

Interfacial conformation energies of stereoregular poly(methyl methacrylate) by infra-red reflection absorption spectroscopy

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Infra-red reflection absorption spectroscopy (i.r.a.s.) has been performed on isotactic (i-) syndiotactic (s-) and atactic (a-) poly(methyl methacrylate) (PMMA) which have been spin-cast on aluminum mirrors. This spectroscopic investigation of the interface has highlighted differences in chain conformation for the stereoisomers at the surface. Indeed, the fraction of carbonyl bonded to the aluminum surface is higher for i-PMMA than for a- and s-PMMA. Furthermore, spectral subtraction combined to the van't Hoff relation, already used by O'Reilly and coworkers^{1,2} for bulk samples, has provided experimental values of the interfacial conformational energy ΔE . These values, calculated from the absorption peaks in the infra-red range 1300–1100 cm^{-1} , are for the highest ones 7.8 kcal mol^{-1} for s-, 5.0 kcal mol^{-1} for a- and 2.1 kcal mol^{-1} for the i-PMMA layer on the aluminum surface. The results show a large increase of the conformational energy of the adsorbed sample as compared to the bulk. Furthermore, the glass transition, which can be deduced from the infra-red spectral subtraction, exhibit a large increase in the case of i-PMMA, while it remains constant for a- and s-PMMA. These results are interpreted in terms of interfacial *gauche* to *trans* conformational changes and restrictions in molecular motions due to strong specific interactions of PMMA on aluminum. © 1997 Elsevier Science Ltd

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INTRODUCTION

The conformation of adsorbed polymer chains has extensively been studied for the last decades. Thus, spectroscopic techniques such as infra-red spectroscopy³, nuclear magnetic resonance (n.m.r.)⁴ and ellipsometry⁵ have been widely used to characterize the structure of an adsorbed layer. Indeed, the adsorbed amount (A), the surface coverage (θ) and the fraction of surface bonded groups (p) can provide information of chain conformation at an interface⁶. Low surface coverage associated with a high fraction of surface bonded groups leads to the assumption of a relatively flat conformation of the adsorbed polymer chains. Moreover, recent studies have pointed out conformational changes, involving chain backbone, which occurs for PMMA at the aluminum surface⁷. The assumed driving force for these local conformational changes is ionic bonds due to the hydrolysis of the ester groups at the aluminum surface^{8,9}. These strong bonds are reinforced by acid–base interactions involving the carbonyl and the aluminum surface hydroxyls¹⁰. However, no experimental values of conformational energy (ΔE), which might be directly affected by the chain rearrangements, have never been reported in the literature, for adsorbed polymers.

Thermal behaviour of thin polymer films has been

investigated by ellipsometry¹¹ and X-ray reflectometry¹² on polymers such as PMMA or P(2)VP spin-cast on SiO_2 wafers. The glass transition temperature (T_g) is found to increase with decreasing film thickness in the case of favourable polymer/substrate interactions. Moreover, experiments carried out by neutron reflectivity^{13,14} showed an increasing density gradient towards the surface. These results can be ascribed to a reduced chain mobility in the interfacial region of length scale 20 nm.

Isotactic and syndiotactic stereoregular PMMA, but also conventional atactic PMMA, have shown varying physical properties such as T_g ¹⁵, chain segment motion (T_1)¹⁶ or chain dimensions in solution ($\langle R_0^2 \rangle$)¹⁷. Since these polymers have the same chemical structure, the differences in physical properties may be analysed in terms of conformation and molecular motion¹⁸. Thus, PMMA's conformational energies ($\Delta E = E_{\text{tg}} - E_{\text{tt}}$), which have been determined with good agreement by Fourier-transform infra-red (FTi.r.) measurements and rotational isomerism state (RIS) calculations¹⁹, increase from i-PMMA to s-PMMA. These higher ΔE values are due to the higher calculated probability of *trans* conformation for syndiotactic PMMA chain as compared to the other isomers²⁰. Moreover, conformational energies of the backbone (ΔE_{bb}) and the side-chain (ΔE_{sc}) can be distinguished from those measurements. Thus, while ΔE_{bb} and ΔE_{sc} are quite different for the a- and the s-PMMA, i-PMMA is suggested to have very

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close values of the conformational energies of the two parts of the chain segment. These local conformational differences, between stereoisomers, coupled to differences in local motion, influence strongly the properties of the global chain such as characteristic ratio (C_∞). Thus, this characteristic ratio, obtained from RIS calculations²⁰, is markedly higher for the i-PMMA than for s-PMMA.

The interfacial behaviour of stereoregular PMMA has already been studied for Langmuir–Blodgett layers at the water/air interface^{21–23}. Thus, pressure–area isotherms and FTi.r. spectroscopy suggest that the i-PMMA is more extended at the interface than the syndiotactic isomer. Although, these studies clearly show the influence of tacticity on the chain interfacial conformation, this parameter has not received much attention in the literature in the field of adsorption or adhesion.

Previous works^{24,25} have already highlighted, using FTi.r. and ellipsometry, a more flattened conformation of i-PMMA chains spin-cast on aluminum surfaces. This work will now focus on the calculation of PMMA interfacial conformational energy using i.r.a.s. These results will be discussed in terms of conformational changes and restriction in chain motion at the interface.

EXPERIMENTAL

Materials

The PMMAs used in the present study are listed in Table 1. Stereoregular atactic samples were purchased from Polymer Source Inc. The tacticity of each sample was determined by ¹H n.m.r. spectroscopy in 10% CDCl₃ solutions, at 400 K, using a Varian XL-200 instrument. Molecular weights were determined by size exclusion chromatography (s.e.c.) using a Waters chromatograph calibrated with PMMA standards. Moreover, intrinsic viscosities $[\eta]$ were measured with a Ubbelohde viscometer. Finally, a Mettler DSC-30 apparatus was used for bulk T_g measurements.

