Synthesis by ATRP of Polystyrene-b-Poly(4-vinylpyridine) and Characterization by Inverse Gas Chromatography

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Abstract: A linear diblock copolymer [Polystyrene-b-Poly(4-vinyl-pyridine)] (PS-b-P4VP) was successfully prepared through Atom Transfer Radical Polymerization (ATRP). This synthesis is performed in two successive steps: using the (1-bromoethyl) benzene as initiatorand and Hexamethyl tris [2(dimethylamino)ethyl] amine as ligands in a protic solvent. The first step of the synthesis allows the realization of block polystyrene having a terminal function; however, Bromine (Br) permits the grafting of the second successive block P4VP. RMN -1H demonstrates that the P4VP block has been grafted onto the PS block. The molecular weight of PS-b-P4VP is determined by size exclusion chromatography, and its thermal stability is examined by TGA. The surface and the thermodynamic properties of this copolymer are studied by inverse gas chromatography (IGC). The new Hamieh Model shows that the synthesized copolymer PS-P4VP has an amphoteric behavior with rather very basic character that is six times stronger than acidic character (in Lewis terms), reflected the presence of acidic and basic groups in the structure of the PS-P4VP copolymer, more particularly the presence of benzenic, methyl and vinylpyridine groups.

Keywords: Radical polymerization, Polystyrene-b-Poly(4-vinylpyridine), Inverse Gas Chromatography, Specific interactions, Acid and Base Constants.

INTRODUCTION

The large family of soft polymer contains a special class of polymers "Block Copolymers" [1]. These latter can be used for consisting at least two fragment of different chemical nature of the polymer, joined together by a junction of covalent bond type.

The synthesis of block copolymers of well-defined structure and composition was carried out by various polymerization techniques: anionic polymerization [2-4], cation polymerization [5-6], the radical polymerization, using different methods. In these block copolymers, the coupling of the two polymers has the advantage to combine their divergent properties differing in a single structure, the hydrophilic blocks and hydrophobic blocks, or ionic blocks and non-ionic blocks, or rigid blocks, soft blocks, amorphous and crystalline blocks.

The copolymer, polystyrene- poly(4-vinyl pyridine) is revealed to be a very interesting copolymer used for technological applications may for example, to compete with conventional copolymers such as polystyrene-polymethylmethacrylate (PS-PMMA).

The atom transfer radical polymerization ATRP is a type of controlled radical polymerization which appeared in 1994. Balance is based on a redox reaction between a transition metal complex and an alkyl halide [7]. This mechanism results from the concept known as karash effect name. It was developed in parallel by Matyjaszewski [8-9] and Sawamoto [10].

An ATRP system is composed of an initiator, a metal halide or complexed with a ligand and of course monomers.

Figure **1** gives a schematic representation of the mechanism of ATRP. Thus an effective ATRP catalyst comprises a transition metal able to extend its coordination sphere and to increase its degree of oxidation, a complexing ligand (L) and a counter ion that can form a covalent or ionic bond with the metal.

The metal complex (Mt/L) is responsible for the haemolytic cleavage of the RX alkyl- halogen bond

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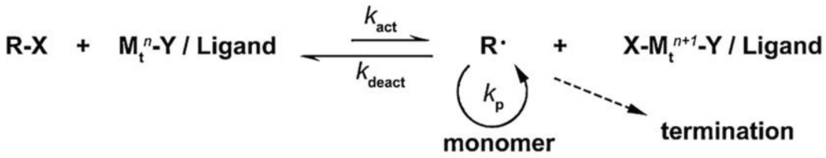

Figure 1: Schematic representation of ATRP mechanism.

which generates the metal complex corresponding to the n+1 oxidation state (n+1 MTX/L) and an organic radical R$^{\bullet}$. The latter can then be spread with a vinyl monomer, with an end or other organic radical or can be reversibly deactivated by MTX n+1 /L to form a dormant polymer chain.

The ATRP is simple to implement and does not require the prior synthesis of complex organic compounds, allow to control the polymerization of all the great families of conjugated monomers such as acrylates, methacrylates and styrenes, can be achieved as in solution or emulsion in water and it allows an excellent functionalization of the polymer ends [11-13].

However the level of control of the polymerization of few conjugated monomers such as vinyl acetate and vinyl chloride is low because the CX bond that is formed weakly reactive and difficult to activate. And the level of control of the polymerization of monomers bearing a chelating group binds to the metal and blocks its action.

Among this decade, Matyjaszewski noted that ATRP is a technique that allows for the synthesis of polymers having a narrow molecular weight distribution (MW) [14], of well–defined block copolymers [15-16] this also enables controlled radical polymerization from the polymerization of a wide range of monomers such as styrenes [17-20] methacrylates [21-22] and a variety of functional monomers.

In particular, the vinyl pyridine (VP) is an attractive monomer having a nucleophilic base pH sensitive. One of these associated polymers, poly (4-vinyl pyridine) linear (P4VP) (based polymer 4VP) and their block copolymers are polymers with high added value due to their broad potential applications.

Of all of these, we can mention, micro and nanostructured polymers [23], the ion exchange resins [24-25], bio sorption on biosensor [26] and microfiltration [27-28].

