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Article

New Advances on the Dispersive and Polar Surface Properties of Poly(styrene-co-butadiene) Using Inverse Gas Chromatography

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Abstract: The dispersive and polar properties of materials, and especially of polymers and copolymers play an important role in several engineering applications implying their surfaces and interfaces. The surface energetic properties of poly(styrene-co-butadiene) have never been studied. We proposed in this study an accurate determination of such properties by using the inverse gas chromatography (IGC) at infinite dilution. Background: The IGC surface technique led to the dispersive and polar properties of poly(styrene-co-butadiene) rubber (SBR) by adsorption of organic solvents at various temperatures. Methods: Our new methodology based on the thermal Hamieh model and the London dispersion interaction energy was used to determine the London dispersion surface energy, the polar acid-base surface energy, and the Lewis acid-base properties of the copolymer. Results: The different surface energy parameters of the SBR were obtained as a function of temperature from the chromatographic measurements. Conclusions: The dispersive and polar free energies of adsorption of the various n-alkanes and polar molecules on poly(styrene-co-butadiene) were determined at different temperatures. A decrease of the London dispersive surface energy and the polar Lewis acid-base surface energies of SBR was highlighted when the temperature increased. It was showed a Lewis amphoteric character of poly(styrene-co-butadiene) with a highest basic constant 10 times larger than its acidic constant.

Keywords: retention volume; adsorption; organic solvents; Hamieh thermal model; London dispersive interaction energy; deformation polarizability; Dispersive and polar surface energy; Lewis's acid-base constants; molecular separation distance

1. Introduction

One of the most widely used synthetic rubbers is the poly(styrene-co-butadiene) (SBR rubber) considered as the most interesting copolymer because of its low manufacture cost and excellent properties, and especially to replace the natural rubber in practically in all industrial uses and applications [1,2].

SBR materials are not only used in the manufacturing of tires, but also in several engineering applications such as roofing barriers, cover trips, wires, footwear, and sport goods. They are also used in reinforced form with inorganic fillers [3–9]. The improvement of the properties of SBR rubber was developed in the literature. Radhakrishnan et al. [10] studied the thermal behaviour of SBR/poly (ethylene-co-vinyl acetate) (EVA) blends. They improved the SBR thermal stability by addition of compatibilizer. Other works were devoted to the determination of the flammability of rubbers, the toxicity of the thermal decomposition, and the combustion products of the vulcanizates [11,12]. Vo et

al. [13] measured the dielectric properties of styrene–butadiene rubber (SBR) composites and deduced the polymer relaxation at the polymer–nanoparticle interface. By adding some fillers such as clays, silica, and carbon black into SBR matrices, it was possible to optimize the mechanical properties [14–25].

Some chemical parameters of SBR were determined by several authors. Diez et al. [26] investigated the solubility, the Flory–Huggins interaction parameters of SBR, and the infinite dilution activity coefficients of various solvents by using the inverse gas chromatography technique. The heat of vaporization and the Hansen solubility parameter of binary solvent poly (styrene-block-butadiene) rubber systems were determined by Benguergoura et al. [27] by investigation of both polar and nonpolar solvents using IGC technique. Whereas, Farshchi et al. [28] used the solubility parameter of SBR to predict the compatibility of solvents with polymer and its interaction parameters.

However, the surface thermodynamic properties of the poly(styrene-co-butadiene) such as the free energy, the enthalpy, and entropy of adsorption, the dispersive and polar surface energies, and the Lewis acid-base properties of this copolymer, were not accurately determined in the literature. This study was devoted to the application of our new methodology for the determination of the different surface thermodynamic parameters of poly(styrene-co-butadiene) using the inverse gas chromatography at infinite dilution [29–39]. This powerful technique experimentally allowed obtaining the net retention time of the n-alkanes and polar solvents adsorbed on the copolymer at different temperatures. The obtained chromatographic measurements led to the London dispersive surface energy of SBR as a function of the temperature using the Hamieh thermal model [40–43] and Fowkes relation [44]. This new model proposed new expressions of the surface area of the adsorbed organic molecules versus the temperature [40] and allowed determining more accurate values of the London dispersive surface energy. Whereas, the polar contributions of the different thermodynamic variables of adsorption were determined applying the London interaction energy given as a function of the deformation polarizability of the various solvents and solid materials [45–51].

2. Materials and Methods

2.1. Solvents and Materials

The poly(styrene-co-butadiene) ($\bar{M}_n = 1.8 \times 10^5 \text{ g/mol}$) and the different n-alkanes, and polar solvents were purchased from Sigma-Aldrich (Beirut, Lebanon). The n-alkanes were the following: n-pentane, n-hexane, n-heptane, n-octane, and n-nonane. Whereas the polar solvents characterized by their donor (DN in J/mol) and acceptor (AN in J/mol) numbers of electrons [52,53] were given as follows:

- The Lewis's acid solvents such as chloroform ($DN=0$, $AN=22.54$) and dichloromethane ($DN=5.02$, $AN=16.27$)
- The amphoteric solvents such as: benzene ($DN=0.42$, $AN=0.72$), ethanol ($DN=80.35$, $AN=43.27$), acetonitrile ($DN=59.01$, $AN=19.65$), and toluene ($DN=16.32$, $AN=3.98$)
- The Lewis's base solvents such as: acetone ($DN=71.15$, $AN=10.49$), ethyl acetate ($DN=71.56$, $AN=6.39$), diethyl ether ($DN=80.35$, $AN=5.91$), cyclohexane ($DN=5.89$, $AN=0.17$), and tetrahydrofuran (THF) ($DN=83.70$, $AN=2.29$)

2.2. Inverse Gas Chromatography

A Focus GC gas chromatograph (Sigma-Aldrich, France) equipped with a flame ionization detector of high sensitivity was used to carry out the measurements of the retention times of the organic solvents adsorbed on SBR copolymer. A stainless-steel column of length 30 cm and 2 mm internal diameter contained 0.5 g of SBR powder. The flow rate of helium used as a carrier gas was optimized to 20 mL/min. A Hamilton microsyringes of a volume of 1 μL was used for the injection of infinite quantity of organic probes for temperatures varying from 30 °C to 70 °C. Each solvent injection was repeated three times to determine the average retention times obtained with a standard deviation of 1%

The net retention time obtained of organic solvents adsorbed on the copolymer was obtained using the methane probe as inert solvent and the first order integration. The net retention volume $V_n(T)$ of the adsorbed solvents was directly deduced as a function of the temperature T from the net retention time measurements.

