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Article

Effect of Tacticity on London Dispersive Surface Energy, Polar Free Energy and Lewis Acid-Base Surface Energies of Poly Methyl Methacrylate by Inverse Gas Chromatography

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Abstract: This research was devoted to study the effect of the tacticity of PMMA on the surface physicochemical properties such as the London dispersive component of the surface energy of the polymer, the polar and dispersive free energies, the Lewis's acid-base surface parameters, and the Lewis acid and base surface energies of atactic, isotactic and syndiotactic PMMAs as a function of the temperature. Inverse gas chromatography (IGC) at infinite dilution was used for the determination of the surface thermodynamic properties of PMMA at different tacticities. The experimental values of the net retention time and volume of model organic molecules adsorbed on the atactic, isotactic and syndiotactic PMMAs, were obtained by IGC technique at infinite dilution. The London dispersion interaction energy was used for the separation of the polar and dispersive energy of the different n-alkanes and polar solvents adsorbed on the different PMMA surfaces. The London dispersive surface energy $\gamma_s^d(T)$ of PMMAs was determined by applying the Hamieh thermal model that took into account the effect of the temperature on the surface area of adsorbed molecules adsorbed. The obtained results showed non-linear variations of $\gamma_s^d(T)$ of atactic, isotactic, and syndiotactic PMMAs with three maxima characterizing the three transition temperatures of PMMAs, T_g , T_g and $T_{liq-liq}$ with a shift of these temperatures with the isotactic and syndiotactic PMMAs. It was showed that the polar interaction free energy $\Delta G_a^p(T)$ also showed the presence of the three above transition temperatures of the polymers. The study showed an important non-linearity variation of the different acid-base parameters in the various polymer surfaces proving the highest effect of the temperature and the tacticity on these parameters. An amphoteric character was highlighted for the different PMMAs. The determination of the enthalpic and entropic Lewis's acid-base parameters showed that the basicity of the atactic PMMA was about four times larger than its acidity outside the neighborhood of the transition temperatures of the polymer. Whereas, the isotactic PMMA was about 2 to 2.5 times more basic than acid, while the syndiotactic PMMA exhibited the highest basicity by showing a surface 5 to 8 times more basic than acid. However, the Lewis acid-base parameters strongly depended on the temperature and sudden variations of these surface parameters were observed around the transition temperatures largely depending on the PMMA tacticity. The determination of the polar acid and base surface energies of the three PMMAs led to the same previous transition temperatures with an important effect of the tacticity of PMMA on the values of these acid-base surface energies.

Keywords: London dispersion equation; recovery fraction; polar enthalpy and entropy; Lewis's acid-base parameters; transition temperatures; intermolecular separation distance

1. Introduction

The tacticity of polymers plays an important role in many industrial processes. Indeed, polymer crystallinity and many macroscopic properties such as the density, glass and melting temperatures, clarity, and stiffness of a polymer depend on it. Furthermore, the determination of polymer tacticity is of crucial interest in the knowledge of polymerization mechanism [1]. The stereochemistry in polymers has been used to influence and control their physical and mechanical properties, as well as begin to control their function. Several studies were devoted to the effect of stereochemistry on mechanical properties, biodegradation, conductivity and in applications of stereodefined polymers for enantioseparation and as supports for catalysts in asymmetric transformations [2].

A tactic polymer is defined as 'a regular polymer, the molecules of which can be described in terms of only one species of configurational repeating unit in a single sequential arrangement [3]. Tacticity then refers to the relative spatial arrangement of substituents along a polymer chain. At that time, three main types of tacticities were distinguished: isotactic, syndiotactic and atactic [1].

It is well-known that the atactic polymers have their pendant groups organized randomly around the principal linear chain of the polymers. They lead to form amorphous and soft materials. Whereas, the syndiotactic polymers are characterized by their pendant groups organized in alternating ways around the principal chain by forming crystal structures. The Tacticity of polymers affects the physical and chemical properties of polymeric materials [4–12]. The isotactic polymers are characterized by pendant groups spatially located on the same side of the principal chain. The crystallinity of polymers strongly depends on their tacticity. In general, the syndiotactic polymers form the most rigid, crystalline structures, while, isotactic polymers exhibit semi-crystalline structure and an amorphous form for atactic polymers. This affects the thermos-mechanic properties of polymers. For example, the highest melting points are obtained with the syndiotactic polymers.

Izzo et al. [4] investigated the effect of polymer tacticity on physico-chemical and biological properties relevant to the use of polymer therapeutics using poly(methacrylic acid) (PMA) as a model polymer. They studied the physicochemical behavior in aqueous solution of atactic and syndiotactic PMAs obtained from hydrolysis of PMMAs.

Grigoriadi et al. [5] studied the effect of tacticity on the ageing kinetics of glassy amorphous polymers at high and low ageing temperatures for atactic, isotactic, and syndiotactic polystyrene using flash-DSC in their glassy state.

The spatial configuration of polymers can be modified by the various parameters of their physicochemical properties. Chat et al. [6] used the dielectric spectroscopy (DS) to study the effect of the tacticity on the glass-transition dynamics of confined polymer films [7].

Several studies were interested in the determination of the tacticity effect on the properties of polymers [11–26]. The polymer tacticity gives information on the arrangement of atoms and/or groups of atoms on the polymer backbone [6]. For poly(methyl methacrylate) (PMMA) and poly(ethyl methacrylates) (PEMA), it has been observed that different spatial configurations of the polymers are characterized by the various relaxation times and the glass-transition temperatures [16–18,27–29].

Hasan et al. [31] investigated the influence of tacticity of the structure formation of Poly(methacrylic acid) by defining an isotactic polymer as consisting only of meso diads (*m*), with two adjacent configurational repeating units with identical orientation, whereas a syndiotactic polymer is made up of only racemo diads (*r*), with two adjacent configurational repeating units with the opposite orientation, while an atactic polymer contains both *m* and *r* diads in a random sequence. With this definition, the tacticity can be further described even more precisely with the introduction of higher-order sequences than diads such, tetrads, and pentads [31].

Zhang et al. [32] considering that the tacticity of polymers is one of the governing microstructural parameters that determines their material properties, used the tacticity engineering to study the thermo-responsive, adhesion and electrical properties of homopolymers by tuning tacticity without compositional variance.

The physical properties of polymer like solubility, mechanical properties, thermal stability, etc. can be affected by the stereoregularity in polymer. Biswas et al. [33] investigated the effect of some physical properties of high molecular weight linear poly(*N*-isopropylacrylamide)s (PNIPAM) having

different isotacticities (m , meso dyad = 47, 62, 68, 81, and 88 %). The effect of tacticity on the transition temperatures were studied by several scientists [33–43].

Nevertheless, we did not find any study in the literature concerning the influence of the tacticity on the surface properties of polymers such as their London dispersive energy, Lewis's acid-base parameters and acid and base polar surface energies. This paper is interested in filling this gap in this research area by studying the effect of the tacticity of poly(methyl methacrylate) on the dispersive component of the surface energy of polymer, the polar and dispersive free energies as well as the various surface variables relative to Lewis's acid-base surface properties.

The technique used in this study is the inverse gas chromatography at infinite dilution that was proved to be a very interesting technique capable to examine the surface properties of solid substrates and to quantify the various surface parameters of interaction between polymers and the adsorbed organic solvents by varying the temperature [44–65].

Different chromatographic methods and molecular models were used in the literature to characterize the physicochemical properties of solid surfaces [39,45–50]. We applied the new method recently developed that utilized the thermal model [51,53,58,59] to determine the London dispersive energy and used the London dispersion equation [56,57] based on the deformation polarizability α_{0X} of the probe and the ionization energies of the solid ε_S and the solvent ε_X with a new chromatographic thermodynamic parameter $\mathcal{P}_{SX}$. By using the thermal model, we compared between the dispersive surface energy of atactic, isotactic and syndiotactic PMMA and by applying the parameter $\mathcal{P}_{SX}$, we determined the polar and dispersive free interaction energy of organic solvents adsorbed on the polymer surfaces, and the Lewis's acid-base surface energy and parameters as a function of the temperature.

2. Methods and Materials

The inverse gas chromatography (IGC) at infinite dilution [44–65] was used to characterize the surface physicochemical properties of PMMA at different tacticities. IGC technique allowed obtaining the experimental values of the net retention time t_n and volume V_n of polar and non-polar adsorbed solvents on the different PMMAs as a function of the temperature. The free energy of adsorption $\Delta G_a^0(T)$ of adsorbed molecules on PMMA surfaces was therefore obtained from Equation 1:

$$\Delta G_a^0 = -RT \ln \frac{V_n(T)}{V_0(T)} \quad (1)$$

Where T is the absolute temperature of the chromatographic column containing the solid material, R the perfect gas constant, and $V_0(T)$ a constant volume depending on the temperature and reference characteristics referred to the two-dimensional state of adsorbed film.

In the case of polar molecules adsorbed on the solid surfaces, two contributions of the free energy of adsorption $\Delta G_a^0(T)$ were distinguished: the London dispersion component ΔG_a^d and the polar or specific component ΔG_a^p (Equation 2)

$$\Delta G_a^0 = \Delta G_a^d + \Delta G_a^p \quad (2)$$

By using our new method recently developed [56,57] that consisted in the separation of the London dispersive and polar components of the free surface, it was possible to obtain the London dispersion energy $\Delta G_a^d(T)$:

$$\Delta G_a^d(T) = -\frac{\alpha_0 S}{H^6} \left[\frac{3N}{2(4\pi\varepsilon_0)^2} \left(\frac{\varepsilon_S \varepsilon_X}{(\varepsilon_S + \varepsilon_X)} \alpha_{0X} \right) \right] \quad (3)$$

Where N is the Avogadro's number, ε_0 the permittivity of vacuum, S denoting the solid particle and X the solvent molecule separated by a distance H , and ε_S and ε_X are the respective ionization energies of the solid and the solvent ε_X .