Surface preparation

Aluminium plates (0.7% Mg, 0.5% Mn, 4.1% Cu, 94.7% Al) were polished with Rotus paper in the increasing order of granulometry (500, 800, 1200). The last polishing step is performed using diamond paste (9 and 3 μ m). Cleaning is obtained in a dichloromethane ultrasonic bath. No acid rehydroxylation treatment was performed on the surface in order to protect the optical mirror of the surface. On the one hand, the obtained aluminium surfaces, were used in this state and on the other hand, the surfaces were gold plated under vacuum for other experiments. This gold surface treatment provides a surface with no specific interaction sites.

Table 1 Characteristics of the PMMA used in that study

PMMA	Tacticity (%) i/h/s	\bar{M}_n (10^{-3} g mol ⁻¹)	I	T_g (°C)	$[\eta]$ 1 mg ⁻¹
i-PMMA	97/03/0	37	1.21	60.6	35.7
a-PMMA	7/39/54	28.5	1.09	104	–
s-PMMA	0/20/80	33	1.05	130.8	21

Spin-coating

PMMAs were dissolved in CHCl₃ at two different concentrations, 5 and 10 g l⁻¹. These solutions were then spin-cast on the aluminum plates with a rotating speed of 2000 rpm and an acceleration of 5000 rpm s⁻¹. The layer was dried at room temperature under vacuum, for at least 2 h.

Ellipsometry

Thickness measurements were carried out at room temperature with a rotating spectroscopic ellipsometer (ES4M Sopra) operating in a wavelength range of 800–350 nm with an incidence angle of 75°. Ellipsometric angles (Ψ , the amplitude attenuation and Δ , the phase difference between the s and p waves) are defined by the equation:

$$R_p/R_s = \tan(\Psi) \exp(i\Delta) \quad (1)$$

where R_p and R_s are the reflection coefficients respectively parallel and perpendicular to the surface plane. These reflection coefficients are related to the film thickness and to the refractive index. Uncovered aluminum surface was taken as a reference and a one layer model was used for thickness calculations (Cauchy law). The PMMA bulk refractive indexes were used for thickness determination. These refractive indexes were determined with a Abbe refractometer on polymer thick films prepared by spin-coating. The refractive index are 1.502 for i-PMMA, 1.499 for a-PMMA and 1.497 for s-PMMA.

Infra-red reflection absorption spectroscopy

The FTi.r. spectrometer was a Bruker IFS-66 equipped with a mercury–cadmium–telluride (MCT) detector. One hundred scans were recorded for good signal to noise ratio. Experiments were performed with a Specac specular reflectance element used in polarized reflection–absorption model. (Polarization is parallel to the incident wave plane.) The incidence angle is fixed at 82° for the best signal recording. At this high angle of incidence, the electric field vector normal to the surface is strengthened and magnifies the adsorption of oscillator oriented towards the surface. The reflectance infra-red element was equipped with a heating cell working in the temperature range 25–160°C. The temperature was monitored directly inside the aluminium plate with a thermocouple inserted as close as possible to the surface. Temperature was controlled to $T \pm 5^\circ\text{C}$. Curve-fitting and spectral subtraction have been performed using Peaksolve²⁶ software. A mixture of Gaussian and Lorentzian band shape has been used to fit the carbonyl absorption band. Free carbonyl frequency has been fixed, during the iterations, at 1740 cm⁻¹ which is the location of the carbonyl stretching vibration resulting from reflectance measurements on gold plated substrates.

RESULTS

PMMA layers, after spin-coating on aluminium mirrors, have been thoroughly characterized. Therefore, the layer thickness has been investigated by spectroscopic ellipsometry in the visible spectral range. This technique has provided values which do not depend on tacticity for

the two concentrations of the solutions which were used. Nevertheless, it has been shown elsewhere²⁵ that for concentrations below 5 g l^{-1} , the thickness of the layer becomes dependent upon the PMMA tacticity. This tacticity dependence of ultrathin PMMA layer (where thickness is less than the gyration radius) will rather complicate our analysis of the i.r.a.s. spectra because of a poor signal to noise ratio. Therefore, 5 g l^{-1} will be the lowest concentration used. The thickness of the PMMA layers, derived from the fit on the Ψ and Δ coefficients, are $150 \pm 20 \text{ \AA}$ for the 5 g l^{-1} spin cast PMMA solutions and $550 \pm 10 \text{ \AA}$ for the 10 g l^{-1} PMMA solutions. These thicknesses, widely higher than the 50 \AA chain gyration radius calculated in θ solvent¹⁷, show that the layer is multimolecular and that chains, which are not directly adsorbed, may remain on the surface after the spin-coating deposition process. This result will be helpful in the further discussions made on the basis of the i.r.a.s. results.

