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Influence of poly(methyl methacrylate) impregnation ratio on the surface properties of fumed silica and on the glassy temperature of poly(methyl methacrylate) using inverse gas chromatographic analysis

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Abstract

The surface properties of poly(methyl methacrylate) (PMMA) impregnated fumed silicas, in a large range of impregnation ratios, were examined using inverse gas chromatography at infinite dilution. It was observed that the dispersive component γ_s^d does not decrease monotonously with the impregnation ratio. Two critical coverage ratios were evidenced corresponding at first to the shielding of the most energetic sites and then to the achievement of total coverage of the silica surface. The influence of the coverage ratio on the glassy temperature (t_g) of the adsorbed PMMA was also studied, which was evidenced down to a very low coverage ratio (1 monomer unit/nm²).

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1. Introduction

The study of macromolecules adsorbed to a solid surface is obviously of a theoretical but also of a practical interest since these systems are developed for many applications, notably in the domain of polymer reinforcement. Indeed, in the manufacturing of high-performance composite materials, the nature and the properties of the polymer–filler or matrix–

fiber interface are of utmost significance, since it is in this region where stresses are transmitted to and distributed over the surface of the reinforcing agent.

In other words, the conformation of macromolecules in the vicinity of polymer–filler interface plays an important role in the filled polymer materials. It is obvious that the conformation will depend on the interaction forces that take place between the filler surface and the monomer units in contact with the former [1,2]. It will depend on the characteristics of both partners: the functionality, the stereochemistry and the molecular mass of the polymer, on one hand, and the chemical nature and the surface morphology of the filler on the other hand. The irregular distribution of both surface functions and geometrical

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structures, in other words, the surface heterogeneity plays certainly a main role in the interactions between both polymer and solid surface [3].

The aim of this work is to demonstrate how coupling inverse gas chromatography in infinite dilution (IGC-ID) measurements with a simple controlled impregnation process, as previously used for the study of the poly(ethylene oxide) (PEO)–talc or PEO–silica interactions [4], will provide interesting information on the polymer–solid interface.

For this study, a fumed silica sample has been selected. Poly(methyl methacrylate) (PMMA) solutions of known concentration in dichloromethane were used for the preparation of impregnated silica samples with coverage ratio varying from 0 up to 36 monomer-units per square nanometre (MU/nm²). The surface properties of the impregnated silica samples have been simply examined using *n*-alkanes as probes for IGC experiments at different temperatures of measurement.

2. Theory

2.1. The principle of inverse gas chromatography

IGC is a simple inversion of conventional gas chromatography. Normally, in IGC measurements, a given amount of solid is packed into a chromatographic column and used as a stationary phase. Several kinds of probe molecules (at infinite dilution or finite concentration) with known properties are injected into the column and eluted through the column by helium used as carrier gas. The fundamental parameter characterising the equilibrium state of partitioning into the column is the net retention volume V_n defined as the amount of carrier gas required to elute the injected probe molecules from the column. Thus, V_n is directly related to the gradient ($\delta I/\delta c$) of the partition isotherm by [5]:

$$V_n = A(1 - Y_0) \cdot \left(\frac{\delta I}{\delta c} \right)_p \quad (1)$$

where I is the concentration of the probe on the solid surface, c the concentration of the probe in the gas phase, P is the equilibrium pressure, A the total surface area of the solid adsorbent in the column, Y_0 the mole fraction of the probe in the gas phase at the

column outlet, and J is the gas compressibility factor given by:

$$J = \frac{3}{2} \frac{\left(\frac{P_{in}}{P_{out}} \right)^2 - 1}{\left(\frac{P_{in}}{P_{out}} \right)^3 - 1} \quad (2)$$

where, P_{in} and P_{out} are, respectively, the pressure of the carrier gas at the inlet of the column and at the outlet of the column.

2.2. Adsorption in infinite dilution conditions

When adsorption takes place at infinite dilution, the interaction between the adsorbed probes is negligible and Henry's law can be applied, i.e. the concentration of the probe on the solid surface is proportional to equilibrium pressure. Thus the term ($\delta I/\delta c$) in Eq. (1) becomes constant and equal to the surface partition coefficient K_s . In this case the V_n is practically independent of the probe concentration [5–8].

