ELSEVIER

Polymer 42 (2001) 1653–1661

polymer

www.elsevier.nl/locate/polymer

Modification of polystyrene glass transition by high pressure methane

M. Ribeiro*, L. Pison, J.-P.E. Grolier

Laboratoire de Thermodynamique et Génie Chimique (UPRES A CNRS 6003, Thermodynamique des Solutions et des Polymères), Université Blaise Pascal, 63177 Aubière, France

Received 28 April 2000; accepted 5 July 2000

Abstract

Polymers are currently processed in many different ways involving elevated temperatures and pressures as well as additional chemicals (mostly gases); this, being typically the case in foaming process. There is then a pressing need to assign the thermophysical properties of polymers in particular states under precise thermodynamic conditions to obtain optimal performances. Thermal, mechanical and/or chemical stresses may induce modifications, possibly permanent, of the glass transition which consequently affect the characteristics of the material. Polystyrene (PS) has been submitted, in a scanning transitiometer (ST), to pressures up to 200 MPa using as hydrostatic fluid either mercury as a neutral fluid or methane as a "chemically active" fluid. Temperature modulated differential scanning calorimetry (TMDSC) has been used to study the thermal behavior, especially the glass transition, of polystyrene modified by high pressure methane, in comparison with polystyrene submitted to high pressure mercury as well as with "non-treated" (native) polystyrene. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Scanning transitiometry; Temperature modulated DSC

1. Introduction

Compressed fluids, particularly in their supercritical state, are widely used in the polymer industry, typically in foam processing. The major advantage using supercritical fluids is the possibility to modify their characteristics (density, viscosity and diffusivity) by only changing the experimental parameters; by controlling these parameters it is then possible to tailor foams having well-defined structures.

Up to now chlorofluorocarbons (CFCs) were widely used as blowing agents in the foaming industry. Presently, international regulation has lead to a ban on CFCs, to be replaced by blowing agents which are less harmful to the ozone layer. Currently, hydrofluorocarbons (HFCs) or hydrochlorofluorocarbons (HCFCs) are being considered instead. However, it is expected that by year 2004 most of these substituted hydrocarbons will eventually be prohibited if they do not have a zero ozone depletion potential (ODP). There is hence a tense competition to select new blowing agents. For this, it is necessary not only to know the thermodynamic properties of these fluids [1] but also to characterize the "interaction" under pressure between such fluids and polymers [2] in order to obtain the product of interest, having the appropriate thermophysical properties and the required structures for specific applications, while keeping similar performance properties.

The present work forms a study in a very active field of research. We report here preliminary results, using the technique of temperature modulated differential scanning calorimetry (TMDSC), of the study of polystyrene modified by scanning transitiometry (ST). Polystyrene (PS) samples were first treated under specific conditions of pressure, induced either by mercury (as a neutral fluid) or a supercritical gas, (more "active" fluid) like methane. Scanning transitiometry is a new technique [2,3] which is used to perfectly control these modifications under pressure. As a matter of fact, methane is an interesting "weakly active" fluid since its interaction with PS is rather weak due to the symmetric geometry and the non-polarizability nature of the molecule of methane.

We compare, in what follows, the results obtained when investigating the initial PS (that is to say, "untreated" PS) with PS "treated" by high pressure transmitted either by mercury or by methane.

2. Description of the techniques

2.1. Scanning transitiometry

Scanning transitiometry is a relatively new technique

---

* Corresponding author. Tel.: +33-473-407191; fax: +33-473-407185.
E-mail address: madeleine.ribeiro@univ-bpclermont.fr (M. Ribeiro).

PII: S0032-3861(00)00521-8

(making use of a transitiometer, actually, a p–V–T calorimeter) which is based on inducing a change in the thermodynamic state of a sample under study by scanning at a low rate (or stepwise) one of the independent variables (p, V, T) and keeping automatically constant the other independent variable. From the output signals recorded simultaneously (rate of heat exchange and variation of the mechanical variable, volume or pressure) a respective pair of thermodynamic derivatives is obtained simultaneously as a function of the scanned variable. The operating instrument performs over wide ranges of pressures and temperatures. The scanning transitiometer used here has been described in detail elsewhere [4]; it allows measurements up to 570 K under pressures up to 400 MPa. Its main characteristic is the possibility to precisely control the three variables p, V or T to induce and monitor thermodynamic changes and transitions and simultaneously measure the energy (i.e. the calorimetrically measured heat) associated with such modifications. To this end, the scanning of the inducing variable must be sufficiently slow in order to keep the system under study close to equilibrium and assure then that the thermodynamic relations are valid. In this way, a transitiometer should be regarded as micro-reactor for model processing.

2.2. Temperature modulated DSC

The TMDSC technique has shown, rather recently, its potential and performances for the thermal characterization of polymeric systems, yielding pertinent information not always accessible by classical DSC. There is still a need for further investigations to better understand the effect of periodically changing scanning rates [5,6]. The mathematical model is well documented [7] and does not need to be developed here. The similarities with dynamic mechanical analysis and with dielectric thermal analysis have brought up many questions and have led to different approaches for TMDSC, characterized by the formalism used to described the signals obtained [8].

