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New approach to characterise physicochemical properties of solid substrates by inverse gas chromatography at infinite dilution

II. Study of the transition temperatures of poly(methyl methacrylate) at various tacticities and of poly(methyl methacrylate) adsorbed on alumina and silica

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Abstract

The determination of the temperature transitions in polymers and more particularly when polymers are adsorbed on oxides is very important in many industrial processes. In this second part, we used inverse gas chromatography (IGC) at infinite dilution to determine the second order transition temperatures of poly(methyl methacrylate) (PMMA) adsorbed (or not) on alumina or on silica. Three types of PMMA were used: atactic (a), syndiotactic (syndio) and isotactic (iso). The IGC technique allowed to obtain the net retention volume V_n and the dispersive component of the surface energy γ_s^d for various theoretical models of molecules, using the results of Part I. By plotting $RT \ln V_n$ as a function of $(1/T)$ or γ_s^d as a function of the temperature T , we proved the presence of three particular temperatures that correspond respectively to the transition temperature relative to β -relaxation (T_β), the glass transition temperature (T_g), and the liquid–liquid transition temperature or order–disorder transition ($T_{1,1}$). Results obtained in this part allowed us to show the effect of the tacticity of PMMA and the recovery fraction of polymer adsorbed on alumina or silica on the transition temperatures.

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1. Introduction

The thermal behaviour of thermoplastic polymers

is unique and responsible for much of their attractiveness as industrially processable materials. In general, amorphous polymers change from hard, brittle, glassy materials at low temperatures to soft, deformable, rubbery materials at high temperatures. This is known as the ‘glass transition’ and occurs over a relatively narrow range of temperatures characterized by the glass transition temperature. In the study of polymers and their applications, it is important to understand the concept of transition

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phenomena and especially, the glass transition temperature, T_g [1–6]. As the temperature of a polymer drops below T_g , it behaves in an increasingly brittle manner. As the temperature rises above T_g , the polymer becomes more rubber-like. Thus, knowledge of T_g is essential in the selection of materials for various applications. In general, values of T_g well below room temperature define the domain of elastomers and values above room temperature define rigid, structural polymers [1].

It is well known that polymer properties strongly depend on temperature. Polymers can be easily affected by abrupt variations of the temperature. In fact, such modifications would induce modifications in the chain segment mobility of polymers. These changes in mobility arising at the glass transition temperatures of bulk polymers can be determined by using thermal methods, like differential thermal analysis or differential scanning calorimetry [7].

Polymers typically display broad melting endotherms and glass transitions as major analytic features associated with their properties. Both the glass and melting transitions are strongly dependent on processing conditions and dispersion in structural and chemical properties of plastics. Characterization of polymers requires a detailed analysis of these characteristic thermal transitions using either differential scanning calorimetry (DSC) or differential thermal analysis (DTA) [8,9]. Temperature scans across the dynamic spectrum of mechanical absorptions are commonly required for characterization of polymers, especially for elastomers. These thermal/mechanical properties are characterized in dynamic mechanical/thermal analysis (DMTA) [10,11]. Additionally, weight loss with heating is a common phenomena for polymers due to degradation and loss of residual solvents and monomers. Weight loss on heating is studied using thermal gravimetric analysis (TGA) [12–15]. The use of electron spin resonance (ESR) and nuclear magnetic resonance (NMR) may help to experimentally validate that the key factor of the glass transition is the change in segmental mobility. An NMR technique will also be useful for samples other techniques cannot handle, such as large samples and different physical forms (liquid, powder, and shapeable or non-shapeable samples) [16,17]. For examining polymer materials, atomic force microscopy (AFM) offers not only the ability

to perform high-resolution profiling of surface morphology and nanostructure and to study some local material properties, but it also allows to characterize the transition temperatures of such polymers [18–22].

However, when adsorbed on oxides, the glass transitions of polymers, and more particularly, of poly(methyl methacrylate) (PMMA) could not be detected by these previous thermal and dielectric methods. Indeed, the amount of polymer involved in this kind (less than 2% w/w) of experiments is too low to provide a significant signal.

In recent years, there has been considerable work done on the characterisation of the glass transition temperature of polymers on flat surfaces [23–31]. It has been shown that the changes in T_g are related to the film thickness, the molecular mass of the polymer and also the nature of the polymer–substrate interactions. An empirical relation has been proposed:

$$T_g(h) = T_g(\text{bulk}) [1 - (\alpha/h)^\delta] \quad (1)$$

where $T_g(h)$ is the measured glass transition for a film of thickness h and α and δ are adjustable parameters.