2.2.1. Determination of standard thermodynamic parameters

At infinite dilution, several standard thermodynamic parameters, such as free energy ΔG_a° , enthalpy ΔH_a and ΔS_a° of adsorption, can be determined according to Katz and Gray [9]. The standard free energy of transferring 1 mole of molecules from the standard gaseous state to a standard adsorption state is related to the V_n by Eq. (3):

$$\Delta G_a^\circ = -RT \ln(V_n) + B \quad (3)$$

where T is the column temperature (in K), R the gas constant and B a constant depending on the reference state and on the total surface area of the solid contained in the column. B is given by Eq. (4):

$$B = RT \ln \left(\frac{P^\circ}{\pi^\circ S g} \right) \quad (4)$$

where S is the specific surface area and g the solid weight in the column. Applying the De Boer's reference state, at $P^\circ = 101.3$ kPa (1 atm) and 273 K where the mean distances between the probe molecules in vapour phase and adsorbed at solid surface

are equal, the spreading pressure π° has a value 0.338 mN/m [10].

It is clear that different reference states will give different ΔG° values. Measuring the retention volume of a probe at different temperature, the enthalpy of adsorption ΔH_a can easily be computed by applying Eq. (5):

$$\Delta H_a = -RT \frac{\partial(L_n V_n)}{\partial\left(\frac{1}{T}\right)} \quad (5)$$

From Eq. (5), we see that the ΔH_a is now independent of reference-state.

2.2.2. Determination of dispersive energy component γ_s^d

The adsorbed probe molecules can exchange different interactions with the solid surface. Generally, the surface energy γ_s can be split into two parts: dispersive γ_s^d and specific γ_s^{SP} energy components:

$$\gamma_s = \gamma_s^d + \gamma_s^P \quad (6)$$

In practice, *n*-alkanes are used to obtain the dispersive component of the surface energy.

For a first approximation, the free energy of adsorption ΔG_a° can be linked with the work of adhesion W_A between the vapour (adsorbat) and the solid stationary phase (adsorbent) per unit surface area:

$$-\Delta G_a^\circ = NaW_A \quad (7)$$

where *N* is Avogadro's number and *a* is the surface area of an adsorbed probe molecule.

When non-polar probes like *n*-alkanes are employed as adsorbats, the work of adhesion is dominated by dispersive interactions at the interface and thus the IGC measurement yields the dispersive components of the surface free energy, γ_s^d , from [11]:

$$W_A = 2(\gamma_s^d \gamma_s^P)^{1/2} \quad (8)$$

Doris and Gray [12] determined γ_s^d from the contribution of a methylene ($-\text{CH}_2-$) group in the alkane series ($\text{C}_n\text{H}_{2n+2}$) to the free energy of adsorption ΔG_{CH_2} , which could be derived from the slope of the linear plot of ΔG_a° of a series of *n*-alkanes versus their carbon atom numbers:

$$\gamma_s^d = \frac{\Delta G_{\text{CH}_2}^2}{4N^2 a_{\text{CH}_2}^2 \gamma_{\text{CH}_2}} \quad (9)$$

where *N* is Avogadro's number, a_{CH_2} is the area covered by one methylene group (0.06 nm^2) [12], and γ_{CH_2} is the surface energy of the pure methylene group surface, i.e. polyethylene, $\gamma_{\text{CH}_2} = 35.6 + 0.058(293 - T)$, in mJ/m^2 [12,13]. ΔG_{CH_2} is obtained from the slope of the straight line obtained when plotting the ΔG_a° of *n*-alkane probes versus their number of carbon atoms.

2.2.3. Limitations of IGC-ID

Finally, it is of the utmost importance to realise that IGC-ID delivers absolute thermodynamic parameters only on a perfectly homogeneous surface, i.e. a surface for which the potential of interaction remains constant from one adsorption site to another one.

No real solid surface could be considered as truly homogeneous and the presence of sites having different potentials of interaction necessarily will influence the IGC-ID behaviour of the probe. On an energetically heterogeneous surface, the residence time of a molecule τ_s on an adsorption site having a characteristic energy of interaction ϵ_s is given by:

$$\tau_s = \tau_s^\circ \exp(\epsilon_s/RT) \quad (10)$$

where τ_s° varies from 10^{-12} to 10^{-13} s [14].