The new method proposed to use the new parameter of interaction $\mathcal{P}_{SX}$ given by

$$\mathcal{P}_{SX} = \frac{\varepsilon_S \varepsilon_X}{(\varepsilon_S + \varepsilon_X)} \alpha_{0X} \quad (4)$$

In the case of n-alkanes (C_n) adsorbed on PMMA, one obtained:

$$RT \ln Vn(C_n) = A \left[\frac{3N}{2(4\pi\varepsilon_0)^2} \mathcal{P}_{SX}(C_n) \right] - B \quad (5)$$

Where A and B are given by:

$$\begin{cases} A = \frac{\alpha_0 S}{H^6} \\ B = \ln V_0(T) \end{cases} \quad (6)$$

The polar free energy ($-\Delta G_a^p(T)$) of polar organic solvents adsorbed on PMMA was obtained from the experimental straight-line of n-alkanes (Equation 7] representing the variations of $RT \ln Vn(C_n)$ against $\frac{3N}{2(4\pi\epsilon_0)^2} \mathcal{P}_{SX}(C_n)$ for different temperatures:

$$-\Delta G_a^p(T) = RT \ln Vn(X) - A \left[\frac{3N}{2(4\pi\epsilon_0)^2} \mathcal{P}_{S-X} \right] + B \quad (7)$$

The use of Equations 8 and 9 led to the determination of the polar enthalpy $-\Delta H_a^p(T)$ and entropy $-\Delta S_a^p(T)$ of organic solvents adsorbed on PMMA:

$$\Delta H_a^p(T) = \frac{\partial \left(\frac{\Delta G_a^p(T)}{T} \right)}{\partial \left(\frac{1}{T} \right)} \quad (8)$$

$$\Delta S_a^p(T) = - \left(\frac{\partial (\Delta G_a^p(T))}{\partial T} \right) \quad (9)$$

The Lewis's enthalpic acid base constants $K_A(T)$ and $K_D(T)$, and entropic acid base parameters $\omega_A(T)$ and $\omega_D(T)$ were obtained from the expressions of $-\Delta H_a^p(T)$ and $-\Delta S_a^p(T)$:

$$-\Delta H^p(T) = DN \times K_A(T) + AN \times K_D(T) \quad (10)$$

$$-\Delta S^p(T) = DN \times \omega_A(T) + AN \times \omega_D(T) \quad (11)$$

Where AN and DN are respectively the Gutmann electron donor and acceptor numbers of the polar solvents [66]. The used values were those corrected by Riddle and Fowkes [67].

Two kinds of probe molecules were used:

- Non-polar molecules such as the n-alkanes (C_n) such as n-pentane (C_5), n-hexane (C_6), n-heptane (C_7), n-octane (C_8), and n-nonane (C_9)
- Polar molecules, divided into three groups:
 - Lewis's acid solvents such as dichloromethane, chloroform, and carbon tetrachloride
 - Basic solvent such as ethyl acetate, diethyl ether, tetrahydrofuran (THF)
 - Amphoteric molecule such as toluene

The isotactic (i), syndiotactic (s) and atactic (a) PMMAs used in this paper, were the same as the polymers previously characterized in other studies by using other classic chromatographic methods and models [34,36,38,39,68]. The previous experimental values of $RT \ln Vn$ of the various n-alkanes and polar molecules adsorbed on i-PMMA, s-PMMA and a-PMMA, obtained from chromatographic measurements, were used to investigate the tacticity effect on the surface physicochemical properties of the different PMMA surfaces.

3. Experimental Results

3.1. London Dispersive Component of Surface Energy of PMMA Polymers

In previous papers [51,54–58,69], a new methodology on the determination of the accurate value of the London dispersive surface energy γ_s^d of materials was proposed. It is based on the thermal effect on the surface areas of organic molecules that are necessary to be known as a function of the temperature to obtain accurate values of $\gamma_s^d(T)$ of solid surfaces.

In this section, the same procedure previously developed [51,54–58,69] was used to determine the $\gamma_s^d(T)$ of the different PMMAs. The determination of the net retention volumes of the various organic molecules adsorbed on i-PMMA, s-PMMA and a-PMMA allowed obtaining $RT \ln Vn$ of such molecules. The obtained results of $RT \ln Vn$ were given in Table S1 ((Supplementary Materials).

The Hamieh thermal model [51,54–58,69] was applied to determine $\gamma_s^d(T)$ the various PMMA surfaces. Figure 1 gave the variations of $\gamma_s^d(T)$ of PMMA at different tacticities as a function of the temperature was plotted on Figure 1.

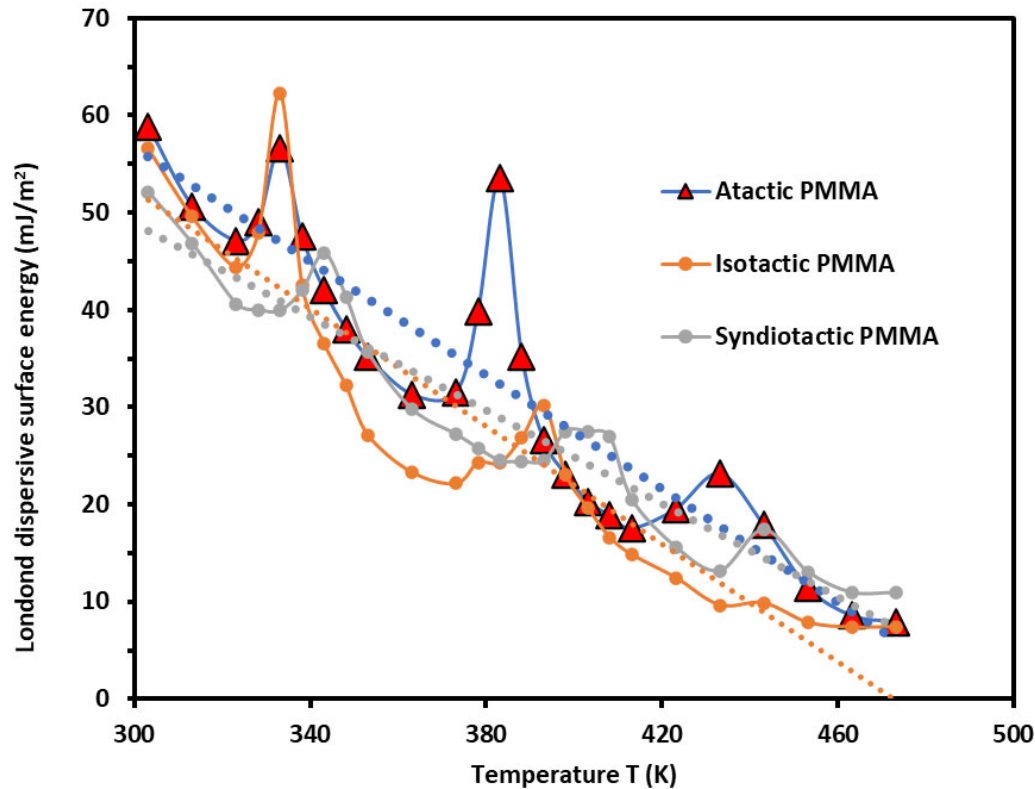


Figure 1. Evolution of the London dispersive surface energy γ_s^d (mJ/m^2) of a-PMMA, i-PMMA and s-PMMA as a function of the temperature T (K) by using the Hamieh thermal model. Dashed lines correspond to linear approximation.

The curves in Figure 1 showed a non-linear evolution of $\gamma_s^d(T)$, contrary to other cases relative to oxides and other solid materials [51,54–58] where the linearity of $\gamma_s^d(T)$ was clearly observed. The precious information collected from Figure 1 showed not only the large variations of $\gamma_s^d(T)$ versus the temperature with permanent change of the slope $\frac{d\gamma_s^d(T)}{dT}$, but also it highlighted an important difference in the behavior of PMMA strongly depending on the tacticity of the polymer. Indeed, larger values of $\gamma_s^d(T)$ of atactic PMMA were globally observed, respectively followed by those of syndiotactic and isotactic. However, an inversion of this tendency between isotactic and syndiotactic PMMAs was found for temperatures lower than 60°C.

The Curves of $\gamma_s^d(T)$ for each of the three examined PMMAs clearly showed three maxima varying from one polymer to another. This interesting observation has to be correlated to the transition phenomena resulting from the influence of the increasing temperature. Indeed, it was showed in previous works [34,36,38,39,68] that the PMMA presents three transition temperatures:

- The beta-relaxation $T_\beta = 60^\circ\text{C}$,
- The glass transition $T_g = 110^\circ\text{C}$,
- The liquid–liquid transitions $T_{liq-liq} = 160^\circ\text{C}$.

The above results were perfectly confirmed by the curves of $\gamma_s^d(T)$ of atactic PMMA in Figure 1 and showed the same values obtained in other works. The presence of the maxima in Figure 1 led to the following Table 1:

Table 1. Values of beta-relaxation, glass transition and liquid-liquid transition temperatures of a-PMMA, i-PMMA and s-PMMA

Transition temperature	T_{β}	T_g	$T_{liq-liq}$
Atactic PMMA	60°C	110°C	160°C
Isotactic PMMA	60°C	120°C	170°C
Syndiotactic PMMA	70°C	130°C	170°C

Table 1 showed that a shift of 10°C was observed in the values of T_g and $T_{liq-liq}$ when passing from atactic-PMMA to isotactic and this shift increases of additional 10°C in the case of syndiotactic PMMA. This shift in the transition temperatures is certainly due to the geometric configuration and position of methacrylate group relatively to the principal chain of PMMA showing that the tacticity of polymer strongly affects the transition temperatures [9,34,36,38,39,68].