2.3. Thermodynamic Methods

The net retention volume of the organic probes adsorbed on SBR led to the free energy of adsorption $\Delta G_a^0(T)$ of the different solvents using the following equation:

$$\Delta G_a^0(T) = -RT \ln V_n(T) + C(T) \quad (1)$$

where R is the perfect constant gas, and $C(T)$ a thermodynamic parameter depending on the temperature and the interaction between the solvent and the polymer.

The free energy of adsorption can be written as follows:

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

Where $\Delta G_a^d(T)$ and $\Delta G_a^p(T)$ are respectively the London dispersive and polar interaction energies.

In the case of the adsorption of n-alkanes (non-polar solvents such as) on SBR, the free interaction energy is equivalent to London dispersive energy:

$$\Delta G_a^0(T) = \Delta G_a^d(T) \quad (3)$$

The determination of the London dispersive component γ_s^d of the surface energy of a solid material was first proposed by Dorris and Gray [54] using the Fowkes's relation [55] and correlating the work of adhesion W_a to the free energy of adsorption by the help of the surface area a of adsorbed molecule and the geometric mean of the dispersive components of the liquid solvent γ_l^d and the solid γ_s^d .

$$\Delta G_a^0 = \mathcal{N} a W_a = 2 \mathcal{N} a \sqrt{\gamma_l^d \gamma_s^d} \quad (4)$$

where $\mathcal{N}$ is Avogadro's number.

Dorris and Gray obtained the dispersive component of the surface energy of a solid by taking the following increment $\Delta G_{-CH_2-}^0$ given by Equation 5:

$$\Delta G_{-CH_2-}^0 = \Delta G^0(C_{n+1}H_{2(n+2)}) - \Delta G^0(C_nH_{2(n+1)}) \quad (5)$$

Where $C_nH_{2(n+1)}$ and $C_{n+1}H_{2(n+2)}$ represent the general formula of two consecutive n-alkanes.

The London dispersive surface energy γ_s^d can be then determined by Equation 6:

$$\gamma_s^d = \frac{\left[RT \ln \left[\frac{V_n(C_{n+1}H_{2(n+2)})}{V_n(C_nH_{2(n+1)})} \right] \right]^2}{4 \mathcal{N}^2 a_{-CH_2-}^2 \gamma_{-CH_2-}} \quad (6)$$

Dorris and Gray used the surface area of methylene group with $a_{-CH_2-} = 6 \text{ \AA}$, independent from the temperature, and the surface energy γ_{-CH_2-} of methylene group given by the following Equation:

$$\gamma_{-CH_2-} (\text{in mJ/m}^2) = 52.603 - 0.058 T \quad (T \text{ in K}) \quad (7)$$

A similar method to determine γ_s^d was also proposed in the literature [31] (Eq. 8):

$$RT \ln(V_n) = 2 \mathcal{N} a (\gamma_l^d \gamma_s^d)^{1/2} + \alpha(T) \quad (8)$$

Where $\alpha(T)$ is a constant only depending on the temperature and the solid surface.

In the above methods, the London dispersive surface energy of the solvents γ_l^d and the surface areas of molecules and methylene group were supposed independent from the temperature. Other

studies [37] proposed a correction of $\gamma_l^d(T)$ and the use of different molecular models of the surface areas of organic molecules such as the geometric model, cylindrical model, spherical model. Kiselev results, Van der Waals (VDW) equation, and the Redlich-Kwong (R-K) equation [37].

In 2020, we proposed new relations of the surface area $a(T)$ of polar and non-polar molecules and the expression of surface area of methylene group $a_{-CH_2-}(T)$ as a function of the temperature to correct the calculation of the London dispersive surface energy of solid materials [40].

The determination of the polar free energy and the polar enthalpy of adsorption was performed by several authors using different reference thermodynamic parameters such as the boiling point of the solvents [29], the vapor pressure of the probes at a fixed temperature [32,33], the London dispersive surface energy γ_l^d [31], the deformation polarizability [34], or the topological index χ_T [35,36]. However, we showed that these various methods cannot be considered as accurate quantitative methods. The only method theoretically well-founded was that based on the deformation polarizability. However, this method was not correctly used in the literature because of several approximations leading to wrong values of the polar free energy. Recently, we proposed the London dispersion interaction energy given by Equation 9:

$$\Delta G_a^d(T) = -\frac{\alpha_{0S}}{H^6} \left[\frac{3N}{2(4\pi\epsilon_0)^2} \left(\frac{\epsilon_S \epsilon_X}{(\epsilon_S + \epsilon_X)} \alpha_{0X} \right) \right] \quad (9)$$

where ϵ_0 is the dielectric constant of vacuum, α_{0S} and α_{0X} the respective deformation polarizabilities of the solid material denoted by S and the organic solvent denoted by X, separated by a distance H , and ϵ_S and ϵ_X their corresponding ionization energies.

Using the previous equations, Equation 9 can be written as follows:

$$RT \ln Vn = \frac{\alpha_{0S}}{H^6} \left[\frac{3N}{2(4\pi\epsilon_0)^2} \left(\frac{\epsilon_S \epsilon_X}{(\epsilon_S + \epsilon_X)} \alpha_{0X} \right) \right] - \Delta G_a^p(T) + C(T) \quad (10)$$

A new chromatographic interaction parameter $\mathcal{P}_{SX}$ was therefore proposed:

$$\mathcal{P}_{SX} = \frac{\epsilon_S \epsilon_X}{(\epsilon_S + \epsilon_X)} \alpha_{0X} \quad (11)$$

The variations of $RT \ln Vn$ of n-alkanes can be then given by Equation 12:

$$\begin{cases} RT \ln Vn(\text{non-polar}) = A \left[\frac{3N}{2(4\pi\epsilon_0)^2} \mathcal{P}_{SX}(\text{non-polar}) \right] + C(T) \\ A = \frac{\alpha_{0S}}{H^6} \end{cases} \quad (12)$$

where A is a dispersive parameter of the polymer.