Subsequent ellipsometry measurements of T_g for PMMA films [32] revealed the strong influence of the substrate on the glass transition of polymer thin films. When decreasing the PMMA film thickness, an increase of the T_g values was observed on Si and in contrast, a decrease for PMMA films on Au. It was suggested that the observed behaviour for PMMA films on Si was due to hydrogen bonding between the polymer and the SiO_2 surface.

No mention is made in the literature of attempts made for the direct determination of the glass transition of the specifically adsorbed polymer on powder. Nevertheless, works pointing out the effect on T_g of fillers have been found [33] which take into account the free and the adsorbed polymer since the ratio of polymer to filler is high. No spectroscopic technique such as ellipsometry or X-ray reflectometry can be used for the characterization of polymer adsorbed onto rough surfaces. However, it is of great interest to know if the same effects as those pointed out on flat surfaces can be found on spherical particles. Therefore, we used inverse gas

chromatography (IGC) on PMMA–alumina or PMMA–silica systems which are known to interact strongly through acid–base interactions and ionic bonds [34]. Moreover, stereoregularity of the polymer has been varied as well as the molecular mass, and the effects investigated.

IGC was used, for thirty years, to characterise glass transitions of polymers [35]. We applied this technique in order to determine the change, as a function of temperature, of the properties of the polymer adsorbed on metallic oxides like alumina or silica and to study the second order transitions of some polymers adsorbed on oxides, and the effect of the tacticity on these transitions. Probes of known properties are injected in the column containing the solid. The retention times of these probes, measured at infinite dilution, allow us to determine the interactions between the organic molecules and the solid, if we suppose that there is no interaction between the probe molecules themselves. IGC at infinite dilution allows to calculate the net retention volume V_n from:

$$V_n = j D_c (t_R - t_0) \quad (2)$$

where t_R is the retention time of the probe, t_0 the zero retention reference time measured with a non adsorbing probe such as methane, D_c the corrected flow-rate and j a correction factor taking into account the compression of the gas [35]. D_c and j are respectively given by the following expressions:

$$D_c = j D_m \cdot \frac{T_c}{T_a} \cdot \frac{\eta(T_c)}{\eta(T_a)} \quad (3)$$

with

$$j = \frac{3}{2} \cdot \frac{\left(\frac{\Delta P + P_0}{P_0}\right)^2 - 1}{\left(\frac{\Delta P + P_0}{P_0}\right)^3 - 1} \quad (4)$$

where D_m is the measured flow-rate, T_c the column temperature, T_a the room temperature, $\eta(T)$ the viscosity gas, P_0 the atmospheric pressure and ΔP the pressure variation.

The free energy of adsorption ΔG^0 of n -alkanes is given by:

$$\Delta G^0 = RT \ln V_n + C \quad (5)$$

where R is the ideal gas constant, T the absolute

temperature and C a constant depending on the reference state of adsorption. In the case of n -alkanes, ΔG^0 is equal to the free energy of adsorption corresponding to dispersive interactions ΔG^d only.

The net retention volume will permit to obtain $RT \ln V_n$ and the free enthalpy of adsorption ΔG^0 of n -alkanes. In the case of n -alkanes, ΔG^0 is equal to the free enthalpy of adsorption corresponding to dispersive interactions ΔG^d only. Studying the evolution of ΔG^d or of $RT \ln V_n$ versus $(1/T)$, we can obtain some interesting physico-chemical properties of polymers and especially, the second order transition temperatures.

A second method was used to detect these transition temperatures. It consists of determining the evolution of the dispersive component γ_s^d of the surface energy of polymer as a function of the temperature. Values of γ_s^d of solid substrates were determined by using the well-known relationship of Fowkes [36] expressing the geometric mean of the dispersive components (exponent ‘d’) of the surface energy of the probe γ_1^d and the solid γ_s^d :

$$\Delta G^0 = \Delta G^d = 2 \mathcal{N} a \sqrt{\gamma_1^d \gamma_s^d} \quad (6)$$

where \mathcal{N} is Avogadro’s number and a the surface area of one adsorbed molecule of the probe. By plotting $RT \ln V_n$ as a function of $2\mathcal{N}a\sqrt{\gamma_1^d}$ of n -alkanes, we can deduce, from the slope of the straight line, the value of dispersive component of the surface energy of the solid [37].

