Anomalous Swelling of a Polystyrene Matrix in Organic Solvents

Gabriel Bernardo,[1,2] **Drahosh Vesely**[3]

[1]*Institute for Polymers and Composites, University of Minho, Campus de Azurem, Guimarães 4800-058, Portugal*
[2]*Institute for Nanostructures, Nanomodelling and Nanofabrication (I3N), University of Minho, Campus de Azurem, Guimarães 4800-058, Portugal*
[3]*Department of Materials, Oxford University, Parks Road, OX1 3PH, UK*

Received 10 July 2008; accepted 15 August 2009
DOI 10.1002/app.31280

ABSTRACT: Swelling behavior of a commercial linear polystyrene, containing a small amount (<5% wt) of mineral oil, has been studied in three different classes of organic solvents (alkanes, alcohols and carboxylic acids) using both gravimetry and light microscopy. A comparison has been made with the results presented in earlier publications using a different linear polystyrene, without mineral oil. It is shown that the polystyrene containing mineral oil absorbs much higher amounts of solvent at lower temperatures then at higher temperatures. This anomalous behavior sharply contrasts with the polystyrene without mineral oil, which at lower temperatures absorbs much less solvent. Light microscopy of the diffusion layer reveals that in the polymer with mineral oil precipitation occurs during diffusion at low temperatures, but not at high temperatures. These results clearly show that the presence of small amounts of mineral oil (in quantities below the detection limit of FTIR) can cause significant changes in the sorption behavior of polymers. These results are interpreted by pre-existing nano-inhomogeneities, formed by the mineral oil, limited miscibility of oil in the polymer phase and high miscibility of solvent in the oil phase. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 2402–2408, 2010

Key words: polystyrene; anomalous swelling; diffusion; precipitation; mineral oil

INTRODUCTION

Diffusion and swelling of polymers in organic solvents has been the subject of research for over 60 years. It is known that when a solvent (either in the liquid or gaseous state), miscible with a polymer, diffuses into a matrix of that polymer, swelling (i.e., mass uptake) occurs until an equilibrium saturation plateau is reached.[1–9] This constant saturated swelling is also attained for noncross-linked polymers[1–5] and is, for the same polymer-solvent system and temperature, a highly reproducible measurable physical quantity. Several different techniques have been used so far to measure this constant saturation plateau including light[1] and electron[2] microscopy, gravimetry,[3–6] FTIR[7,8] and neutron and x-ray reflectivity measurements.[9] Previous studies[2–5] have also shown that in polymer-solvent systems the amount of solvent mass uptake always increases with increasing temperature and therefore the corresponding solubility diagrams are of the upper critical solubility temperature type.

Polymer microstructure in the diffusion layer is rarely investigated and the origin of the opacity often observed[10] does not get the attention it might deserve. On the other hand, theoretical consideration of microvoids (or holes) and their filling up during diffusion is not new and played a major role in explanation of diffusion rate using the concept of dual mode sorption.[11–17] Filling up voids has been observed *in situ*[18] and a new approach to diffusion has been recently suggested.[19–21] It has been previously reported[22,23] that a small addition of mineral oil can change the low temperature mechanical behavior of polystyrene. The addition of vegetable oil to PS has also been reported[24] to change the UV absorption and photoluminescence properties.

In the present work we report on the anomalous swelling behavior [apparent lower critical solubility temperature (LCST)] of a commercial polystyrene matrix containing <5% of mineral oil (as mentioned in the product specification) and show that the presence of mineral oil, even in quantities close to the detection limit of FTIR, can affect substantially the swelling behavior of a commercial polymer. This is of a significant scientific relevance because it is, as far as we know, the first time in the literature that

---

Correspondence to: G. Bernardo (gabriel.bernardo@dep.uminho.pt).

Contract grant sponsor: Fundação para a Ciência e a Tecnologia; contract grant number: SFRH/BD/4908/2001.

such an anomalous swelling behavior has been reported and correlated with composition of the commercial polymer samples as well as with the occurrence of precipitation during solvent diffusion. This work highlights the fact that much precaution is needed when studying the swelling behavior of commercial polymer samples, especially if these contain additives even in very small quantities, and emphasizes the fact that swelling studies should be accompanied by *in situ* diffusion studies under a light microscope to detect the occurrence of possible anomalies during the diffusion and swelling processes.

EXPERIMENTAL

Polymers and solvents

Two different polystyrenes, which from now on we shall designate simply as polystyrene 1 (PS1) and polystyrene 2 (PS2), and a mineral oil have been obtained from Sigma-Aldrich with the following specifications:

PS1 – catalog number 43,010-2 ($M_w = 230{,}000$, $M_n = 140\ 000$, MFI 7.5 g/10min, $T_g = 94°C$)

PS2 – catalog number 44,114-7 ($M_w = 350{,}000$, $M_n = 170{,}000$, MFI 3.4 g/10 min, $T_g = 95°C$), containing <5% mineral oil.

