Synthesis and Characterization of Polydimethylsiloxane end-Modified Polystyrene from Poly(Styrene – co –Vinyltriethoxysilane) Copolymers

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In this paper, we report the synthesis of polystyrene end- capped with three- short- arm PDMS (PS-(PDMS)$_3$) using poly(styrene – co –vinyltriethoxysilane) copolymers as precursors. These materials were obtained in a two-step process; first, two random copolymers of poly(St – co – VTES) having different molecular weight, and vinyltriethoxysilane content were prepared via free radical polymerization. The materials thus obtained, were treated with an excess of dimethyldimethoxysilane to produce PS-(PDMS)$_3$ by co-condensation of alkoxysilane groups. The formation of the copolymers was confirmed by proton nuclear magnetic resonance, infrared spectroscopy, and gel permeation chromatography. Surface properties of films formed by casting the copolymers on a glass sheet were studied by Atomic force microscopy (AFM), and water contact angle measurements. We found that PS-(PDMS)$_3$ copolymers exhibit a hydrophobic behavior, showing water contact angles close to values early reported for block copolymers composed by PS and PDMS segments, and comparable with the corresponding value of PDMS.

Keywords: *Silane, Polydimethylsiloxane, Polystyrene, Water Contact Angle*

1. Introduction

Segmented copolymers composed of polystyrene (PS), and polydimethylsiloxane (PDMS) combine the outstanding properties of silicone polymers and polystyrene. Silicones are highly stable against radiation and chemical agents, present good gas permeability, low surface tension, and most of them are nontoxic and biocompatible. On the other hand, PS based materials present capability of transmitting light, dimensional stability, and high tensility and flexibility which allow them being used in numerous industrial applications.

The fact that PMDS exhibits a hydrophobic behavior has encouraged the synthesis of copolymers containing it, as an alternative for obtaining polymeric materials with tailored surface properties. For example, it has been reported that the presence of segments of PDMS in materials such as PMMA – b – PDMS – b – PMMA [1] , PEO – b – PDMS [2], PDMS – b – PEG [3], and PDMS – b – PEMA [4] confers them hydrophobic character. In the specific case of copolymers composed of PS and PDMS, Jiang et al., [5] studied the surface properties of PS–b–PDMS–b – PS, and found that their water contact angle ranges between 87.7 – 97 °, depending on the length of the PS segments. In other report Guan et al., [6] found that the water contact angle of PS – b – PDMS is 109.9 °.

Block copolymers containing PDMS segments may be synthesized by techniques such as anionic polymerization [7-9], atom transfer radical polymerization [10, 11], and reversible addition-fragmentation chain transfer polymerization [12].

Although, this methodologies have been widely used at academic level, have several drawbacks; for instance, high purity of the reagents is required, must be carried out in absence of air, involve the use of harmful or not commercially available chemicals, and require tedious purification of the products. These limitations could hamper the widespread usage of this kind of material at large scale.

In this paper, we report the synthesis and surface properties of Polystyrene Three-Arm PDMS (PS-(PDMS)$_3$) in two steps. First, poly(St – co – VTES) macrosilanes are prepared via free radical polymerization. Afterwards, PS-(PDMS)$_3$ is obtained by reaction of the macrosilane precursor with dimethyldimethoxysilane (DMDMS) through the hydrolysis, and co-condensation of alkoxy silane groups. In previous studies, we found that poly(St – co – VTES)´s can be used as a reactive macrosilanes for the modification of silica surfaces[13] and as precursors for the synthesis of PS/silica nanocomposites [14].

2. Experimental part

2.1. Materials

Styrene (St) 99%, vinyltriethoxysilane (VTES) (97%), triethylamine and dimethyldimethoxysilane (DMDMS) (95%) were purchased from Sigma-Aldrich. 2,2-Azobis-isobutyronitrile (AIBN), was supplied by Akzo Novel, and methanol, toluene, butanol, heptane and tetrahydrofuran (THF) by Merck.