However, the surface area a of a molecule adsorbed on a solid substrate is not known with a good accuracy. In Part I, we proposed various models giving the molecular areas of n -alkanes: geometrical model, cylindrical molecular model, liquid density model, BET method, Kiselev results and the model using the two-dimensional Van der Waals’ constant b that depends on the critical temperature and pressure of the liquid. The Redlich–Kwong equation, (see [38–53]) transposed from three-dimensional space to two-dimensional space was also used to calculate the areas of organic molecules. To obtain qualitative results concerning the various polymers used in this study, we applied the different models above giving the surface area of the molecule in order to determine the variations of γ_s^d of the solid as a function

of the temperature and possibly deduce some properties concerning the transition phenomena in PMMA, especially when the polymer is adsorbed on solid substrates like alumina or silica.

2. Materials, equipment and IGC procedure

Many chemical products were used in this study. α -Alumina (α - Al_2O_3), obtained by the Bayer method, from Sigma–Aldrich (St. Quentin Fallavier, France), was in powder form with particle sizes comprised between 0 and 200 μm . It contained small quantities of Na_2O (about 200 ppm relatively to Al_2O_3) and of other mineral impurities (SiO_2 : 810 ppm and CaO : 450 ppm). It exhibited a specific surface area equal to 1.5 m^2/g and a density equal to 3.97 m^2/g .

The silica was obtained from Degussa (Frankfurt, Germany), in powder form. The silica analysed here had a very high specific surface area, 105 m^2/g (determined by BET method). Its density was 2.2 m^2/g . Three types of poly(methyl methacrylate) were used: atactic PMMA (a), isotactic PMMA (iso) and syndiotactic PMMA (s) all synthesised by anionic polymerisation were purchased from Polymer Source (Montreal, Canada).

Further, we used some model organic polar molecules such as toluene, ethanol, diethyl ether, ethyl acetate, acetone, tetrahydrofuran (THF), CCl_4 , CHCl_3 , CH_2Cl_2 , CH_3CN and C_6H_6 , which are characterized by their donor and acceptor numbers [54,55]. We also used *n*-alkanes (C_5H_{12} , C_6H_{14} , C_7H_{16} , C_8H_{18} , C_9H_{20} , $\text{C}_{10}\text{H}_{22}$, etc.) as non-polar molecules. All organic molecules used in this study were purchased from Prolabo (Strasbourg, France).

Measurements of retention volumes of molecules were carried out with a DELSI GC 121 FB Chromatograph from Delsi Instruments (Suresnes, France) equipped with a flame ionisation detector of high sensitivity. The retention data were obtained with a stainless steel column of length 15 cm to 30 cm and 2 mm internal diameter packed with 1 to 2 g of polymer or oxide powders.

In this part, we used PMMA (at various tacticities), silica or alumina particles (about 1.5 g) having diameters between 100 and 200 μm , which

were introduced in the column. Helium (He) was selected as carrier gas at a flow-rate of about 25 ml min^{-1} . Before measurements, the polymer or oxide particles were conditioned in the column under a He flow during 12 h at 120 $^\circ\text{C}$, so as to eliminate physically adsorbed impurities. Here, IGC under infinite dilution conditions was used with minor amounts of gaseous solutes injected so as to approach near zero surface coverage permitting to neglect lateral interactions between adsorbed molecules and the observation of symmetrical chromatographic peaks. IGC measurements at infinite dilution were performed by varying the temperature from 20 $^\circ\text{C}$ to 180 $^\circ\text{C}$. The retention times obtained by this study allowed to obtain the net retention volume using Eq. (1).

The same procedure was used with PMMA (at various tacticities) adsorbed on alumina or silica, with the same experimental conditions.

3. Experimental

3.1. Adsorption of PMMA on α -alumina or on silica

3.1.1. Method

The polymer was dissolved in a chloroform solution containing α -alumina (or silica) powder. The solution obtained was stirred for 48 h and the residue decanted was washed three times with 25 ml of CHCl_3 to suppress any trace of PMMA non directly adsorbed on Al_2O_3 (or on silica). The surface coverage fraction θ was determined by DRIFT (diffuse reflectance infrared spectroscopy). The following formula was applied:

$$\theta = \frac{A}{A_{\text{Max}}} \cdot 100 \quad (7)$$

where A is the absorbance of the carbonyl groups for a given sample and A_{Max} the maximum absorbance recorded for a totally saturated alumina (or silica) surface.