The variations of $\gamma_s^d(T)$ of each PMMA are composed by four parts of parabolic arcs represented by parabolic equations as shown in Table 2 and having the following general form:

$$\gamma_s^d(T) = aT^2 + bT + c$$

Table 2. Equations of $\gamma_s^d(T)$ of different PMMAs with the corresponding linear regression coefficients in the case of parabolic interpolation.

Atactic PMMA		
Equation of $\gamma_s^d(T)$	R ²	Temperature interval
$\gamma_s^d(T) = 0.0451T^2 + 28.851T + 4657.9$	0.935	303.15K - 333.15K
$\gamma_s^d(T) = 0.0282T^2 - 20.47T + 3745.4$	0.9722	333.15K - 378.15K
$\gamma_s^d(T) = 0.0408T^2 - 33.635T + 6940.9$	0.9477	378.15K - 423.15K
$\gamma_s^d(T) = 0.0091T^2 - 8.647T + 2061.4$	0.9902	423.15K - 473.15K
Isotactic PMMA		
Equation of $\gamma_s^d(T)$	R ²	Temperature interval
$\gamma_s^d(T) = 0.0299T^2 - 19.277T + 3152$	0.9398	303.15K - 333.15K
$\gamma_s^d(T) = 0.0342T^2 - 25.053T + 4607.6$	0.9557	333.15K - 393.15K
$\gamma_s^d(T) = 0.0077T^2 - 6.795T + 1501.7$	0.9925	393.15K - 443.15K
$\gamma_s^d(T) = 0.0051T^2 - 4.787T + 1121.9$	0.9896	443.15K - 473.15K
Syndiotactic PMMA		
Equation of $\gamma_s^d(T)$	R ²	Temperature interval
$\gamma_s^d(T) = 0.0051T^2 - 4.790T + 1121.9$	0.9485	303.15K - 343.15K
$\gamma_s^d(T) = 0.0115T^2 - 8.900T + 1740.8$	0.9900	343.15K - 403.15K
$\gamma_s^d(T) = 0.0099T^2 - 8.798T + 1967.3$	0.9569	403.15K - 443.15K
$\gamma_s^d(T) = 0.0108T^2 - 10.079T + 2370$	1.000	443.15K - 473.15K

Table 2 showed the large difference between the $\gamma_s^d(T)$ of the different PMMAs with various tacticities with a sensitive variation as a function of the temperature. The parabolic interpolation was obtained for the various cases with good linear regression coefficients. The variations of $\gamma_s^d(T)$ are submitted to the magnitude of the second order transition temperatures and also to the tacticity of PMMA as it was shown in Figure 1.

The linear interpolation shown in Table 3 was obtained with a moderate value of the linear regression linear. This bad correlation is due to the non-linearity of the London dispersive energy as a function of the temperature for the different PMMAs.

Table 3. Equations of $\gamma_s^d(T)$ of different PMMAs with the corresponding linear regression coefficients with a linear approximation.

	Equation of $\gamma_s^d(T)$	R ²	Temperature interval
Atactic PMMA	$\gamma_s^d(T) = -0.292T + 144.37$	0.8368	303.15K - 473.15K
Isotactic PMMA	$\gamma_s^d(T) = -0.303T + 143.16$	0.8491	303.15K - 473.15K
Syndiotactic PMMA	$\gamma_s^d(T) = -0.240T + 120.8$	0.8368	303.15K - 473.15K

However, Table 3 allowed to obtain some useful information on the surface entropy $S_s = -\frac{d\gamma_s^d}{dT}$, the London dispersive energy $\gamma_s^d(0K)$ at 0K and the intrinsic temperature $T_{int.}$ of PMMA surfaces. These values were given in Table 4.

Table 4. Values of the surface entropy $S_s = -\frac{d\gamma_s^d}{dT}$, the London dispersive energy $\gamma_s^d(0K)$ at 0K and the intrinsic temperature $T_{int.}$ of a-PMMA i-PMMA and s-PMMA.

	$S_s = -d\gamma_s^d/dT$ (mJ $\times$ m ⁻² $\times$ K ⁻¹)	$\gamma_s^d(0K)$ (mJ $\times$ m ⁻²)	$T_{int.}(K)$
Atactic PMMA	0.292	144.37	494.1
Isotactic PMMA	0.303	143.16	472.6
Syndiotactic PMMA	0.240	120.8	503.8

The values of the surface characteristics of the different PMMAs showed an important difference in the behavior of PMMA following its tacticity. It seems that the obtained values of the intrinsic temperatures $T_{int.}$ correspond to degradation temperatures of PMMAs and can be considered as a specific identity of the polymer.

3.1. Polar Free Surface Energy of Atactic, Isotactic and Syndiotactic PMMAs

Using the values of the deformation polarizability α_{ox} and the ionization energies of the various n-alkanes and polar molecules adsorbed on the different PMMA surfaces obtained from Handbook of Physics and Chemistry [70], it was possible to study the variations of $RT\ln Vn$ as a function of the chromatographic parameter $\frac{3N}{2(4\pi\epsilon_0)^2}\mathcal{P}_{S-X}$ of the different solvents, and therefore to deduce the values of the free polar surface energy ($-\Delta G_a^p(T)$) of polar solvents adsorbed on three studied PMMAs. The obtained results were given in Table 5

Table 5. Values of ($-\Delta G_a^p(T)$ kJ/mol) of polar molecules adsorbed respectively on atactic, isotactic and syndiotactic PMMAs versus the temperature.

Polar free energy of atactic PMMA							
Temperature T(K)	CCl ₄	CH ₂ Cl ₂	CHCl ₃	Diethyl ether	THF	Ethyl acetate	Toluene
303.15	10.047	19.251	14.493	15.248	19.777	16.627	11.951
313.15	10.142	18.357	13.862	14.794	19.179	16.162	11.585
323.15	10.303	17.750	13.399	14.416	18.845	15.830	11.442
328.15	10.433	17.669	13.278	14.259	18.889	15.755	11.561
333.15	10.642	17.926	13.323	14.166	19.257	15.828	11.961
338.15	10.621	17.193	12.884	13.904	18.679	15.479	11.526
343.15	10.638	16.636	12.532	13.665	18.266	15.198	11.244
348.15	10.676	16.168	12.229	13.447	17.938	14.959	11.033
353.15	10.729	15.768	11.962	13.242	17.673	14.749	10.878
363.15	10.865	15.098	11.494	12.854	17.267	14.384	10.679

373.15	11.081	14.759	11.178	12.521	17.185	14.163	10.758
378.15	11.342	15.218	11.285	12.442	17.767	14.323	11.335
383.15	11.682	15.988	11.514	12.403	18.664	14.617	12.180
388.15	11.479	14.558	10.824	12.058	17.371	13.963	11.140
393.15	11.408	13.673	10.371	11.792	16.616	13.543	10.566
398.15	11.435	13.186	10.086	11.582	16.256	13.295	10.331
403.15	11.476	12.754	9.827	11.382	15.950	13.070	10.144
408.15	11.850	12.756	9.922	11.500	16.078	13.204	10.372
413.15	11.627	12.174	9.424	11.019	15.621	12.744	10.013
423.15	11.940	12.230	9.255	10.729	15.944	12.693	10.431
433.15	12.367	12.723	9.224	10.476	16.727	12.831	11.230
443.15	12.147	10.846	8.317	9.886	15.066	11.893	10.015
453.15	12.172	9.778	7.776	9.494	14.219	11.360	9.451
463.15	12.310	9.164	7.383	9.138	13.845	11.019	9.285
473.15	12.276	8.131	6.767	8.597	13.044	10.414	8.814
Polar free energy of isotactic PMMA							
Temperature T(K)	CCl ₄	CH ₂ Cl ₂	CHCl ₃	Diethyl ether	THF	Ethyl acetate	Toluene
303.15	9.422	14.973	11.160	15.214	17.783	15.139	11.652
313.15	9.579	14.564	10.848	14.812	17.121	14.694	11.374
323.15	9.760	14.259	10.605	14.441	16.553	14.331	11.174
328.15	9.943	14.504	10.689	14.334	16.646	14.457	11.401
333.15	10.269	15.363	11.071	14.330	17.328	15.059	12.148
338.15	10.120	14.192	10.454	13.969	16.068	14.088	11.188
343.15	10.147	13.788	10.220	13.741	15.539	13.712	10.874
348.15	10.198	13.485	10.041	13.539	15.103	13.414	10.639
353.15	10.231	13.105	9.833	13.329	14.592	13.058	10.338
363.15	10.401	12.806	9.635	12.975	14.011	12.701	10.129
373.15	10.625	12.735	9.544	12.655	13.652	12.521	10.117
378.15	10.804	12.970	9.615	12.537	13.740	12.637	10.338
383.15	10.955	13.096	9.636	12.400	13.722	12.671	10.471
388.15	11.121	13.277	9.678	12.268	13.759	12.745	10.649
393.15	11.326	13.611	9.781	12.161	13.952	12.936	10.956
398.15	11.297	13.014	9.509	11.928	13.210	12.416	10.465
403.15	11.344	12.718	9.363	11.737	12.768	12.127	10.232
408.15	11.400	12.466	9.238	11.556	12.367	11.872	10.034
413.15	11.482	12.320	9.155	11.384	12.074	11.698	9.930
423.15	11.687	12.183	9.055	11.068	11.642	11.467	9.850
433.15	11.891	12.051	8.958	10.751	11.213	11.241	9.776
443.15	11.933	11.393	8.645	10.315	10.245	10.615	9.277
453.15	12.152	11.328	8.582	10.009	9.880	10.440	9.259
463.15	12.437	11.521	8.595	9.719	9.789	10.457	9.468
473.15	12.492	11.059	8.311	9.232	9.025	9.972	9.163