Light mineral oil—catalog number 33,077-9

As diffusing solvents we have used three different types, namely: alkanes (octane, decane, dodecane, tetradecane and hexadecane), alcohols (1-decanol) and carboxylic acids (myristic acid). Two additional solvents, namely chloroform and hexane, were used in the purification of PS2. All these organic solvents were purchased from Sigma–Aldrich and were all of purity >99%.

Calculation of solvent mass uptake

In this work we express solvent mass uptake as a percentage in mass, X_L, of solvent uptake using the formula:

$$X_L = \left(\frac{m_L}{m_L + m_{\mathrm{PS}}}\right) \times 100 \qquad (1)$$

where m_L is the mass of liquid penetrant (g) and m_{PS} is the mass of dry polystyrene (g).

Experimental procedure

In the present work we study the swelling behavior of PS2 using gravimetry and also the *in situ* diffusion of organic solvents into PS2, using light microscopy. The swelling behavior of PS1 has been studied in our previous work,[3–5] and in the present work we use PS1 only to perform some *in situ* diffusion studies with light microscopy to compare the results with the corresponding results obtained with PS2.

To characterize polystyrenes 1 and 2 by FTIR spectroscopy, the polystyrene granules were compression molded (on a hot press at temperature of 180°C and pressure of 3 tons) into very thin films with thicknesses of ~ 0.1 mm. These thin films were placed between potassium bromide (KBr) windows, put in the sample holder and analyzed by FTIR. Infra-red spectra were obtained on a Perkin–Elmer FTIR spectrometer, at room temperature. Sixty-four scans were averaged for each sample.

To characterize the different polystyrenes by ^{1}H-NMR, small samples were dissolved on $CDCl_3$ and analyzed on a Varian VXR 300 MHz NMR spectrometer.

Before the swelling experiments we have performed some preliminary tests to find out if PS2 was a linear polymer or if it had some amount of cross-linking. We have tested the solubility of PS2 samples in several different organic solvents and they have dissolved completely in: cyclohexane, benzene, 4-heptanone, cyclohexanone, and tetrahydropyran. These results clearly show that PS2 is a matrix of a linear polymer, i.e., there are no chemical cross-links in our samples.

To perform the swelling studies of PS2, the polymer granules as purchased from Sigma-Aldrich, were also compression molded at the same temperature and pressure as above into thin flat samples with thicknesses of ~ 0.45 mm, 0.85 mm and 1.70 mm (measured with a micrometer). The sample thicknesses were determined by metallic molds with appropriate thicknesses. After compression at high temperature, the samples were allowed to cool down slowly at normal atmospheric pressure to avoid possible stresses that could have remained if the samples had been cooled quickly. The PS2 samples, with approximate dimensions of 10 mm × 10 mm × thickness, have been placed inside beakers with solvent in a oven at constant temperature, as measured with a mercury thermometer with a precision of 0.5°C. At time intervals, the samples were removed from the solvent (after quenching with cold solvent in the case of solvents with melting points well below room temperature), their surfaces were carefully cleaned with absorbent paper and the samples were weighted on an analytical balance. Finally they were returned back to the solvent and put inside the oven. The experiments were run until full saturation has been attained and no more weight increase observed.

For each system and temperature, at least five samples have been tested. The scatter of data between the individual samples has been less than

