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Study of the transition phenomena of poly(α-*n*-propyl) methacrylates adsorbed on silica by Inverse Gas Chromatography (IGC)

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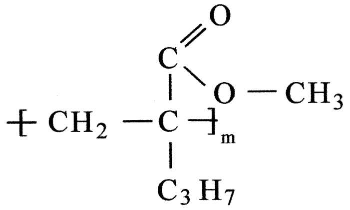
Abstract. Inverse gas chromatography at infinite dilution was used in this paper to characterise the superficial and interfacial properties of solid substrates as oxides, polymers or polymers adsorbed on oxides. Especially, we studied the transition phenomena in PMMA and poly(α-n-alkyl) methacrylate adsorbed on silica or in their bulk phases. In the case of PMMA (adsorbed on silica or not), the study of the evolution of RTlnVn as a function of 1/T for different n-alkanes, proved that IGC technique allowed to determine with a good accuracy the various transition temperatures: 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 same study was also realised with poly(α-n-propyl) methacrylate. The glass transition temperatures of this polymer (*C3*) adsorbed in its bulk phase or on silica were determined. We also showed an important effect of the adsorption of polymer on oxide on the shift in the value of *Tg*.

1. INTRODUCTION

This study is the result of a fruitful collaboration between three laboratories: Laboratory of Study and Characterisation of Amorphous and Polymers (LECAP, University of Rouen)), Institute of Chemistry of Surfaces and Interfaces (ICSI-CNRS, Mulhouse) and Laboratory of Analytical Chemistry, Materials, Surfaces and Interfaces (CHAMSI, Lebanese University, Beirut).

Poly(α-n-propyl) methacrylates synthesised and characterised in the Laboratory of Macromolecular Materials (L2M-INSA, Rouen)[1] and studied in this paper has the following formula:



$$-\!\!\left[CH_2-\underset{C_3H_7}{\overset{C(=O)-O-CH_3}{C}}\right]_m$$

Figure 1. Poly(α-n-propyl) methacrylate, noted *C3*

In a previous study, Godard, Saiter et al. [2] had determined the enthalpy relaxation in polymethyl (alpha-n-alkyl) acrylates and the effect of the length on the thermal properties of polymers. They investigated by DSC the structural relaxation of these polymers in which it is possible to change the length of the alkyl chain, evaluated the Narayanaswamy parameter, x, which controls the relative contribution of temperature and of structure to the relaxation time, the apparent activation energy.

The results obtained by Godard, Saiter et al. [2, 3] on two acrylates showed that the parameter x increases with the lateral chain length, that is to say, that the temperature effects increase as the length of the alkyl chain is increased.

Godard et al. [4] studied the phenomena transition in PMMA and polymethyl (α-n-propyl) acrylates and demonstrated the following results:

- A weak transition in PMMA (noted *C1*) at a temperature comprised between -150 et -100°C was observed and attributed to a transition γ, that corresponds to the rotation of final methyl group of the lateral chain.
- Another transition between -100 et 0°C corresponding to a transition β relative to the movement of ester groups for *C3*.
- The third transition with a very important amplitude, corresponding to a glass transition, observed above 0°C. This transition temperature decreases from *C1* to *C3* :

Table 1. Tg values of *C1* and *C3*

Polymer	*C1*	*C3*
Tg (°C)	110	72

We proposed in this paper to study the transition temperatures of these two polymers.

2. INVERSE GAS CHROMATOGRAPHY AND PROCEDURE

IGC technique was used, for thirty years, to characterise glass transitions of polymers [5]. We applied this technique in order to determine the change, as a function of temperature, of the properties of some polymers and to study the second order transitions of such polymers adsorbed on oxides. 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 interactions between the probe molecules themselves.

IGC technique at infinite dilution allows to calculate the net retention volume V_n from:

$$V_n = j\,D_c\,(t_R - t_0) \tag{1}$$

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 [5]. D_c and j are respectively given by the following expressions:

$$D_c = jD_m \frac{T_c}{T_a}\frac{\eta(T_c)}{\eta(T_a)} \tag{2}$$

and

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

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 :

$$\Delta G^0 = RT \ln V_n + C \tag{4}$$

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 $RTlnV_n$ 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 $RTlnV_n$ versus $(1/T)$, we can obtain some interesting physico-chemical properties of polymers and especially, the second order transition temperatures.

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 paper, we used PMMA, poly (α-n-propyl) methacrylate, 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 about 25 $ml.min^{-1}$. Before measurements, the polymer or oxide particles were conditioned in the column under a He flow during 12 hours at 120°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 done by varying the temperature from 20°C to 180°C. The retention times obtained by this study allowed to obtain the net retention volume using Eq. (1).

The same procedure was used when polymer was adsorbed on silica, with the same experimental conditions.

3. TRANSITION PHENOMENA OF *C1* AND *C3* DETERMINED BY IGC AND DISCUSSION

By analysing the curves $RTlnV_n = f(1/T)$ of PMMA obtained by *IGC* at infinite dilution three transitions can be in general distinguished : β-transition, α-transition or glass transition, and l-l-liquid-liquid or order-desorder transition . These three particular transition temperatures were obtained with PMMA and PMMA/SiO_2. However, when silica was used without PMMA, we did not observe any change in the concavity of the curves obtained when plotting the evolution of *RTlnVn* (the curves obtained with silica A130 are linear).