With regard to the synthesis of homo and some block of VP copolymerization, several approaches have already been performed by ATRP by Matyjaszewski [29] and by other researchers, such as Wan and Yang [30-31].

One of the problems of polymerization by ATRP, 4VP resides in the fact that the monomer 4VP and the block polymer 4VP are strong coordinating ligands which may both contribute to the fixation of the metal catalysts in this system. Matyjaszewski *et al*. [29] have therefore proposed the use of multidentate ligand hexamethyl tris [2 dimethyl amino) ethyl amine] (Me6 – TREN) which can compete with the pyridine units in respect of copper complexation. However, the synthesis of Me6 – TREN is not easy and the product is relatively expensive. Wang [31] selected a macrocyclotetraamine,5,5,7,12,12,14-hexamethyl-1,4,8,1-tetra-azamacrocyclotetradecane (Me6 aneN4) as ligand in the ATRP VP blocks also proved effective, a further alternative has been proposed by Huang [32]; he proposes a radical polymerization by atom transfer in two steps using commercial available ligands such as N,N,N,N,N-pentamethyldiethylenetriamine (PMDETA), 2,2- bipyridine (Bipy), 4,4-dinonyl-2,2dipyridyl (dNBipy), however, still relatively complex synthesis.

Due to this technical difficulty, the polymerists turned to other types of radical polymerization to synthesize PS – P4VP. For example, Zhoe and al. [33] have used the 4-hydroxyl-2,2,6,6-tetramethylpiperidine as a catalyst using NMP (Nitroxyde Mediated Polymerization) technique. Damet and al. [34] were able to prepare PS-P4VP with a polydispersity index DPn of less than 1.13 DPn using 2.2'- azobisisobutyronitrile (Aiban) as catalyst by using RAFAT technology (reversible addition fragmentation transfer).

It is necessary to know the superficial characteristics of polymers in the bulk phase of gold in the adsorbed state in order to understand and forecast of their behaviours. Inverse gas chromatography (IGC) is capable to characterize the area properties (area, energy, heat of adsorption, and specific interaction of the surface area) of polymeric materials [35] and recently pharmaceuticals [36-39].

IGC is a real source of physiochemical data [40]. It can be applied to observe the interaction between polymers and organic solvent systems under the conditions approaching infinite dilution of the volatile component [41]. It can be also used to determine the glass transition temperature (Tg) of polymers or amorphous pharmaceuticals and to study the plasticizing effect of water on these materials [42]. This technique is adequate to determine the Lewis acid-base properties of thermoplastic and thermosetting polymer insulating materials [43] or to analyze the area of cellulosic multipurpose office paper [44]. Many other studies were devoted to conducting polymers by al Saigh and al. [45,46], and Boukerma and al. [47] and Bailey and al. [48]. ICG is also used to determine the solubility parameters of some solid surfaces as titanate modified silica gel [49] or to compare the surface energies of crystalline, amorphous, and ball milled lactose [50], also to determine the heterogeneous surfaces [51] and textile their products and physico-chemical properties [52], and to determine surface energy and surface area of powdered materials [53,54].

The technique of ICG is able to analyze the solvent-solvent interactions [55], the area properties of clays [56,57], nanomaterials and clay-polymer composites [58,59] and nanoparticles with respect to their specific surface area, particle size and morphology [60].

The target of this work is, the synthesis of diblock copolymers of the type PS-P4VP by two successive ATRP using (1-bromoethyl)benzene as an initiator, as well as the characterization of the polymer, and to its physic- chemical properties by IGC.

METHODS OF IGC

IGC Technique

The superficial phenomena, glass transitions, surface energy and acid-base properties of solid materials, for over 30 years, was determined by inverse gas chromatography (IGC) [61]. This technology aimed to identify the changes, as a function of temperature, of the superficial properties of some polymers and of those adsorbed on oxides. Probes of known properties are injected into the column containing the solid. The retention times of these probes, measured at infinite dilution, allow us to determine the interactions between model organic molecules and the solid, if we assume there is no interaction between the probe molecules themselves. Measurements were carried out with a DELSI GC 121 FB chromatograph equipped with a flame ionization detector of high sensitivity. The data retention was obtained with a stainless steel column 15-30 cm long and 2 mm internal diameter packed with 1-2 g of polymer powders.

Retention Volume

The net retention volume V_n, is the volume of carrier gas through the column from the introduction of the probe until the output of the maximum of the peak of the inferred methane retention volume V_0.This volume serves to determine the thermodynamic quantities. It is influenced by the retention time according to the following relation:

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

Where Dc represents the corrected carrier gas given by the following equation (2). The flow rate correction is given by:

$$D_c = j\,D_m\left(1+\frac{P(H_2O)}{P\,atm}\right)\frac{Tc}{Ta} \tag{2}$$

Dm is the measured flow rate of the carrier gas with the bubble flow meter at the outlet of the column. *Tc* and *Ta* are respectively the column temperature and the ambient temperature at the time of flow measurement, *Patm* et P_{H2O} are respectively the atmospheric pressure at the time of analysis and the saturation vapour pressure of water at *Ta*.

The coefficient j for James Martin [62] takes account of the compressibility of the gas in the column under the action of the charge loss *ΔP* in the column:

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

This coefficient is always less than or equal to 1 [63].