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2.2. Synthesis of copolymers P(S – co – VTES)

Styrene and VTES were copolymerized in solution, using toluene as solvent and AIBN (0.1 wt%) as free radical initiator. Copolymers with two different feed molar ratio of the monomers (St: VTES) 2:3 and 4:1 were synthesized, and designated as S1 and S2, respectively. The polymerization was carried out at 70 °C, until obtaining yields close to 20%.

The polymerization reactions were stopped by the addition of an excess of methanol at room temperature. The product was recovered by filtration and purified by successive precipitations from a THF solution by the addition of methanol. After purification, the samples were thoroughly rinsed with methanol until not residual monomer was detected by UV-visible spectroscopy; the final product was dried at 60 ºC under reduced pressure during 48 hours.

2.3. Synthesis of PS-(PDMS)₃

PS modified with PDMS was prepared from random copolymers poly(styrene – co – VTES) through the hydrolysis and co-condensation of alkoxy groups contained in both, VTES units and DMDMS monomer. The reaction of S1 and S2 with DMDMS was carried out in solution using a mixture of toluene/butanol as solvent in weight ratio 1:1. In a typical synthesis, 1 g of S1 or S2, and 1 g of DMDMS were dissolved in 20 mL of the solvent mixture. 2.3 mL of water was added to promote the hydrolysis of the alkoxy groups, and triethylamine was used as a catalyst.

The reaction was carried out at 65 °C for 72 hours, PS-(PDMS)₃ materials were precipitated by the addition of an excess of butanol, filtered, dried at room temperature under reduced pressure, and then rinsed with heptane to remove any residual of DMDMS and PDMS. Finally, the materials were dried at 60 °C.

2.4. Characterization techniques

Infrared analysis: 2 mg of the corresponding sample was dissolved in a minimum amount of THF, and then dropped on a ZnSe window to form a film; the samples were dried at 60 °C to eliminate any residual THF. The spectra were collected with 16 scan in a FTIR Perkin Elmer spectrum one.

^{1}H NMR spectra were recorded on a Bruker AMX-300 spectrometer operated at 300 MHz for [1]H. Samples were dissolved in CDCl₃ and the spectra were recorded at 303 K. Chemical shifts (δ) were expressed in ppm respect to the CDCl₃ signals, and TMS was used as internal standard.

Molecular weight and distribution were measured by GPC in a Waters HPLC equipped with a differential refraction index detector. The analyses were performed in THF at a flow rate of 0.8 mL/min using a HR 4E column. The calibration curve was constructed with standards of polystyrene.

DSC Thermograms of the samples were acquired in a Temperature-Modulated Differential Scanning Calorimeter (TM-DSC) TA Instrument Q100. The samples were heated from room temperature to 200 °C at 30 °C/min, and then cooled to 0 °C. Finally, the thermograms were acquired from 0 °C to 200 °C heating at 10 °C/min. Scanning Electron Microscopy (SEM) images and EDX spectra were acquired in a JEOL JSM–6490LV microscope at 20 kV.

Water contact angle and Atomic Force Microscope (AFM) analyses were performed on films formed by casting a solution of the copolymer in THF on a smooth glass sheet,

the samples were annealed at 90 °C for 24 h. AFM images, surface roughness and grain size were measured in a Park Scientific Instrument Company (PSI) equipment. Water contact angle measurements were carried out using the sessile drop method in OCA Dataphysics 15 equipment at 22 °C and 45% relative humidity.