The free polar energy $\Delta G_a^p(\text{polar})$ of the adsorbed polar solvents on SBR can be obtained by the following Equation:

$$\Delta G_a^p(T, \text{polar}) = RT \ln Vn(T, \text{polar}) - A \left[\frac{3N}{2(4\pi\epsilon_0)^2} \mathcal{P}_{SX}(\text{polar}) \right] - C(T) \quad (13)$$

The values of $\Delta G_a^p(T, \text{polar})$ obtained by Equation 13 versus the temperature led to the enthalpy ($-\Delta H_a^p$) and entropy ($-\Delta S_a^p$) of adsorption of polar solvents on the copolymer using Equation 14:

$$\Delta G_a^p(T) = \Delta H_a^p - T \Delta S_a^p \quad (14)$$

The determination of the enthalpic (K_A , K_D) and entropic (ω_A , ω_D) Lewis's acid-base constants of PBR copolymer were determined by Equations 15:

$$\begin{cases} (-\Delta H^p) = K_A \times DN + K_D \times AN \\ (-\Delta S_a^p) = \omega_A \times DN + \omega_D \times AN \end{cases} \quad (15)$$

where DN and AN are, respectively, the corrected electron donor and acceptor numbers of the polar molecule.

The London dispersive surface energy $\gamma_s^d(T)$ of PBR as a function of the temperature was obtained using the Hamieh thermal model. Whereas, the polar (or acid-base) contribution of the surface energy $\gamma_s^p = \gamma_s^{AB}$ of the poly(styrene-co-butadiene) was calculated by applying the Van Oss et al.'s method [56] (Equation 16):

$$\gamma_s^p = 2\sqrt{\gamma_s^+ \gamma_s^-} \quad (16)$$

where γ_s^+ and γ_s^- are respectively the Lewis acid and base surface energies of the solid material.

The Van Oss et al. [56] method used two solvents such as ethyl acetate (base B) and dichloromethane (acid A), characterized by the following parameters:

$$\begin{cases} \gamma_A^+ = 5.2 \text{ mJ/m}^2, \gamma_A^- = 0 \\ \gamma_B^+ = 0, \gamma_B^- = 19.2 \text{ mJ/m}^2 \end{cases} \quad (17)$$

Using the expression $\Delta G_a^p(T)$ of the polar solvents given by:

$$\Delta G_a^p(T) = 2Na(T) (\sqrt{\gamma_l^- \gamma_s^+} + \sqrt{\gamma_l^+ \gamma_s^-}) \quad (18)$$

we deduced the Lewis acid and base surface energies of the copolymer by Equations 19:

$$\begin{cases} \gamma_s^+(T) = \frac{[\Delta G_a^p(T)(B)]^2}{4N^2[a_B(T)]^2\gamma_B^-} \\ \gamma_s^-(T) = \frac{[\Delta G_a^p(T)(A)]^2}{4N^2[a_A(T)]^2\gamma_A^+} \end{cases} \quad (19)$$

Therefore, the total surface energy $\gamma_s^{tot.}$ of SBR can be obtained from Equation 20:

$$\gamma_s^{tot.} = \gamma_s^d + \gamma_s^p \quad (20)$$

3. Experimental Results

3.1. London Dispersive Surface Energy of the SBR Copolymer

The chromatographic measurements led to the values of $RT\ln V_n(T)$ of the adsorbed solvents as a function of the temperature. The results were given were given in Tables S1 ((Supplementary Materials). In Figure 1 we gave the evolution of $RT\ln V_n(T)$ of the different organic solvents adsorbed on SBR versus the temperature.

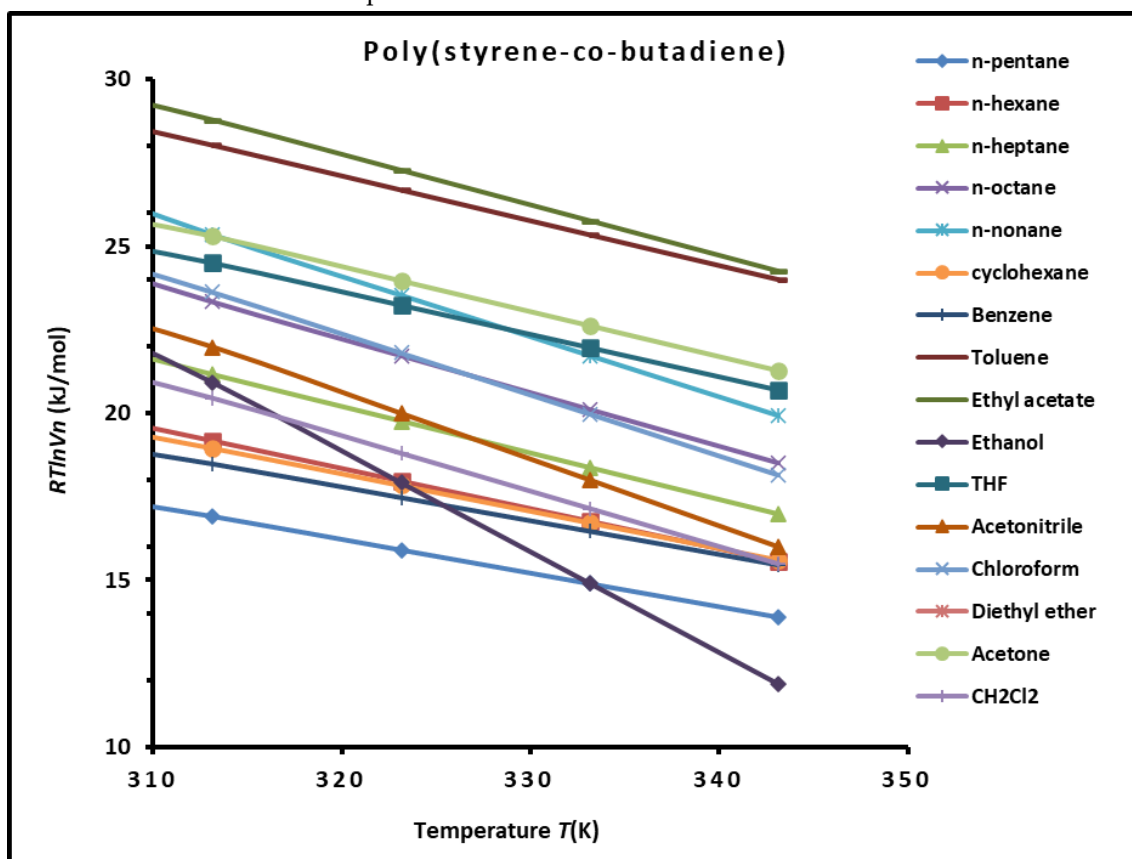


Figure 1. Variations of $RT\ln Vn$ (kJ/mol) of organic solvents adsorbed on poly(styrene-co-butadiene) against the temperature.