The specific retention volume *Vg* is also used; it can report the net retention volume to the unit mass of adsorbent and to the temperature 0 ˚C:

$$V_g = \frac{Vn}{ma}\frac{273}{Tc} \tag{4}$$

Method of Papirer and al.

Several methods were employed to determine first, the specific interactions exchanged between polar molecules and a solid surface as polymers or oxides and second to obtain the acid- base interactions [64-69]. Hamieh and al studied the physicochemical properties of many oxides [70-82] and polymers in bulk phase or when adsorbed on oxides [83-95] by modeling the various models used in inverse gas chromatography and by applying Papirer method [64-66].

Papirer and al. developed the method by giving the most precise specific free enthalpy of interaction between a probe and a solid. When plotting $RT \ln Vn$ against $\ln P_0$, Papirer and al have obtained a straight line, where P_0 is the vapour pressure of the probes [64-66]. For a homologous series of n-alkanes (from n-pentane C5 to n-decane C10), Papirer and al. wrote the following equation:

$$RT \ln Vn = A \ln P_0 + B \tag{5}$$

Where A and B are two constants depending on the nature of the solid substrate. If polar probes (as for example Toluene) are injected into the column, specific interactions are made between these probes and the solid surface and ΔG^0 is now given by:

$$\Delta G^o = \Delta G^d + \Delta G^{SP} \tag{6}$$

We can deduce the various values of the free specific enthalpy ΔG^{SP} of the polar molecules at different temperatures, by using Papirer and al. approach.

Then by plotting ΔG^{SP} of the polar molecules as a function of the temperature from the equation:

$$\Delta G^{SP} = \Delta H^{SP} - T\,\Delta S^{SP} \tag{7}$$

We can deduce the specific enthalpy (ΔH^{SP}) and entropy (ΔS^{SP}) of interaction between the copolymer and the polar molecules.

Determining ΔG_a^{SP} at different temperatures is used to draw the straight line of variation of ΔG_a^{SP} in function of T. The slope of this line is equal to ΔS_a^{SP} and intercepts to ΔHa^{SP}.

The Method of Gutmann

One of the uses of Inverse gas chromatography is to evaluate Lewis type acid- base interactions, exchanged between a solid surface and polar molecules. Gutmann [96] classified the polar molecules by assigning an electron donor (ND) and a number of electron acceptor (NA) which realizes respectively the acidity and the basicity of the molecule. In analogy to the approach of Gutmann, Papirer and al [97] proposed to characterize the solid by two parameters K_A and K_D respectively reflect the basic and the acidic character of the solid. These two constants measure the ability of the solid to develop respectively the acid and base interactions with basic, acidic or amphoteric probes. They are connected to the specific enthalpy ΔH_a^{SP} through the following equation:

$$-\Delta H_a^{SP} = K_A.ND + K_D.NA \tag{8}$$

Where K_A and K_D respectively represent the acidic and the basic character of the solid. Also NA and ND represent the donor number and the electron acceptor of the probe according to the scale of Gutmann [96].

Equation 8 can be written as:

$$\frac{-\Delta Ha^{SP}}{NA} = \frac{ND}{NA} K_A + K_D \tag{9}$$

The representation of $\frac{-\Delta Ha^{SP}}{NA}$ in function of $\frac{ND}{NA}$ gives in general a straight line of slope K_A and intercept K_D.

EXPERIMENTAL

Materials

In this experiment the following materials were used: Styrene (S) and 4-vinylpyridine (4-VP) that were distilled from calcium hydride before use. Cu(II)Br is used in solid state. N,N,N',N'',N''-pentaméthyldiethylenetriamine (PMDETA), Me6-TREN (Tris hexamethyl [2 (dimethylamino) ethyl] amine), toluene, methanol and initiator 1- phenylethylbromide were used without special purification. All chemicals were purchased from the Sigma-Aldrich.

Preparation of PS-Br Macro Initiator by the ATRP of Styrene

A typical polymerization is done as follow: CuBr (0,3mmol) was placed in a 25 mL schlenck tube by 3 cycle's vacuum-nitrogen and it is equipped with a magnetic bar. Toluene (10 mL), styrene (144.3 mmol) and PMDETA (0.3-0.18 mmol) were added sequentially and the solution was stirred for 20 min to form the Cu complex. The initiator 1-phenylethylbromide is then added. The shlenck tube is then placed in a thermostatically controlled oil bath at 110°C and submitted to magnetic stirring.

The appearance of dark green colour is obvious and the mixture becomes progressively more viscous. At the end of reaction, the crude reaction is then diluted in tetrahydrofuran and restless with an amberlites IR-120 (form H) cationic (3-5 g) for 30-60 minutes to eliminate the CuBr /PMDETA catalyst. Then the mixture is passed on a neutral alumina column.

The polymer is then precipitated in excess methanol filtered and dried in vacuum oven at 60°C during the night.