3. Results and Discussion

3.1. Characterization of P(St – co – TEVS) macrosilanes

Figure 1 presents the ^{1}H-NMR spectrum of sample S1, resonance peaks found between 6.5 and 7.4 ppm are assigned to aromatic protons in styrene (c, d and e); whilst the signals between 0.9 and 2.2 ppm are due to aliphatic C – H (a, b and g). Although the spectrum is essentially composed by signals due to PS, the presence of one small peak centered at 0.2 ppm, assigned to the H(h) in the alpha position to the silicon atom; in addition to peaks between 3 and 4 ppm due to the ethoxy groups (i and j) of the VTES units, and some silanol groups produced by their partial hydrolysis, prove that the copolymerization took place. Molar fraction of VTES in the copolymers, shown in table 1, was estimated from ^{1}HNMR spectra[15], as follows:

$$\chi_{VTES} = \frac{A_{0.2\,ppm} * 5}{A_{0.2\,ppm} * 5 + A_{7\,ppm} * 2} \tag{1}$$

$A_{0.2ppm}$ and A_{7ppm} stand for the area of the peaks centered at 0.2 and 7 ppm, respectively.

Molecular weight (M_n), and polydispersity (M_w/M_n) measured by GPC for copolymers S1 and S2, are summarized in table 1. It is seen that the molecular weight depends on the concentration of VTES, larger M_n is obtained reducing the amount of VTES. This behavior is indicative of the occurrence of chain transference afforded by the presence of VTES, and agrees with results early reported by Seno et al. for the radical polymerization of vinyltrimethoxysilane [16].
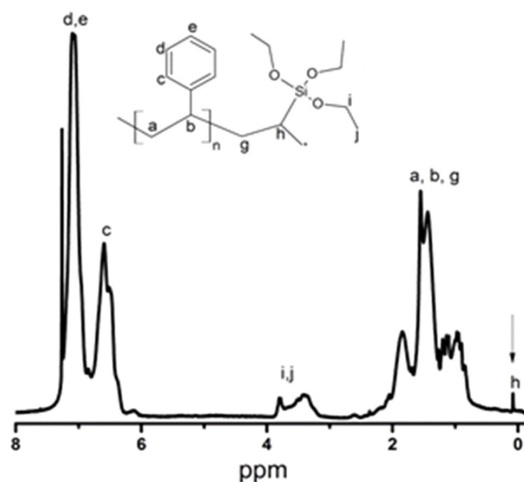

Fig 1. ^{1}H-NMR spectrum of macrosilane S1. The presence of VTES units is corroborated by the signal at 0.2 ppm which is assigned to the H atom in C bounded to the silicon atom.

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Table 1. GPC and ^{1}H NMR results for the macrosilane precursors, and PS end-capped 3-short-arm PDMS.

| Sample	GPC		^{1}HNMR		Average Composition
	M_n (KDa)	M_w/M_n	χ_{VTES}	χ_{DMS}	
S1	2.7	2.0	0.040		St_{26}-co- $VTES_1$
S1- 3 PDSM	5.9	2.1		0.30	St_{26}- $(DMS_3)_3$
S2	17	1.9	0.007		St_{163}-co-$VTES_1$
S2– 3 PDMS	18	2.0		0.15	$St_{163.5}$ –$(DMS_7)_3$
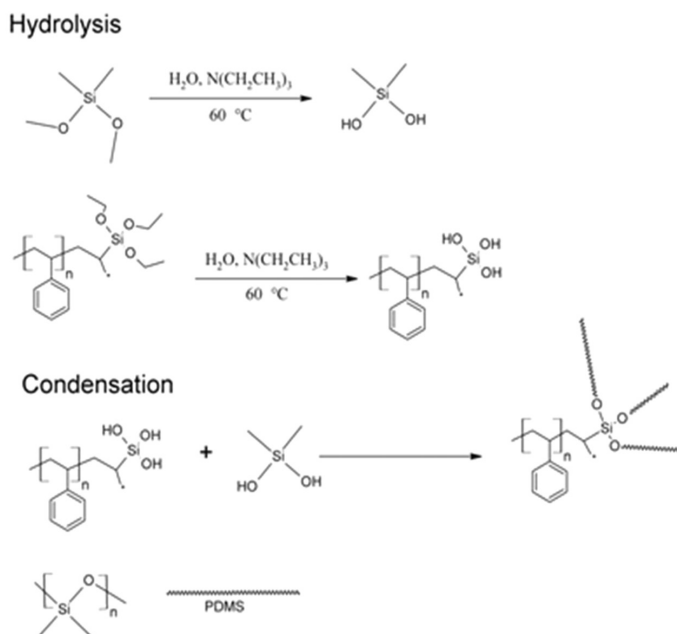
Fig 2. The reaction overall of the synthesis of PS $(PDMS)_3$.