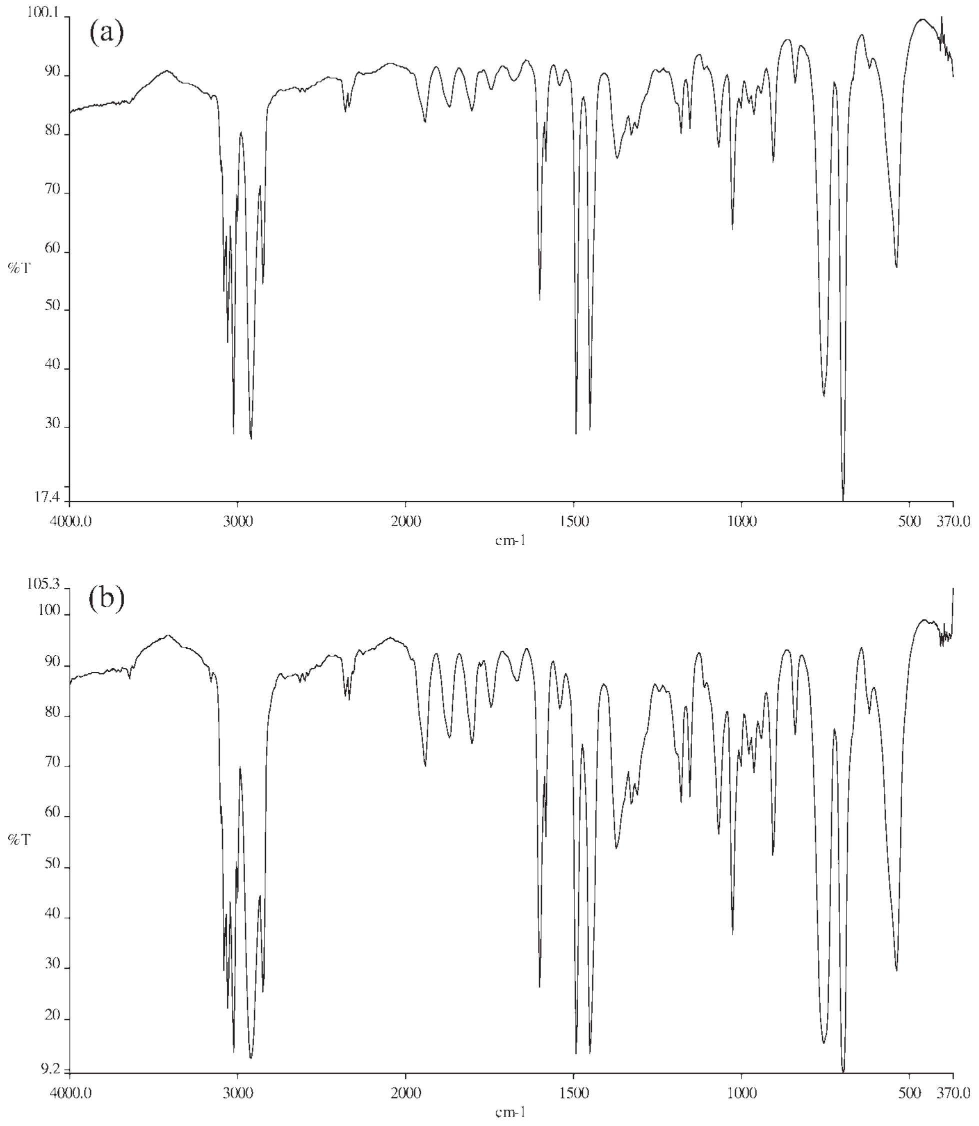

Figure 1 FTIR spectra of: (a) PS1 and (b) PS2.

5% at full saturation, and for average data and repeated test less than 2%.

We have observed that the solubility data cannot be obtained with the same accuracy and precision as in the case of PS1, as reported earlier.[3–5] Furthermore the concentration levels attained at saturation with PS2, are not as stable as in the case of swelling of PS1.

In this work we have also performed *in situ* light microscopy diffusion studies of the diffusion of solvents into PS1 and PS2, using a technique described previously.[18] Thin flat polymer samples were compressed between two glass slides at high temperature (~ 150°C) on a hot plate and cooled down slowly to room temperature. The samples were then placed on a hot stage (Reichert) at selected temperatures (65 and 125°C), under a light microscope. When a thermal equilibrium was reached, solvent was introduced and the progress of the diffusion front observed and recorded by a digital camera at selected time intervals. A lens with a long working distance (and thus low magnification and resolution) had to be used with the hot stage.

Blending of PS1 with light mineral oil has been achieved by using a specially constructed laboratory blender with a temperature controller. Batches of four grams were blended in a sealed chamber for 15 s to obtain a homogeneous mixture at 150°C.

Removal of mineral oil from PS2 has been achieved by making use of the different solubility of polystyrene and mineral oil in chloroform and in hexane. PS2 has been dissolved in a small amount (50 mL) of chloroform by stirring vigorously the mixture until a highly viscous, transparent and colorless liquid has been obtained. By adding a large amount of hexane (250 mL), a white solid precipitates which is polystyrene. Mineral oil is soluble both in chloroform and in hexane and for that