In TMDSC, a modulated temperature profile is applied and the heat flow response is subsequently analyzed using Fourier transforms. The total heat flow obtained after deconvolution represents the sum of two distinguishable contributions, because the response to the imposed temperature modulation is different depending on the phenomena submitted to the temperature changes. One component, called reversing heat flow, is linked to the heat capacity change; the modifications that depend on the temperature scanning rate can be cycled by alternating heating and cooling effects. The second component is linked to the kinetics and is called non-reversing heat flow, by opposition to the first one. Modifications appearing in this signal depend only on the temperature. Typically, the increase of heat capacity characterizing the glass transition of polymers appears in the reversing heat flow, without other overlapping effects, whereas the enthalpic relaxation effects occurring during the glass transition are observed in the non-reversing heat flow.

The ratio of the oscillating heat flow amplitude to the oscillating temperature amplitude yields the heat capacity information; once calculated, the contributions of the reversing and of the non-reversing heat flows to the total heat flow HF_{tot} noted respectively as HF_{rev} and $HF_{\text{non-rev}}$, are obtained using the following relations:

- HF_{rev} signal = −average temperature scanning rate × heat capacity signal (conventionally, on heating a negative sign is necessary because an endothermic effect in the sample, i.e. heat consumption, creates a negative ΔT between the sample and the reference).
- $HF_{\text{non-rev}}$ signal = HF_{tot} signal − HF_{rev} signal.

3. Experimental

The experiments were carried out with a polystyrene (PS) of the atactic type provided by Fibran SA (Thessaloniki, Greece), in the form of pellets.

Different samples of polystyrene were submitted to different “treatments” to induce modifications under well-defined conditions. The controlled conditions were obtained by the transitiometric method. Two series of samples were “treated” on heating and then on cooling in the range 303–453 K with a fixed scanning rate of 0.16 K min^{-1} under isobaric conditions of 50, 100, 150 and 200 MPa. In one series the pressure was transmitted to the sample by a “neutral” hydraulic fluid, mercury. In the other series the pressure was transmitted by a more “active” hydraulic fluid, methane; under the operating conditions methane was in the supercritical state. After the last cooling back to room temperature, the pressure was released and the samples removed and stored at room temperature, under atmospheric pressure.

For the thermal analysis study at atmospheric pressure, a thermal analyzer MDSC 2920 from TA Instruments was used; it was equipped with a refrigerated cooling system (RCS) provided with the instrument and used to cool the measuring system and to operate it in the range 200–620 K. Argon from RCS was circulated (120 ml min^{-1}) in the cooling head. A nitrogen flow (20 ml min^{-1}) was also used to purge the cell. In a previous work [9], we have shown that an optimization of the modulation parameters is necessary before performing a study. These conditions have been taken into account for the present investigations with PS.

For comparing the modified samples within a series of pressures and between the two series, a common “reference” material was prepared in order to isolate the modifications brought by the pressure. This reference sample was a native (as-received) sample of PS which was submitted under isobaric normal condition (atmospheric pressure) to the thermal treatment, i.e. heating and subsequent cooling at

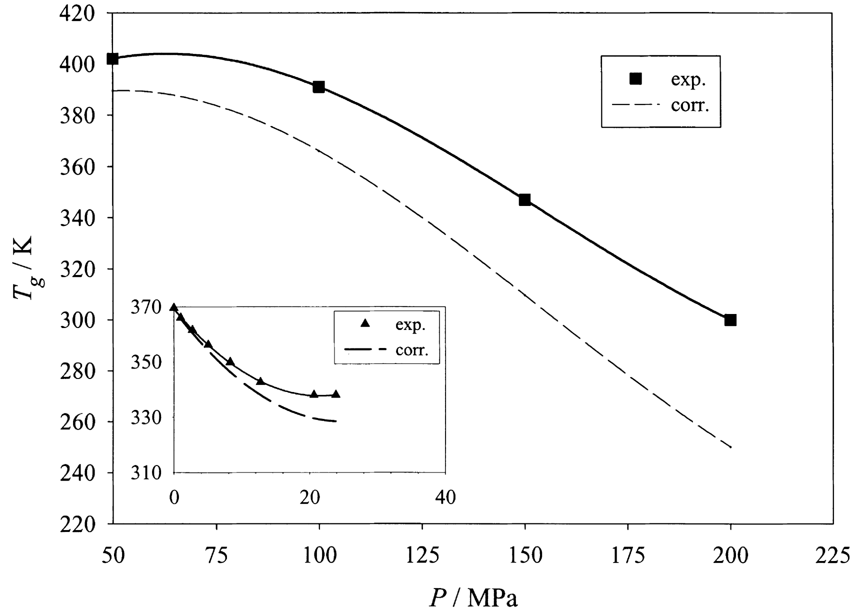


Fig. 1. Glass transition temperature for the system PS-CH_4 plotted against the gas pressure; The symbols ▲ [10] and ■ represent literature values and our set of data, respectively; dashed lines are for both data after correction for the hydrostatic pressure effect.

the same rate of 0.16 K min^{-1} rate; in this way all compared materials were supposed to have, at least, the same initial thermal history.