Furthermore, in order to characterize the chain conformation at the interface, the fraction of segments bound to the surface was calculated from infra-red spectra. While spectrometric techniques such as X-ray photoelectron spectroscopy (X.p.s.)⁸ and inelastic electron tunnelling spectroscopy (IETS)⁹ have provided the experimental evidence of the PMMA ester group cleavage on the aluminium surface, no such information can be obtained from the i.r.a.s. spectra, as previously mentioned in the literature⁷. On the one hand, this can be explained both by a rather poor hydroxylation state of the aluminium surface, which is used just after cleaning in dichloromethane. On the other hand, the spin-coating deposition process may not allow chemical reaction to proceed further since the contact time of the solution on the aluminium plate is

only a few seconds before drying. These two reasons may lead to only a few ionic bonds but on the contrary to numerous acid-base interactions. These interactions which occur between the carbonyl and the surface hydroxyl groups are known to shift, towards lower frequencies, the adsorption band of the carbonyl²⁷. Thus, infra-red reflectance studies of a solvent cast thin PMMA film on gold substrate has shown that the carbonyl peak is located at 1740 cm^{-1} . This frequency is considered as a reference for the free carbonyl since no specific interactions are expected for PMMA on gold. Otherwise on aluminium, as shown in *Figure 1*, a part of the carbonyl peak, due to acid-base interactions, is shifted towards lower frequency (1730 cm^{-1}). Curve-fitting analysis allows the calculation of the fraction of carbonyl groups, involved in acid-base interactions, $f_{\text{C=O}}^{\text{ab}}$ by the equation:

$$f_{\text{C=O}}^{\text{ab}} = \frac{A_{\text{C=O}}^{\text{ab}}}{A_{\text{C=O}}^{\text{ab}} + \frac{\epsilon_{\text{C=O}}^{\text{ab}}}{\epsilon_{\text{C=O}}^{\text{f}}} A_{\text{C=O}}^{\text{f}}} \quad (2)$$

where $A_{\text{C=O}}^{\text{ab}}$ and $A_{\text{C=O}}^{\text{f}}$ the peak fitted integrated intensity of the 1730 cm^{-1} peak and of 1740 cm^{-1} peak, respectively. The ratio of the molar absorption coefficients has not been found in the literature for the PMMA/aluminium system. The fraction of acid-base bonded carbonyls, reported in *Figure 2*, have been calculated using a ratio equal, to a first approximation²⁸, to unity. However, it is likely for these values, ranging from 0.37 to 0.63 to be overvalued because of a molar absorption coefficient in fact higher than unity²⁹. The surface-bonded carbonyl fraction is found to decrease from isotactic to syndiotactic PMMA. Moreover, this tendency is enhanced for the

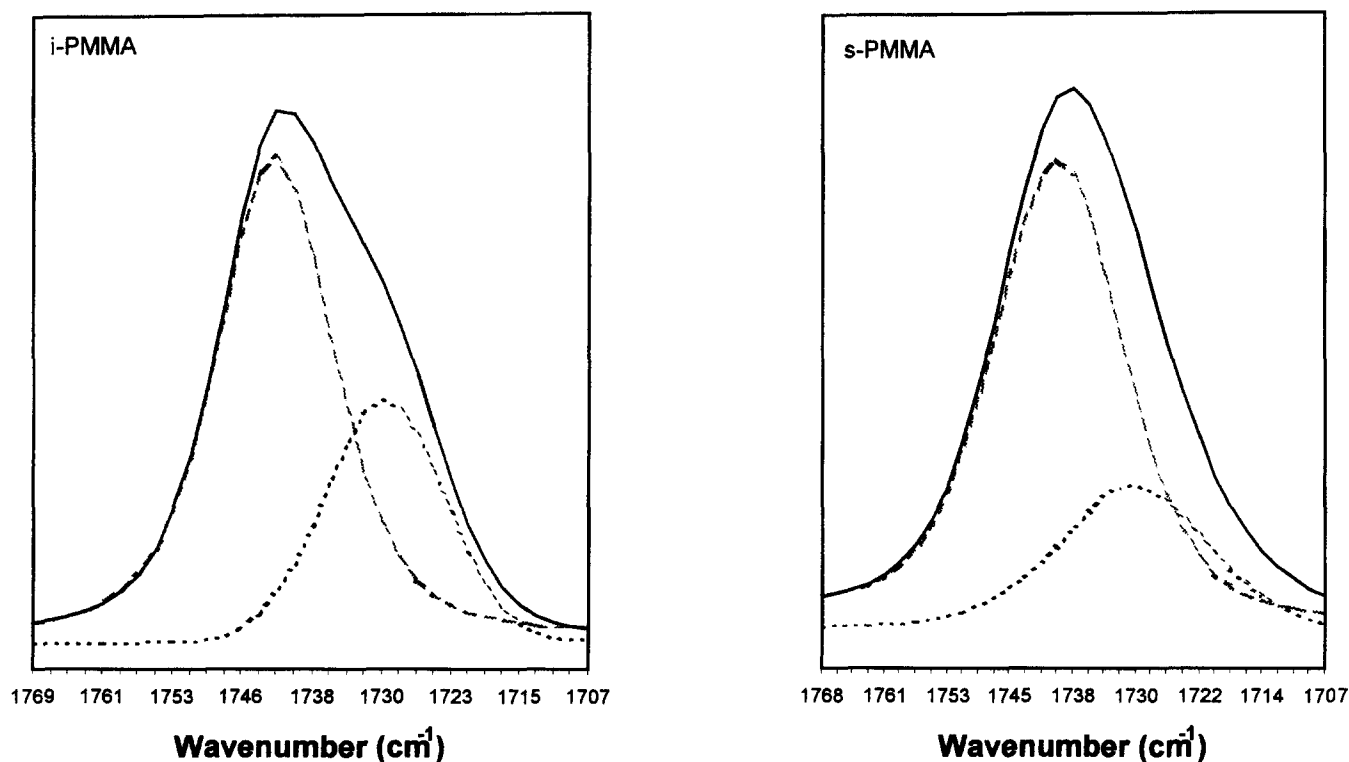


Figure 1 Curve-fitted infra-red carbonyl area of i- and s-PMMA spin-cast on aluminium mirrors. The i.r.a.s. spectra were recorded at 25°C on a layer with a thickness of 150 \AA . The solid curve represents the overall carbonyl peak, the dotted line represents the bonded carbonyl area and the dashed curve represents the free carbonyl area