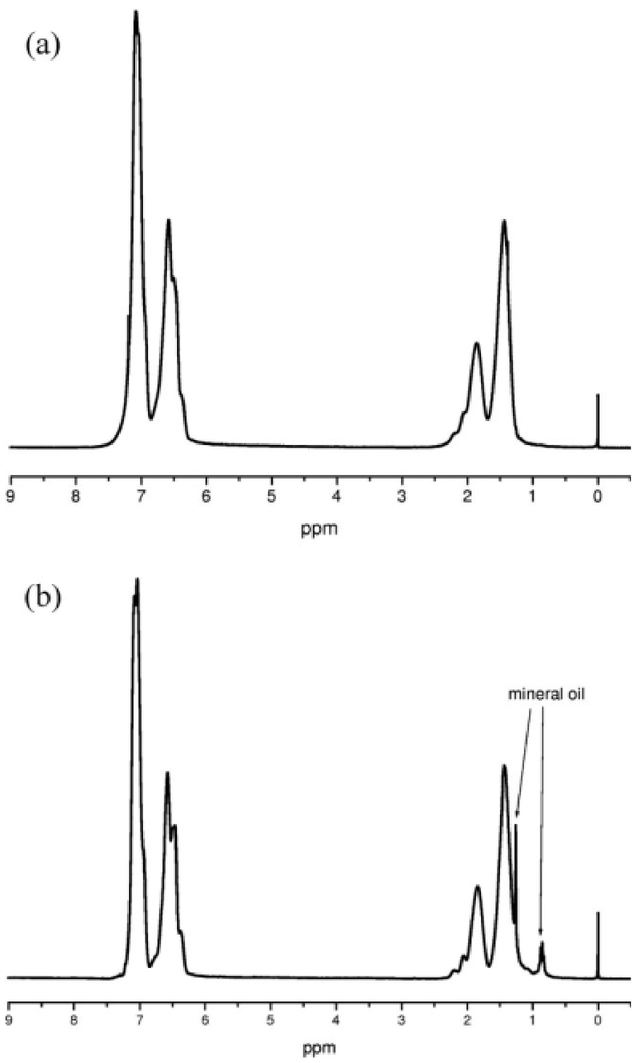

Figure 2 ^{1}H-NMR spectra of: (a) PS1 and (b) PS2.

reason does not precipitate. Then the solid was filtrated in a büchner funnel and washed with hexane. Finally it was carefully dried under high vacuum at 170°C for 5 h. The resulting solid was then analyzed by ^{1}H-NMR using the same procedure as before.

RESULTS AND DISCUSSION

The FTIR spectra of both PS1 and PS2 are shown in Figure 1. There are no detectable differences between these two polymers. The presence of mineral oil in PS2 cannot be detected in the FTIR spectrum, because of its small concentration ($\leq 5\%$), and the overlap of C—H vibrations of oil and PS.

Figure 2 shows the ^{1}H-NMR spectra of PS1 and PS2. As shown in Figure 2(b), the ^{1}H-NMR of PS2 shows a small group of peaks in the interval 0.85–0.88 ppm and another peak at 1.26 ppm which clearly identify the presence of the mineral oil.[25,26] These peaks correspond to aliphatic functional groups of the mineral oil.[25,26] It is possible that other peaks from mineral oil might also be present in the interval 1–2 ppm[25,26] but in that case they are overlapped by the peaks from the aliphatic protons of polystyrene.

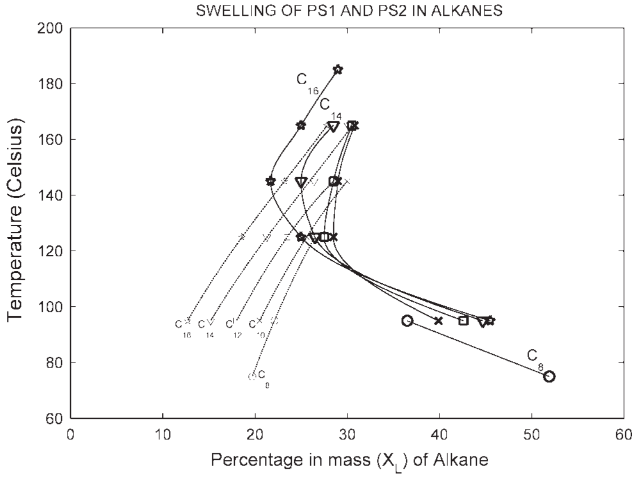

Figure 3 Swelling of polystyrene matrices in linear alkanes: (o) octane (C_8); (x) decane (C_{10}); (□) dodecane (C_{12}); (▽) tetradecane (C_{14}); (five-pointed star) hexadecane (C_{16}). Dark solid lines represent the swelling results in PS2 as obtained in the present work; Thin dashed lines represent the swelling results in PS1 as obtained in our previous work.[5]

Figure 3 shows the mass uptake of alkanes by PS2 as a function of temperature. The results reported previously[3] for the swelling of PS1 in alkanes are also shown for comparison. The results clearly demonstrate that PS2 has an anomalous swelling behavior as it absorbs much more solvent at lower temperatures than at higher temperatures. The occurrence of possible dissolution of PS2 at higher temperatures, which could in part explain this anomalous