3.1.2. Effect of the tacticity of polymer adsorbed on alumina

In a previous paper [56], we studied the variations

of surface coverage (in %) of PMMA (at different tacticities adsorbed on aluminium and proved an important effect of the tacticity of the polymer on its adsorption on alumina: the more the polymer is syndiotactic, the more the surface coverage is high. This result is assumed to be due to the low surface area occupied by a syndiotactic chain as compared to an isotactic one. Therefore, the low spreading out of syndiotactic chains enables the adsorption of more PMMA chains at the alumina surface area. We also proved that if the concentration of the polymer is higher than 3 g/l a layer saturated in polymer is obtained, whatever the polymer tacticity or molecular mass. These differences in the chain conformation and in the chain packing at the interface may lead to differences in the chain mobility that are expected to be detected by inverse gas chromatography. Section 4 will give the results relative to the transition phenomena and the chain mobility in PMMA, by using IGC.

3.1.3. Adsorption of atactic PMMA on SiO₂

In this section, we give some of the results of atactic PMMA adsorbed on silica previously obtained in another study [57]. We choose a volumetric rate of silica equal to 1.82% (v/v), that means 2 g of silica in 20 ml of chloroform, with various concentrations of PMMA. For a volumetric rate of silica equal to 1.82% (v/v), we varied the polymer concentration in the solution and consequently changed the rate (τ) of PMMA–SiO₂. After an equilibrium time $t = te$, we separated the floated part by centrifugation and determined by IR spectroscopy the equilibrium concentration of polymer using the variation of the peak area of the band relative to the carbonyl group. The adsorption isotherm was determined by plotting the rate of the bound polymer, Γ , as a function of the equilibrium concentration C_{eq} (in g/l) of PMMA:

$$\Gamma = \frac{(C_0 - C_{eq})V}{1000.m} \quad (8)$$

where C_0 is the initial concentration of PMMA (g/l), V (l) the final volume of the solution and m the silica mass initially engaged (g).

This study showed that after three treatments, the quantity of polymer adsorbed on the silica surface

does not evolve and the bound polymer rate remains constant after three treatments. For the determination of the adsorption isotherms, we took a contact time equal to 48 h corresponding to an equilibrium situation where the polymer concentration in the solvent and the quantity of polymer adsorbed have no effect on the adsorption limit. We also proved that the equilibrium concentration C_{eq} of PMMA linearly depends on the initial concentration C_0 even if the concentrations are relatively high.

However, the study of polymer/oxide rates showed that the bound polymer quantity increases with the polymer rate τ , and seems to tend to a limit value for τ values higher than 0.75 (g/g) for the couple PMMA–SiO₂ corresponding to an initial concentration higher than 25 g/l [41].

In our case, we verified that our isotherms are of Langmuir type-1 by using Eq. (9):

$$\frac{C_{eq}}{\Gamma} = \frac{1 + BC_{eq}}{B\Gamma_m} = \frac{1}{B\Gamma_m} + \frac{C_{eq}}{\Gamma_m} \quad (9)$$

where Γ_m is the quantity of polymer necessary to form one monolayer and B the Langmuir constant.

From these isotherms [57], we determined the quantity of polymer adsorbed corresponding to a monolayer by knowing the value of the slope of the curve given by Eq. (9).

3.2. Surface energy and transition temperatures of PMMA– α -Al₂O₃ and PMMA–SiO₂

We analyzed, in this study, the variations of the dispersive component of the surface energy of α -alumina and silica A130 as a function of temperature, for all the models of molecular areas, and showed that the variation of γ_s^d of α -alumina or silica is monotonous and decreases with increasing temperature. These curves do not show any transition phenomena.

However, the variations of γ_s^d of PMMA are not monotonous as a function of the temperature T . In Fig. 1, we observed three maxima of temperatures that can indicate the various transition temperatures of the polymer.

On the other hand, we plotted in Figs. 2 and 3 the variation of γ_s^d when PMMA was adsorbed respectively on silica A130 and on alumina.

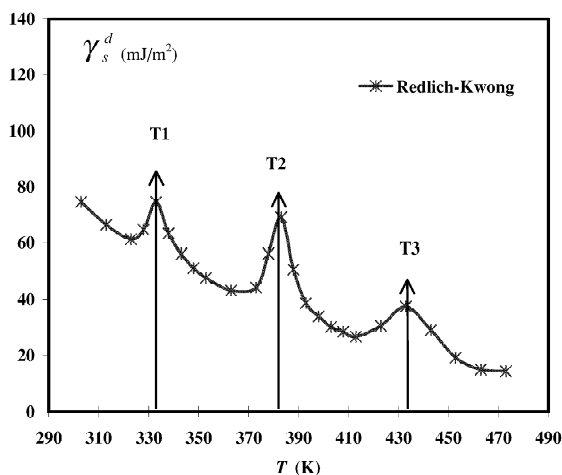


Fig. 1. Variation of the dispersive component of the surface energy (in mJ/m^2) of atactic PMMA as a function of the temperature T (in K) using the Redlich–Kwong model of molecule surface areas.