Preparation of PS-b-P4VP by the ATRP of 4-VP

The synthesis of PS-b-P4VP is done as follow. The PS-Br macro initiator was dried overnight in a vacuum oven. By 3 cycles vacuum-nitrogen, CuBr (0.3 mmol) was placed into a dry 25-mL schlenck tube equipped with a magnetic bar. 4-VP (15.9 mmol), methanol (5mL) and Me6- TREN (0.3-0.18 mmol) were added sequentially. The solution is agitated for 20 minutes at room temperature for the formation of the Cu complex. The Macroinitiator (PS-Br) is then added (0.3 mmol). The schlenk tube is then placed in a thermostatically controlled oil bath at 80°C and magnetically stirred. Once a dark green colour appears, the reaction mixture becomes progressively more viscous. Periodically, tests (0.1 mL) are removed for analysis. At the end of reaction, and in order to eliminate the CuBr / Me6-TREN, crude reaction is then diluted in the DMF and disturbed by amberlites IR-120 (form H) cationic (3-5 g) for 30-60 minutes. Then the mixture is passed on a neutral and precipitated alumina in 10% water/ methanol column. The obtained polymers are redissolved in DMF and precipitated in ether, then filtered and dried in oven at 60˚C for 10 hrs.

Preparation of the Chromatography Column

After introducing the PS-P4VP copolymer into chromatographic column, its synthesized powdered form can be used as a solid material.

The stages of preparation of the column are simplified and summarized as below: 0.49 g of PS-b-P4VP copolymer was weighed, then the mixture is placed in a volume of 50 ml (THF) and stirring using a magnetic stirrer for 24 hours at room temperature. After stopping stirring, centrifugation (3000 rounds/min) for 25 minutes. The product is drying in an oven at 40^0C (for 12 hours). Then, the powder is sieved by means of two sieves (0.4 and 0.25 mm), followed by filling the column with the powder of the copolymer using the vortex to help the powder to enter the column (1h). Then the column is conditioned at 40^0C for 12 hours (the column is connected to the chromatograph injector side) to avoid contamination of the detector.

The column was then attached to the gas chromatograph, fitted with a flame ionization detector. Helium is used as a carrier gas; its flow rate is equal to about 25 cm^3. min^{-1}. The temperature of the injector and of the detector always exceeded the oven temperature by about 50˚C. Very small volumes of solute vapours were injected so as to approach linear condition gas chromatography.

Characterization

It can be employed to measure the molecular weight and the molecular weight distribution by using size- exclusion chromatography (Shimadzu LC-20 AD) coupled with a differential refractometer detector (Shimadzu RID- 10A). The samples were prepared in a 2 ml vial by dissolving about 10 mg of polymer in THF. The solution was filtered (syringe filter of 0.2 μm) then 100 μL of the filtrate is injected through two columns (Waters Styragel 100 Å and 500) covered by the continuous phase (THF) at a flow rate of 100 μL/min. ^{1}H-NMR study was performed on a 500 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent. Solutions with PS concentration of about 50 mg/ml were placed in tubes with 5mm in diameter.

Description of the Chromatography in Gas Phase Apparatus

Chromatographic apparatus is made up of several parts:

Injector

It is the part where the mixture of probes are injected and evaporated, it aims to facilitate its passage from the injector to the column, and the inlet temperature must be higher than that of the furnace. The injection is done by using a micro syringe.

The Column

It is formed from a solid support and a tube of stainless steel, glass or Teflon (for the analysis of corrosive products). When it passes from the injector to the column, the mixture of the probes migrates there through with a carrier gas (inert gas in the column) and the individual products are separated according to their molecular weight (the lighter get out of the column first) or to their polarity get out first from the column. If the column is non-polar the reverse will happen.

The Detector

At the end of the column, the products pass into a detector where they are analyzed. Since separated,

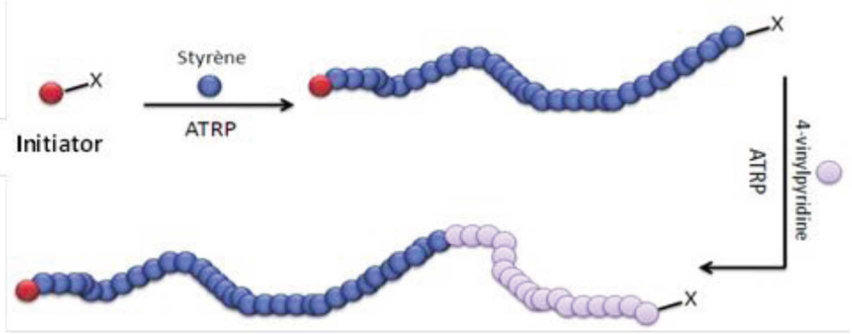

Figure 2: Schematic representation of the used synthesis strategy for PS-P4VP

each product gives a signal in the form of a peak (Gauss). The surface of this peak is proportional to the mass or volume concentration of the product in the mixture.

RESULTS

In Figure **2**, the synthetic approach for the PS-b-P4VP block copolymers is depicted. Initially, it was decided to grow a well-defined polystyrene chain from the phenylethylbromide initiator and resulted chain end functionalized PS acted as a polymeric initiator for the next controlled polymerization of 4-vinylpyridine.