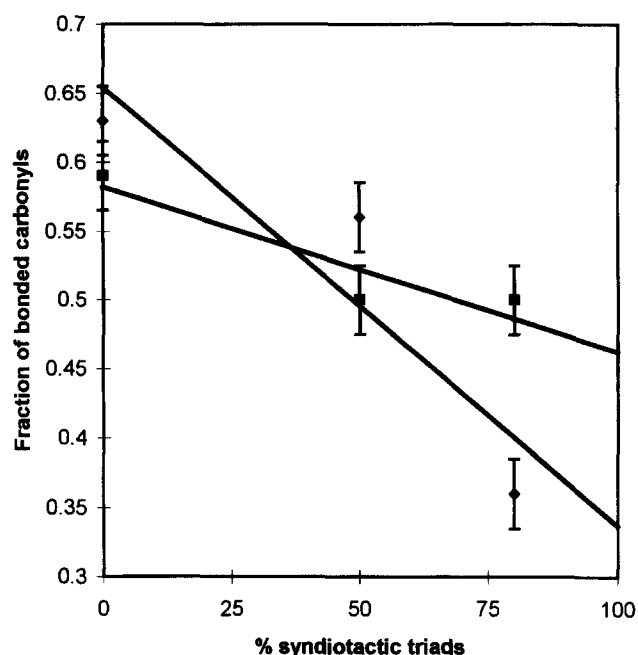


Figure 2 Evolution of the fraction of bonded carbonyls (on aluminium surface) with the percentage of syndiotactic triads

lowest layer thickness because of a more direct investigation of the chains bonded to the surface. The signal provided by these interfacial polymer chains is probably partially screened by the non-adsorbed chains for the 550 Å layer thickness. The dependence between tacticity and bond carbonyl fraction tends to prove that the surface configuration of the adsorbed layer depends strongly on the PMMA stereoregularity. Thus, isotactic PMMA chains are supposed to lay in a more flattened configuration on the aluminium surface, than the syndiotactic isomer. It is likely for this phenomenon to result from a high ability of *i*-PMMA to favour interfacial acid-base interactions by local conformational changes. This ability of conformational changes has been pointed out, using RIS calculations, by Vacatello and Flory²⁰ and Sundararajan¹⁹. Thus, the driving force for these interfacial conformational changes, whatever the tacticity, is the strong interactions with the surface. However, as the chemical structure of the tactic PMMA is identical, the differences in the structure of the adsorbed layer may originate in differences in the dynamic or the thermodynamic of the conformational rearrangements. Moreover, besides the assumption taking into account the local conformation, the overall chain conformation can also be counted on. Thus, chain dimensions in the chloroform solvent, deduced from the intrinsic viscosity, given in Table 1, are higher for the *i*-PMMA than for the syndiotactic isomer. Isotactic chains, assumed to be highly extended in solution, may present towards the aluminium surface more ester groups than the *s*-PMMA chains. These syndiotactic chains, relatively coiled, may bond only a few groups before they collapse on the surface. The thermodynamic of the conformational changes will be studied by i.r.a.s. through the conformational energies of the bulk and the adsorbed PMMA, while the glass transition will provide information on the dynamics of the adsorbed PMMA chains.

Several workers have analysed the infra-red spectra of

stereoregular PMMA and made band assignments which are available in the literature^{30,31}. Although no ambiguity remains on the assignment of much of the high intensity peaks, the attribution of the 1300–1100 cm⁻¹ range is still not cleared up. However, it is commonly agreed that the $\nu_a(\text{C-O-C})$ is responsible, at least partly, for the multiple absorption peaks in the spectral region³⁰. Otherwise, it is well known that this infra-red range is sensitive to PMMA chain conformation³². Thus, many of the shifts in frequency or changes in peak intensity, in the 1300–1100 cm⁻¹ region, can be ascribed to conformational changes. Besides, this range has been the most suitable infra-red region, used by O'Reilly and Mosher¹, for their calculations of the conformational energies ΔE of stereoregular PMMA. Thus, our analysis of the infra-red spectra, described hereafter and based on spectral subtraction, will focus on the 1300–1100 cm⁻¹ infra-red region. The i.r.a.s. spectra, recorded at 25°C are shown on Figure 3 for the three tactic PMMA. The four peaks, of high intensity, are pointed as ν_1 , ν_2 , ν_3 and ν_4 . The spectrum, recorded at room temperature, will be named *term spectrum*, and used in the following relation:

$$\begin{aligned} \text{Result spectrum} &= \text{sample spectrum} \\ &- k \times (\text{term spectrum}) \end{aligned} \quad (3)$$

where *sample spectrum* is a spectrum recorded at a temperature above 25°C, and *k* is a constant, equal to unity for our calculations. The *result spectra* are the difference spectra obtained at different temperatures as shown on Figure 4. The peaks obtained from that method are both increasing and decreasing bands and their heights will be named $A_+(\nu)$ and $A_-(\nu)$ respectively. These peaks are gathered in four doublets pointed as d_1 , d_2 , d_3 and d_4 . However, in contrast to the bulk, where each doublet allows the calculation of a conformational energy, d_1 and d_3 (sometimes d_4 for *s*-PMMA) are the only workable doublets on i.r.a.s. spectra. Thus, the van't Hoff energy ΔE , henceforward named conformational energy, can be calculated from these peaks