Polar free energy of syndiotactic PMMA							
Temperature T(K)	CCl ₄	CH ₂ Cl ₂	CHCl ₃	Diethyl ether	THF	Ethyl acetate	Toluene
303.15	9.704	16.617	13.631	15.200	16.129	13.339	11.448
313.15	9.879	16.212	13.363	14.978	15.709	12.965	10.664
323.15	10.028	15.714	13.055	14.733	15.199	12.476	10.121
328.15	10.138	15.625	12.986	14.642	15.093	12.442	9.935
333.15	10.259	15.581	12.939	14.559	15.031	12.470	9.343
338.15	10.416	15.691	12.969	14.506	15.116	12.701	11.685
343.15	10.594	15.893	13.038	14.458	15.293	13.068	16.158
348.15	10.646	15.560	12.853	14.326	14.953	12.704	13.145
353.15	10.673	15.123	12.624	14.180	14.510	12.198	11.800
363.15	10.809	14.608	12.344	13.950	13.968	11.670	11.126
373.15	11.001	14.337	12.182	13.759	13.661	11.473	10.155
378.15	11.091	14.178	12.092	13.660	13.483	11.342	9.749
383.15	11.190	14.056	12.021	13.570	13.341	11.259	9.829
388.15	11.309	14.017	11.982	13.488	13.283	11.293	9.622
393.15	11.444	14.041	11.971	13.417	13.287	11.408	10.293
398.15	11.646	14.333	12.065	13.380	13.561	11.891	13.616
403.15	11.755	14.278	11.999	13.262	13.493	11.937	13.468
408.15	11.905	14.333	12.013	13.226	13.527	12.062	10.553
413.15	11.879	13.723	11.757	13.076	12.890	11.309	7.576
423.15	12.004	13.210	11.520	12.858	12.328	10.781	7.563
433.15	12.235	13.114	11.441	12.694	12.192	10.819	7.746
443.15	13.534	14.036	12.398	13.561	13.081	11.903	7.539
453.15	12.543	12.452	11.078	12.240	11.439	10.311	4.992
463.15	12.772	12.352	10.999	12.073	11.299	10.345	4.800
473.15	12.779	11.679	10.632	11.688	10.574	9.720	4.785

The comparison between the polar interaction free energy of the different PMMAs shown in Table 5 for the different polar organic molecules globally, highlighted higher values of ($-\Delta G_a^p(T)$) in the case of atactic PMMA followed by syndiotactic PMMA and isotactic PMMA. A higher basic interaction was observed in all PMMAs showing their higher basicity with an important amphoteric character (Table 5).

The effect of the tacticity on the adsorption of polar solvents on PMMA was shown in Figure 2. The curves of the adsorbed polar molecules plotted on Figure 2 also showed a specific signature at the various transition temperatures previously highlighted by the variations of the London dispersive surface energy. The shift in the transition temperatures was also observed in Figure 2 for the different PMMAs. The results presented in Figure 2 showed an important variation in the behavior of the different polymers. The atactic PMMA exhibited the highest values with the various solvents followed by syndiotactic and isotactic PMMAs.

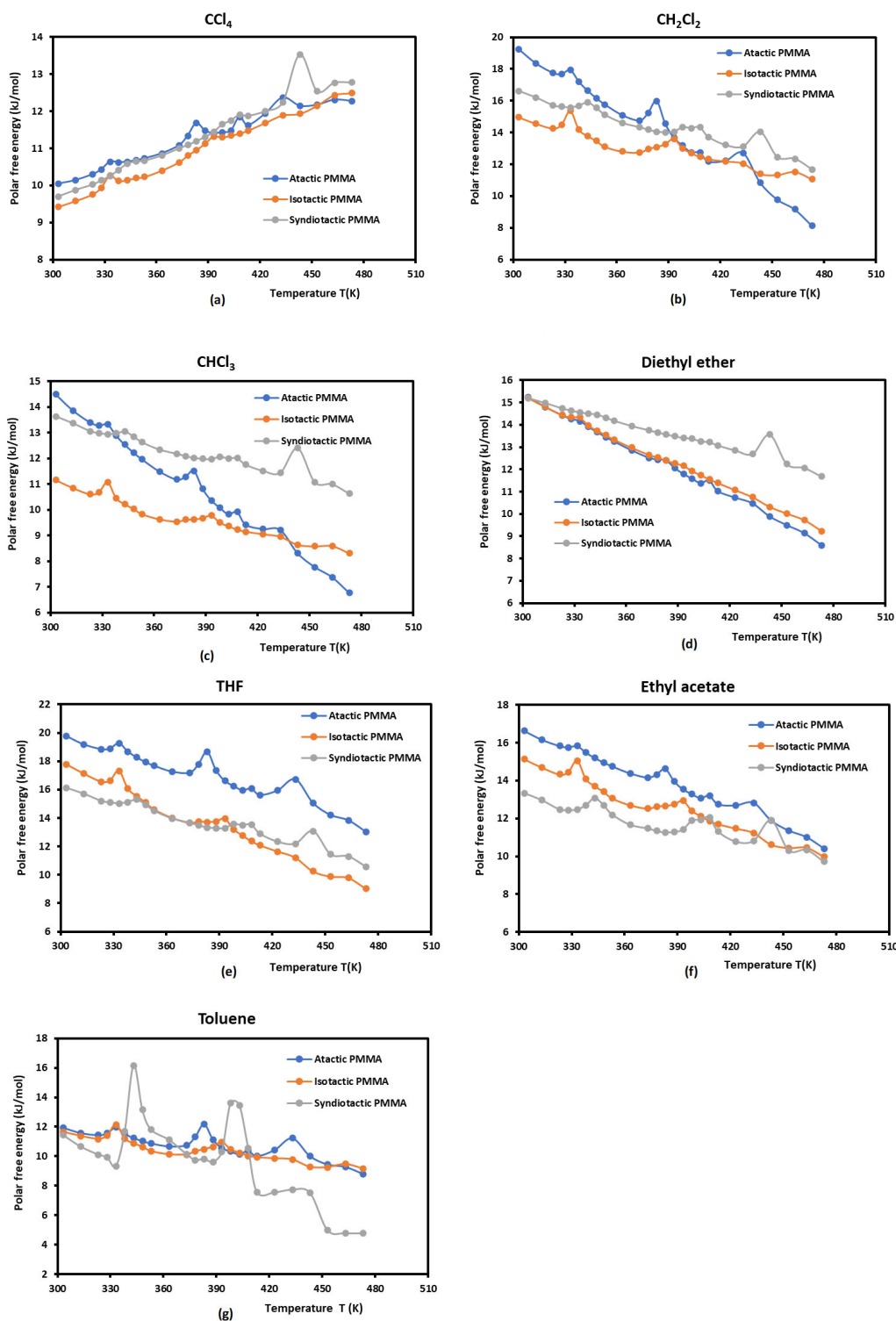


Figure 2. Variations of the polar free interaction energy ($-\Delta G_a^p(T)$) (kJ/mol) of different polar solvents adsorbed on atactic, isotactic and syndiotactic PMMAs as a function of the temperature: (a) CCl_4 ; (b) CH_2Cl_2 ; (c) CHCl_3 ; (d) diethyl ether; (e) tetrahydrofuran (THF); (f) ethyl acetate; and (g) toluene.

The variations of ($-\Delta G_a^p(T)$) of adsorbed solvents on PMMAs led to the determination of their polar enthalpy ($-\Delta H_a^p(T)$) and entropy ($-\Delta S_a^p(T)$) as a function of the temperature. The obtained

values of $(-\Delta H_a^p(T))$ and $(-\Delta S_a^p(T))$ of the adsorbed solvents on the various PMMAs were given in Tables S2 and S3, and their variations were plotted on Figure 3.