The average composition of the copolymers, listed in table 1, was calculated with the M_n value measured by GPC, and the corresponding molar fraction of VTES estimated from ^{1}HNMR. Considering that VTES promotes chain transference to the monomer, and its relative reactivity ratios is two magnitude orders smaller than the corresponding value for styrene [13], it can be concluded that the copolymers are mainly composed by styrene, and contain one VTES unit mostly found at the end of each chain.

3.2. Characterization of PS-(PDMS)_3

PS-(PDMS)_3 samples were synthesized from the reaction of two copolymers poly(St-co-VTES) having different molecular weight, and an excess of DMDMS. The global reaction implies the hydrolysis of the alkoxy groups, catalyzed by triethylamine, and their posterior condensation. Figure 2 summarizes the steps through poly(styrene – co – VTES) precursors react with DMDMS. VTES units present three ethoxy groups which are hydrolyzed and co-condensate with hydrolyzed DMDMS, resulting in PS chains ended with three-short-arm PDMS.

Figure 3 compares the normalized infrared spectrum of S1 precursor with the corresponding polysiloxane modified sample (S1-(PDMS)_3) in the region of 2000 to 600 cm⁻¹. Both samples present infrared absorptions that are
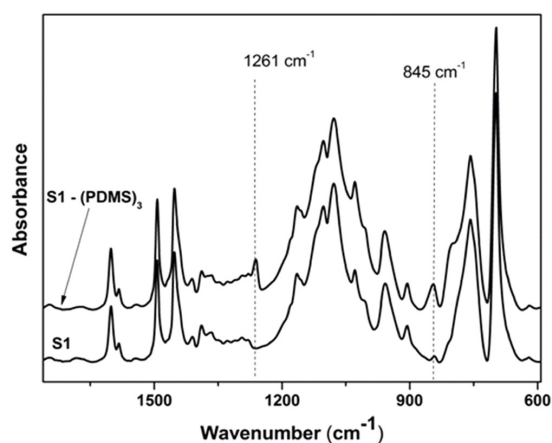
Fig 3. Infrared spectrum of the macrosilane precursor S1 and the corresponding S1- (PDMS)_3.

characteristic of polystyrene such as, aromatic ring stretching at 1600 and 1500 cm⁻¹, and also absorption bands due to Si-O-C (at 1105 and 1079 cm⁻¹), and C-O stretching (at 1167 and 960 cm⁻¹). The sample (S1 –(PDMS)_3) shows

two peak at 1261 and 845 cm^{-1} which are characteristic of Si-CH$_3$ linkages [17].

Figure 4 presents the ^{1}H-NMR spectra for samples obtained from precursors S1 and S2 (S1-(PDMS)$_3$ and S2-(PDMS)$_3$, respectively). Both samples exhibit resonance peaks also seen in the precursors, which are assigned to PS (Figure 1). A sharp signal at 0.2 ppm is due to the methylene protons of PDMS. The absence of signals between 3 and 4 ppm, due to -Si – O –CH$_2$ – CH$_3$ and –Si –OH, ratifies that Poly(St-co-VTES) samples were modified by co-condensation with DMDMS and accounts for a complete hydrolysis of the alkoxy groups in the macrosilane precursor.