As example we gave on figures 2 and 3 the evolution of $(RTlnV_n)$ as a function of $(1/T)$ respectively for PMMA (*C1*) and for the couple PMMA adsorbed on silica (*C1*/SiO_2) when the recovery fraction (θ) is less than 1. The molecule probes injected into the column are here chosen between the n-alkanes (from n-pentane C5, to n-nonane C9).

Results obtained from the curves of figures 2 and 3 and concerning the various PMMAs are summarised in the table 2:

Table 2. Transition temperatures of *C1* and *C1* adsorbed on silica (*C1*/SiO_2).

Transition type	*C1*	*C1*/SiO_2 ($\theta = 1$)	*C1*/SiO_2 ($\theta < 1$)
β -Transition	60 °C	60 °C	70 °C
glass Transition	110 °C	115 °C	125 °C
l-l Transition	160 °C	160 °C	170 °C

These transitions are really affected by the experimental method, experimental conditions, the molecule nature, the polymer morphology, its tacticity and when polymer is adsorbed on oxides. It is worth noting that the glass transition temperature increases when the PMMA is adsorbed on reactive polar surface as silica as compared to the T_g value recorded for the same polymer in its bulk phase. The same behaviour is observed for the liquid-liquid transition temperature.

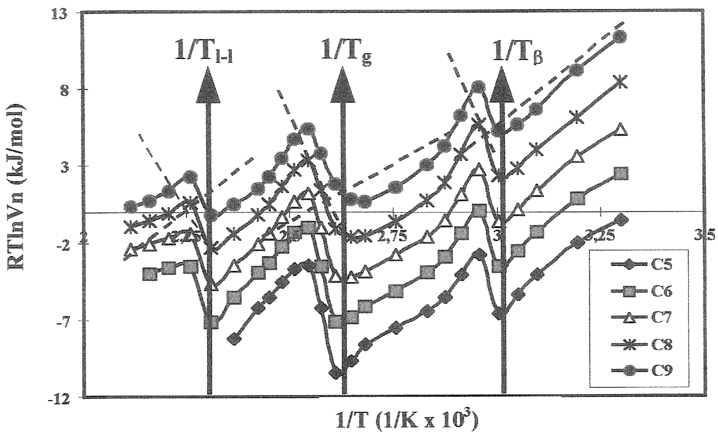


Figure 2. Variation of $RTlnV_n$ versus *1/T* for *C1* polymer for the different n-alkanes (C5 to C9).

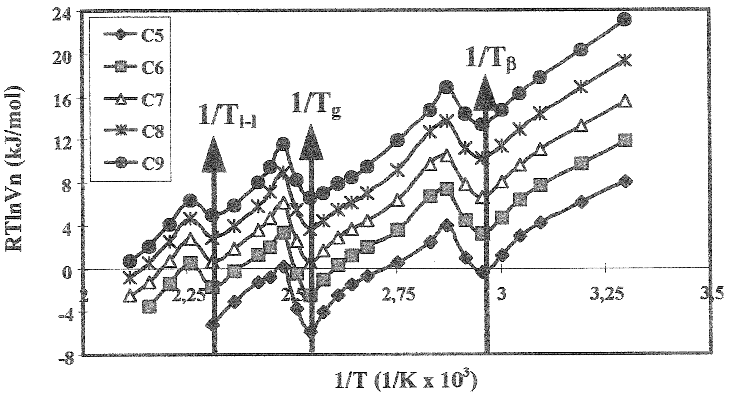


Figure 3. Evolution of *RTlnVn* of PMMA adsorbed on silica A130 (recovery fraction $\theta < 1$) as a function of (*1/T*) for the different n-alkanes

A similar study was done with poly(α-n-propyl) methacrylate (*C3*) in bulk phase and when this polymer is adsorbed on silica A130 for two cases, the first one was realised for an adsorption of *C3* on silica obtained with a monolayer of polymer and the second studied when the recovery fraction is less than 1. We also observed a glass transition temperature (figure 4) equal to 71°C that confirmed exactly the results obtained by Godard and Saiter [4] by using IGC technique.

On figures 5 and 6 we plotted the variations of RTlnVn of polymer *C3* adsorbed on silica for the two cases ($\theta = 1$ and $\theta < 1$) as a function of 1/T with n-alkanes. Figures 5 and 6 showed a shift in the glass transition temperature respectively in the two previous cases.

Table 3. Glass transition temperatures of *C3* and *C3* adsorbed on silica (*C3*/SiO_2).