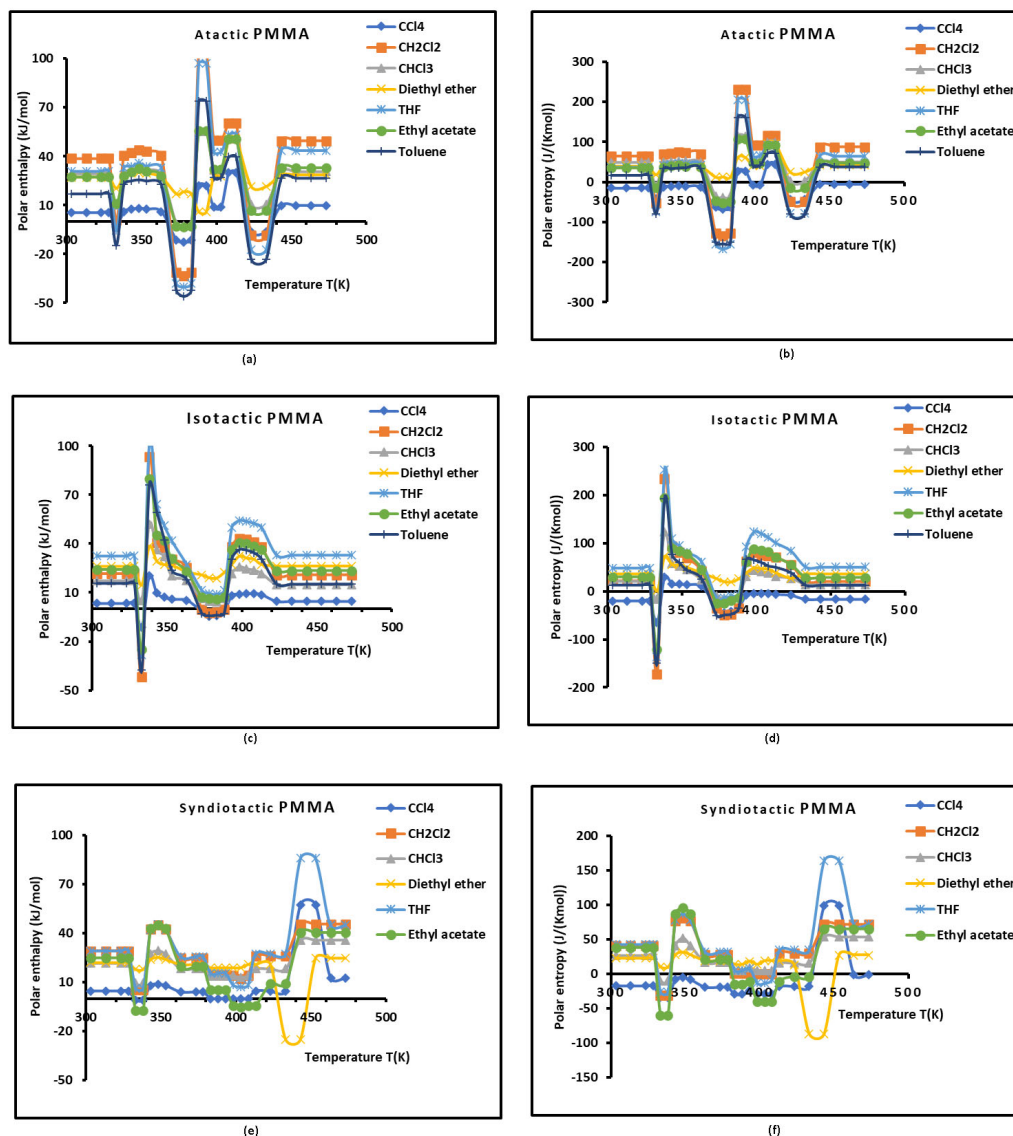


Figure 3. Variations of the polar interaction enthalpy $(-\Delta H_a^p(T) \text{ (J/mol)})$ and entropy $(-\Delta S_a^p(T) \text{ (JK}^{-1}\text{mol}^{-1}))$ of polar solvents adsorbed on atactic, isotactic and syndiotactic PMMAs as a function of the temperature: (a) $(-\Delta H_a^p(T))$ of atactic PMMA (b) $(-\Delta S_a^p(T))$ of atactic PMMA; (c) $(-\Delta H_a^p(T))$ of isotactic PMMA; (d) $(-\Delta S_a^p(T))$ of isotactic PMMA; (e) $(-\Delta H_a^p(T))$ of syndiotactic PMMA; (f) $(-\Delta S_a^p(T))$ of syndiotactic PMMA.

It was observed that the different curves on Figure 3 clearly reflected the various behaviors of the PMMAs based on their tacticities. Three minima of each curve were observed for all PMMAs. These minima elucidated the presence of the three transition temperatures for the different polymers with a shift of these temperatures for the isotactic and syndiotactic PMMAs.

The positive values of $(-\Delta H_a^p(T))$ evoked a adsorption rather than desorption process, while the negative ones significance a desorption reaction. This led to conclude that the interaction between the polar solvents and PMMAs is repulsive and the transition phases are characterized by smaller polar interactions. The comparison between the polar entropy change $(-\Delta S_a^p(T))$ of the solvents adsorbed on the various polymers in general showed an ordered and organized surface of polymers

remaining constant for temperatures lower than the beta-relaxation temperature ($T < T_\beta = 60^\circ\text{C}$), whereas, the disorder dramatically increased around T_β , then decreased after this transition temperature and stabilized between the temperature interval $T_\beta < T < T_g$.

This process continued by repeating the same evolution with a maximum disorder of the surface groups of the different PMMAs around each transition temperature. These observations were more accentuated with the atactic PMMA, and the more ordered case was obtained with the syndiotactic PMMA justifying its higher crystallinity relative to other PMMAs.

Figure 3 showed the non-linearity variations of $(-\Delta H_a^p(T))$ and $(-\Delta S_a^p(T))$ against the temperature and this will strongly affect the Lewis acid-base properties which was detailed in the next section.

3.3. Lewis's Acid-Base Properties

The results in Tables S2 and S3, and Figure 3 with the thermodynamic relations 10 and 11 led to the determination of the enthalpic acid base parameters K_A and K_D and the entropic acid base parameters ω_A and ω_D of atactic, isotactic and syndiotactic PMMAs versus the temperature. The non-linearity of $(-\Delta H_a^p(T))$ and $(-\Delta S_a^p(T))$ of adsorbed solvents necessarily implied the strong variations of the acid-base parameters of PMMAs as a function of the temperature. The values of the different enthalpic and entropic acid-base parameters of PMMAs at different tacticities were presented in Table 6 as a function of the temperature and led to the corresponding curves in Figure 4. The information collected from Table 6 and Figure 4 are very numerous and precious.

- The three examined polymers are more basic than acidic in Lewis terms. The basicity of the tactic PMMA is about four times greater than its acidity outside the neighborhood of the transition temperatures of the polymer (Table 6 and Figure 4). Whereas, the isotactic PMMA is about 2 to 2.5 times more basic than acid, while the syndiotactic PMMA exhibits the highest basicity by showing a surface 5 to 8 times more basic than acid, of course outside the neighborhood of the transition temperatures of the polymer (Table 6 and Figure 4).
- The Lewis acid K_A parameter of atactic PMMA is comparable to that of the isotactic PMMA with a slightly higher value in the isotactic PMMA, but greater than that of syndiotactic PMMA. However, the basicity of the latter polymer is higher than those of atactic and isotactic PMMAs. In fact, the alternate acrylate groups present in syndiotactic PMMA principal chain confer the highest basicity of this polymer, whereas, the methyl groups in isotactic and atactic PMMAs give the highest Lewis acidity.
- The Lewis amphoteric character given by the values of $(K_D + K_A)$ and $(\omega_D + \omega_A)$ which are shown in Table 6 and Figure 4 led to the conclusion that the highest amphoteric surface is obtained with the syndiotactic PMMA, respectively followed by the atactic PMMA and isotactic PMMA, certainly due to the highest activity of the surface groups of syndiotactic PMMA.
- Once again, the curves plotted in Figure 4 showed the three transition temperatures with sudden changes around each transition temperature with a drop in the values of the different acid-bases parameters at these transition temperatures of the three polymers. The different parameters rapidly increase after reaching the different minima to be stabilized on positive parameter stages between two transition temperatures of PMMA.
- The changes in the values of the different acid-base parameters in atactic PMMA are higher than those happened in isotactic and syndiotactic PMMAs. This is due to the random distribution of the acrylate groups in the PMMA principal chain.
- An important effect of the temperature on the Lewis acid-base properties of the various PMMAs was highlighted (Table 6 and Figure 4).

Table 6. Values of the enthalpic acid base parameters K_A , K_D , K_D/K_A and $(K_D + K_A)$, and the entropic acid base parameters ω_A , ω_D , ω_D/ω_A and $(\omega_D + \omega_A)$ of PMMA as a function of the temperature.

Atactic PMMA								
T(K)	K_A	K_D	$K_D + K_A$	K_D/K_A	$10^3 \cdot \omega_A$	$10^3 \cdot \omega_D$	$10^3(\omega_D + \omega_A)$	ω_D / ω_A
303.15	0.304	1.260	1.565	4.142	0.43	0.52	0.95	1.22
313.15	0.304	1.260	1.565	4.142	0.43	0.52	0.95	1.22
323.15	0.304	1.260	1.565	4.142	0.43	0.52	0.95	1.22
328.15	0.304	1.260	1.565	4.142	0.43	0.52	0.95	1.22
333.15	-0.018	-0.033	-0.051	1.847	-0.56	-3.43	-3.99	6.16
338.15	0.317	1.459	1.775	4.602	0.46	1.09	1.56	2.36
343.15	0.317	1.459	1.775	4.602	0.46	1.09	1.56	2.36
348.15	0.317	1.459	1.775	4.602	0.46	1.09	1.56	2.36
353.15	0.317	1.459	1.775	4.602	0.46	1.09	1.56	2.36
363.15	0.317	1.459	1.775	4.602	0.46	1.09	1.56	2.36
373.15	-0.313	-1.063	-1.376	3.397	-1.23	-5.71	-6.93	4.65
378.15	-0.343	-0.508	-0.851	1.478	-1.23	-5.71	-6.93	4.65
383.15	-0.313	-1.063	-1.376	3.397	-1.23	-5.71	-6.93	4.65
388.15	0.876	3.081	3.957	3.518	1.93	6.11	8.04	3.17
393.15	0.876	3.081	3.957	3.518	1.93	6.11	8.04	3.17
398.15	0.411	1.630	2.042	3.966	0.69	1.44	2.13	2.07
403.15	0.411	1.630	2.042	3.966	0.69	1.44	2.13	2.07
408.15	0.453	3.784	4.237	8.350	0.79	6.62	7.41	8.40
413.15	0.453	3.784	4.237	8.350	0.79	6.62	7.41	8.40
423.15	-0.128	-0.259	-0.388	2.016	-0.61	-3.12	-3.73	5.13
433.15	-0.128	-0.259	-0.388	2.016	-0.61	-3.12	-3.73	5.13
443.15	0.418	1.667	2.085	3.989	0.67	1.40	2.08	2.08
453.15	0.418	1.667	2.085	3.989	0.67	1.40	2.08	2.08
463.15	0.418	1.667	2.085	3.989	0.67	1.40	2.08	2.08
473.15	0.418	1.667	2.085	3.989	0.67	1.40	2.08	2.08
Isotactic PMMA								
T(K)	K_A	K_D	$K_D + K_A$	K_D/K_A	$10^3 \cdot \omega_A$	$10^3 \cdot \omega_D$	$10^3(\omega_D + \omega_A)$	ω_D / ω_A
303.15	0.344	0.717	1.060	2.084	0.61	-1.03	-0.42	-1.68
313.15	0.344	0.717	1.060	2.084	0.61	-1.03	-0.42	-1.68
323.15	0.344	0.717	1.060	2.084	0.61	-1.03	-0.42	-1.68
328.15	0.344	0.717	1.060	2.084	0.61	-1.03	-0.42	-1.68
333.15	-0.211	-1.628	-1.838	7.730	-1.08	-8.20	-9.28	7.59
338.15	0.964	3.531	4.494	3.664	2.45	7.28	9.72	2.98
343.15	0.427	1.066	1.493	2.498	0.78	1.52	2.30	1.95
348.15	0.427	1.066	1.493	2.498	0.78	1.52	2.30	1.95
353.15	0.427	1.066	1.493	2.498	0.78	1.52	2.30	1.95
363.15	0.427	1.066	1.493	2.498	0.78	1.52	2.30	1.95
373.15	0.153	-0.119	0.034	-0.778	0.12	-3.21	-3.10	-27.41