4. Results and discussion

There is not much information available in the literature on calorimetric study of plasticization of polymers at high pressures, above say 50 MPa, induced by gases. O'Neill and Handa [10] have reported data concerning the plasticization of PS using methane (CH_4), ethylene (C_2H_4) and carbon dioxide (CO_2), under relatively small pressures up to 6.0, 8.8 and 35.9 MPa for CO_2, C_2H_4 and CH_4, respectively. For our part, we deliberately worked at much higher pressures. Plasticization is well characterized by the shift of the temperature of the glass transition, T_g. Actually, when pressure is induced by a gas, both plasticization and hydrostatic effects contribute to the shift of T_g. If plasticization tends to lower T_g because of the gain of mobility of the polymeric chains, the hydrostatic effects raises it by diminishing the free volume. We have then plotted, Fig. 1, the data of O'Neill and Handa for the system PS-CH_4 together with our measurements. As shown by the literature data, the plasticization effect is quite weak and tends to level off at about 30 MPa. Experimental data by O'Neill and Handa [10] and our present values represent the combination of hydrostatic and plasticization effects. "Pure" plasticization effect is obtained by subtracting the hydrostatic effect. O'Neill and Handa have estimated an average value of the change of T_g with the hydrostatic pressure p_{hyd}, of $dT_g/dp_{hyd} = 0.004$ K MPa^{-1}. Our measurements were corrected by a value of $dT_g/dp_{hyd} = 0.0025$ K MPa^{-1}, deduced from our measurements under the same conditions (scanning rate and pressures) realized under pressure of mercury. CH_4 is assumed to be a non-plasticizing gas but our results show that at higher pressures, plasticization overtakes the hydrostatic effect, probably due to higher solubility of the gas in the PS at higher pressures; this kind of behavior has been suggested for high enough pressures [10]. Evidently, plasticization is not as important as at lower pressure; a dT_g/dp of about -0.005 K MPa^{-1} in the range of 50–200 MPa is obtained, whereas O'Neill and Handa have determined a dT_g/dp of -0.02 K MPa^{-1} up to 35.9 MPa.

Table 1
Densities of modified PS as a function of CH_4 pressure

CH_4 pressure (MPa)	Density (g cm^{-3})
0.1	1.05
50	1.03
100	0.78
150	0.94
200	0.76

Our results and those given by O'Neill and Handa cannot be directly compared since on one hand, both sets of data do not correspond to the same pressure range, and on the other hand, the temperature T_g used by the authors is the value taken at the onset of the transition whereas we have selected the value corresponding to the end of the transition. This choice resulted from the nature of the transition which is relatively less marked due to the fact that under pressure, the difference of enthalpy between glassy and liquid states is rather small. We observed that the end of transition should be more reproducible when reaching the more stable liquid state. This choice does not change the general view of the

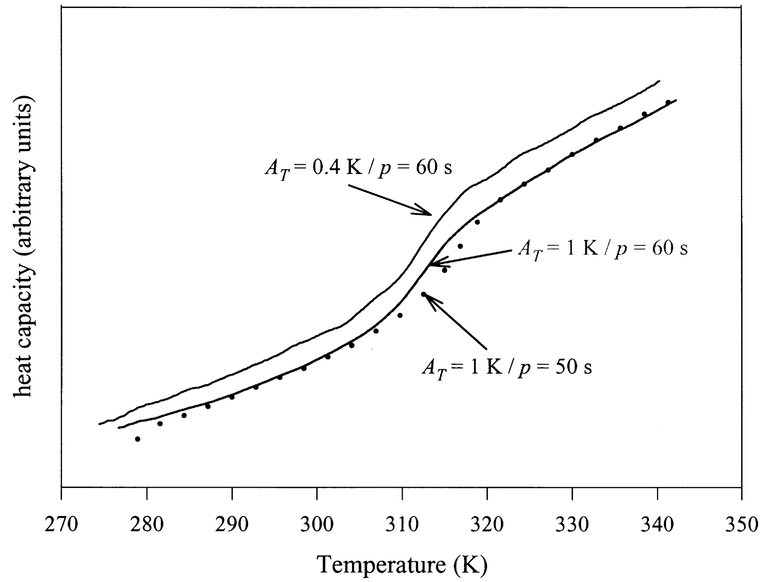


Fig. 2. Variation of the temperature of the glass transition, for the same polymeric sample, with the modulation parameters, amplitude and period; three pairs of experimental parameters have been used, $A_T = 1\ K/p = 50$ s; $A_T = 1\ K/p = 60$ s; $A_T = 0.4\ K/p = 60$ s.

polymer behavior under pressure but it may lead to a difference of temperature of about 20 K in the determination of T_g. The plasticization of PS using CH_4 seems to be possible but it is necessary to apply high pressure, i.e. 200 MPa, in order to obtain approximately the same shift of the T_g than with ethylene (C_2H_4) under 9.0 MPa! In this respect CH_4 cannot really be considered as a good plasticizing gas. However, determination of the density of the modified sample, see Table 1, has shown that the PS obtained has the characteristics of a foam, with a decrease of density of about 25% after "treatment" under 200 MPa of methane.

All pressure-modified samples have been studied at atmospheric pressure by TMDSC. In order to apply the same thermal treatment, all the samples were investigated under the same conditions of modulation, that is to say with an amplitude $A_T = 0.5$ K, a period $p = 60$ s and an average scanning rate $q = 2\ \text{K min}^{-1}$. Noticeably, because of its nature, the glass transition is heating rate dependent and also frequency dependent as shown in Fig. 2. In Fig. 2 are represented, as an example, three runs obtained with samples of the same polymer, undergoing a glass transition under different conditions of modulation; the pairs of parameters used are the following, $A_T = 1\ K/p = 50$ s; $A_T = 1\ K/p = 60$ s and $A_T = 0.4\ K/p = 60$ s. Keeping a constant value of the period of 60 s and changing the amplitude from 0.4 to1 K yields the same temperature of the glass transition.