For example, for a τ_s° value equal to 10^{13} , the residence time on a site having a characteristic energy of interaction equal to 50 kJ/mol, is equal to about 10 μs . Admitting that all the sites have the same energy of interaction, that means that the solid surface is homogeneous, a retention time of 2 min will correspond to 12,000 elementary adsorption steps.

Moreover, the probe can migrate on the surface and falls down in the potential wells corresponding to the sites having the highest energy of interaction, thus, increasing the contribution of the latter to the overall retention time. Then, the overall retention time is a complex function of the number of sites, their characteristic energies of interaction and their capture radius. Consequently, the thermodynamic data delivered by the IGC-ID can only be used for the comparison of solid surfaces presenting a close analogous structure, and is particularly interesting for

Table 1
Surface area fractal dimensions of the fumed silica sample (Wacker HDK-S13)

Surface area N ₂ (m ² /g)	Surface area CTAB (m ² /g)	$R_{\text{CTAB}/\text{N}_2}$	D_s CTAB–N ₂	D_s SAXS
131	133	1.02	2.0	2.0

the detection of surface modification. In this study, we have taken advantage of this selectivity of the IGC-ID to the more interactive sites for detecting the progressive killing of the more energetic sites by a PMMA-controlled impregnation of the silica surface according to the method proposed by Ref. [4].

3. Materials and methods

3.1. Silica sample

The fumed silica sample, HDK-S13 from Wacker-Chemie was selected for this study. The specific surface area of this sample was determined by nitrogen and cetyltrimethylammonium bromide (CTAB) adsorption whereas its surface roughness in terms of surface fractal dimension was assessed by relating the CTAB surface area to the nitrogen one (SET) or by small angle X-ray scattering (SAXS) [15] (Table 1).

One sees that the silica HDK-S13 exhibits a surface fractality equal to 2, whatever the technique used. Therefore one can conclude that this silica is flat at the molecular level as schematically shown in Fig. 1 and that all silanol groups are accessible to interaction with the polymer.

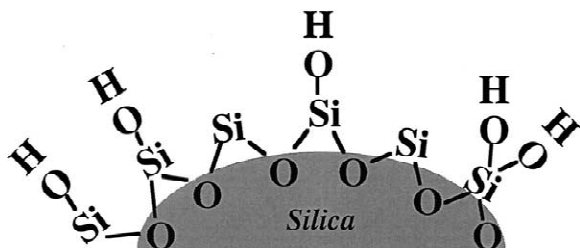


Fig. 1. Schematic representation of HDK-S13 silica surface.

3.2. Inverse gas chromatographic measurements

Before filling the columns, the very fluffy fumed silica has to be pressed in an IR die. The silica pellets are carefully crushed and sieved. The silica particles having sizes comprised between 80 and 400 μm were then selected. These particles after impregnation were packed into a stainless steel column having an internal diameter of 2.17 mm and a length of 30 cm.

The column was then attached to a gas chromatograph (IGC HP5730A), fitted with a flame ionisation detector. Helium was used as carrier gas; its flow-rate was equal to about 25 $\text{cm}^3 \text{min}^{-1}$. The temperatures of the injector and detector always exceeded the oven temperature by about 50 $^\circ\text{C}$. Very small volumes of solute vapours were injected so as to approach linear condition gas chromatography. With alkanes, very symmetrical peaks were recorded and the retention times were simply measured from the peak maximum position using a Perkin-Elmer LCI-100 integrator.

The precision of the measurement was as follows.

- For the retention time: 0.005 min.
- For the column temperature: 0.1 $^\circ\text{C}$.
- For the atmospheric pressure: ± 20 Pa.
- For the pressure drop: ± 100 Pa.

Therefore net retention volumes were known with a precision equal to about 0.5%. Consequently we found that the absolute error for the free energy of adsorption could be estimated to be ± 2 kJ and ± 0.5 mJ m^{-2} for the dispersive component (γ_s^d) of the surface free energy probes.