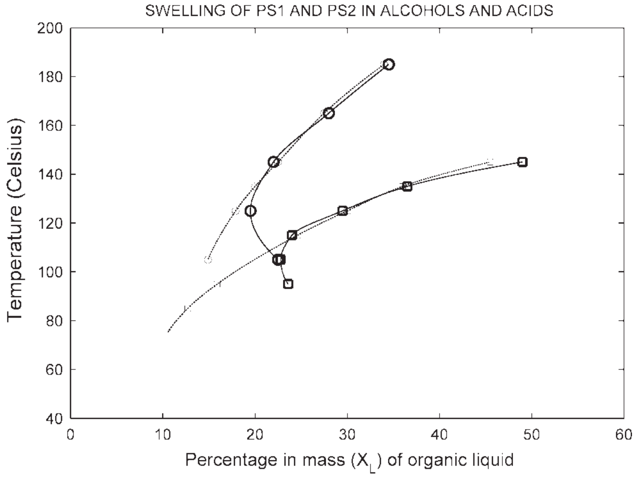

Figure 4 Swelling of polystyrene matrices in 1-decanol (□) and in myristic acid (O). Dark solid lines represent the swelling results in PS2 as obtained in the present work; Thin dashed lines represent the swelling results in PS1 as obtained in our previous work.[3,4]

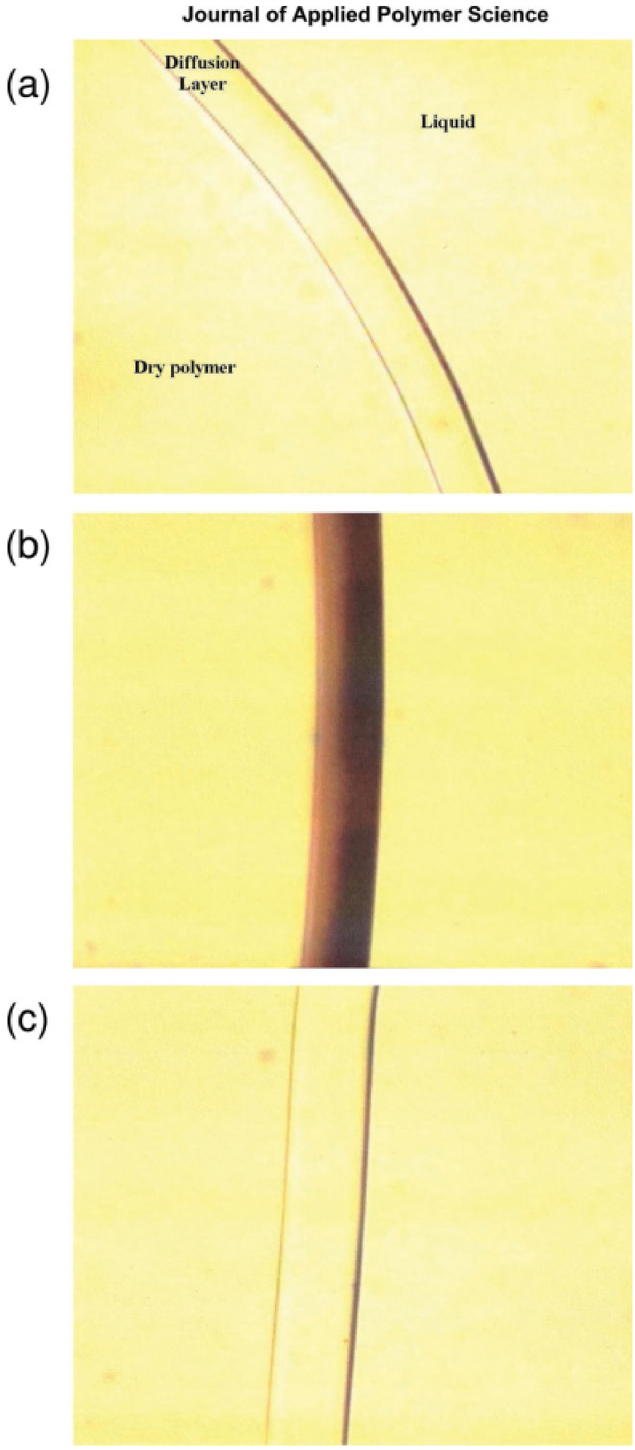

Figure 5 Light microscopy pictures of the diffusion of alkanes into polystyrene matrices: (a) diffusion of dodecane into PS1, at 65°C, for 60 minutes, (b) diffusion of dodecane into PS2, at 65°C, for 60 minutes, (c) diffusion of dodecane into PS2 at 125°C, for 2 minutes. [Color figure