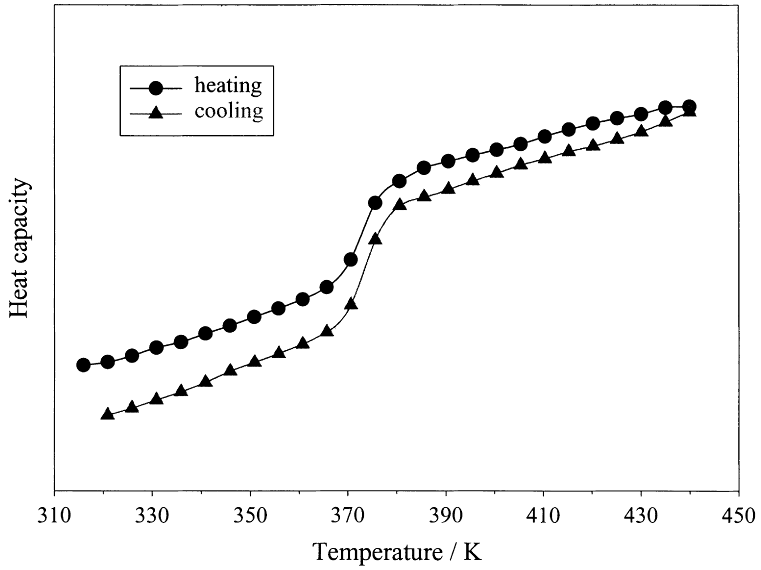


Fig. 3. Study of the glass transition of the initial PS, using quasi-isothermal conditions with $A_T = 0.5\ K/p = 60$ s, on heating and on cooling.

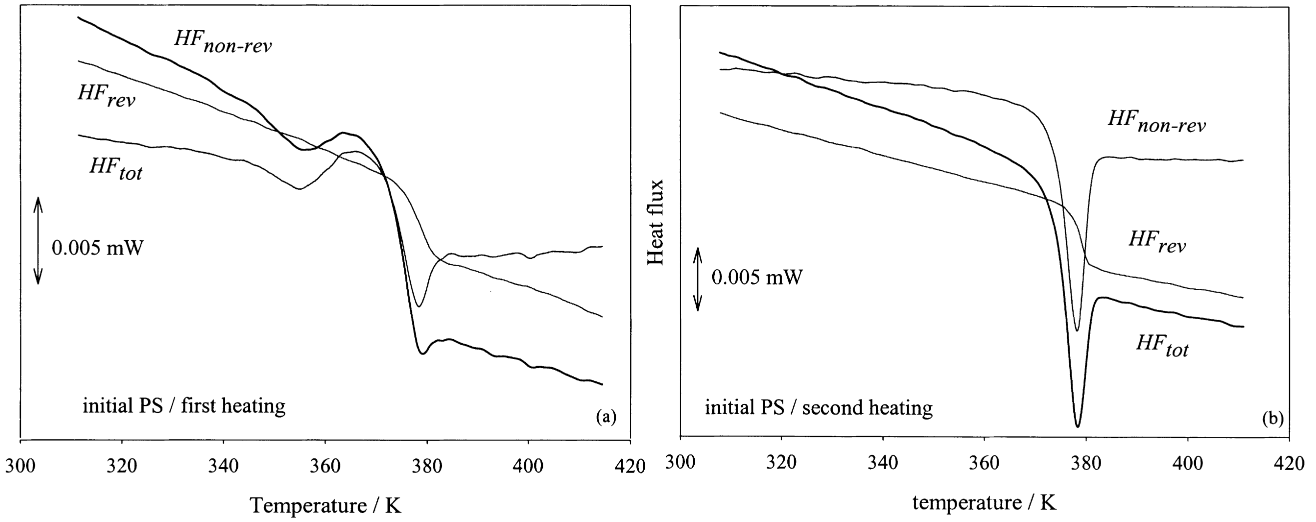


Fig. 4. TMDSC thermograms. (a) Separation of the total heat flow into the reversing and non-reversing heat flux for initial PS (as received), on first heating. (b) Separation of the total heat flow into the reversing and on-reversing heat flux for the same PS, on second heating after cooling at 0.16 K min^{-1}.

But using a fixed amplitude of 1 K and changing the period from 50 to 60 s induces a shift of the glass transition temperature of the order of 2.5 K. This imposed us to keep a fixed period for all measurements.

Using TMDSC, it has also been shown that accurate results can be obtained with a specific mode of modulation, called quasi-isothermal mode [3]. Using this particular profile of the scanning rate, the equilibrium state can be approached and maintained since only a small thermal perturbation is applied to the sample. As a matter of fact, a small modulation is superimposed to an isotherm, in such a way that the mean scanning rate is zero. Fig. 3 shows the results obtained when studying a PS sample under quasi-isothermal conditions, with an amplitude of 0.5 K and a period of 60 s. For the study of the glass transition, these conditions seem to be appropriate since the same temperature of the transition can be obtained on heating as on cooling; this is never the case in classical DSC runs because of the crossing from metastable state (frozen state) to equilibrium state (liquid state). The results presented in this paper have been obtained in the continuous mode, i.e. with a modulation superimposed to a ramp of temperature. In this way, the benefits of the technique can be gained using advantageously the continuous mode of modulation and we can determine not only the glass transition temperatures of different samples of PS but also the corresponding enthalpies of relaxation. In order to do so, it is necessary to maintain a ramp of temperature during the measurements.