The RMN-^{1}H spectrum of polystyrene (Figure **3a**) has a set of two massifs. The massifs located between 6.2 and 7.2 ppm corresponds to the aromatic protons of the polystyrene (c,d); all bytes observed between 0.7 to 2.4 ppm corresponds to the protons attached to the aliphatic functions CH and CH_2 of the polystyrene (a,b). The RMN-^{1}H spectrum gives a ratio of integration $I_a/2=$

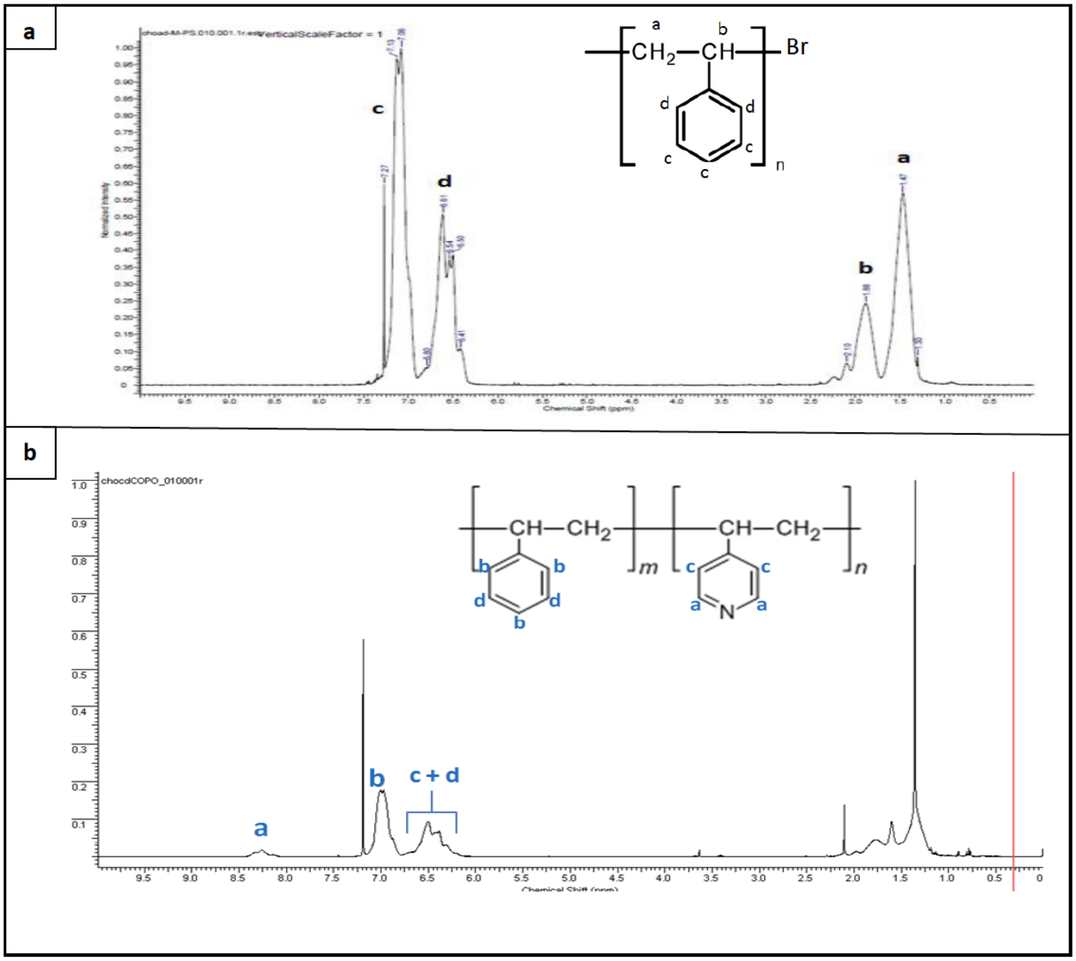

Figure 3: 1H-NMR spectra of (**a**) PS, (**b**) PS-b-P4VP in $CDCl_3$

Table 1: Characteristics of the Polystyrene Batches Synthesized by ATRP Using SEC Technique

Code	Temperature of synthesis (°C)	Polymerization time	Mn, By SEC (g/mol)	Polymerization index PI	Yield %
PS-a	110	4h	25900	1,21	30
PS-b	110	6h	38300	1,28	39
PS-c	110	8h	41000	1,25	37
PS-d	110	10h	44000	1,33	32

$I_b/1 = I_d/2 = Ic/3$. This is in agreement with the structure of the molecule of the PS block, and confirms the synthesis of the polymer.

The RMN-^{1}H spectrum of the obtained copolymer PS-P4VP (Figure **3b**) shows two peaks between 6.2 ppm and 8.2 ppm corresponding to the aromatic protons of the copolymer as described in Figure **3** peaks at 1.4 ppm and 1.75 ppm appear and allow to identify respectively aliphatic hydrogens corresponding to the CH_2 and CH groups.

The steric exclusion chromatography (SEC) allows the analysis of the molar weight of the polymer.

Several batches of polystyrene were synthesized with a ratio of monomer over initiator ($[M]_0/[I]_0$) equal to 481. Indeed, in ATRP, this ratio is the degree of theoretical polymerization that would be obtained if the conversion was total. All polymerizations were carried out at 110˚C using (1-Bromoethyl) benzene as an initiator and the characteristics of the samples are summarized in Table **1**.