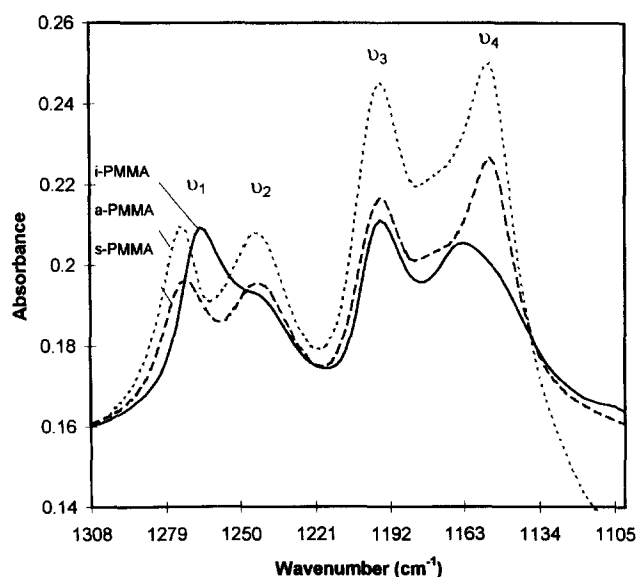


Figure 3 I.r.a.s. spectra of *i*- (solid curve), *a*- (dotted curve), and *s*-PMMA (dashed curve) spin-cast on aluminium mirrors with a thickness of 550 Å. These spectra are recorded at 25°C and named *term spectra* for the spectra subtraction

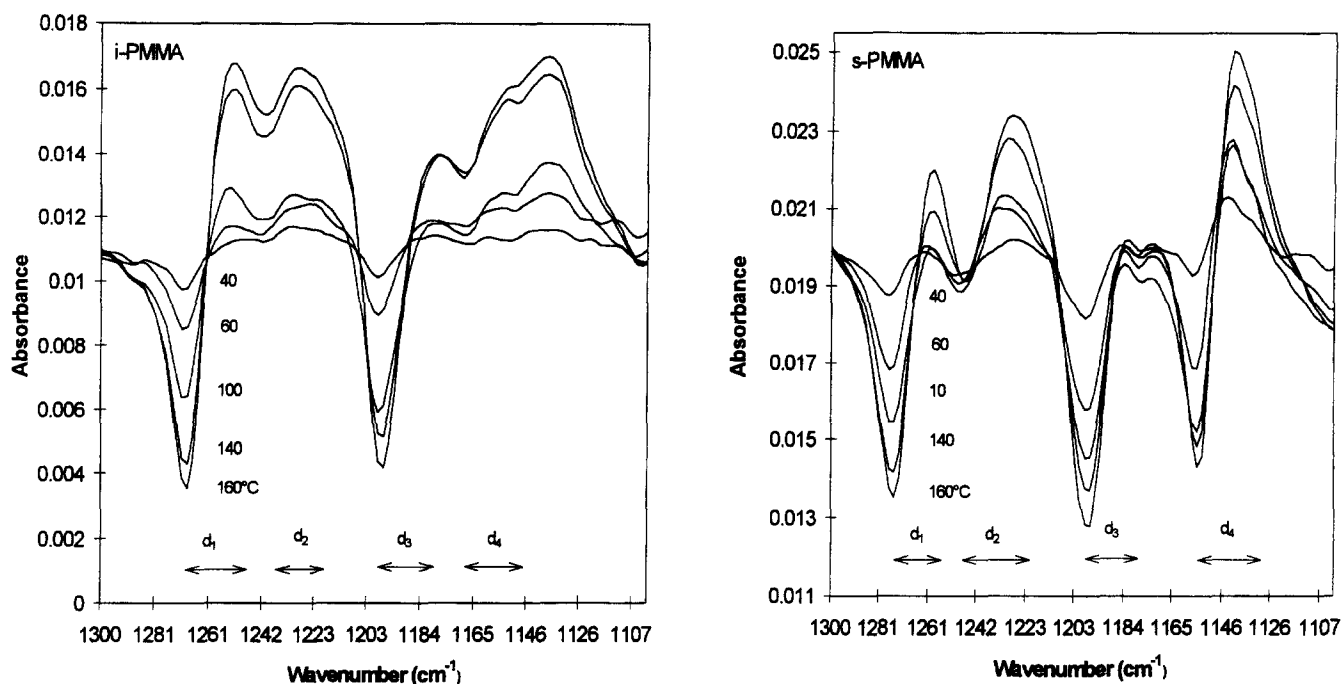


Figure 4 Difference spectra, with a term spectra at 25°C, of i- and s-PMMA spin-cast on aluminium. The thickness of the layer is 150 Å. d_1 , d_2 , d_3 and d_4 , represent the doublets resulting from spectra subtraction

intensity through the relations:

$$\Delta E = -R\delta[\ln\{A_+(\nu)/A_-(\nu)\}]/\delta(1/T) \quad (4)$$

$$= -R\delta \ln K/\delta(1/T) \quad (5)$$

where R is the ideal gas constant, T the temperature, and K the equilibrium constant defined by:

$$K = [A_+(\nu)/\alpha_+]/[A_-(\nu)/\alpha_-] \quad (6)$$

where a_+ and α_- are the extinction coefficients of the increasing or decreasing band under study. The ratio of the extinction coefficients is found to be independent of the temperature as confirmed by other workers^{1,2}. This can be checked by plotting A_- vs A_+ for the different temperature. The linear curve, which is obtained, shows that the ratio of the extinction coefficients is independent of the temperature, that means that those coefficients do not depend on temperature or have the same temperature dependence. Thus, these coefficients will not have any contribution in the calculations. Otherwise, as many of the bands, in the spectral region of interest, are sensitive to the glass transition, the slope of the curve $\ln(A_{\pm}) = f(1/T)$ changes at this temperature as previously mentioned by O'Reilly *et al.* Thus, *Figure 5* shows that the glass transition can easily be detected from these curves whatever the PMMA tacticity. Furthermore, while the glass transition of the s- and a-PMMA seems to remain unchanged as compared to the bulk, at 130 and 105°C, respectively, the i-PMMA exhibit a glass transition increase of about 30°C, from the bulk (60, 6°C) to the absorbed state (90°C). This T_g increase, already observed by other workers^{11,12}, will be discussed further in terms of restriction in molecular mobility. Otherwise, the conformational energies are calculated by linear regression analysis and the regression coefficients are found between 0.89 and 0.97. These coefficients are worse than the 0.97–0.99 obtained from transmission spectra of bulk polymers. This is probably due, in reflectance studies, to differences in the surface reflectivity

with the temperature but also to the control of the temperature at the surface. Moreover, reflectance spectra, which exhibit a lower signal-to-noise ratio than transmission spectra, can generate these relatively low regression coefficients.