The alkane probes used were purchased from Sigma–Aldrich as high purity grade products and used without further purification.

3.3. Impregnation protocol

A PMMA solution of known concentration in dichloromethane was prepared. On the other hand, a known amount of fumed silica was dispersed in 25 ml of the same solvent. By adding increasing volumes of the PMMA solution to this silica dispersion, a large scale of impregnation ratios (τ) expressed in mg of PMMA per g of silica, corresponding to defined coverage ratio (θ) of the surface in terms of monomer units per square nanometre

Table 2
The characteristics of the PMMA impregnated silica samples

Ref. samples	τ (mg/g)	θ (MU/nm ²)
HDK-S13	0	0
HDK-S13/PMMA/1.08	10.87	0.5
HDK-S13/PMMA/2.17	21.75	1
HDK-S13/PMMA/4.35	43.50	2
HDK-S13/PMMA/8.60	86.00	4
HDK-S13/PMMA/12.95	129.5	6
HDK-S13/PMMA/17.40	174.0	8
HDK-S13/PMMA/21.75	217.5	10
HDK-S13/PMMA/26.10	261.1	12
HDK-S13/PMMA/51.80	518.0	24
HDK-S13/PMMA/77.70	777.0	36

(MU/nm²), was scanned. θ is related to τ by Eq. (11):

$$\theta = \tau \frac{6023}{M_{\text{MU}} S} \quad (11)$$

where M_{MU} is the PMMA monomer unit molecular mass (100 g/mol) and the specific surface area of the silica (131 m²/g) and τ is given in mg/g θ expressed in MU/nm² (Table 2).

The PMMA monomer unit molecular area (a_{MU}) could be assessed from the molecular volume of the monomer unit, computed from PMMA bulk density (ρ_{PMMA}), according to the equation:

$$a_{\text{MU}} = 2/3 \sqrt{\frac{\rho_{\text{PMMA}}}{M_{\text{MU}}}} \quad (12)$$

where ρ_{PMMA} is the PMMA density equal to 1.19 g/cm³, hence unit area (a_{MU}) could be estimated to have a value of 27 Å²/MU. It is known that such estimation from the bulk density leads to an underestimated value of about 20%, therefore we will admit a value of 31 Å²/MU. Then, if all the MU would be in contact with the surface, 3.1 MU/nm² could be necessary to form a so-called “MU monolayer”, on the silica surface.

4. Results and discussion

4.1. Free energies of adsorption (ΔG_a°) of alkane probes

The surface properties of the impregnated silica

samples were simply examined using *n*-alkanes as probes for IGC experiments. In a first step, the evolution of the standard free energy of adsorption of *n*-alkanes was examined. Fig. 2 displays their evolution with the number of carbon atoms of the *n*-alkanes used for probing the surface properties of the fumed silica before and after adsorption of PMMA at different impregnation ratios.

It is observed that the standard free enthalpies decrease readily with increasing impregnation ratios until the coverage ratio reaches a value of 8 MU/nm². Over this ratio a stabilisation of the surface properties of the impregnated is evidenced, suggesting a complete coverage of the silica surface by a continuous film of polymer. In order to have a close insight of the surface properties with the impregnation ratio the values of γ_s^d were computed from the slope of the straight lines representing ΔG_a° versus the number of carbon alkanes, according to the Doris and Gray approach.

4.2. Dispersive component of the surface energy γ_s^d

Fig. 3 shows the variation of the London component of surface energy (γ_s^d) measured at 80 °C of PMMA impregnated HDK-S13 samples with MU coverage ratio.

Obviously, the dispersive component (γ_s^d) does not decrease monotonously with the impregnation ratio, but two break points can be observed corre-

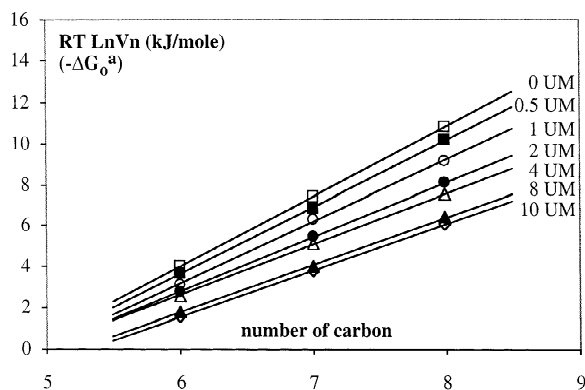


Fig. 2. Variation of $-\Delta G_a^\circ$ of alkane probes, with their number of carbon atoms, on some PMMA impregnated samples at different MU coverage ratios, measured at 100 °C.