The molar fraction of DMDMS as well as the average composition of the materials (listed in table 1) were estimated by ^{1}HNMR[15], using the area under the signals in the region 6.5-7.5 ppm, and the peak at 0.2 ppm. The larger fraction of PDMS was achieved when S1 was used as precursor, which is due to the larger amount of VTES that increases the probability that the co-condensation reaction takes place. The average number of DMS units per arm was calculated as follows:

$$DMS / arm = \frac{\chi_{DMS}}{3\chi_{VTES}} \qquad (2)$$

χ_{VTES} and χ_{DMS} are the molar fraction of VTES and DMS in the precursor and modified PS, respectively. The average composition of samples prepared from precursor S1 and S2 are St$_{26}$-(DMS$_3$)$_3$ and St$_{163}$-(DMS$_7$)$_3$, respectively. EDX analysis of St$_{163}$-(DMS$_7$)$_3$ is shown in figure 5, the surface exhibited a homogenous composition; the average molar ratio C/Si was 53 which is comparable to the average composition determined by ^{1}HNMR.

According to data listed in table 1, and the molecular weight distribution plots of sample S1 and St$_{26}$- (DMS$_3$)$_3$ shown as illustration in figure 6, the M$_n$ value measured by GPC increases on the presence of –[O – Si(CH$_3$)$_2$]$_n$ arms. Although these values were determined using a relative calibration curve, and the presence of PDMS units can alter the interaction between the polymer chains and the solvent, it can be deduced that the hydrodynamic dimensions of PS–(PDMS)$_3$ chains are lager compared to macrosilane precursors.

Figure 7 presents the DSC thermograms of PS-(PDMS)$_3$ samples, the precursor, and a PS sample (M$_n$=10 KDa) chosen as a reference. Both S1 and S2 exhibit a T$_g$ lower than the corresponding value for PS, probably due to the plasticizing effect exerted by the pendant ethoxy groups on the VTES. However, T$_g$ of PS in the PDMS modified copolymers is close to value obtained for the reference, this behavior could presumably, be related to the segments segregation due to the poor affinity between PS and PDMS.

Topographic AFM images of PS-(PDMS)$_3$ samples casted from a THF solution are shown in figure 8. According to the images, the copolymer chains are forming aggregates; the largest molecular weight for sample S2-(PDMS)$_3$
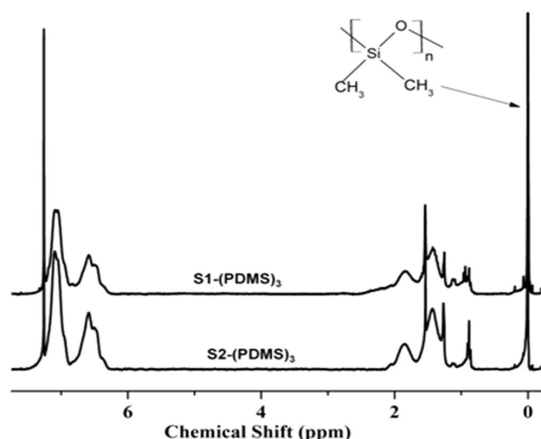

Fig 4. ^{1}H-NMR of the material PS–(PDMS)$_3$ spectrum of samples S1 – (PDMS)$_3$ and S2 – (PDMS)$_3$.
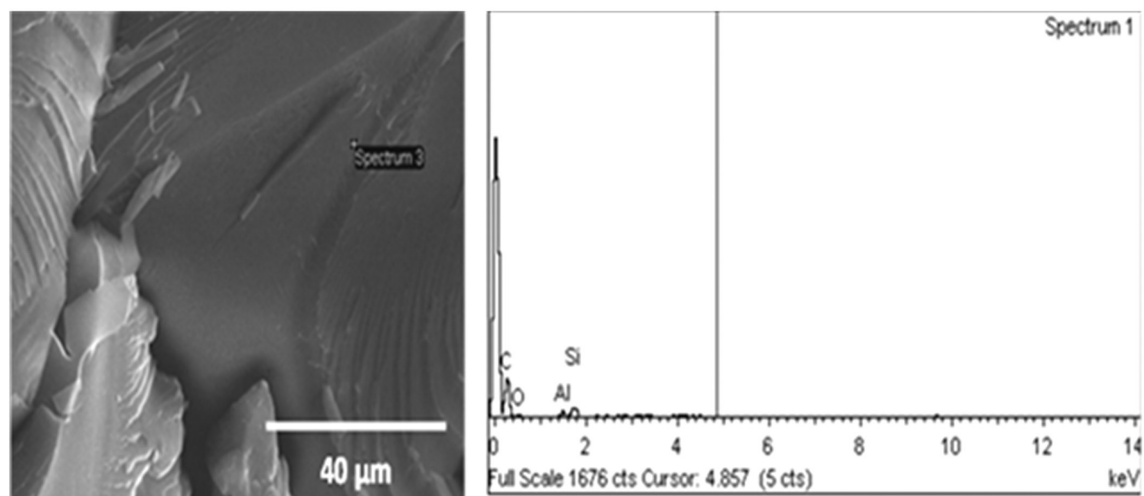