The results obtained for the native (initial) PS are shown in Fig. 4a and b for, respectively, the PS studied "as received" and the PS reheated after a cooling rate of 0.16 K min^{-1}. The separation of the total heat flow enables not only the observation of the exact and identical temperature of the glass transition of the given sample through the reversing heat flow but also the quantitative evaluation of its history, in terms of thermal, mechanical and/or chemical contributions. This latter information is "contained" in the peak (the endotherm) exhibited by the non-reversing heat flow — see Fig. 4a; integration of this peak yields the amount of energy characterizing quantitatively then the non-reversing changes undergone by the sample. One of the major advantages of the TMDSC technique is undoubtedly the possibility to access directly in a single run, these two different parameters.

Samples of PS submitted to different pressures induced by mercury maintain their glassy aspect. TMDSC measurements yielded an identical glass transition temperature (as observed on the reversing heat flow), independently of the pressure applied, as it is shown in Fig. 5a and b, for pressures of 50 and 150 MPa, respectively; this shows that, if the temperature of the glass transition varies during temperature scans under pressure, it is not modified in an irreversible manner by pressure. These results are not surprising; the hydrostatic pressure to which the sample is submitted does not modify the internal structure of the PS since there is no real interaction between mercury and PS. The increase of the glass transition temperature, during measurements under pressure of mercury, is only due to the decrease of the free volume. This effect being reversible, the free volume increases again when the PS is decompressed until atmospheric pressure and the energy barrier between the two states, glassy and liquid, is crossed again at the same temperature. Nevertheless, the nature of the glassy state that has been formed by cooling under pressure of mercury of the molten polymer is apparent from the non-reversing heat flow signals of different pressure-densified PS samples, as represented in Fig. 6. The runs, at atmospheric pressure, of the samples modified by pressure show a typical shape, with different extents of enthalpic peaks. As shown in Fig. 7, the temperature range of the total phenomenon seems to increase with pressure. We have represented in Fig. 7 the difference of temperature ΔT, between the onset temperature