The conformational energies are different above and below T_g . Thus, the values above T_g , reported in *Table 2*, are ranging from 1.5 to 7.8 kcal mol⁻¹ while the conformational energies below T_g , listed in *Table 3*, are ranging from 1.1 to 3.0 kcal mol⁻¹ for the spin-cast layers. These last values are calculated from the d_1 doublet, since less accurate results are obtained from the other doublets. Above T_g , the d_1 and d_3 doublets provide the more reproducible values. Since backbone motions are presumed to be frozen in at temperature below T_g , the conformational energies calculated at those temperatures, may only refer to changes in side-chain conformations. Above T_g , as the side-chain and the backbone motions are allowed, the calculated energies may represents ΔE_{bb} but also ΔE_{sc} . The fact that conformational energies, below T_g , only involve side-chain conformational changes, may explain the high ΔE , obtained above T_g where both backbone and side-chain conformational changes may occur. It can be observed from *Table 2* that the ΔE values, corresponding to the spin-cast layers, are always higher than those of the bulk samples as calculated by O'Reilly *et al.* and confirmed by our measurements. The differences, observed between the values of O'Reilly and our values, obtained both from classical transmission experiments, can be ascribed to differences in tacticity and molecular weight of the polymers under study. Whatever the bulk values chosen as references, these results show a large increase in the conformational energy at a surface. This is, to our knowledge, the first, really quantifiable experimental evidence of conformational changes in PMMA chains at the interface. Moreover, when comparing the values in *Tables 2* and *3*, the increase in conformational energy is higher for the temperature above T_g than below T_g .

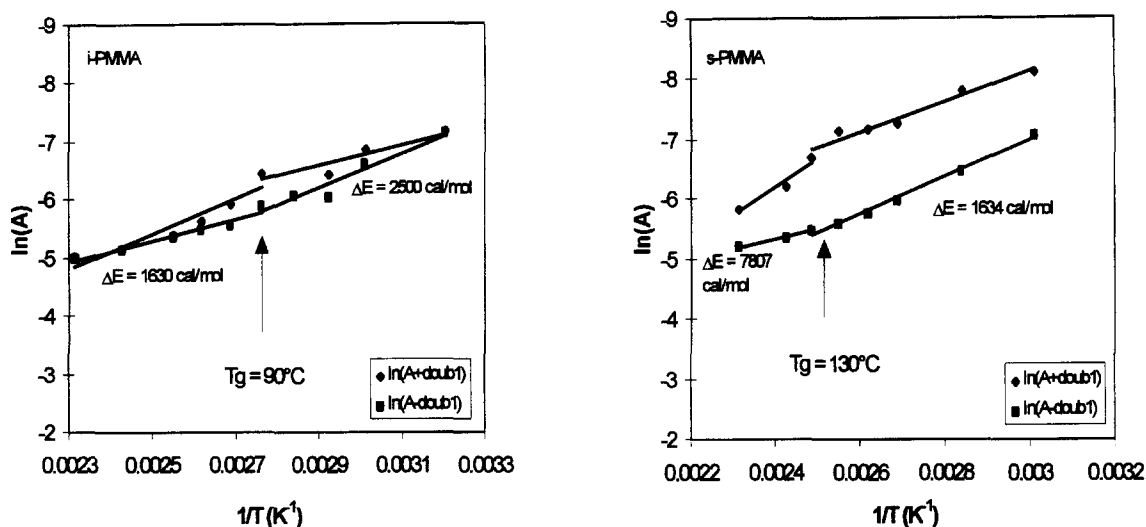


Figure 5 Van't Hoff plot of the logarithm of the absorbance as a function of the reciprocal temperature for the d_1 doublet. The glass temperature is defined by the intersection between the two straight lines plotted from the experimental points. The thickness of the layers studied here is 150 Å

Table 2 Conformational energies, of bulk and spin-cast PMMA layers on aluminium, calculated from infra-red spectra at $T > T_g$. The above values are calculated from the d_1 doublet and the values, given below, from the d_3 or d_4 doublet. The values given between brackets are those calculated by O'Reilly and Mosher¹

		ΔE of bulk PMMA (kcal mol ⁻¹)	ΔE of PMMA layers (550 Å), (kcal mol ⁻¹)	ΔE of PMMA layers (150 Å), (kcal mol ⁻¹)
i-PMMA	d_1	1.14 ± 0.06 (0.75 ± 0.02)	1.5 ± 0.1	1.6 ± 0.1
	d_3	(0.35)	1.8 ± 0.2	2.1 ± 0.2
a-PMMA	d_1	1.99 ± 0.05 (1.42 ± 0.01)	5.0 ± 0.4	4.6 ± 0.4
	d_3	(0.84 ± 0.4)	2.0 ± 0.2	2.2 ± 0.2
s-PMMA	d_1	3.20 ± 0.2 (2.00 ± 0.2)	4.3 ± 0.4	7.8 ± 0.6
	d_3	(1.26 ± 0.1)	2.5 ± 0.3	7.8 ± 0.5