behavior, has been monitored by FTIR of the solvent after the sample has been fully saturated and also by residue after solvent has evaporated. In all cases considered in this work no solubility of PS2 has been detected. Figure 4 shows the results of swelling of PS2 in 1-decanol and in myristic acid as a function of temperature. The results reported previously for the swelling of PS1 in 1-decanol[3] and in myristic acid[4] are also shown for comparison. Again, an anomalous swelling behavior is visible in these cases at lower temperatures. There are inflexion points in the swelling curves at about 120°C for myristic acid and at about 100°C for 1-decanol. We could not find any relationship with T_g of PS (95°C). This has been expected as the plasticization effect of solvents dominates the diffusion process. The temperature range selected has been dictated by melting and boiling points of the solvents as well as by time required for full saturation. Other alcohols and carboxylic acids have also been tested with PS2 and the same anomalous swelling behavior has always been observed.

To better understand the differences observed in the mass uptake of organic solvents by PS1 (Refs. 3–5) and PS2 (present work) we have performed some *in situ* light microscopy diffusion studies, as described earlier. Some results from the light microscopy *in situ* diffusion experiments are in Figure 5.

Figure 5 (a) shows the *in situ* diffusion of dodecane into PS1 at 65°C, 60 min after the beginning of diffusion. It can be clearly seen that the diffusion layer is transparent and homogeneous, i.e., no precipitation occurs. We have repeated this experiment with PS1 using several different solvents and at several different temperatures (from room temperature to 160°C) and the results were always the same: during the diffusion of organic liquids into PS1, the diffusion layer is always transparent and homogeneous at all temperatures investigated.

Figure 5 (b) shows the *in situ* diffusion of dodecane into PS2 at 65°C, 60 min after the beginning of diffusion. As this picture shows, the advancement of

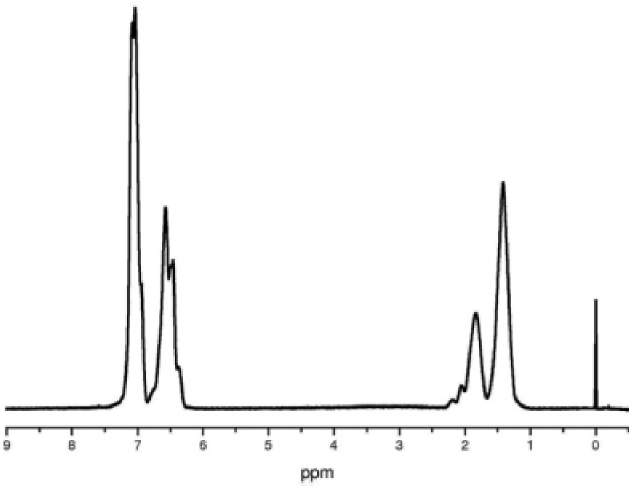

Figure 6 ^{1}H-NMR spectrum of purified PS2.