3.3. Results obtained by using $RT \ln V_n = f(1/T)$

The results obtained with n -alkanes when we plotted the evolution of $RT \ln V_n = f(1/T)$ of non-polar molecules interacting on silica, PMMA, PMMA–silica and on PMMA–alumina are given respectively in Figs. 4–7.

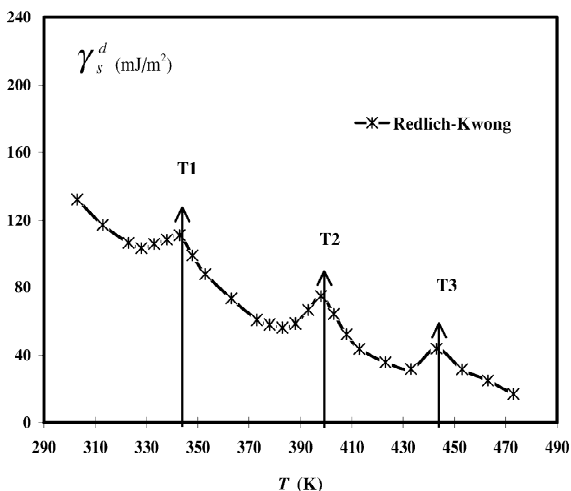


Fig. 2. Variation of the dispersive component of the surface energy (in mJ/m^2) of atactic PMMA (with 5 g/l) adsorbed on silica A130 as a function of the temperature T (in K) using the Redlich–Kwong model of molecule surface areas.

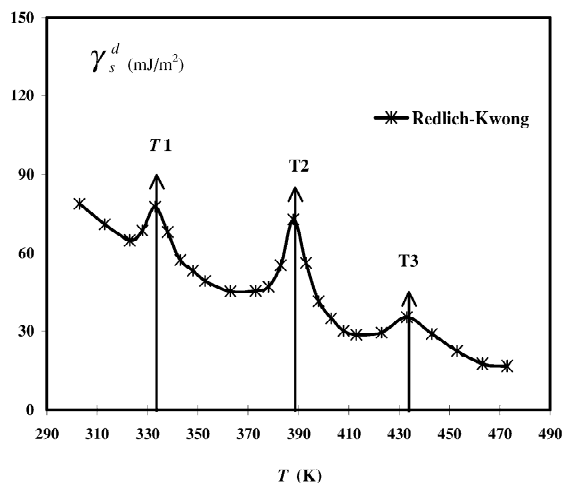


Fig. 3. Variation of the dispersive component of the surface energy (in mJ/m^2) of atactic PMMA (with 5 g/l) adsorbed on alumina as a function of the temperature T (in K) using the Redlich–Kwong model of molecule surface areas.

The results obtained by studying the evolution of $RT \ln V_n$ of the various alkanes as a function of the reciprocal temperature ($1/T$) are in good agreement with the results concerning the dispersive component of the surface energy of various PMMAs adsorbed on α -alumina or silica. As an example, we gave in Figs. 5–7 the results obtained with PMMA, PMMA–silica and PMMA–alumina. The curves obtained from $RT \ln V_n = f(1/T)$ and from $\gamma_s^d = f(T)$ for various PMMAs gave the same results. Three particular temperatures were obtained in every case, they correspond to the transition temperatures in

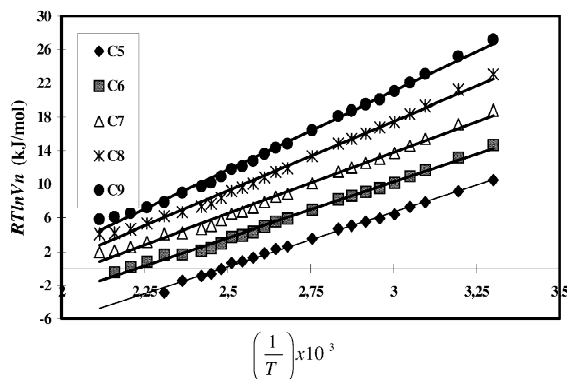


Fig. 4. Evolution of $RT \ln V_n$ of silica A130 as a function of $(1/T)$ for the different n -alkanes, T is expressed in K.