The variations of $RT\ln Vn$ of the adsorbed organic solvents adsorbed on PBR shown in Figure 1 showed linear evolution for the solvents. Indeed, the temperature interval is located out of the transition temperatures of the copolymer. This justified the linearity variations of the thermodynamic parameter such as $RT\ln Vn$ as a function of temperature

The representation of $RT\ln Vn$ given in Table S1 versus $2Na(T)\sqrt{\gamma_l^d(T)}$ of n-alkanes adsorbed on SBR at different temperatures led to linear variation of the Londo dispersive surface energy $\gamma_s^d(T)$ using the variations of the surface area $a(T)$ of solvents obtained from the Hamieh thermal model [40]. The results of $\gamma_s^d(T)$ of SBR obtained by applying the other molecular models and that used by Schultz et al. [31] were compared in Figure 2 to those of the Hamieh thermal model [40].

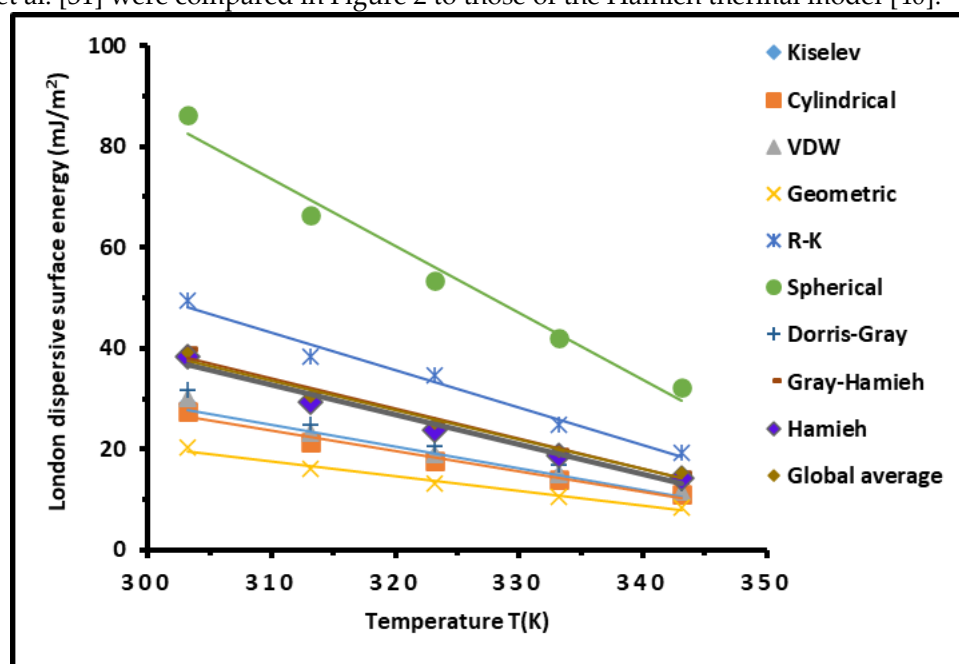


Figure 2. Variations of the London dispersive surface energy γ_s^d (mJ/m^2) of SBR as a function of the temperature T (K) using the different molecular models compared to Hamieh thermal model.

Figure 2 showed large differences in the values of the London dispersive surface energy of SBR obtained from the use of the various molecular models. The highest values of γ_s^d were obtained by the spherical model representing an overestimation of the dispersive surface energy, while the smallest values were those of the geometric model. Whereas, the accurate values were obtained by those of the Hamieh thermal model [40] that took into account the thermal effect on the surface area of organic molecules. The global average obtained by taking the mean average of all models coinciding with the values of the thermal model.

The deviation between the various molecular models and the Hamieh thermal model can be more clarified by determining the equations of $\gamma_s^d(T)$ of the copolymer versus the temperature. The results were given in Table 1 including the values of the dispersive surface entropy ε_s^d , the extrapolated values $\gamma_s^d(T = 0K)$ and the maximum of temperature T_{Max} defined by: $T_{Max} = -\frac{\gamma_s^d(T=0K)}{\varepsilon_s^d}$ for SBR.

Table 1. Equations $\gamma_s^d(T)$ of SBR obtained by the various molecular models compared to the Hamieh thermal model, ε_s^d , $\gamma_s^d(T = 0K)$, and T_{Max} .

Molecular model	$\gamma_s^d(T)$ (mJ/m ²)	$\varepsilon_s^d = d\gamma_s^d/dT$ (mJ m ⁻² K ⁻¹)	$\gamma_s^d(T = 0K)$ (mJ/m ²)	T_{Max} (K)	R ²
Kiselev	$\gamma_s^d(T) = -0.43 T + 158.83$	-0.43	158.83	367.66	0.9809
Cylindrical	$\gamma_s^d(T) = -0.40 T + 148.22$	-0.40	148.22	368.61	0.9815
VDW	$\gamma_s^d(T) = -0.45 T + 165.22$	-0.45	165.22	367.40	0.9808
Geometric	$\gamma_s^d(T) = -0.29 T + 108.25$	-0.29	108.25	370.09	0.9821
Redlich-Kwong	$\gamma_s^d(T) = -0.74 T + 271.53$	-0.74	271.53	368.28	0.9811
Spherical	$\gamma_s^d(T) = -1.32 T + 483.45$	-1.32	483.45	365.59	0.9795
Dorris-Gray	$\gamma_s^d(T) = -0.45 T + 165.93$	-0.45	165.93	371.13	0.9817
Gray-Hamieh	$\gamma_s^d(T) = -0.60 T + 219.89$	-0.60	219.89	366.91	0.9799
Hamieh	$\gamma_s^d(T) = -0.59 T + 215.36$	-0.59	215.36	365.45	0.9793
Global average	$\gamma_s^d(T) = -0.59 T + 215.19$	-0.59	215.19	367.5	0.9824

The results given in Table 1 showed that the Hamieh thermal model applied to Dorris-Gray method and Fowkes equation gave identical values of ε_s^d , $\gamma_s^d(T = 0K)$, and T_{Max} compared to the averages values, whereas, a large deviation was observed with the other models. However, all molecular models approximately gave the same values of the maximum temperature $T_{Max} = 367.5 \pm 2.5$ K. This temperature can be considered as an important thermodynamic intrinsic characteristic of the copolymer.