Table 3 Conformational energies, of bulk and spin-cast PMMA layers on aluminium, calculated from infra-red spectra at $T < T_g$. The values are calculated from the d_1 doublet. The values given between brackets are those calculated by O'Reilly and Mosher¹. The value pointed with an asterisk is a presumed value

		ΔE of bulk PMMA (kcal mol ⁻¹)	ΔE of PMMA layers (550 Å), (kcal mol ⁻¹)	ΔE of PMMA layers (150 Å), (kcal mol ⁻¹)
i-PMMA		< 0.70*	1.1 ± 0.2	2.5 ± 0.3
a-PMMA		1.45 ± 0.16 (0.80 ± 0.05)	1.5 ± 0.3	3.0 ± 0.4
s-PMMA		1.52 ± 0.23 (0.950 ± 0.12)	1.4 ± 0.2	1.6 ± 0.2

Backbone conformational changes seem then to be, at least energetically, predominant in the interfacial chain rearrangement. Indeed, stating that *gauche* to *trans* conformational change is the only parameter responsible for an increase in conformational energy implies that the adsorption of PMMA on aluminium may lead to a large increase in interfacial *trans* states.

The ratio of *gauche* to *trans* states is related to the conformational energy as shown in the following relation:

$$n_g/n_t = 2 \exp(-\Delta E/RT) \quad (7)$$

where n_g and n_t are respectively the population of *gauche* and *trans* states and R the ideal gas constant. Performing these calculations, on bulk polymers above T_g , has pointed out that the ratio of *gauche* to *trans* states is strangely higher for the i-PMMA (0.28) than for the s-PMMA (0.067). This tendency, resulting from R.I.S.

calculations, has already been mentioned by Flory *et al.*²⁰. Otherwise, calculations performed on the PMMA layers exhibit a large decrease of the *gauche* to *trans* ratio, for s-PMMA (3.6×10^{-4}) and for i-PMMA (0.13), as compared to the bulk values. The interfacial loss in the population of *gauche* state is larger for i-PMMA, than for a- and s-PMMA, however, the population of *gauche* states remains sizable for the isomer on the aluminium surface. In contrast, the population of *gauche* states for s-PMMA at the interface becomes quite insignificant.

Is this increase in conformational energy (or increase in *trans* states) preferentially due to the strong interactions between PMMA and aluminium or can it be ascribed to a reduction in chain entropy (simple confinement effect) at the interface? The answer can be, at least partially, obtained by performing the spectroscopic investigations on PMMA spin-cast on gold plated substrates. Indeed, no specific interactions are expected

between the gold surface and the PMMA. The conformational energies, at $T > T_g$, focus on the d_1 doublet, are reported on Table 4. It can be observed, from that table, a slight increase of the conformational energies, on the gold plated surface, as compared to the bulk values. Furthermore, this increase is lower than that observed on aluminium. Hence, it can be deduced from these values that the screening of the aluminium superficial functional groups, provided by the gold layer, lowers the increase in interfacial conformational energy. The slight increase of ΔE , on gold as compared to the bulk, can then be ascribed by reduced chain entropy of the layer that is likely to favour some conformational changes. In other words, the interactions created by the PMMA with the surface of the major factor in the large increase of the ΔE at the interface.

The high level of interaction of i-PMMA with the surface, determined from the carbonyl shifted area, argues for a flattened conformation of the isotactic chains at the aluminium surface. Moreover, the spectral subtraction has provided an accurate method to forecast the glass transition of PMMA, as shown in Figure 5. The 30°C increase in the glass transition of i-PMMA, on the aluminium as compared to the bulk, can also support the assumption of the spreading out of isotactic chain on the surface, maximizing their contact area with the surface. This spreading out allows the establishment of numerous interaction of the ester groups, along the chain, with the surface, which may highly restrict the chain backbone motions. Moreover, the T_g , measured on the i-PMMA layer spin-cast on gold, remains constant, at 60°C, as compared to the bulk. On aluminium as well as on gold, s- and a-PMMA keep a constant T_g at 130 and 105°C, respectively. Similar thermal behaviour has already been observed for a-PMMA thin layers¹¹. Glass transition increases of about 6° on SiO₂, while a slight decrease has been found on gold plated silicon wafers. Moreover, Poly(2-vinylpyridine) on SiO₂ exhibit a larger T_g increase of 20–50°C¹². The restriction of chain mobility of macromolecules in the interphase may originate in the interactions of the polymer with the substrate. Thus, strong PMMA/aluminium interactions may be responsible for the T_g increase of i-PMMA thin layer. The fact that the other tactic PMMAs do not show any changes can be due to the sensitivity of the technique we used, which can probably not detect variations of T_g lower than 10°C. 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. Thus, the level of side-chain acid-base interactions with the substrate, depending on PMMA tacticity, may have a significant contribution to the increase of T_g .