378.15	0.153	-0.119	0.034	-0.778	0.12	-3.21	-3.10	-27.41
383.15	0.153	-0.119	0.034	-0.778	0.12	-3.21	-3.10	-27.41
388.15	0.153	-0.119	0.034	-0.778	0.12	-3.21	-3.10	-27.41
393.15	0.501	1.338	1.839	2.668	1.00	0.49	1.50	0.49
398.15	0.501	1.338	1.839	2.668	1.00	0.49	1.50	0.49
403.15	0.501	1.338	1.839	2.668	1.00	0.49	1.50	0.49
408.15	0.501	1.338	1.839	2.668	1.00	0.49	1.50	0.49
413.15	0.501	1.338	1.839	2.668	1.00	0.49	1.50	0.49
423.15	0.347	0.728	1.076	2.097	1.00	0.49	1.50	0.49
433.15	0.347	0.728	1.076	2.097	0.63	-0.99	-0.37	-1.58
443.15	0.347	0.728	1.076	2.097	0.63	-0.99	-0.37	-1.58
453.15	0.347	0.728	1.076	2.097	0.63	-0.99	-0.37	-1.58
463.15	0.347	0.728	1.076	2.097	0.63	-0.99	-0.37	-1.58
473.15	0.347	0.728	1.076	2.097	0.63	-0.99	-0.37	-1.58
Syndiotactic PMMA								
T(K)	K_A	K_D	$K_D + K_A$	K_D/K_A	$10^3 \cdot \omega_A$	$10^3 \cdot \omega_D$	$10^3 (\omega_D + \omega_A)$	ω_D / ω_A
303.15	0.276	1.452	1.728	5.262	0.46	1.14	1.60	2.47
313.15	0.276	1.452	1.728	5.262	0.46	1.14	1.60	2.47
323.15	0.276	1.452	1.728	5.262	0.46	1.14	1.60	2.47
328.15	0.276	1.452	1.728	5.262	0.46	1.14	1.60	2.47
333.15	0.355	-7.527	-7.172	-21.189	0.69	-25.75	-25.06	-37.30
338.15	0.355	-7.527	-7.172	-21.189	0.69	-25.75	-25.06	-37.30
343.15	0.237	6.367	6.603	26.907	0.34	14.74	15.08	42.88
348.15	0.237	6.367	6.603	26.907	0.34	14.74	15.08	42.88
353.15	0.237	6.367	6.603	26.907	0.34	14.74	15.08	42.88
363.15	0.220	1.888	2.108	8.591	0.30	2.01	2.32	6.60
373.15	0.220	1.888	2.108	8.591	0.30	2.01	2.32	6.60
378.15	0.220	1.888	2.108	8.591	0.30	2.01	2.32	6.60
383.15	0.143	0.961	1.104	6.703	0.11	-0.46	-0.35	-4.25
388.15	0.143	0.961	1.104	6.703	0.11	-0.46	-0.35	-4.25
393.15	0.496	-8.578	-8.082	-17.310	1.01	-24.79	-23.79	-24.65
398.15	0.411	-8.490	-8.079	-20.645	0.79	-24.58	-23.79	-31.17
403.15	0.413	-8.464	-8.052	-20.514	0.79	-24.51	-23.72	-30.94
408.15	0.413	-8.464	-8.052	-20.514	0.79	-24.51	-23.72	-30.94
413.15	0.605	-8.652	-8.047	-14.291	1.28	-24.99	-23.71	-19.53
423.15	0.290	0.185	0.475	0.639	0.47	-2.19	-1.72	-4.69
433.15	0.259	-0.401	-0.143	-1.552	0.39	-3.54	-3.15	-8.98
443.15	0.590	5.780	6.369	9.796	1.12	10.32	11.44	9.24
453.15	0.624	6.415	7.039	10.283	1.19	11.79	12.98	9.86
463.15	0.451	1.105	1.556	2.453	0.80	0.10	0.90	0.12
473.15	0.451	1.105	1.556	2.453	0.80	0.10	0.90	0.12

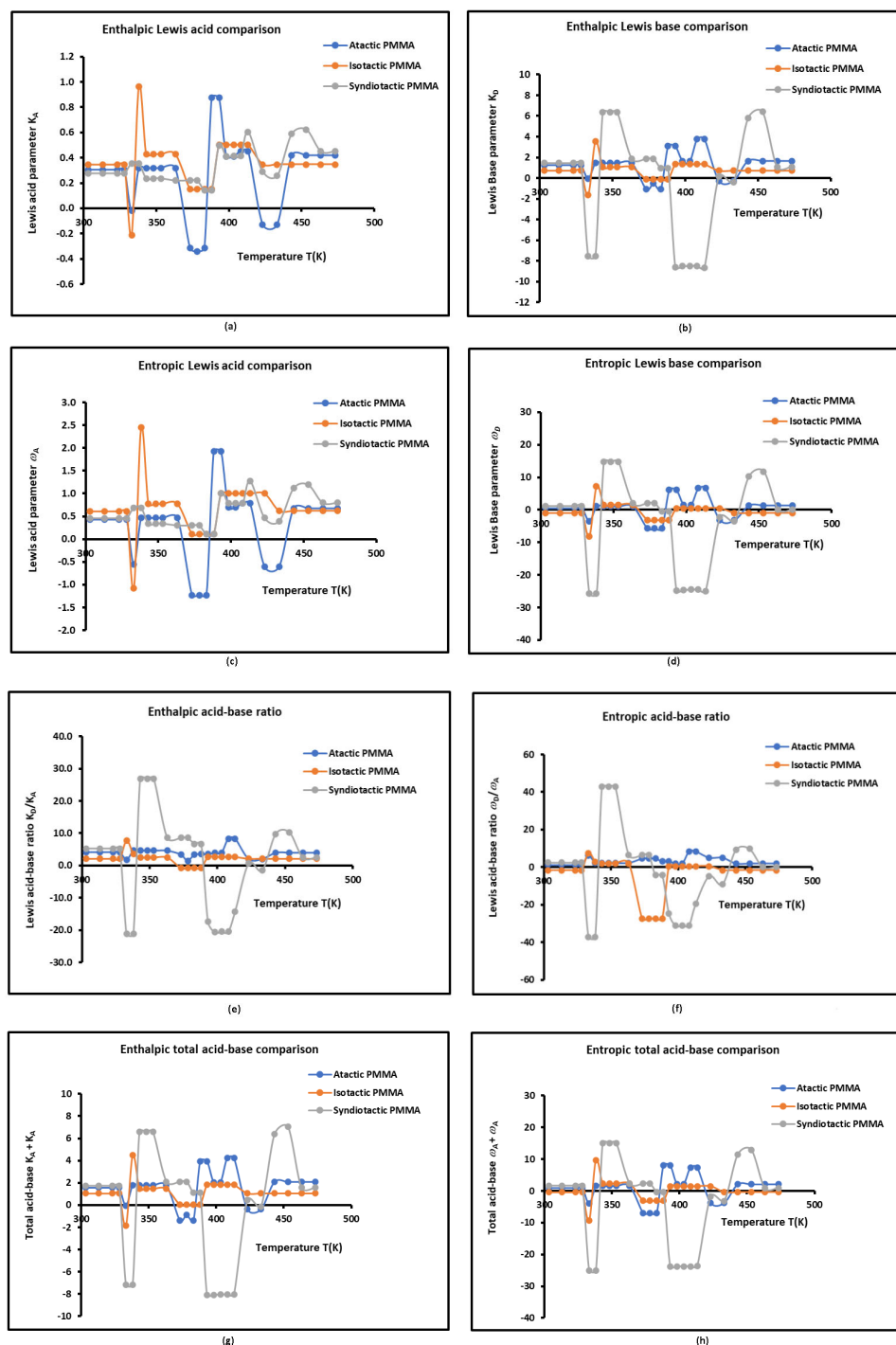


Figure 4. Comparison between the various enthalpic and entropic acid-base parameters of atactic, isotactic and syndiotactic PMMAs versus the temperature: (a): K_A , (b): K_B , (c): ω_A , (d): ω_B , (e): K_D/K_A , (f): ω_D/ω_A , (g): $(K_D + K_A)$, and (h): $(\omega_D + \omega_A)$.

3.4. London Dispersive Free Energies of PMMAs and Dispersion Factor

The values of the dispersion factor A and the London dispersive free energies $\Delta G_a^d(T)$ of organic solvents adsorbed on the various PMMAs at different temperatures were obtained from Equations 3 and 5. The obtained results of $\Delta G_a^d(T)$ were given reported in Table S4 and Figure 5.