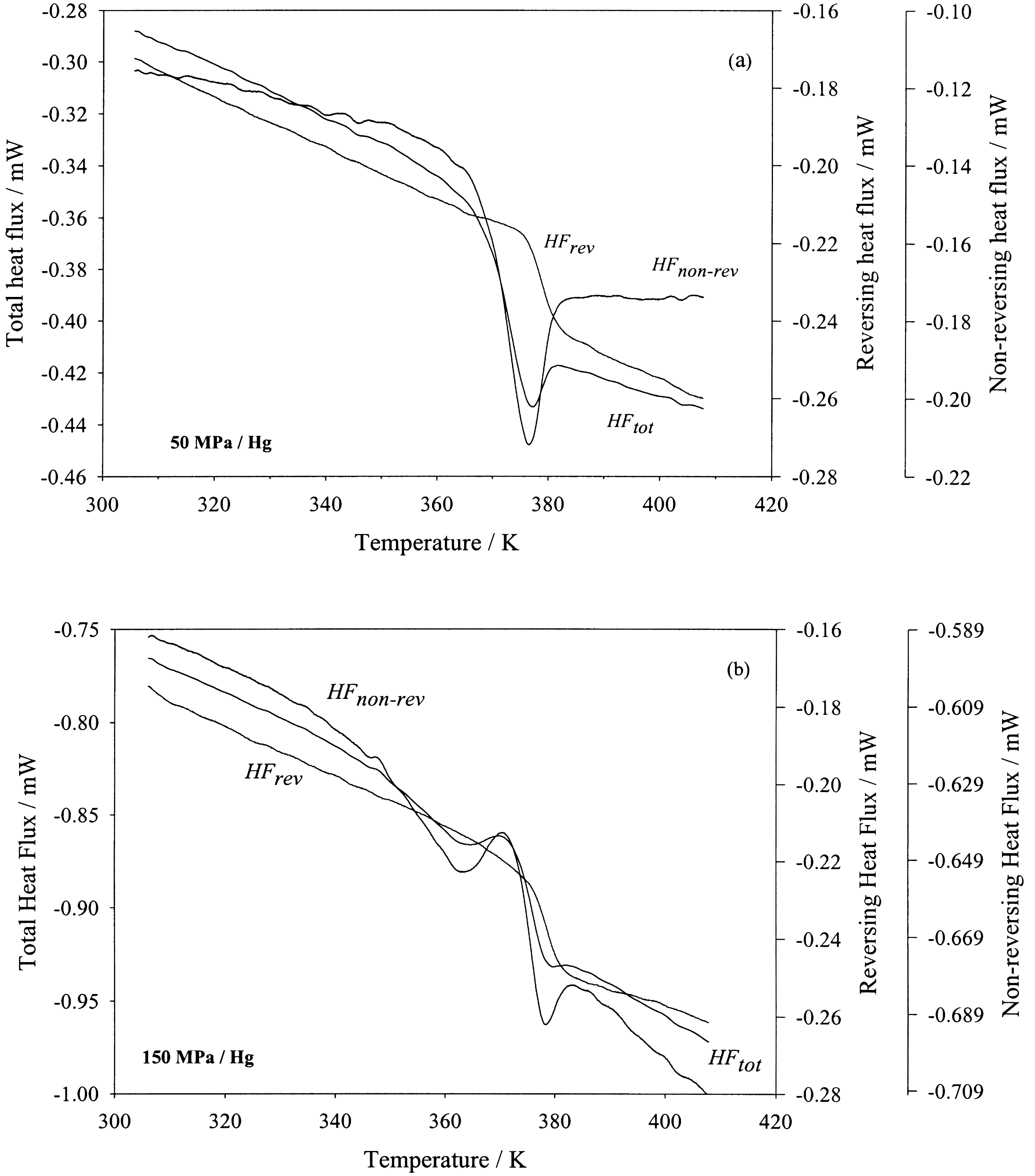


Fig. 5. TMDSC thermograms of PS modified by high pressure induced by mercury. (a) Separation of the total heat flow into the reversing and non-reversing heat flux for a 50 MPa pressure modified PS. (b) Separation of the total heat flow into the reversing and non-reversing heat flux for a 150 MPa pressure modified PS.

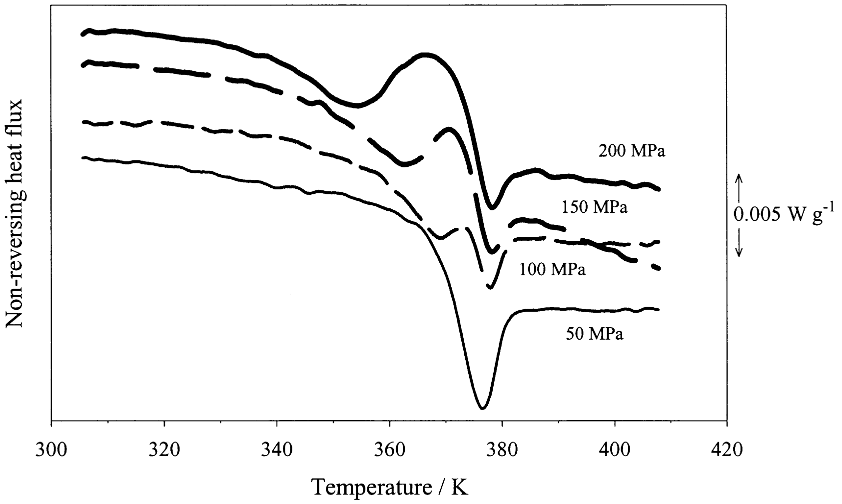


Fig. 6. Atmospheric pressure TMDSC scans of the PS samples cooled under high pressure of mercury. Non-reversing heat flux obtained for the four applied pressures, 50, 100, 150 and 200 MPa (the curves have been shifted for clarity).

and the final temperature, of the entire phenomenon. A sub-T_g endothermic peak appears, — see Figs. 5 and 6 — shifted to lower temperature. Only the temperature of the end of the large transition, i.e. the end of the second peak, the more "classical relaxation peak", remains quasi-constant. This behavior can be explained as an attempt by the densified glass to undergo a glass transition. But the molecular organization does not allow the creation of an equilibrium liquid state and the glass reverts to a "new" enthalpic state (and entropic state as well); this glassy state relaxes progressively until it reaches the energy barrier to access the stable liquid state. The integration of the different peaks shows a small decrease of the intensity of the first peak (from 1.7 down to $1.2_5\,\mathrm{J\,g^{-1}}$) as the pressure decreases, peak which eventually blends in a unique peak at 50 MPa. Different trials were made in order to separate the two peaks at this pressure by adjusting the modulation parameters, but the results did not change.

Although the interactions between methane and PS are weak, measurements realized under CH_4 have led to modifications of the sample. We have obtained in the transitiometer (due to the geometry of the measuring cell) a cylindrically molded PS. The aspect of the sample has also changed. The PS lost its glassy appearance; it became opaque, close to a micro-foam aspect (this is confirmed by the additional density measurements showing the decrease of the density of the treated PS, see Table 1). Fig. 8a and b shows the curves obtained by TMDSC for PS modified under two different pressures of methane, 50 and 150 MPa, respectively. Remarkably, the temperature of the glass transition does remain identical, independent of the pressure of methane. This transition undergone by the sample seems to be reversible, not only for PS treated under