Transition type	*C3*	*C3*/SiO_2 ($\theta = 1$)	*C1*/SiO_2 ($\theta < 1$)
Glass transition	71 °C	79 °C	88 °C

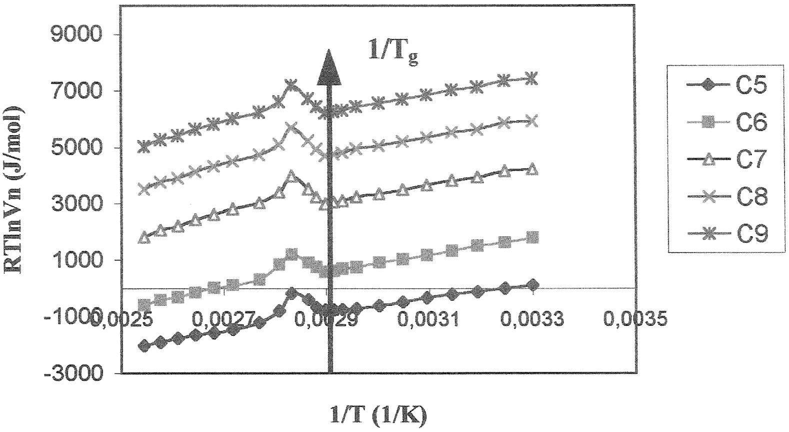


Figure 4. Variation of $RTlnV_n$ versus $1/T$ for polymer $C3$ for the different n-alkanes (C5 to C9).

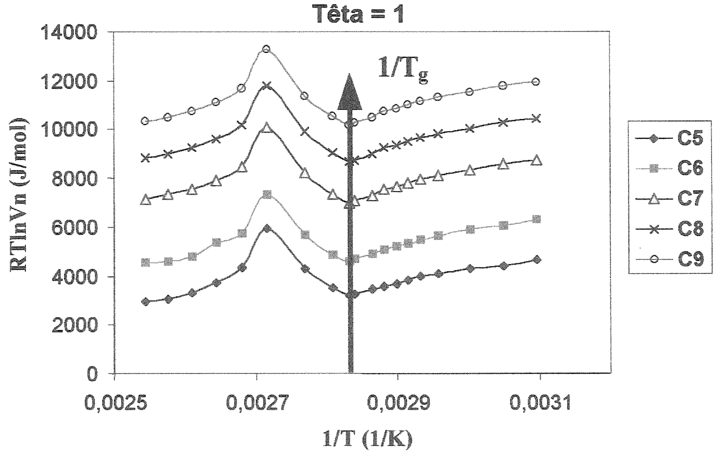


Figure 5. Variation of $RTlnV_n$ versus $1/T$ for $C3$ adsorbed on silica ($\theta = 1$) for the different n-alkanes (C5 to C9)

The results obtained highlighted the effect of lateral chain on the adsorption and physico-chemical properties of poly(α-n-propyl) methacrylate and especially on the glass transition temperature *Tg*. The variation of *Tg* from 110 °C for *C1* to 71 °C for *C3* clearly shows that the increase of α-lateral chain length leads to a decrease of *Tg* (Table 4):

Table 4. Values T_g for *C1* and *C3*

Polymer	*C1*	*C3*
Tg (°C)	110	71

This decrease of T_g when the carbon atom number increases in the lateral chain can be attributed to an inner plastification effect created by the increase of the lateral chain length. If we admit that *Tg* is representative of the compacity of the polymer, we can deduce that the higher *Tg* is, the higher the polymer compacity is.

Note that the difference between *Tg* before and after adsorption of polymer on silica, ΔT_g, increases from *C1* to *C3* (Table 5):

Table 5. Variation of ΔT_g for *C1* and *C3* after adsorption on silica

ΔT_g (°C)	*C1*	*C3*
$\theta = 1$ (Cn/SiO_2)	5	8
$\theta < 1$ (Cn/SiO_2)	15	17

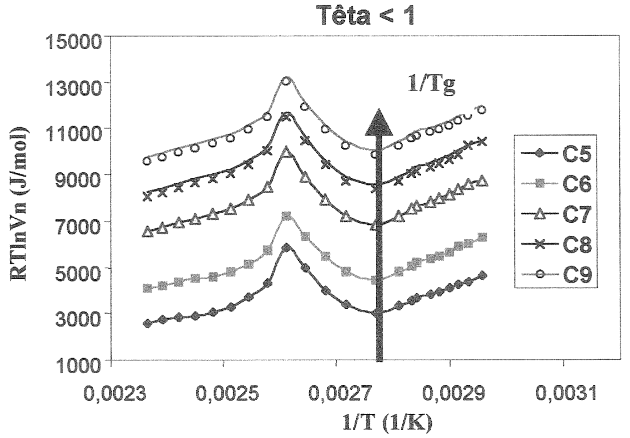


Figure 6. Variation of $RTlnV_n$ versus *1/T* for *C3* adsorbed on silica ($\theta < 1$) for n-alkanes (C5 to C9).

4. CONCLUSION

In this paper, we showed that 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, PMMA and poly(α-n-alkyl) methacrylate adsorbed on silica or in their bulk phases. We proved that IGC technique 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_{ll} 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 that mentioned in the literature.

We also determined the glass transition temperatures of polymer (*C3*) even when the polymer was adsorbed on silica and proved an important effect of the adsorption on the shift in the value of *Tg*.

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