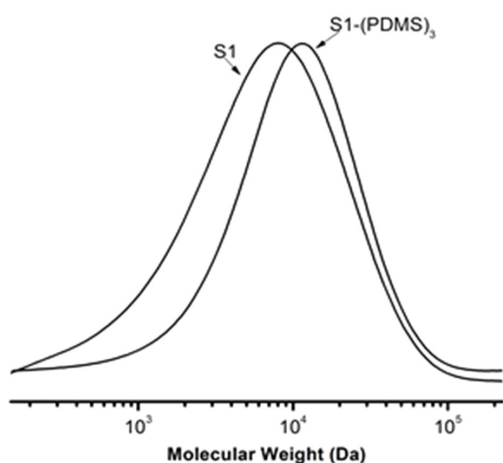**Fig 5.** EDX spectrum for sample S2-(PDMS)$_3$.

Fig 6. Molecular weight distribution for sample S1 and S1-(PDMS)₃.

corresponds to the largest aggregates size, and also to the highest roughness, measured as the root mean square of the deviation of the height from the standard plane (RSM); according to the values in table 2. From SEM images for sample S2-(PDMS)$_3$ (Figure 9), it is observed that a low magnification, (850x) the surface looks smooth, and present some cracks which are characteristic of polystyrene, however, at higher magnification (8000x) the surface looks rough, which corroborates the results obtained by AFM.

Figure 10 shows the water contact angles of each of the surfaces. It is seen that the contact angle correlates with the amount of PDMS in the copolymer, i.e. S1- (PDMS)$_3$, that according to the previously mentioned results, has the larger molar fraction of PDMS, presents the most pronounced hydrophobic character. The contact angle of both samples is larger than 85.4 ± 0.7°, value reported for PS homopolymer by Carre under the same experimental conditions herein used [18].
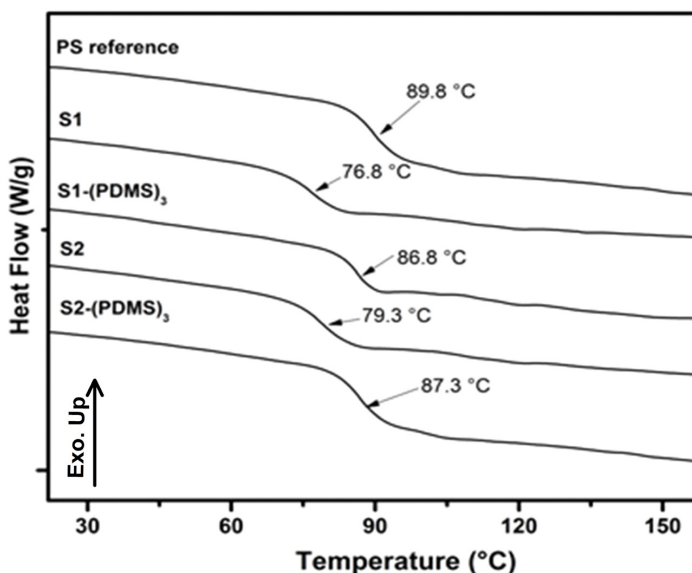