Results analysis by SEC allowed the calculation of the molar weights of the synthesized polystyrene block (Table **1**). We note that the molar weight distribution is narrow and varies according to the synthesis from 25,900 to 44,000 g/mol. This result allows concluding that the polymerization reaction is well controlled.

Furthermore, according to Patten and al. [98], the polydispersity index (PI) for the polymers synthesized by ATRP should be between 1.21 and 1.33. This result is in good agreement with the literature [98-99].

Moreover, after all the obtained results, the sample titled "PS-c" represents the type of polymer that has the average molecular weight that is the most similar to that required to synthesize the copolymer PS-P4VP.

The molar masses of the copolymers synthesized were determined by SEC.

Analysis of the results obtained by SEC and presented in Table **2** demonstrates that the P4VP block has been grafted onto the PS block. As expected the chain length of the block increases with a reaction time. the polydispersity index is a bit high but its stability (about 3.5) highlights the perfect control of the second step of the thermal stability of diblock copolymer PS-P4VP, as well as the two polymers of the reference PS and PVP were studied by thermo gravimetric analysis (TGA) in a temperature range between 30˚C to 800˚C as presented in Figure **4** below.

Polymerization of P4VP Block by ATRP

The appearance of two major thermal phases was detected from the analysis of TGA spectra of the linear polymers and diblock copolymer by two steps.

In the First step, polystyrene analysis shows no loss in mass or thermal transition before the degradation phase of the polymer which appear at around 400˚C.

In the second step, the analysis of the spectrum of this polymer P4VP presents first a loss in mass at 80^0C which corresponds to a water loss due to probable hydration of the polymer and a glass transition temperature (Tg) at 160˚C. The degradation

Table 2: Characteristics of PS-P4VP Copolymers Synthesized by ATRP in Two Stages

Code	Mn PS-OH (g/mol)	Temperature of the reaction (°C)	Reaction time	Mn PVP, by SEC (g/mol)	PI
PS-P4VP.a	41000	80	12h	5200	3.5
PS-P4VP.b	41000	80	15h	5500	3.6
PS-P4VP.c	41000	80	18h	5900	3.5
PS-P4VP.d	41000	80	24h	6300	3.7

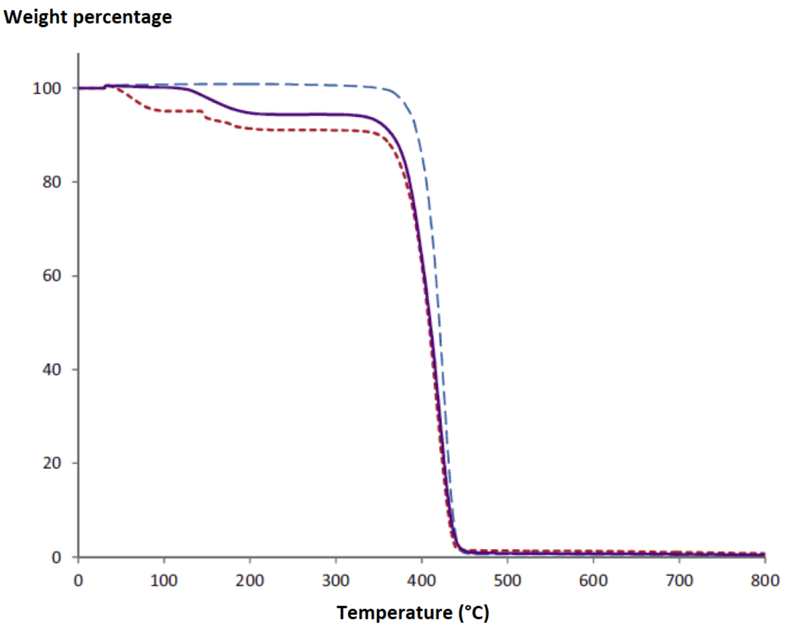

Figure 4: TGA analysis of ---- PS ------- PVP ——PS-PVP.

temperature of the homopolymer is comparable to that of the PS in the order of 380˚C.

Finally, the GTA spectrum of the copolymer PS-P4VP is a composition of two previous spectra of the two homopolymers and has a first inflection point at 160^0C corresponding to the glass transition of the P4VP block and a sharp drop in weight due to the degradation of the copolymer to 400^0C.

CGI allows to give the retention volumes obtained from different probes (n-alcanes and polar). These volumes allow the determination of *RTlnVn* values of different polar probes (Figure **5**) as well the determination of the values of their specific interactions ΔG^{SP} representing the difference between the value of *RTlnVn* and the corresponding point to its projection on the axis of $RTlnVn=f(log\ P_0)$.

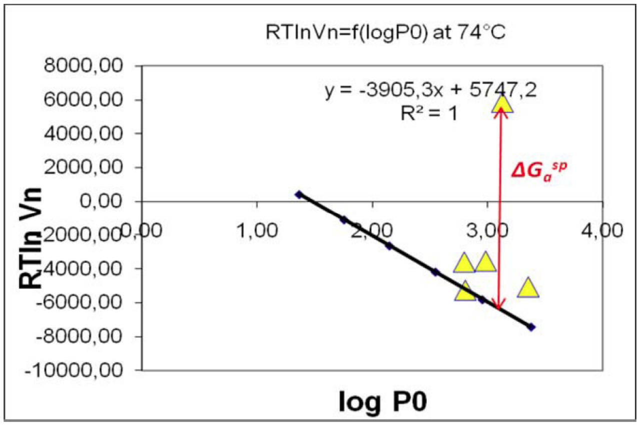

Figure 5: Example of *RTlnVn* in function of *log P0* for n-alcanes and polar probes adsorbed on the copolymer.