3.3. Variations of Polar Free Surface Energy ($-\Delta G_a^p(T)$) of SBR Copolymer

Using the Equations 9 to 14 relative to the adsorption of n-alkanes and polar molecules on SBR copolymer, we obtained the variations of the polar free surface energy ($-\Delta G_a^p(T)$) of polar solvents versus the temperature. The results given in Table S2 allowed classifying the polar solvents in increasing order of their polar free interaction energy ($-\Delta G_a^p(T)$) as follows:

Cyclohexane < Benzene < Dichloromethane < Chloroform < Toluene < THF < Ethanol < Acetonitrile < Ethyl acetate < Acetone < Diethyl ether

The above classification slightly varied when the temperature increases from 303.15K to 343.15 for solvents such as THF, ethanol, and acetonitrile. The results showed that the highest values of ($-\Delta G_a^p(T)$) was obtained with diethyl ether proving the highest basic character of the copolymer (Figure 3).

The curves plotted in Figure 3 showed linear variations of ($-\Delta G_a^p(T)$). This linearity is due to the temperature interval that was located outside of the transition temperature of SBR.

The different equations of ($-\Delta G_a^p(T)$) were given in Table 2 for the polar molecules. This allowed obtaining the polar enthalpy and entropy of adsorption of the various polar solvents using Equation 14 and consequently led to the Lewis acid-base constants of the copolymer.

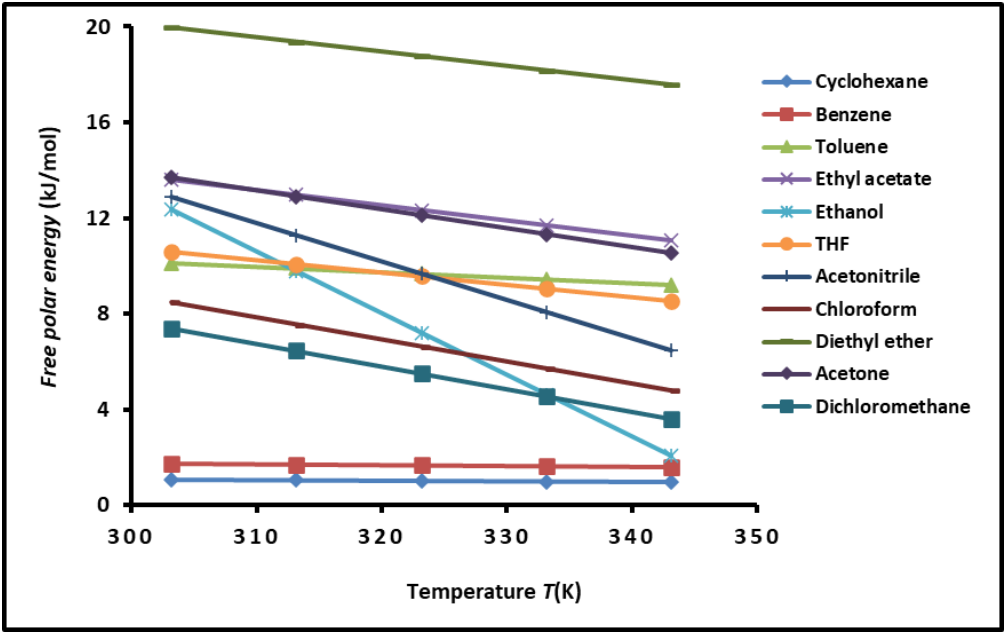


Figure 3. Variations of the polar free interaction energy ($-\Delta G_a^p(T)$) (kJ/mol) of polar organic molecules adsorbed on SBR copolymer as a function of temperature.

Table 2. Equations of the polar free energy ($-\Delta G_a^p(T)$) as a function of temperature for the different polar solvents adsorbed on SBR.

Probes	Equation of ($-\Delta G_a^p(T)$) (kJ/mol))
Cyclohexane	$(-\Delta G_a^p(T)) = -0.0032T + 2.060$
Benzene	$(-\Delta G_a^p(T)) = -0.0027T + 2.542$
Toluene	$(-\Delta G_a^p(T)) = -0.023T + 17.108$
Ethyl acetate	$(-\Delta G_a^p(T)) = -0.0627T + 37.598$
Ethanol	$(-\Delta G_a^p(T)) = 0.2574T + 90.377$
THF	$(-\Delta G_a^p(T)) = -0.0522T + 26.434$
Acetonitrile	$(-\Delta G_a^p(T)) = -0.1103T + 91.466$
Chloroform	$(-\Delta G_a^p(T)) = 0.0918T + 76.300$
Diethyl ether	$(-\Delta G_a^p(T)) = -0.0593T + 37.928$
Acetone	$(-\Delta G_a^p(T)) = -0.0791T + 57.669$
Dichloromethane	$(-\Delta G_a^p(T)) = -0.0689T + 36.204$

3.4. Lewis Acid-Base Constants of Poly(styrene-co-butadiene)

The equations of ($-\Delta G_a^p(T)$) given in Table 2 led to the values of the polar enthalpy and entropy of adsorption of the adsorbed polar molecules. The results were given in Table 3.

Table 3. Equations of the polar enthalpy ($-\Delta H_a^p$) and entropy ($-\Delta S_a^p$) of adsorption polar solvents on SBR copolymer as a function of temperature.

Probes	$(-\Delta S_a^p)$ (J/k.mol)	$(-\Delta H_a^p)$ (kJ/mol))
Cyclohexane	3.2	2.060
Benzene	2.7	2.542
Toluene	23.0	17.108

Ethyl acetate	62.7	32.598
Ethanol	257.4	90.377
THF	52.2	26.434
Acetonitrile	160.3	61.466
Chloroform	91.8	36.300
Diethyl ether	59.3	37.928
Acetone	79.1	37.669
Dichloromethane	68.9	36.204

The values in Table 3 allowed drawing in Figure 4 the variation of $(-\Delta H_a^p)/AN$ and $(-\Delta S_a^p(T))/AN$ of the adsorbed organic molecules as a function of their DN/AN .