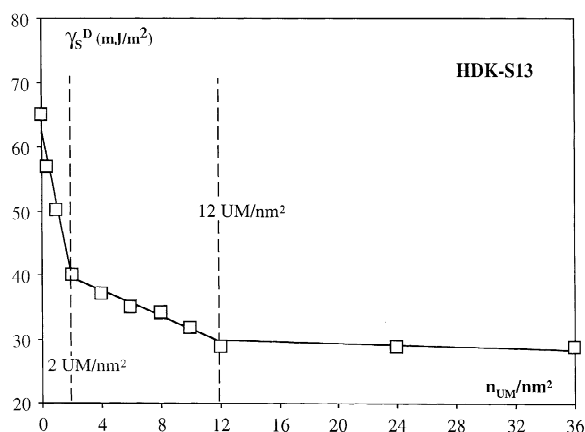


Fig. 3. Variation of the dispersive component γ_s^d of the surface energy of PMMA impregnated HDK-S13 samples with the MU coverage ratio, measured at 100 °C.

sponding to critical MU densities corresponding to 2 and 12 MU/nm^2 .

The first decrease could be attributed to the quick shielding of the most energetic sites, possibly highly polarisable stressed siloxane bridges. Then between 2 and 12 MU/nm^2 the polymer covers progressively the residual free surface, until the formation of a thick film of polymer that occurs above 12 MU/nm^2 . Then, it remains stable and independent of the coverage ratio.

Looking at γ_s^d , one has a look at the potential of interaction of all the components of the composite surface at low coverage ratio below 2 MU/nm^2 , that means the uncovered free silica surface and the adsorbed macromolecules. On the contrary, the examination of the evolution of the glassy temperature and its intensity gives access only to information on the polymer part of the impregnated silica.

4.3. Determination of the PMMA temperature transitions

IGC is a very convenient and very sensitive method for the detection of the glassy transition (t_g) of a thin film of polymer deposited on a solid surface [16]. For this purpose, one has to determine ΔG_a° at different temperatures around the temperature transition. In case of PMMA adsorbed on a solid, one observes two transition temperatures at 60 and 105 °C attributed, respectively, to the β transition

and the glassy temperature transition and corresponding to two minima in the plot of $-\Delta G_a^\circ/T$ versus the reciprocal temperature. Such typical plots are depicted in Fig. 4, for three *n*-alkane probes and a coverage ratio of 4 MU/nm^2 .

The evolution of the free adsorption energy with the temperature was studied for the different coverage ratios of the silica by the PMMA, in both ranges of temperature around the t_g temperature and β transition temperature.

4.3.1. Variation of the t_g transition temperature with the coverage ratio

The variation of $-\Delta G_a^\circ/T$ versus the reciprocal temperature is plotted in Fig. 5.

The following points are worth noting.

- (i) It is possible to observe the t_g down to very low coverage ratios, e.g. only 1 MU/nm^2 corresponding obviously to isolated macromolecules scattered on the silica surface, whereas a surface density 3.1 MU/nm^2 is at least necessary to cover all the solid surface.
- (ii) The T_g is independent of the impregnation ratio and remains equal to the same as for the bulky polymer, which is equal to 105 °C [17].
- (iii) The jump of surface properties corresponding to the glassy transition increases with the impregnation ratio, proof that a part of the MU are immobilised on the silica surface and not concerned by the transition phenomena.
- (iv) A continuous increase of the $-\Delta G_a^\circ/T$ at a