Once ΔG^{SP} is determined for different temperatures it is possible to trace its variation in function of the temperature. A straight line can be obtained and whose slope gives the value of ΔH^{SP} and by the intercept we get $-\Delta S^{SP}$.

The obtained value of ΔH^{SP} is used to determine the values of K_A and K_D (in our case this equation is treated using the classical model and the model of Hamieh [68-69]. Mamieh model was used on many oxides and polymers and gave interesting results on the acid base properties of solids [72, 74-76, 79-80, 85, 89, 91, 93].

It is recalled here that the classical model is given by:

$$-\Delta H^{SP} = K_A.ND+K_D.NA \qquad (11)$$

With NA and ND the electron acceptor and donor numbers, respectively.

While Hamieh's model [69] corrected the relationship (11) and proposed a new relationship by adding a third parameter *K* reflecting the amphoteric character of the oxide or polymer according to:

$$(-\Delta H^{sp}) = K_A\ DN + K_D\ AN - K\ DN\ AN \qquad (12)$$

By dividing by *AN*, we obtain:

$$-\frac{\Delta H^{sp}}{AN} = K_A\frac{DN}{AN} + K_D\text{-}K\ .DN \qquad (13)$$

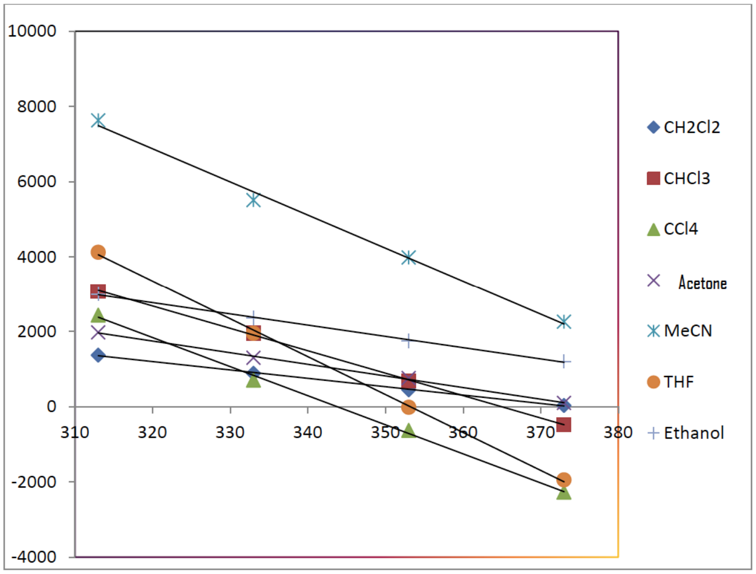

Figure 6: Variation of ΔG^{SP} as a function of the temperature of polar molecules adsorbed on the copolymer.

Equation (13) can be symbolically written as:

$$X1 = K_D + K_A X_2 - K X_3 \quad (14)$$

Where $X_1 = -\dfrac{\Delta H^{sp}}{AN}$, $X_2 = \dfrac{DN}{AN}$, $X_3 = DN$ and $K = K(K_A, K_D)$

X_1, X_2 and X_3 are known for every polar molecule, whereas K_D, K_A and K are the unknown of the problem.

By using N probes, relationship (14) will allow us to write the following equations:

$$\sum_{i=1}^{N}(X_1)_i = K_D N + K_A \sum_{i=1}^{N}(X_2)_i - K\sum_{i=1}^{N}(X_3)_i \quad (15)$$

$$\sum_{i=1}^{N}(X_1X_2)_i = K_D \sum_{i=1}^{N}(X_2)_i + K_A \sum_{i=1}^{N}(X_2)_i^2 - K\sum_{i=1}^{N}(X_2X_3)_i \quad (16)$$

$$\sum_{i=1}^{N}(X_1X_3)_i = K_D \sum_{i=1}^{N}(X_3)_i + K_A \sum_{i=1}^{N}(X_2X_3)_i - K\sum_{i=1}^{N}(X_3)_i^2 \quad (17)$$

One obtains a linear system given by the equations (15-17) at three unknown numbers: K_D, K_A and K. The matrix representing this linear application is a symmetrical one; we deduce that the problem (15-17) has a unique solution for $N \geq 3$. We applied this method to calculate the acid-base constants of our copolymer.