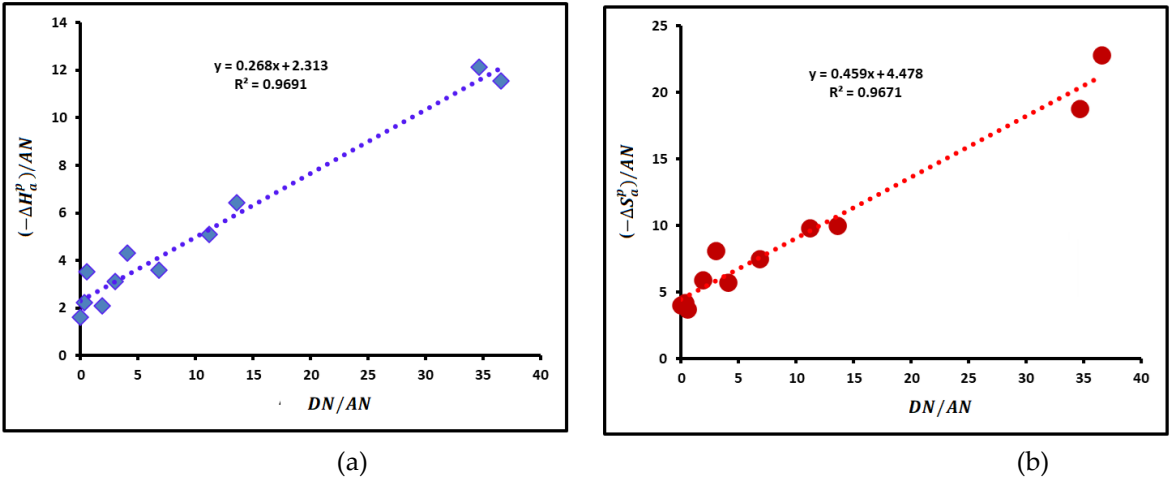


Figure 4. Variations of $(-\Delta H_a^p)/AN$ (a) and $(-\Delta S_a^p(T))/AN$ (b) of the various organic solvents adsorbed on SBR as a function of the ratio of donor number on acceptor number of electrons DN/AN of the polar molecules.

The linear variations of $(-\Delta H_a^p)/AN$ and $(-\Delta S_a^p(T))/AN$ shown in Figures 4 led to the values of the enthalpic and entropic Lewis acid-base constants of the SBR copolymer using Equations 15. The results given in Table 4 clearly showed the highest basic character of the poly(styrene-co-butadiene). The highest donor capacity of electrons of SBR led to a Lewis basicity which is about 8.6 times larger than its acidity. A similar result was observed in the values of the Entropic Lewis acid and base of SBR.

Table 4. Values of the various enthalpic (K_A, K_D) and entropic (ω_A, ω_D) Lewis's acid-base constants of the SBR copolymer, with the corresponding linear regression coefficients.

Lewis's acid-base parameter	Values	R ²
K_A	0.268	0.9691
K_D	2.313	0.9691
K_D/K_A	8.631	0.9691
$(K_D + K_A)$	2.581	0.9691
$10^3 \times \omega_A$	0.459	0.9671
$10^3 \times \omega_D$	4.478	0.9671
ω_D/ω_A	9.756	0.9671
$10^3 \times (\omega_D + \omega_A)$	4.937	0.9671

The comparison of the results obtained with the poly(styrene-co-butadiene) to those obtained in a recent study [57] with another copolymer such as polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) showed that SBR is 3.5 times more basic and 2.8 more acidic than PS-*b*-P4VP. This is certainly due to the presence of butadiene in SBR copolymer that exhibits larger Lewis acid-base constants.

3.5. Dispersive Free Energy and Interaction Distance Between the Solvents and SBR Copolymer

Using the London interaction equation and the chromatographic data, we determined the dispersive free energy of interaction between the different solvents and the copolymer. The results given in Table S3 were plotted in Figure 5.

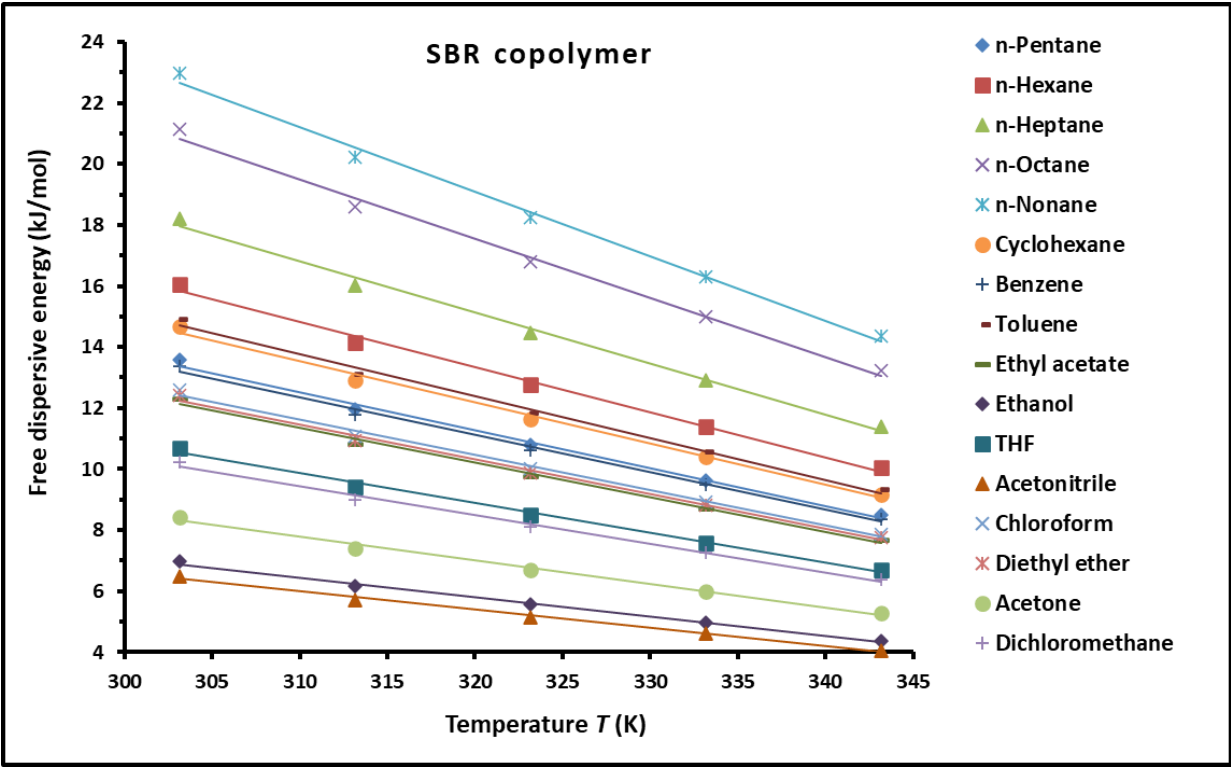


Figure 5. Variations of the free dispersive energy ($-\Delta G_a^d(T)$) of the different organic solvents adsorbed on the SBR as a function of the temperature T (K).

The curves in Figure 5 showed linear variations of the free dispersive energy ($-\Delta G_a^d(T)$) of all adsorbed organic solvents versus the temperature T (K). The highest value of the free dispersive energy was obtained in the case of n-alkanes exhibiting the highest carbon atom number.

