. Kumar, S. K., Chhabria, S. P., Reid, R. C. and Suter, U. W., *Macromolecules*, 1987, **20**, 2550.
22. Pradhan, D., Chen, C. and Radosz, M., *Ind. Eng. Chem. Res.*, 1994, **33**, 1984.
23. Condo, P., Sanchez, I. C., Panayiotou, C. G. and Johnston, K. P., *Macromolecules*, 1992, **25**, 6119.
24. Yada, N., Kumagai, K. and Watanabe, K., *J. Chem. Eng. Data*, 1991, **36**, 142.
25. Sousa, A. T., Fialho, P. S., Nieto de Castro, C. N., Tufeu, R. and Le Neindre, B., *Fluid Phase Equilib.*, 1992, **80**, 213.
26. Yada, N., Kumagai, K., Tamatsu, T., Sato, H. and Watanabe, K., *J. Chem. Eng. Data*, 1991, **36**, 12.
27. Tufeu, R., Subra, P. and Plateaux, D., *J. Chem. Thermodynam.*, 1993, **25**, 1219.
28. Walsh, D. J. and Dee, G. T., *J. Supercrit. Fluids*, 1989, **2**, 57.
29. Sanchez, I. E. and Lacombe, R. H., *J. Phys. Chem.*, 1976, **80**, 2352.
30. Daneshvar, M. and Gulari, E., *J. Supercrit. Fluids*, 1992, **5**, 143.
31. Desmarest, Ph., Hamedí, M., Tufeu, R. and Cansell, F., in *Proceedings of the 3rd International Symposium on Supercritical Fluids*, Vol.2. 1994, p. 287.