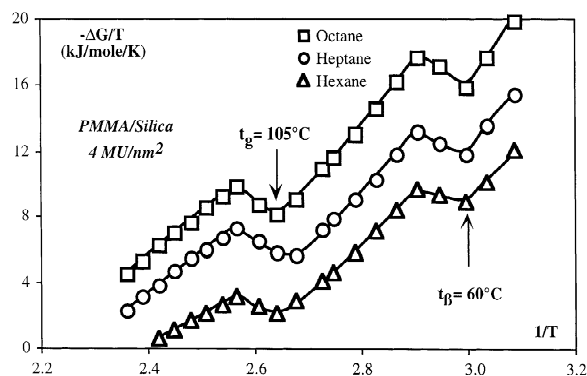


Fig. 4. Variation $-\Delta G/T$ of *n*-hexane, *n*-heptane and *n*-octane, with the reciprocal temperature, for PMMA impregnated HDK-S13 silica samples, at different MU coverage ratios, from below the t_β temperature to above the t_g temperature.

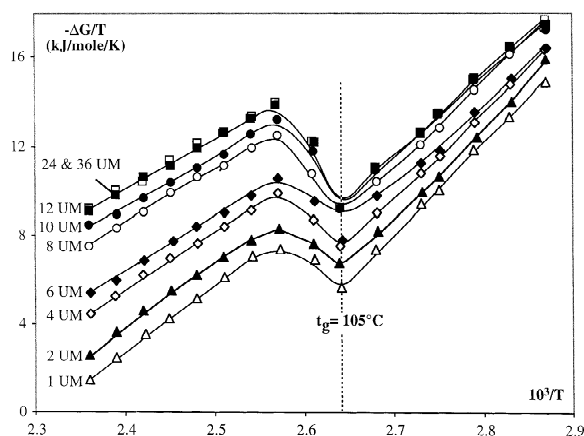


Fig. 5. Variation $-\Delta G/T$ of *n*-octane, with the reciprocal temperature, for PMMA impregnated HDK-S13 silica samples, at different MU coverage ratios, around the t_g transition temperature.

given coverage ratio is observed up to a coverage ratio of 12 MU/nm². Over this critical MU surface density, also evidenced previously by the observation of the variation of γ_s^d with the coverage ratio, the plots overlay completely, testifying to the formation of a thick PMMA film.

4.3.2. Variation of the t_β temperature transition with the coverage ratio

In the same way as for the t_g temperature evolution, we have also studied the variation of $-\Delta G_a^\circ/T$ with the reciprocal temperature, in a temperature around 60 °C in order to evidence the influence of the coverage ratio on the β temperature transition. This evolution is displayed in Fig. 6.

We observe again that β transition can be detected down to a coverage ratio as low as 1 MU/nm² corresponding to isolated macromolecules scattered on the silica surface and that t_β is also independent of the impregnation ratio and the same as for the bulky polymer: 60 °C [16]. As previously, the intensity of the β transition decreases with decreasing impregnation ratios.

From the slope of the linear parts of the previous plots, versus the reciprocal temperature, we have access to the enthalpies of adsorption

- at temperatures lower than the β temperature ($-\Delta H1$),

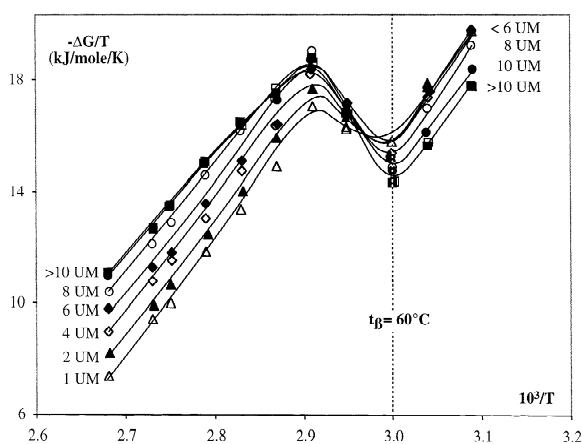


Fig. 6. Variation of the adsorption enthalpy of *n*-octane, with the MU coverage ratios, for PMMA impregnated HDK-S13 silica samples, impregnated at different MU coverage, around the t_β transition temperature.

- in the temperature range between the two transition temperatures ($-\Delta H2$)
- over the t_g temperature ($-\Delta H3$).