The values of the free dispersive energy of adsorption led to those of the interaction distance H between the solvents and the copolymer. In Figure 6, we plotted the evolution of $H(T)$ against the temperature. A linear variation of $H(T)$ was obtained. The separation distance increased when the temperature increased. This is totally in good agreement with the concept of the thermal agitation.

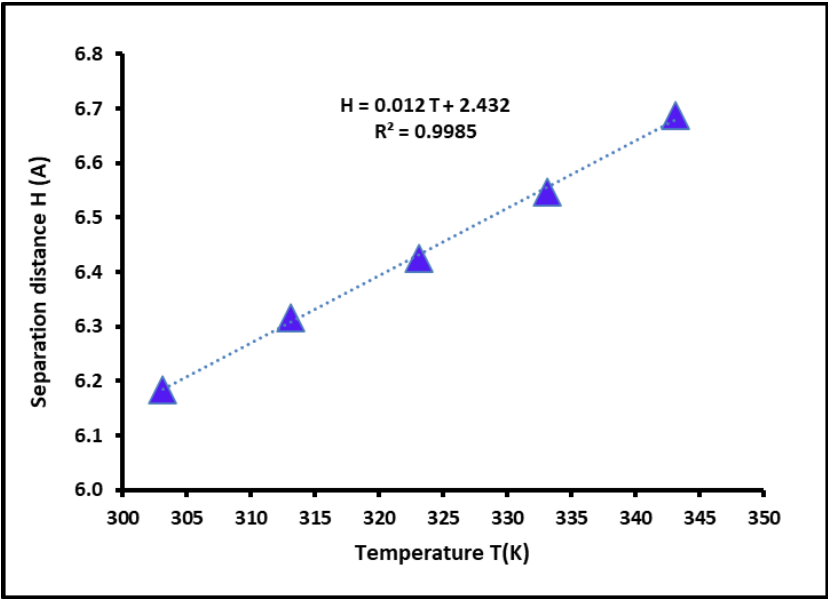


Figure 6. Variations of the interaction distance $H(T)$ (Å) of the SBR as a function of temperature T (K).

3.6. Determination of Polar Acid-Base Surface Energies and Total Surface Energy of the Copolymer

The values of the polar Lewis acid γ_s^+ and base γ_s^- surface energies of the SBR copolymer with respect of temperature were obtained by applying the Van Oss et al.'s method [56] (Equations 16-19). The polar acid-base surface energy $\gamma_s^{AB} = \gamma_s^p$ of the copolymer was determined using Equation 20. Whereas, the total surface energy of the copolymer $\gamma_s^{tot.}$ was obtained by summing the two polar and dispersive contributions. The values of the different polar acid and base surface energies of the SBR given in Table 5 allowed drawing their variations in Figure 7 as a function of temperature.

Table 5. Values of the polar acid and base surface energies γ_s^+ , γ_s^- , the polar surface energy γ_s^p , the London dispersive surface energy γ_s^d , and the total surface energy $\gamma_s^{tot.}$ (mJ/m²) of the SBR copolymer versus the temperature.

T(K)	γ_s^-	γ_s^+	γ_s^p	γ_s^d	$\gamma_s^{tot.}$
303.15	56.95	28.17	80.11	38.36	118.47
313.15	41.59	25.10	64.62	29.47	94.08
323.15	29.09	22.26	50.90	23.75	74.65
333.15	19.17	19.65	38.82	18.69	57.50
343.15	11.57	17.25	28.25	14.28	42.53

The comparison between the different surface energy components of the copolymer showed the highest values of polar acid surface energy due to the highest basic character of the surface groups of the copolymer blocks. The results in Table 4 showed that the London dispersive surface energy is equivalent to the half of the polar surface energy of the PS-*b*-P4VP diblock copolymer, whereas, the lowest surface energy was obtained for the basic surface energy component, because of the weaker acid force of the surface groups of the copolymer.

The variations of the various surface energy components plotted in Figure 7.

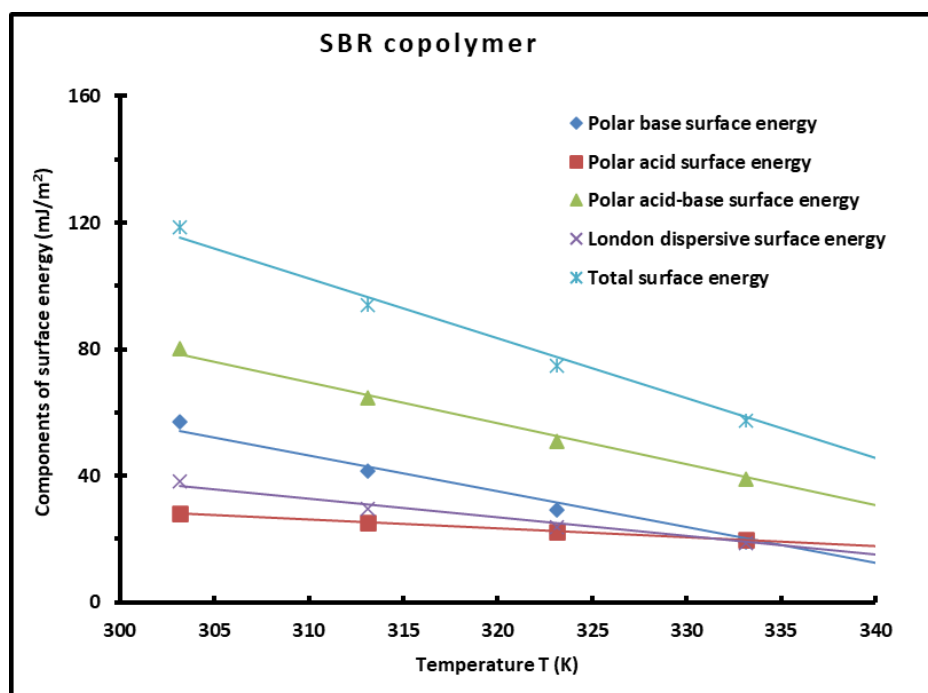


Figure 7. Variations of the polar acid and base surface energies γ_s^+ , γ_s^- , the polar surface energy γ_s^p , the London dispersive surface energy γ_s^d , and the total surface energy γ_s^{tot} . (mJ/m²) of the SBR as a function of the temperature.