The Classical Method

The determination of K_A and K_D by the conventional method is done by plotting $-\Delta H^{SP}/NA$ *as a (ND/NA).*

Determining ΔG^{SP} allows us to calculate, for each molecule, the values of ΔH^{SP} and ΔS^{SP}. Figure **6** shows the variation of ΔG^{SP} in function of the temperature for polar molecules. The Curves in Figure **6** show many lines with excellent correlation coefficients. ΔH^{SP} and ΔS^{SP} values are shown in the following table:

The numbers of electron donors and acceptors for used polar molecules are given in Table **4.**

Table 3: Values of ΔH^{SP} and ΔS^{SP} for Polar Molecules

Molecules	ΔH^{SP} ($J\ mol^{-1}$)	ΔS^{SP} ($J\ K^{-1} mol^{-1}$)
CH_2Cl_2	8330	22
$CHCl_3$	21760	60
CCl_4	26580	77
Acetone	11610	31
MeCN	35080	88
THF	35610	101
EtOH	12378	30

Table 4: Values of *NA* and *ND* for Used Polar Molecules

Molécules	*NA*	*ND*	*ND/NA*	$-\Delta H^{SP}$ / *NA* (J/mol)
CH_2Cl_2	13.5	2.97	0.22	616.7
$CHCl_3$	18.7	0	0	1164
CCl_4	2.3	0	0	11554
Acetone	8.7	42.63	4.9	1334.71
MeCN	16.3	35.37	2.17	2152
THF	1.9	50.01	26.32	18744
EtOH	35.9	50	1.40	344.79

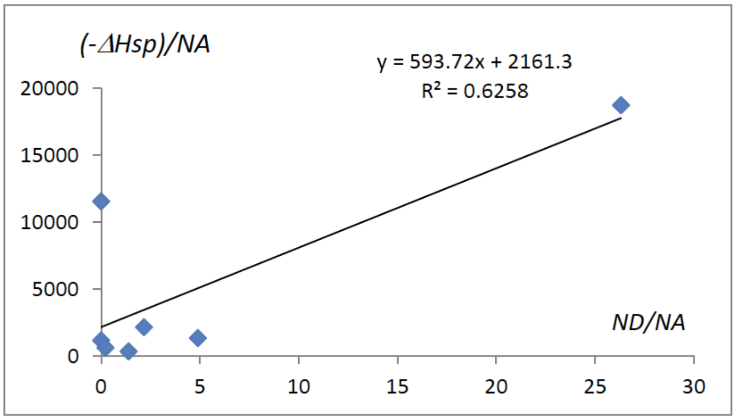

Figure 7: Variation of - $\Delta H_{SP}/NA$ as a function of *ND/NA* for the synthetized copolymer.

If we draw the variation of - $\Delta H^{SP}/NA$ as a function of (*ND/NA*), one should find a straight line according to the classical model, thus Figure **7** does not show a linear relationship at all. According to the classical model a simple mathematical calculation used to obtain the values of K_A and K_D:

K_A = 594 *(J mol^{-1})* and K_D = 2160 *(J mol^{-1})*

However, the linear regression coefficient r^2 for this model is so far from 1; then, the classical model is not respected here, even if the results show a basic and acid character.

Hamieh Model

This allows us to apply in this case Hamieh model [69] that was already mentioned above. The mathematical calculation using equations 15 to 17 shows:

K_A = 771 (J mol^{-1}),

K_D = 4550 *(J mol^{-1}),*

K= 127 (J mol^{-1})

Therefore, these obtained results with new model clearly show that the synthesized copolymer PS-P4VP has an amphoteric behavior with rather very basic character that is six times stronger than acidic character (in Lewis terms). These results are also confirmed by the strong interactions shown in Table **3** with the acidic and basic polar molecules.

These results also reflected the presence of acidic and basic groups in the structure of the PS-P4VP copolymer, more particularly the presence of benzenic, methyl and vinylpyridine groups. These groups are strongly correlated to the acid base character in Lewis terms.

CONCLUSION

Controlled ATRP polymerization type was employed in the synthesis of linear diblock copolymer PS-P4VP. This synthesis was carried out by two successive steps with the initiator (1-Bromoethyl) benzene. Hexamethyl tris [2(dimethylamino)ethyl] amine (Me6-TREN) was used as ligands in a protic solvent.

Chemical analysis of the product obtained by RMN-^{1}H allowed demonstrating the success of the second step of the synthesis.

The molar weight of this copolymer was determined by size exclusion chromatography. The thermal stability of PS-P4VP diblock copolymer was investigated by TGA, the two peaks corresponding to the glass transition of P4VP block at 160^{0}C and the mass loss observed around 400˚C due to the thermal degradation of the polymer confirmed the product obtained.

The IGC technique was used to study the superficial properties and the thermodynamic properties of PS-P4VP the different values of *Vn* at various temperatures, obtained after adsorption of several probe molecules on the solid copolymer. Results allowed to calculate the thermodynamic values of $\Delta G_a^{SP}, \Delta H_a^{SP} et\ \Delta S_a^{SP}$, that were used to calculate the values of K_D and K_A of copolymer by using classical model and the new Hamieh model. The obtained results clearly demonstrated that the synthesized diblock copolymer is of an amphoteric character with stronger basic constant in Lewis terms.

The future scope for research in this area will be the determination of physicochemical of polymers and polymers adsorbed on oxides and more particularly the highlighting of transition phenomena and acid-base properties in Lewis terms for such solid substrates.

Compliance with Ethical Standards

Conflict of Interest

On behalf of all authors of this paper, the corresponding author Tayssir Hamieh declares that he has no conflict of interest.

This article does not contain any studies with human participants or animals performed by any of the authors.

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