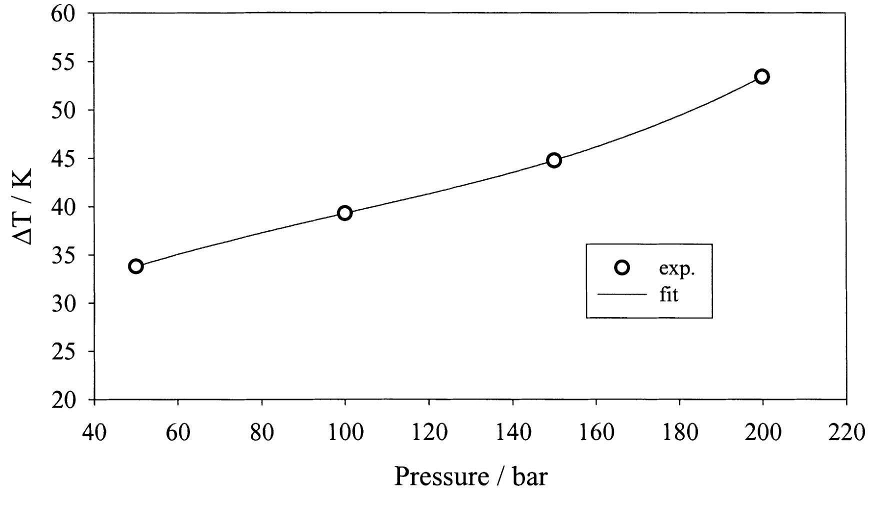
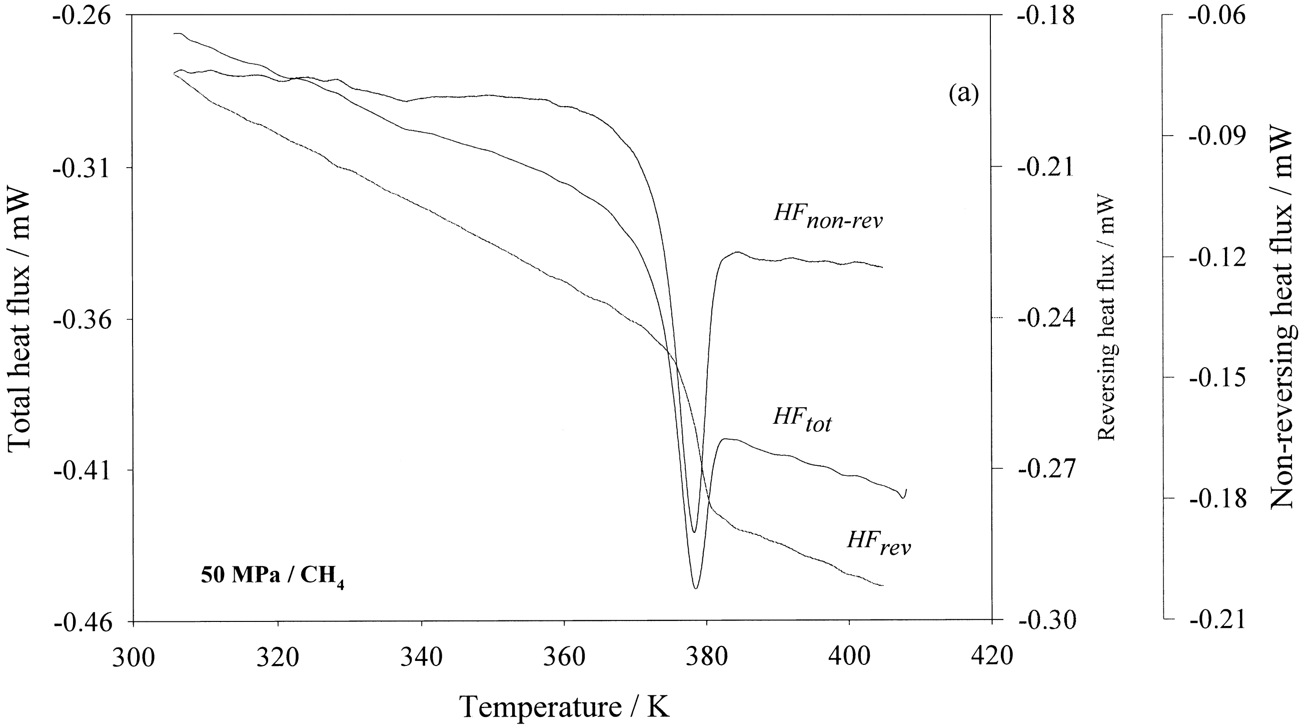


Fig. 7. Temperature range for the enthalpic effect as a function of pressure of mercury. ΔT is the difference of temperature between the onset point and the final point of the entire phenomenon shown in Fig. 6.