Figure 7 clearly showed linear variations of the surface energy components of SBR copolymer. This linearity is a direct consequence of non-existence of transition temperatures in the interval temperature [300K, 350K]. In several previous works, a non-linear variation of the different components of the surface energy of polymers was observed around the transition temperatures was proved with the presence of a maximum of surface energy at these temperatures. [61–63,77].

Furthermore, knowing the polar free energy ($-\Delta G_a^p(X)$) of a polar molecule (X) with a surface area a_X and the polar surface energy γ_s^p of SBR copolymer, we determined the polar surface energy $\gamma_l^p(X)$ of the organic molecules using Equation 21:

$$\gamma_l^p(X) = \frac{(-\Delta G_a^p(X))^2}{4N^2 a_X^2 \gamma_s^p} \quad (21)$$

The polar surface energy $\gamma_l^p(X)$ of the solvents adsorbed on SBR was then calculated for the different temperatures versus the temperature and represented in Figure 8. An increase of the polar surface energy of the solvents was observed when the temperature increased, except for ethanol where a decrease of γ_l^p was found. The results in Figure 8 showed that the highest value of γ_l^p was obtained with diethyl ether and acetone adsorbed on SBR, due to the highest basic character of the copolymer.

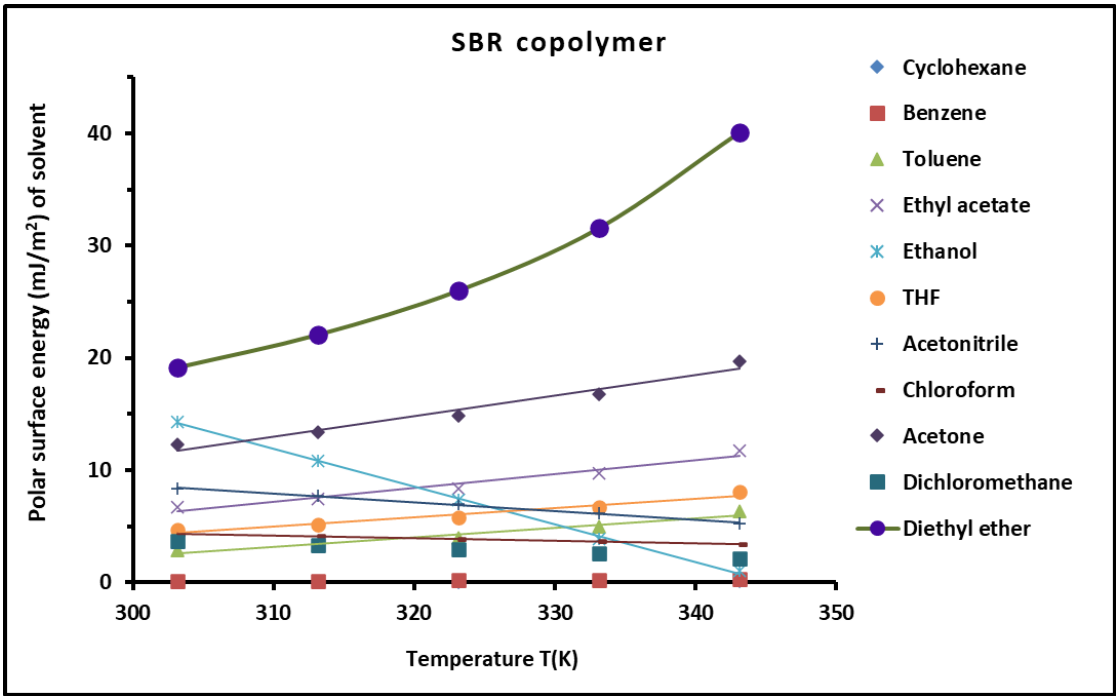


Figure 8. Evolution of the polar component of the surface energy $\gamma_I^p(T)$ (mJ/m²) of polar solvents adsorbed on the SBR copolymer as a function of temperature. .

4. Conclusions

The inverse gas chromatography technique at infinite dilution was utilized for the determination of the surface energetic properties of poly(styrene-co-butadiene) as a function of temperature. Several molecular models were applied to calculate the London dispersive surface energy of SBR copolymer. The obtained results were corrected by applying the Hamieh thermal model taking into account the temperature effect. A linear relation of the London dispersive surface energy $\gamma_s^d(T)$ of SBR was obtained as a function of temperature showing a decrease in the values of $\gamma_s^d(T)$ when the temperature increased. An intrinsic maximum temperature of the copolymer equal to 365.5K was observed.

The London interaction equation was used to quantify the polar free energy, the polar enthalpy, and the polar entropy of organic solvents adsorbed on the poly(styrene-co-butadiene). This recently proved to be the more accurate chromatographic method to determine the physicochemical properties of solid materials such as the Lewis acid-base parameters and the polar acid-base surface energy of polymers. The results showed that SBR copolymer is 8.63 times more basic than acidic with an acidic constant equal to 2.313 and a basic constant of 0.268. It was also showed an interaction distance H between the solvents and the copolymer increasing with the temperature and varying from 6 Å to 6.9 Å governed by the following equation $H(T) = 0.012T + 2.432$.

The application of our new method led to values of the acid γ_s^+ and base γ_s^- surface energies, the polar acid-base surface energy γ_s^p , the London dispersive surface energy γ_s^d , and the total surface energy $\gamma_s^{tot.}$ of the copolymer for the different temperatures. The variations of the different components were obtained as a function of temperature and given in the following table:

Surface energy component	Equation
Polar base surface energy	$\gamma_s^-(T) = -1.132T + 397.42$
Polar acid surface energy	$\gamma_s^+(T) = -0.273T + 110.70$
Polar acid-base surface energy	$\gamma_s^p(T) = -1.295T + 471.08$
London dispersive surface energy	$\gamma_s^d(T) = -0.590T + 215.36$
Total surface energy	$\gamma_s^{tot.}(T) = -1.885T + 686.43$

All surface energy components of SBR copolymer linearly decreased when the temperature increased

Supplementary Materials: The following supporting information can be downloaded at the website of this paper posted on Preprints.org, Table S1. Values of $RT\ln V_n$ (kJ/mol) of solvents adsorbed on SBR as a function of the temperature. Table S2. Variations of the polar free energy $\Delta G_a^p(T)$ (kJ/mol) of different polar solvents adsorbed on SBR copolymer as a function of temperature. Table S3. Variations of dispersive free energy $\Delta G_a^d(T)$ (kJ/mol) of different solvents adsorbed on SBR copolymer as a function of temperature.

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