Fig 7. DSC thermograms for a PS reference, precursors and the corresponding samples end-capped with 3-short-arm PDMS.
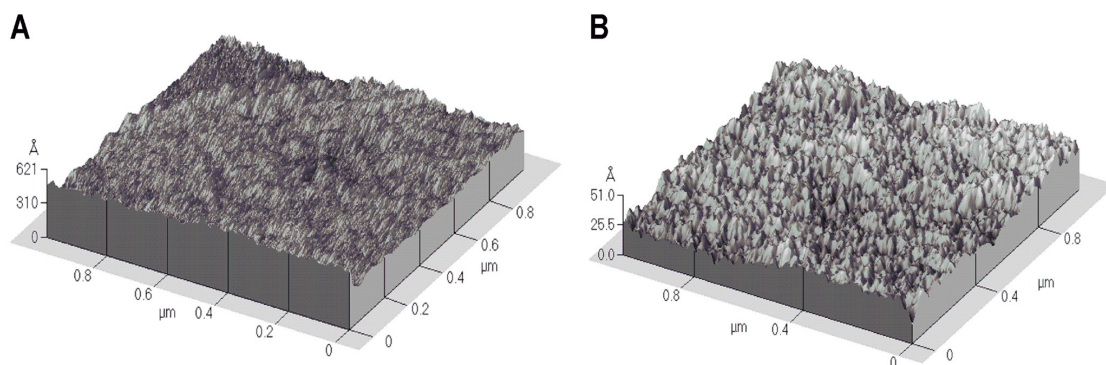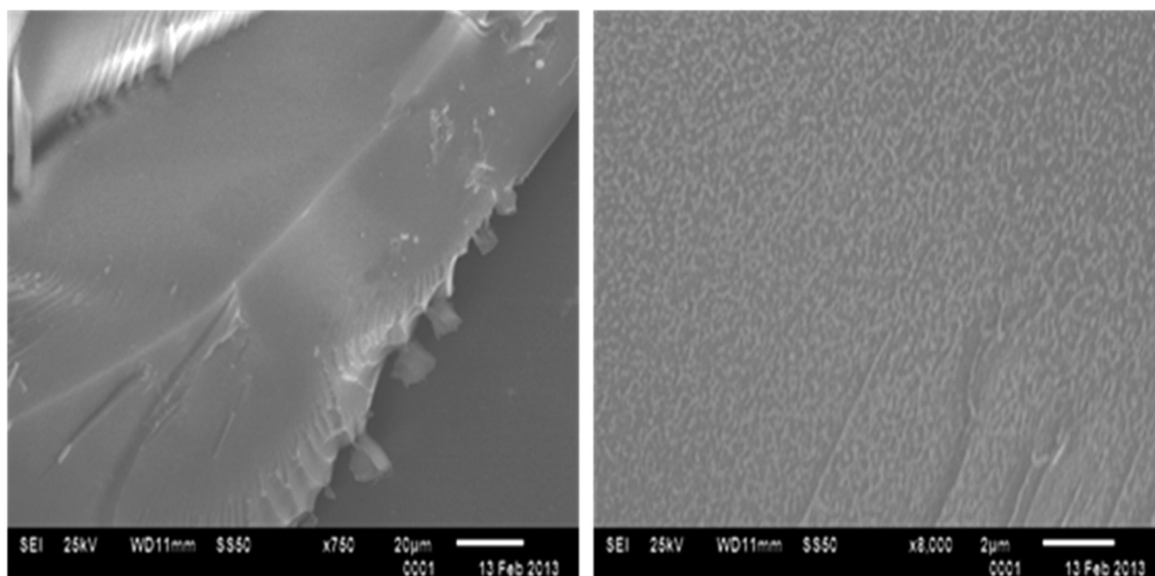

Fig 8. AFM topographic images for A. S1-(PDMS)₃ and B. S2-(PDMS)₃ casted from a THF solution on a smooth glass surface.