The values of Table S4 showed a dispersive interaction energy of atactic PMMA stronger than those of isotactic and syndiotactic PMMAs. The curves of Figure 5 highlighted the presence of the three transition temperatures of PMMAs confirming those previously obtained.

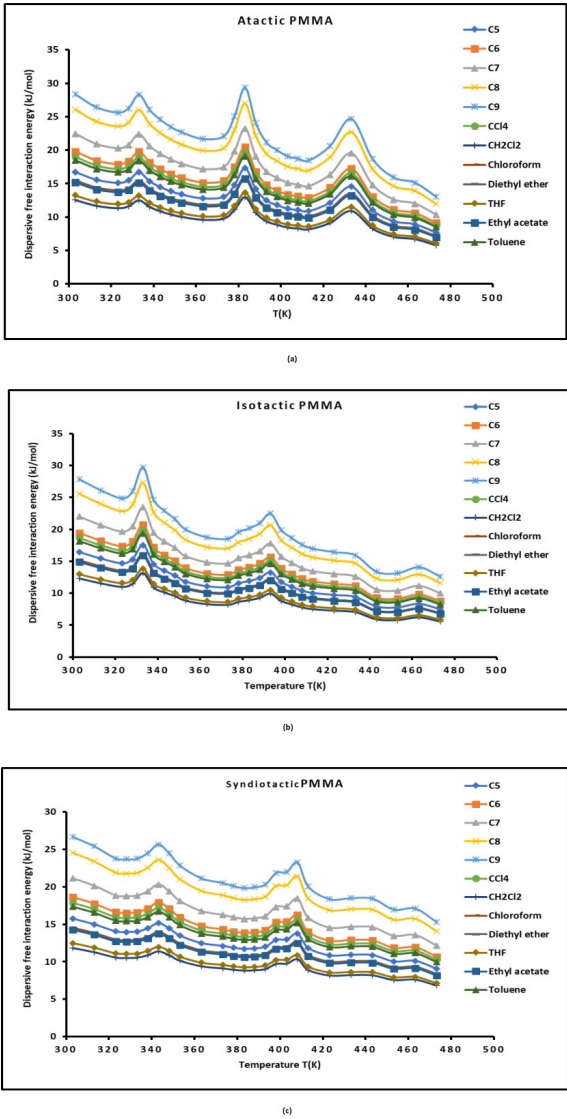


Figure 5. Dispersion free energy ($-\Delta G_a^d(T)$) (kJ/mol) of polar solvents adsorbed on atactic, isotactic and syndiotactic PMMAs as a function of the temperature: **(a)** atactic PMMA, **(b)** atactic PMMA, and **(c)** isotactic PMMA.

The values of the dispersion factor A and the separation distance H of the various PMMA polymers deduced from equation 5 were given in Table S5. The curves of A and H also showed the presence of the three transition temperatures of the various PMMAs (Figure 6) with a shift in their values from tactic PMMA to another. Even if one observed slight variations of the parameters A and H against the temperature, the transition phenomena were clearly elucidated.

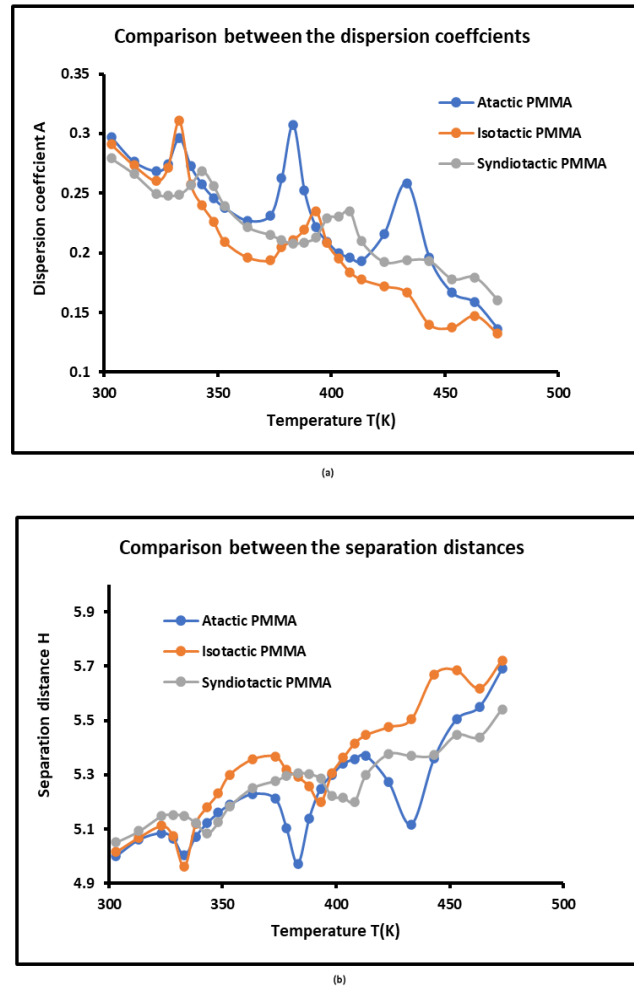


Figure 6. Variations of the dispersion coefficient A (a) and separation distance H (b) of atactic, isotactic and syndiotactic PMMAs as a function of the temperature.

It was shown in Figure 6b that the average separation distance H between the solvents adsorbed on PMMA surfaces increased when the temperature increased justifying the effect of the thermal agitation on the separation distance. A larger separation distance was observed with the isotactic PMMA with the respect of the two other PMMAs, certainly due to the lower attractive free interaction energy.

3.5. Lewis Acid-Base Surface Energies of PMMAs and Polar Component of the Surface Energy of Polar Molecules

The Lewis acid γ_s^+ and base γ_s^- surface energies of atactic, isotactic, and syndiotactic PMMA were determined using the following Van Oss's relation [67]:

$$-\Delta G_a^p(X - Polar) = 2N a_X \left(\sqrt{\gamma_{IX}^- \gamma_s^+} + \sqrt{\gamma_{IX}^+ \gamma_s^-} \right) \quad (12)$$

Where γ_{IX}^+ and γ_{IX}^- are the respective acid and base surface energies of the polar molecule X adsorbed on polymer surface with a_X the surface area of the adsorbed solvent.

Knowing that the experimental values of Lewis acid-base energies of ethyl acetate (EA) and dichloromethane (CH_2Cl_2) are respectively given by $\gamma_{EA}^+ = 0$, $\gamma_{EA}^- = 19.2 \text{ mJ/m}^2$ and $\gamma_{\text{CH}_2\text{Cl}_2}^+ = 5.2 \text{ mJ/m}^2$, $\gamma_{\text{CH}_2\text{Cl}_2}^- = 0$; we were able to determine the values of γ_s^+ and γ_s^- of PMMAs by using equations (13):

$$\begin{cases} \gamma_s^+ = \frac{[\Delta G_a^{sp}(T) (EA)]^2}{4N^2[a(EA)]^2\gamma_{EA}^-} \\ \gamma_s^- = \frac{[\Delta G_a^{sp}(T) (CH2Cl2)]^2}{4N^2[a(CH2Cl2)]^2\gamma_{CH2Cl2}^+} \end{cases} \tag{13}$$

The polar acid-base surface energy γ_s^{AB} of PMMAs was then determined from equation (14):

$$\gamma_s^{AB} = 2\sqrt{\gamma_s^+\gamma_s^-} \tag{14}$$

The determination of γ_s^{AB} of PMMAs with the values of the London dispersive surface energy previously discussed in this paper, led to the determination of the Lifshitz – Van der Waals (LW) surface energy γ_s^{LW} (or total surface energy of the polymer) by using equation (21):

$$\gamma_s^{LW} = \gamma_s^d + \gamma_s^{AB} \tag{15}$$

The values of the different polar acid and base surface energies γ_s^+ , γ_s^- , and γ_s^{AB} (mJ/m²) of atactic, isotactic and syndiotactic PMMAs as a function of the temperature were given in Table 7.

The atactic PMMA exhibited the highest polar basic surface energy γ_s^- , whereas the syndiotactic PMMA presented the highest polar acid surface energy. However, the atactic PMMA had the highest polar acid-base surface energy γ_s^{AB} due to its highest amphoteric character.

Table 7. Values of the polar acid and base surface energies γ_s^+ , γ_s^- , and γ_s^{AB} (mJ/m²) of atactic, isotactic and syndiotactic PMMAs as a function of the temperature.