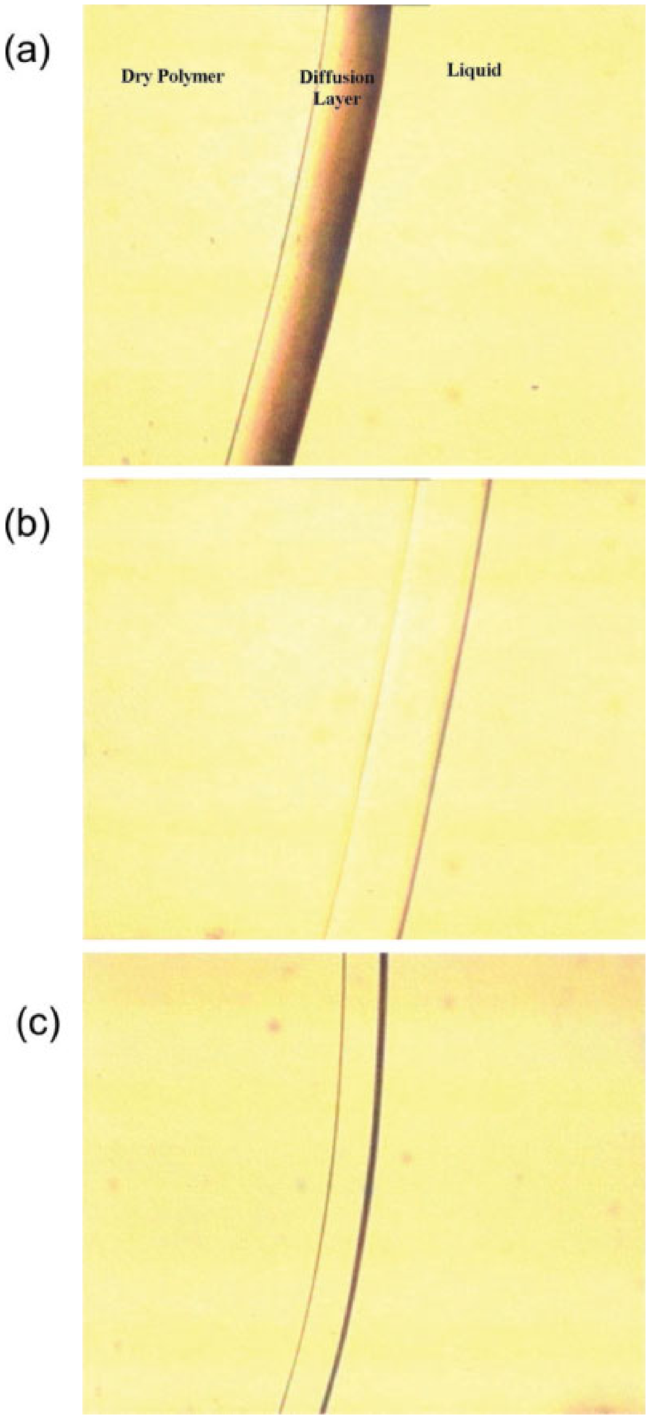

Figure 7 Light microscopy pictures of the diffusion of alkanes into polystyrene matrices: (a) diffusion of dodecane into PS1 (+mineral oil) at 65°C, for 60 minutes, (b) diffusion of dodecane into PS1(+mineral oil) at 125°C for 3 minutes, (c) diffusion of dodecane into PS2 purified at 65°C, for 60 minutes. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the diffusion front at this temperature is accompanied by the opacity of the diffusion region. These light microscopy results can only be interpreted as formation of inhomogeneities, i.e. precipitates. At such low temperatures (<90°C), we have always observed the occurrence of precipitation during diffusion in PS2 for all organic solvents tested.

We have also studied *in situ* diffusion of organic solvents into PS2 at a temperature well above T_g of PS2 (95°C). Figure 5(c) shows the result for dodecane diffusing into PS2 at 125°C, 2 min after the beginning of diffusion. Contrary to what had been observed before in the diffusion of dodecane at 65°C, in this case at 125°C, the diffusion layer is transparent, i.e., there is no precipitation. We have also studied the *in situ* diffusion of other organic solvents into PS2 at 125°C, and we have never observed precipitation.

To better understand the role played by mineral oil in these anomalous PS2 results and to differentiate between the contribution of the mineral oil and that of the polymer matrix, some additional experiments have been performed. On the one hand we have blended PS1 with mineral oil, as described earlier, and we have performed *in situ* light microscopy diffusion studies on the resulting sample. On the other hand we have removed the mineral oil from PS2, using the procedure described earlier, and we have performed *in situ* light microscopy diffusion studies on the purified sample, whose ^{1}H-NMR is shown in Figure 6. As Figure 6 shows our purification method was efficient at removing the mineral oil.

The *in situ* light microscopy results of the solvent diffusion into PS1 (+ mineral oil) and into PS2 purified are shown in Figure 7. Figure 7(a) shows the diffusion layer of dodecane into PS1 with mineral oil at 65°C after 60 min. The precipitation in the diffusion layer is very similar to PS2 [compare Figs. 5(b) for PS2 and 7(a) for PS1 + oil]. Figure 7(b) shows the diffusion layer of dodecane into PS1 with mineral oil at 125°C after 2 min. Contrary to what has been observed in the diffusion of dodecane at 65°C into PS1 with mineral oil and similarly to what has been observed in the diffusion of dodecane into PS2 at 125°C in this case the diffusion layer is transparent, i.e., there is no precipitation. Figure 7(c) shows the diffusion layer of dodecane into purified PS2 at 65°C after 60 min. No precipitation is visible indicating clearly the role of mineral oil in the formation of inhomogeneities and associated enhanced solubility.

Some preliminary results have also shown that, at low temperatures (65°C), purified PS2 swells much less in alkanes than PS2.

We can therefore conclude that the anomalous swelling behavior observed at lower temperatures must be related to the occurrence of precipitation during diffusion. A possible explanation is the "hole filling," as suggested in Refs. 11–17. This would however explain only the behavior at lower temperature, but not in the whole temperature range, as at high temperatures we would expect to obtain more precipitation, contrary to observation.