Table 2. Surface properties of PS end-capped 3-short-arm PDMS.

Sample	AFM		Water contact Angle (°)
	Roughness RMS (nm)	Grain Size (nm)	
S1- 3 PDSM	2.28	32±4	109.6
S2 -3 PDMS	4.30	68±6	100.4

Fig 9. SEM images for sample S2-(PDMS)$_3$ casted from a THF solution on a smooth glass surface at two different magnifications 750x and 8000x.
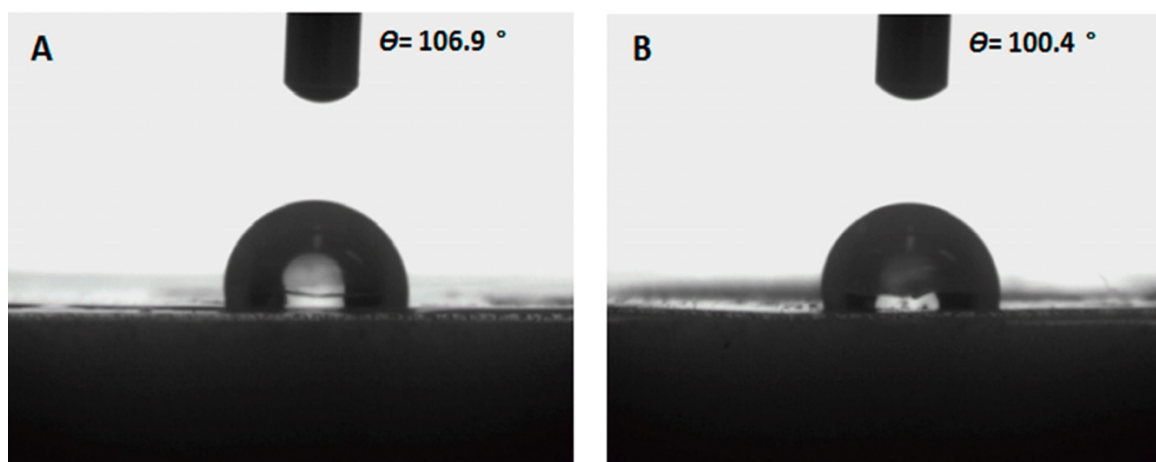
Fig 10. Static water contact angles of A. S1-(PDMS)$_3$, and B. S2-(PDMS)$_3$ casted on a glass surface.

The increase on the hydrophobicity of the surfaces can be attributed to the roughness and chemical composition of the surface. Rough surfaces present larger contact angle due to the increased of the solid – liquid interface, as previously described [19, 20].

On the other hand, the presence of PDMS segments decreases the surface energy, and therefore the affinity between water and the surface decreases. Given that the samples were casted on a glass surface, which is hydrophilic, presumably, the PDMS segments were oriented to the air/solid interphase. It has been reported that phenyl rings in PS can interact with silanol groups on the glass trough electron donor – acceptor interactions [21], whilst PDMS segments are highly hydrophobic. It is corroborated by the fact that the water contact angle of the samples herein studied are close to the corresponding value for PDMS homopolymer, which according to Mata and coworkers is around 113°[22], and comparable with the corresponding values early reported for PS-*b*-PDMS[6], and PS-*b*-PDMS-*b*-PS[5].

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4. Conclusions

PS-(PDMS)$_3$ was synthesized by co-condensation of poly(St – co –VTES) with DMDMS. The method herein used overcomes some of the disadvantages of living polymerization techniques which are used to prepare segmented copolymers. The reactions can be carried out under air atmosphere, and the reagents do not need to be exhaustively purified. However, the materials herein reported presented water contact angles close to the values reported for block copolymers based on the same polymer segments, and comparable with the water contact angle reported for PDMS homopolymer. The methodology we report can be applied to other vinyl copolymers which can be modified in similar way to obtain hydrophobic materials.

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