T(K)	Atactic PMMA			Isotactic PMMA			Syndiotactic PMMA		
	γ_s^-	γ_s^+	γ_s^{AB}	γ_s^-	γ_s^+	γ_s^{AB}	γ_s^-	γ_s^+	γ_s^{AB}
303.15	203.75	108.73	297.68	123.27	90.13	210.82	151.82	69.97	206.14
313.15	183.42	101.70	273.16	115.44	84.06	197.02	143.04	65.44	193.50
323.15	169.77	96.59	256.11	109.56	79.16	186.25	133.06	59.99	178.69
328.15	167.38	95.20	252.46	112.78	80.16	190.16	130.89	59.37	176.30
333.15	171.41	95.61	256.03	125.91	86.53	208.76	129.50	59.34	175.32
338.15	156.91	90.97	238.96	106.91	75.36	179.52	130.68	61.25	178.94
343.15	146.17	87.28	225.89	100.41	71.04	168.91	133.41	64.53	185.56
348.15	137.38	84.13	215.02	95.56	67.65	160.81	127.25	60.68	175.74
353.15	130.01	81.38	205.72	89.82	63.79	151.39	119.60	55.66	163.18
363.15	118.03	76.64	190.22	84.91	59.76	142.47	110.49	50.45	149.32
373.15	111.70	73.58	181.32	83.16	57.51	138.31	105.40	48.28	142.68
378.15	118.18	74.88	188.14	85.83	58.30	141.48	102.57	46.95	138.79
383.15	129.80	77.62	200.74	87.09	58.32	142.53	100.32	46.05	135.93
388.15	107.09	70.48	173.76	89.07	58.72	144.64	99.29	46.10	135.31
393.15	94.01	65.98	157.52	93.16	60.20	149.77	99.14	46.82	136.26
398.15	87.01	63.28	148.40	84.75	55.19	136.79	102.80	50.62	144.27
403.15	81.01	60.87	140.44	80.55	52.40	129.94	101.53	50.77	143.59
408.15	80.65	61.82	141.22	77.02	49.97	124.08	101.82	51.59	144.95
413.15	73.10	57.31	129.46	74.87	48.29	120.25	92.89	45.13	129.50
423.15	73.07	56.31	128.29	72.51	45.96	115.46	85.25	40.62	117.70
433.15	78.33	57.00	133.64	70.27	43.74	110.89	83.23	40.53	116.15
443.15	56.38	48.50	104.59	62.22	38.64	98.07	94.44	48.59	135.48
453.15	45.40	43.84	89.22	60.93	37.02	94.99	73.62	36.11	103.13
463.15	39.51	40.86	80.36	62.44	36.80	95.87	71.77	36.02	101.68
473.15	30.81	36.16	66.75	56.99	33.15	86.93	63.57	31.50	89.50

The values in Table 7 led to draw the curves of Figure 7 giving the polar acid-base surface energy γ_s^{AB} (mJ/m²), the London dispersive surface energy γ_s^d (mJ/m²), and the Lifshitz – Van der Waals surface energy γ_s^{LW} (mJ/m²) of atactic, isotactic and syndiotactic PMMAs as a function of the temperature. It was interesting to notice that the different curves of Figure 7 gave the same shape of the

previous curves obtained in the study of the various surface thermodynamic parameters again highlighting the three transition temperatures of the PMMAs.

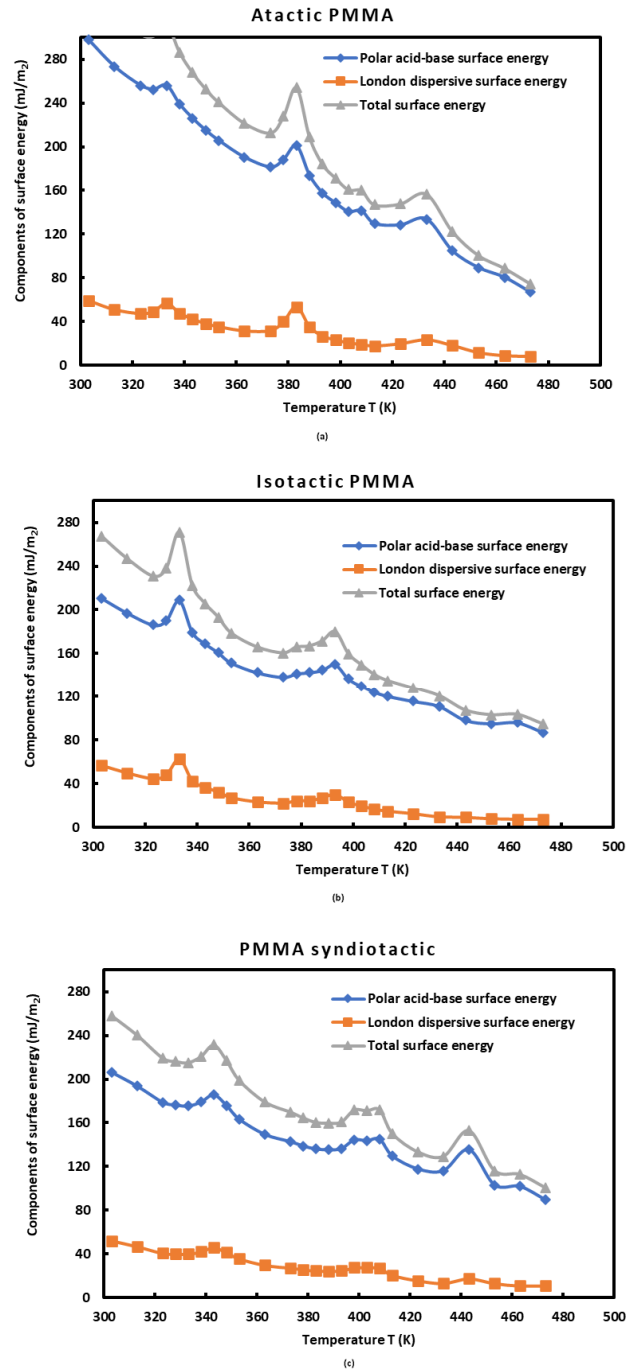


Figure 7. Evolution of the polar acid-base surface energy γ_s^{AB} (mJ/m²), the London dispersive surface energy γ_s^d (mJ/m²), and the Lifshitz – Van der Waals surface energy γ_s^{LW} (mJ/m²) of atactic, isotactic and syndiotactic PMMAs as a function of the temperature.

These results led to the determination of the polar free energy γ_l^p of polar molecules adsorbed on the various PMMAs with the help of the polar components of the surface energy of PMMA γ_s^p using relation 16 and the previous results.

$$\begin{cases} -\Delta G_a^p(X) = 2N a_x \sqrt{\gamma_s^p \gamma_l^p} \\ \text{or } \gamma_l^p = \frac{(-\Delta G_a^p(X))^2}{4N^2 a_x^2 \gamma_s^p} \end{cases} \quad (16)$$

Table S56 reported the values $\gamma_l^p(T)$ of the polar solvents adsorbed on the atactic, isotactic, and syndiotactic PMMAs. The results in Table S6 showed that the highest values of $\gamma_l^p(T)$ was obtained with dichloromethane for the three PMMAs, due to their strong Lewis basicity. However, it was noticed that the different values of $\gamma_l^p(T)$, even if their decrease when the temperature increases, are very small relative to their dispersive components.

4. Conclusions

The effect of tacticity on London dispersive surface energy, polar free energy and Lewis's acid-base surface energies of PMMA was studied. The technique used was the inverse gas chromatography at infinite dilution consisting in the experimental determination of the net retention time and volume of model organic molecules adsorbed on the atactic, isotactic and syndiotactic PMMAs. Our new methodology used in this study was that based on the London dispersion interaction energy applied for the separation of the polar and dispersive energy of the different n-alkanes and polar solvents adsorbed on the different polymer surfaces. The London dispersive component of the surface energy of the different polymers was determined by applying the Hamieh thermal model that took into account the thermal effect on the surface area of molecules adsorbed on the solid surfaces. This study showed non-linear variations of $\gamma_s^d(T)$ of the different PMMAs with three maxima highlighting the three transition temperatures of PMMA, T_g , T_g and $T_{liq-liq}$ with a shift of 10°C in the values of T_g and $T_{liq-liq}$ when passing from atactic-PMMA to isotactic and an additional shift of 10°C in the case of syndiotactic PMMA. The curves of $\gamma_s^d(T)$ were assimilated to four parts of perfect parabolic equations with an important difference in the values of $\gamma_s^d(T)$ between atactic, isotactic and syndiotactic. The polar interaction free energy $\Delta G_a^p(T)$ of polar solvents adsorbed on PMMAs was calculated as a function of the temperature. The variations of $\Delta G_a^p(T)$ also showed the presence of the three transition temperatures of the polymers. The obtained results showed large differences in the behavior of the different polymers. The determination of the Lewis acid-base properties of PMMAs as a function of the temperature. The non-linearity of the different acid-base parameters was observed in all polymer surfaces proving the highest effect of the temperature and the tacticity on these parameters. The results showed that the basicity of the tactic PMMA is about four times greater than its acidity outside the neighborhood of the transition temperatures of the polymer. Whereas, the isotactic PMMA is about 2 to 2.5 times more basic than acid, while the syndiotactic PMMA exhibits the highest basicity by showing a surface 5 to 8 times more basic than acid. The Lewis acid K_A parameter of atactic PMMA had a value comparable to that of the isotactic PMMA, but greater than that of syndiotactic PMMA. However, the basicity of the latter polymer was higher than those of atactic and isotactic PMMAs.

It was shown that the average separation distance between the organic molecules and the polymers depends on the temperature. It increased when the temperature increased. The slight variations of the separation distance also highlighted the three transition temperatures of the different PMMAs.

This work also determined the values of polar acid-base surface energy γ_s^{AB} (mJ/m²), the London dispersive surface energy γ_s^d (mJ/m²), and the Lifshitz – Van der Waals surface energy γ_s^{LW} (mJ/m²) of atactic, isotactic and syndiotactic PMMAs as a function of the temperature. The curves representing the variations of these surface parameters showed the same tendency of the curve shape highlighting the three transition temperatures of the PMMAs.

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Table S1. Values of $(RT \ln V_n)$ in kJ/mol) of organic solvents adsorbed on PMMA particles as a function of the temperature for the different tacticities. Table S2. Values (in kJ/mol) of polar enthalpy $(-\Delta H_a^p(T))$ of polar solvents adsorbed on the various PMMAs as a function of the temperature different temperatures. Table S3. Values (in kJ/mol) of polar entropy $(-\Delta S_a^p(T))$ of polar solvents adsorbed on the various

PMMA as a function of the temperature different temperatures. Table S4. Values of (London dispersive free energies $\Delta G_a^d(T)$ in kJ/mol) of organic solvents adsorbed on the various PMMA particles as a function of the temperature for the different tacticities. Table S5. Values of the dispersion coefficient A and separation distance H of atactic, isotactic and syndiotactic PMMAs as a function of the temperature. Table S6. Values (in mJ/m²) of the polar free energy γ_l^p of the polar molecules adsorbed on the various PMMAs as a function of the temperature different temperatures

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