We can suggest a simple explanation for this phenomenon as follows. The oil is mixed with the polymer at processing temperature, i.e. at about 180°C. At this temperature it would be fully dissolved. When cooled down, the solubility is reduced and some phase separation will occur. This separation cannot be detected using light microscopy as the oil phase is too small (at molecular level) and cannot scatter light, and/or the refractive indexes are too close (1.5916 for PS and 1.4680 for oil). When solvent diffuses in, it will quickly reach equilibrium with the polymer matrix. The oil phase on the other hand is separated and can absorb large volume of the solvent, before equilibrium is reached. The precipitates will therefore grow in size, until the corresponding solubility limit of the solvent in the oil is reached. With increasing temperature more and more oil is dissolved in the polymer matrix and less and less is separated. There will therefore be smaller or fewer precipitates. The total volume of solvent is therefore the sum of the solvent in the polymer and in the oil phase. This behavior is not related to LCST, as on cooling more precipitation occurs, not less as would be expected.

CONCLUSIONS

In this work, the observation of an anomalous swelling behavior during solvent diffusion into a polystyrene matrix (containing <5% mineral oil) has been reported. The observation of such an anomalous swelling behavior has been correlated with the observed occurrence of precipitation during diffusion at lower temperatures, which is shown to be caused by the presence of mineral oil in the samples. The system of polymer-oil-solvent is a ternary system, and must be studied in this context, as e.g. for block copolymers.[27,28]

As far as we know, this is the first time in the literature that the observation of precipitation during solvent diffusion has been correlated with the occurrence of anomalous swelling. These results strongly suggest that much precaution is needed when studying the swelling of commercial polymer samples, especially if these have not been characterized properly. The use of light microscopy to detect possible anomalies during diffusion can be recommended.

References

1. Thomas, N. L.; Windle, H. Polymer 1982, 23, 529.
2. Parker, M. A.; Vesely, D. J Polym Sci Part B: Polym Phys 1986, 24, 1869.
3. Bernardo, G.; Vesely, D. Eur Polym J 2007, 43, 938.
4. Bernardo, G.; Vesely, D. Eur Polym J 2007, 43, 4983.
5. Bernardo, G.; Vesely, D. J Appl Polym Sci 2008, 110, 2393.
6. Seo, J.; Han, C.-S.; Han, H. J Polym Sci Part B: Polym Phys 2001, 39, 669.
7. Elabd, Y. A.; Sloan, J. M.; Tan, N. B.; Barbari, T. A. Macromolecules 2001, 34, 6268.
8. Hong, S. U.; Barbari, T. A.; Sloan, J. M. J Polym Sci Part B: Polym Phys 1998, 36, 337.
9. Mukherjee, M.; Singh, A.; Daillant, J.; Menelle, A.; Cousin, F. Macromolecules 2007, 40, 1073.
10. Kwei, T. K.; Zupko, H. M. J Polym Sci A-2 1969, 7, 867.
11. Meares, P. J Am Chem Soc 1954, 76, 3415.
12. Barrer, R. M.; Barrie, J. A.; Slater, J. J Polym Sci 1958, 27, 177.
13. Crank, J. The Mathematics of Diffusion; Oxford: New York, 1975; p 266.
14. Chan, A. H.; Koros, W. J.; Paul, D. R. J Memb Sci 1978, 3, 117.
15. Patton, C. J.; Felder, R. M.; Koros, W. J. J Appl Polym Sci 1988, 35, 21.
16. Vieth, W. R. Diffusion In and Through Polymers; Hanser: NY, 1991; p 29.
17. Neogi, P. Diffusion in Polymers; M. Dekker: NY, 1996; p 173.
18. Morrissey, P.; Vesely, D. Polymer 2000, 45, 865.
19. Vesely, D. Polymer 2001, 42, 4417.
20. Zhu, M.; Vesely, D. Eur Polym J 2007, 43, 4518.
21. Vesely, D. Int Mater Rev 2008, 53, 299.
22. Anderson, S. L.; Grulke, E. A.; Delassus, P. T.; Smith, P. B.; Kocher, C. W.; Landes, B. G. Macromolecules 1995, 28, 2944.
23. Armeniades, C. D.; Baer, E.; Rieke, J. K. J Appl Polym Sci 1970, 14, 2635.
24. Duraes, J. A.; Drummond, A. L.; Pimentel, T. A. P. F.; Murta, M. M.; Bicalho, F. S.; Moreira, S. G. C.; Sales, M. J. A. Eur Polym J 2006, 42, 3324.
25. Khan, M. A.; Ahmad, I.; Ishaq, M.; Shakirullah, M.; Jan, M. T.; Rehman, E.; Bahader, A. Fuel Process Technol 2003, 85, 63.
26. Owrang, F.; Mattsson, H.; Olsson, J.; Pedersen, J. Thermochim Acta 2004, 413, 241.
27. Matsen, M. W. Macromolecules 1995, 28, 5765.
28. Hong, K. M.; Noolandi, J. Macromolecules 1983, 16, 1083.