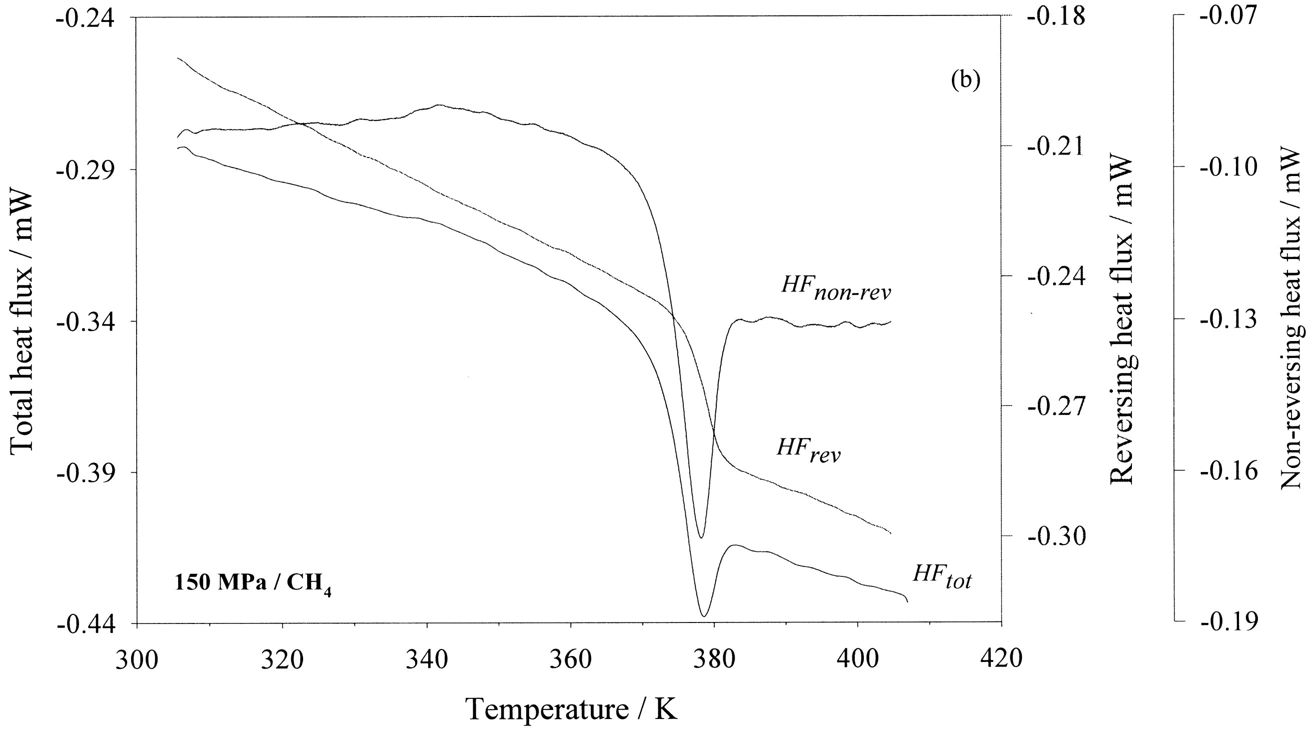


Fig. 8. TMDSC thermograms of PS modified by high pressure induced by methane. (a) Separation of the total heat flow into the reversing and non-reversing heat flux for a 50 MPa pressure modified PS. (b) Separation of the total heat flow into the reversing and non-reversing heat flux for a 150 MPa pressure modified PS.

hydrostatic pressures induced by mercury but also for PS modified by high pressure methane. Most likely methane behaves as a solvent of PS; it tends to “lubricate” the chains of the polymer, increasing their mobility leading then to a decrease of the glass transition temperature during runs performed under pressure. After decompression, the mobility of the chains is limited again and T_g stays unchanged. The modifications of the aspect (opacity) is a direct result of the foaming effect. The only changes that can be noticed, by comparison with the initial PS, appear in the non-reversing signals. As a result of the constraint applied on the polymer, i.e. thermal (the same for all samples), mechanical and chemical, the effect of pressure can be observed as a main endothermic peak in the non-reversing heat flow. The quasi disappearance of the first peak (as seen in Fig. 6) can be explained by an increase of the enthalpy of the polymer due to gas sorption. As a matter of fact, the thermograms obtained after an identical study on 1-year old samples, i.e. on samples after possible partial diffusion of the gas, show that a sub-T_g peak does appear.

A more systematic study covering a more extended range of pressures should be carried out in order to establish a dependence, as a function of the applied pressure of gas, of the enthalpic peak(s). Integration of the peak for the two pressures 50 and 150 MPa gives apparently a quasi-constant enthalpy of about 2.9_5 J g^{-1}, whereas the average value for the hydrostatic pressure modified PS is 2.7 J g^{-1}.

5. Conclusions

When PS is submitted to high pressure, its glass transition is consequently modified. Methane, regarded as a non-plasticizing gas, is able to diminish the T_g when the pressure is significantly increased. One can observe that the contribution of the hydrostatic pressure effect and of the plasticization effect is largely dependent on the pressure. At high pressure plasticization seems to overtake the hydrostatic effect, but the interactions between CH_4 and PS are not strong enough to modify in an irreversible way the physical properties of PS. In this sense, this work has to be regarded as a preliminary study. Further measurements will include the study of new blowing agents such as CO_2, HFC134a, (1,1,1,2 tetrafluoroethane) or HCFC142b (1-chloro1,1-difluoroethane).

Moreover, quasi-isothermal experiments using TMDSC should be performed in order to compare, with a good precision, the variation of heat capacity ΔC_p of the modified PS. In the present work ΔC_p, measured at the inflection point of the glass transition appearing in the reversing signal, does not allow the observation of a pressure dependence. A value of about 0.12–0.14 J g^{-1} K^{-1} seems to be the mean value in both cases (mercury and methane “treated” PS).

Acknowledgements

Financial support through the Brite Euram Program No. 97-4154 “Interactions between gases and polymers at high pressures. Polymer foaming process” is highly appreciated.

References

[1] Wong B, Zhang Z, Handa YP. J Polym Sci Part B: Polym Phys 1998;36:2025.
[2] Randzio SL, Grolier J-PE. Anal Chem 1998;70:2327.
[3] Ribeiro M. PhD thesis. Université Blaise Pascal, France, 1998.
[4] Randzio SL. Chem Soc Rev 1996;25:383.
[5] Menczel JD, Judovits L. J Therm Anal Calorimet 1998;54:419.
[6] Ribeiro M, Grolier J-PE. Proceedings of the 4th Symposium/Workshops on Pharmacy and Thermal Analysis. PhandTA, Mars Karlsruhe, Germany, vol. 4, 1999. p. 23–6, other.
[7] Reading M, Elliott D, Hill VL. J Therm Anal 1993;40:949.
[8] Reading M. J Therm Anal Calorimet 1998;54:411.
[9] Ribeiro M, Grolier J-PE. J Therm Anal Calorimet 1999;57:253.
[10] O’Neill ML, Handa YP. In: Seyler RJ, editor. Assignment of the glass transition: STP 1249, Philadelphia, PA: American Society for Testing and Materials, 1994. p. 165.