4.4. Variation of enthalpies of adsorption above and below the t_g and t_β temperature transitions

The values of the adsorption enthalpies on *n*-octane on impregnated fumed silica were computed by least square linearisation for the three temperature domains previously defined. Their evolutions with the impregnation ratio are displayed in Fig. 7.

Concerning adsorption enthalpies, the impregnated silicas behave differently depending on the considered domain of temperature.

Over the t_g temperature, an important jump of the surface property is observed between the unmodified silica and the first coverage ratio corresponding to 1 MU/nm². Then, the enthalpy decreases more slowly until a coverage ratio of 10 MU/nm² is reached, above this last value, the enthalpy remains quite constant. This critical value is 2 MU/nm² lower than the one observed when looking at the variation of γ_s^d with the coverage ratio, testifying that the influence of the surface on the MU mobility occurs before the formation of a thick film.

Between the t_g temperature and the β temperature, the enthalpies of adsorption follow exactly the same

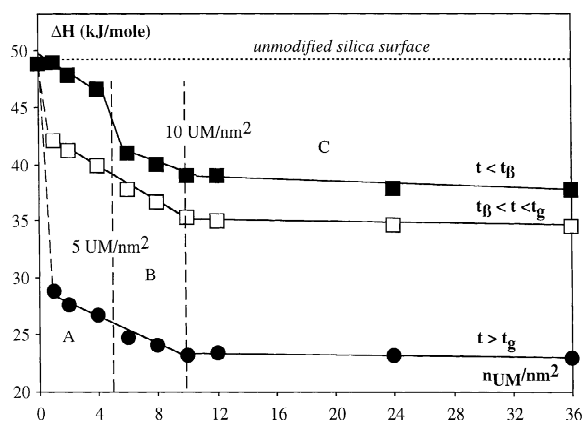


Fig. 7. Variation of the adsorption enthalpy ΔH of *n*-octane, with the MU coverage ratios, for PMMA impregnated HDK-S13 silica samples, impregnated at different MU coverage, from below the t_β temperature to above the t_g temperature.

trend, only the initial decrease is less intensive than previously.

Finally, having a look to the evolution of the enthalpies of adsorption at temperature lower than the β transition temperature, one observes a new jump that occurs between 4 and 5 MU/nm^2 . It could be attributed to the transition between a silica surface covered with isolated scattered macromolecules and with macromolecules in close contact, forming a continuous film. This transition was previously observed when looking at the variation of γ_s^d with the coverage ratio.

5. Conclusion

In conclusion, coupling IGC measurements and modification through controlled coverage of silica by a polymer appears to be a powerful way to get information on the polymer–solid interface.

This new approach permits

(i) estimation of the number of monomer units

(MU) necessary to cover the whole surface of the silica;

(ii) detection of the glassy transition temperature (t_g) and that of the β transition down to a very low coverage ratio equal to only 1 MU/nm^2 ;

(iii) evidence of three modes of adsorption of the macromolecules, depending on the coverage ratio. The first mode observed for a coverage ratio lower than 4 MU/nm^2 , which corresponds to some isolated macromolecules scattered on the silica surface, the second, for a coverage ratio between 4 and 12 MU/nm^2 , corresponding to the formation of a monolayer made of close-packed macromolecules. Finally the third one is evidenced where obviously there is the formation of a thick PMMA film.

These three different modes of adsorption of the PMMA macromolecules are schematised in Fig. 8.

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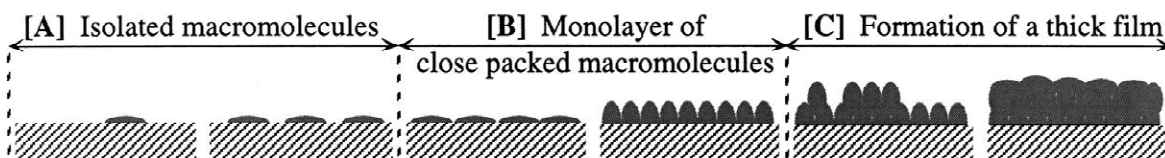


Fig. 8. Schematic representation of the three modes of adsorption of PMMA macromolecules depending on the impregnation ratio.

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