The calculated conformational energy of i-PMMA, lower than that of the other isomers, runs somewhat

Table 4 Conformational energies, of bulk and spin-cast PMMA layers on gold plated aluminium, calculated from infra-red spectra at $T > T_g$. The values are all calculated from the d_1 doublet. The values given between brackets are those calculated by O'Reilly and Mosher¹

	ΔE of bulk PMMA (kcal mol ⁻¹)	ΔE of PMMA layers (150 Å), (kcal mol ⁻¹)
i-PMMA	1.14 ± 0.03 (0.72 ± 0.02)	1.4 ± 0.2
a-PMMA	1.99 ± 0.05 (1.42 ± 0.01)	2.6 ± 0.4
s-PMMA	3.20 ± 0.21 (0.20 ± 0.22)	3.6 ± 0.5

counter to the assumption made above. Indeed, a flattened conformation of polymer chain at a surface will inevitably result from *gauche* to *trans* conformational changes, which should then increase the conformational energy. Thus, a crucial question remains: why are the conformational energies of the adsorbed i-PMMA lower than those of a- and s-PMMA, since the isotactic chains are assumed to be more flattened at the surface? No direct answer can be provided for now. However, two assumptions can be made on the basis of our results. The first assumption should be supported by Figure 6, which shows a schematic description of the adsorbed state of i- and s-PMMA chains. Thus, the spin-cast layer can be roughly divided into two regions. On the one hand, an area close to the aluminium surface, where the i.r.a.s. polarized beam reflects, which provides a high part of the recorded infra-red signal. This region is known to be a zone of highly restricted mobility¹¹. This region is on the order of the macromolecule size, which means 100 Å. On the other hand, the rest of the layer. The interfacial zone, where chain motion is partially hindered, is likely to hinder conformational changes from a stable *trans* state (stabilized by the interactions with the surface) to a *gauche* state. Thus, this may provide no measurable signal to the infra-red spectra, and hence no information to the conformational energy. No experimental evidence of this restricted conformational change has been found in the literature. However, the assumption of a region of restricted mobility combined with the increasing density gradient, towards the surface, in PMMA thin layers^{13,14} can support our talk. Therefore, we can reasonably assess that no real conformational changes may occur in a dense region of restricted mobility. Nevertheless, motions, which do probably not lead to stable conformational states, are still allowed for the adsorbed chains since T_g is still measurable for each layer of PMMA isomer.

Otherwise, the rest of the layer, distant from the interface, is assumed to be nearly isotropic for the i-PMMA since no long loops or tails are supplied by the adsorbed chains. On the contrary, for s-PMMA, only loops or tails which are propagating in the layer may generate some anisotropy. Thus, chain aggregation which is known to occur in s-PMMA¹⁸ can perhaps be responsible for the quasi-non-remaining *gauche* conformational states at the aluminium surface. The second assumption will take into account the conformational entropic consideration. Indeed, relation (6) can be rewritten as follows:

$$n_g/n_t = 2 \exp(-\Delta H/RT_e + \Delta S/R) \quad (8)$$

where ΔH is the conformational enthalpy, ΔS the conformational entropy and T_e the equilibrium temperature. Thus, the conformational entropic parameter ΔS is assumed to be constant with temperature for bulk polymers which simplify greatly the calculations. However, it is probably improper to neglect the entropy variation, with temperature, for PMMA layers on the aluminium surface. Indeed, the entropic parameter, for anisotropic distributed PMMA chains in the spin-cast layer, will certainly have a major effect on the calculated values of the conformational energy.

CONCLUSION

I.r.a.s. spectroscopy, equipped with a heating cell, has

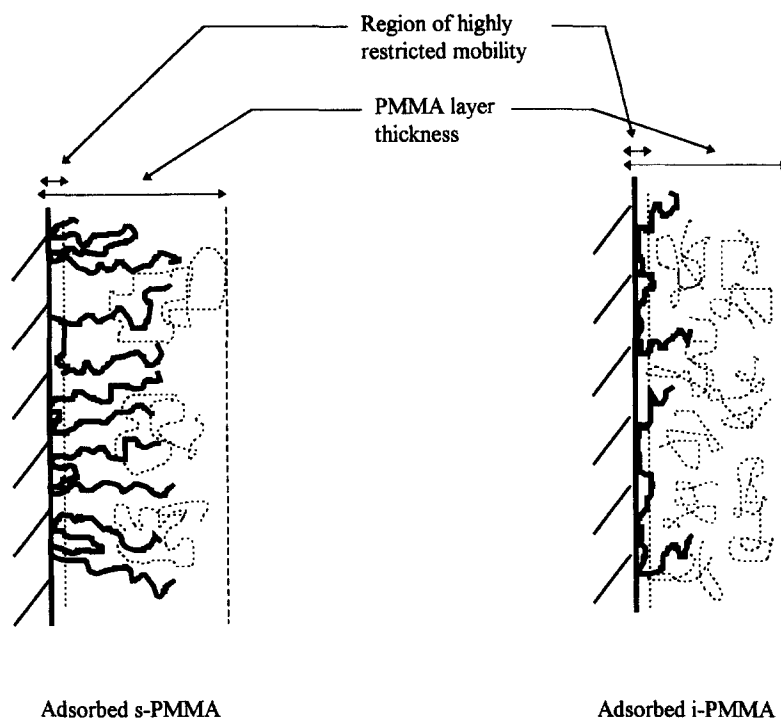


Figure 6 Scheme of the assumed structure of the adsorbed i- and s-PMMA layer at the aluminium surface

been shown as a powerful tool for probing the PMMA/aluminium interface. Thus, the structure of the PMMA spin-cast layers, deduced from the fraction of bonded carbonyls, has highlighted a more flattened structure of the i-PMMA chains at the interface, as compared to the other isomer chains. Moreover, the T_g of the polymer layers, derived from the difference infra-red spectra, increases for the i-PMMA layer, while it remains constant for the other isomers. Finally, a significant achievement in the understanding of the interfacial polymer conformation, is the possible calculation of the conformational energies at the surface. Thus, the calculated values, largely higher than those obtained from the bulk, allows us to forecast an increase in the interfacial *trans* conformation of the adsorbed polymer chains. The gold plated surface does not lead to such an increase in ΔE . Despite these results, some critical questions remain on the meaning of the calculated interfacial conformational energies, depending upon the tacticity of the polymer.

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