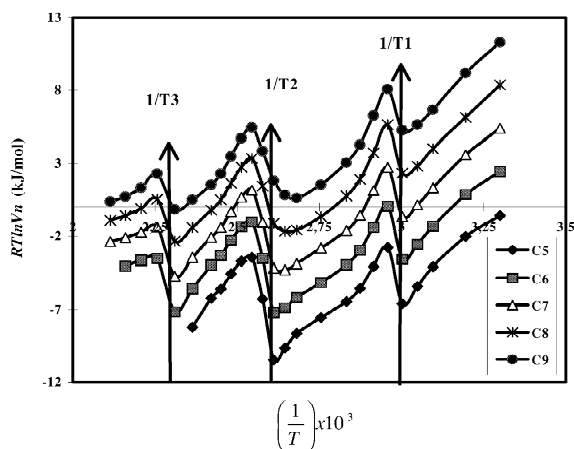


Fig. 5. Evolution of $RT \ln V_n$ of atactic PMMA as a function of $(1/T)$ for the different n -alkanes, T is expressed in K.

PMMA. However, when silica or alumina are used without PMMA, we do not observe any change in the concavity of the curves obtained when plotting the evolution of γ_s^d or $RT \ln V_n$ (see for example the linearity of the curves obtained with silica A130 in Fig. 4).

Many other experiences were done when PMMA was adsorbed on α -alumina or on silica by varying the tacticity of the polymer. The study of the variation of the dispersive component of the surface energy of atactic, isotactic and syndiotactic PMMA, adsorbed on α -alumina (or on silica), as a function of the temperature, also showed a change in the vari-

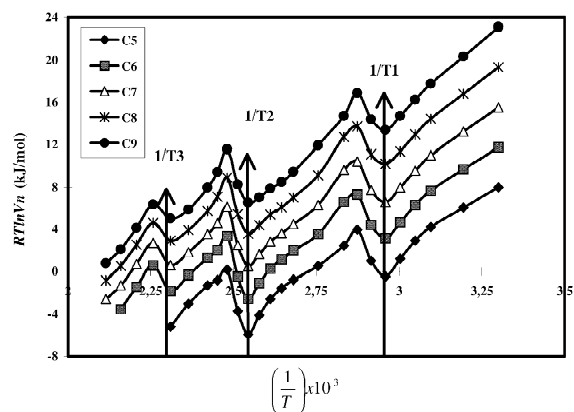


Fig. 6. Evolution of $RT \ln V_n$ of atactic PMMA (with 5 g/l) adsorbed on silica A130 as a function of $(1/T)$ for the different n -alkanes, T is expressed in K.

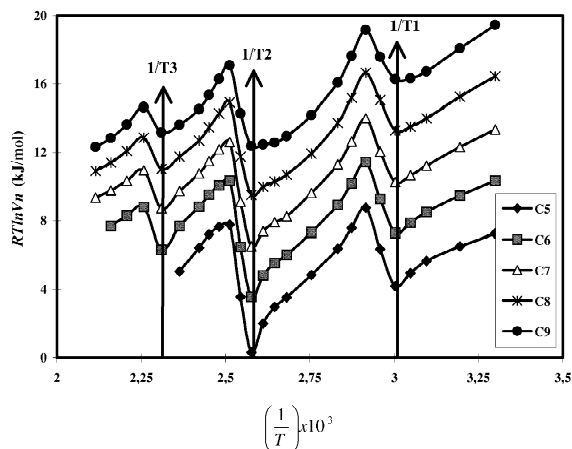


Fig. 7. Evolution of $RT \ln V_n$ of atactic PMMA (with 5 g/l) adsorbed on alumina as a function of $(1/T)$ for the different n -alkanes, T is expressed in K.

ation of γ_s^d versus the temperature. The maxima of the curves obtained correspond to transition temperatures of the polymer adsorbed on to the solid. The results obtained by IGC concerning the transition temperatures, summarised in Table 1, are in good agreement with the values measured by DSC. T_β (here T_1) represents the transition temperature of β -relaxation, T_g (T_2) the glass transition temperature and $T_{l,1}$ (T_3) the liquid–liquid transition or order–disorder transition. To compare between the transition temperatures of atactic, isotactic and syndiotactic PMMA in the bulk phase or adsorbed on alumina or on silica, we plotted the curves of $RT \ln V_n = f(1/T)$ in Figs. 8–10 which clearly showed an important effect of the tacticity of PMMA on the values of the various transition temperatures.

Table 1 shows that three transition temperatures

Table 1
Values of transition temperatures of the various PMMA

Sample	T_β (°C)	T_g (°C)	$T_{l,1}$ (°C)
a-PMMA	60	110	160
a-PMMA–SiO ₂ A130	60	115	160
a-PMMA– α -Al ₂ O ₃	60	120	170
i-PMMA	–	60	120
i-PMMA–SiO ₂ A130	–	100	140
i-PMMA– α -Al ₂ O ₃	–	110	150
s-PMMA	70	130	170
s-PMMA– α -Al ₂ O ₃	70	135	170
s-PMMA–SiO ₂ A130	70	130	170

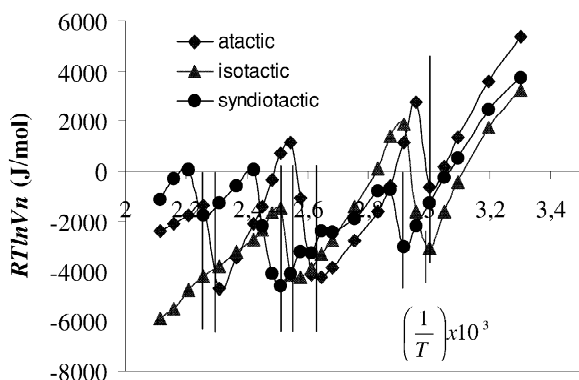


Fig. 8. Comparison between the curves of $RT \ln V_n = f(1/T)$ of atactic, isotactic and syndiotactic PMMA (in the bulk) for *n*-heptane as an example, T is expressed in K.

can be observed on a- and s-PMMA but only two transitions on the isotactic PMMA. This observation is consistent with the conclusions drawn by other workers [33,34,58,59] who show that the β -relaxation and the glass transition are partially merged for the highly isotactic isomer. It is worth noting that the glass transition temperature increases when the PMMA is adsorbed on a reactive polar surface such as alumina as compared to the T_g value recorded for the same polymer in its bulk phase. Moreover, this increase of T_g ranges from 5 for an s-PMMA to 50 degrees for the i-PMMA. The same behavior is observed for the liquid–liquid transition temperature.

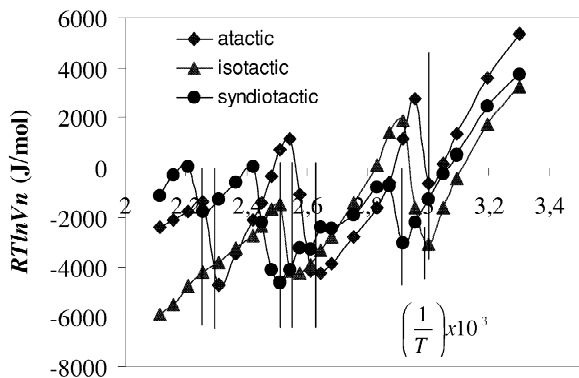


Fig. 9. Comparison between the curves of $RT \ln V_n = f(1/T)$ of atactic, isotactic and syndiotactic PMMA adsorbed on alumina for *n*-heptane as an example, T is expressed in K.

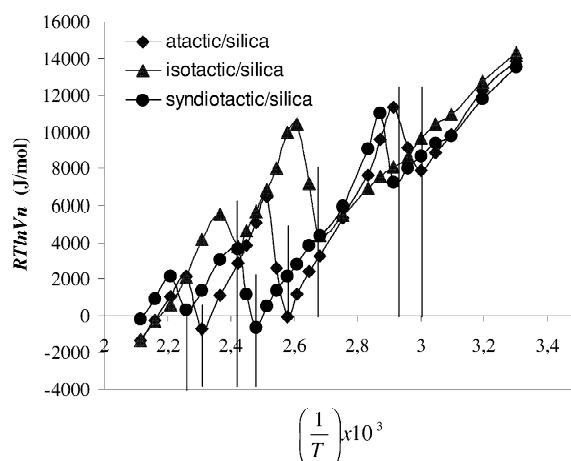


Fig. 10. Comparison between the curves of $RT \ln V_n = f(1/T)$ of atactic, isotactic and syndiotactic PMMA adsorbed on silica for *n*-heptane as an example, T is expressed in K.

4. Discussion

The maxima of γ_s^d indicate the presence of transition temperatures (glass or local transition). In general, we observed with PMMA three principal maxima that reflect the motions leading to reorganization and rearrangement of the various groups or chain segments of the polymer. The change in the retention mechanism of the probes at the transition temperatures is attributed to an increased molecular mobility of the polymer segments, allowing for the penetration of the probes into the polymer layer. Indeed, for a polymer below T_g , the penetration of the solute molecules in the bulk polymer is precluded and retention proceeds only by surface adsorption. Then, at glass transition, the penetration of the probe molecules begins; however, due to an initially slow rate of diffusion of the solute into and out of the polymer, non equilibrium conditions prevail. This can explain the decrease in the retention volume with temperature at T_g . As the temperature is increased, the diffusion coefficient rises sharply which leads to equilibrium conditions.

It can be observed that the maxima of γ_s^d correspond to the minima of the curves of the evolution of $RT \ln V_n$ as a function of $(1/T)$. This indicates that three transition temperatures are present, β -relaxation, glass transition and liquid–liquid transition. The

results obtained by IGC concerning the transition temperatures were summarised in table.

With IGC, we demonstrated the presence of PMMA transitions which are likely to be ascribed to β -relaxation, glass transition and other liquid–liquid transitions. Another assumption is that the adsorbed layer which is likely to be non homogeneous over the total thickness (with train segments having highly restricted mobility, and loops and tail segments with higher mobility) gives rise to different transitions depending on the locus of the chain segments in the layer.

5. Conclusions

In this part, we showed that the inverse gas chromatography technique at infinite dilution can be strongly used to characterise the superficial and interfacial properties of solid substrates as oxides, polymers or polymers adsorbed on oxides. Especially, we studied the superficial properties of silica, alumina, PMMA with different tacticities and PMMA adsorbed on alumina and silica. We proved that IGC allowed to determine the transition temperatures of PMMA (adsorbed or not): T_β , the transition temperature relative to β -relaxation, T_g , the glass transition temperature and T_{l-l} the liquid–liquid transition temperature or order–disorder transition. The values obtained in this study and confirmed by two different ways are in good agreement with those mentioned in the literature.

Looking at the glass transition, the adsorbed i-PMMA exhibits a large shift of T_g of about 50 °C as compared to the bulk T_g (from 60 °C for bulk PMMA to 110 °C for the adsorbed polymer). In contrast, no major effect of the adsorption on T_g seems to occur for the a- and s-PMMA. The T_g increase of adsorbed i-PMMA, is supported by the assumption of the spreading out of isotactic chains on the surface plane, maximising their contact area with the surface. This has already been studied by other groups and published elsewhere [60,61]. This spreading out allows the establishment of numerous interactions of the ester groups along the chain with the surface, which may highly restrict the chain backbone motions. Therefore, the restriction of chain mobility of macromolecules in the interfacial region

may originate in the interactions of the polymer with the substrate. Thus, strong PMMA–alumina or PMMA–silica interactions may be responsible for the T_g increase of the adsorbed i-PMMA. However, as the nature of the polymer–substrate interactions remains constant whatever the PMMA tacticity, there must be other effects acting on the T_g of thin layers.

6. Nomenclature

a	Surface area of molecule
A	Absorbance of the carbonyl groups for a given sample
A_{Max}	Maximum absorbance recorded for a totally saturated alumina (or silica) surface
AN	Acceptor number of electrons
B	Langmuir constant.
C	Constant depending on the reference state of adsorption
C_0	Initial concentration of PMMA
C_{eq}	Equilibrium concentration
DN	Donor number of electrons
D_c	Corrected flow-rate
D_m	Measured flow-rate
j	Correction factor taking into account the compression of a gas
N	Avogadro's number
P_0	Vapour pressure of a probe
P_a	Atmospheric pressure
R	Ideal gas constant
t_0	Zero retention reference time
te	Equilibrium time
t_R	Retention time of a probe
T	Absolute temperature
T_c	Column temperature
T_a	Room temperature
T_g	Glass transition temperature
T_{l-l}	Liquid–liquid transition
T_β	Transition temperature of β -relaxation
V_n	Net retention volume
γ_l^d	Dispersive component of the surface energy of the probe (liquid)
γ_s^d	Dispersive component of the surface energy of the solid
ΔG^0	Free enthalpy of adsorption
ΔG^d	Free enthalpy of adsorption corresponding to dispersive interactions

ΔP	Pressure variation.
η	Viscosity gas
Γ	Rate of the bound polymer
Γ_m	Quantity of polymer necessary to form one monolayer
θ	The surface coverage fraction

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