Modified Diblock Copolymer Bearing Fluoro Groups and Evaluation of its Hydrophobic Properties

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Summary: The major scope of the presented work is the characterization and evaluation of hydrophobicity of novel copolymers of the PS-b-$PB_{1,2}$ type, modified with perfluorooctanoyl chloride [PS: polystyrene, $PB_{1,2}$: poly(butadiene) with 100% 1,2-microstructure]. Fluoro atoms in polymers can create hydrophobic surfaces with low surface energy. The fluorinated groups can migrate and possible orient in the outermost surface of the polymeric thin film. Characterization in the modified block copolymer was conducted with carbon nuclear magnetic resonance (^{13}C-NMR) and thermogravimetric analysis (TGA) to evaluate the structure. Contact angle measurements were also conducted to verify the hydrophobicity of the fluorinated copolymer. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to depict the structure of the material. The obtained results showed that indeed the fluorinated copolymer exhibits high hydrophobicity (low surface energy material) with significant structural differences from its precursor.

Keywords: atomic force microscopy (AFM); contact angle; fluoropolymers; polybutadiene

Introduction

Polymers bearing fluorine atoms are considered to be a very important class of polymeric materials. These polymers exhibit unique properties and the most important is considered to be hydrophobicity.[1] Besides hydrophobicity, fluoropolymers have many other interesting properties, such as chemical inertness, thermal stability, low relative permittivity, lipophobicity, low friction coefficient.[2–5] Due to these properties, many applications such as coatings, microfiltration, microelectronics, antifouling, antiwetting and optics can be envisaged.[3,6–11] It is therefore clear that the most significant property of fluoropolymers is their hydrophobicity which eventually leads to modified surface properties. In the literature, novel low energy fluorinated poly(amide urethane) block copolymers have been reported.[12,13]

The existance of -F- atoms or groups (-CF_3 or –CF_2-) on a surface leads to significant hydrophobicity exhibiting contact angles higher than 90°.[1] Side chains containing different fluoro-groups such as -CH_2-, -CH_3, -CF_2- and -CF_3 are responsible for the orientation in the material surface, thus affecting the hydrophobicity. The length and the chemical components (e.g. -CH_2- and -CF_2-) of the side group are very important and play significant role for achieving low surface energy hydrophobic materials. Maximum orientation of -CF_3 without the presence of -CH_2-, -CH_3 or -CF_2- in the outermost surface leads to desirable results.

Side-groups should be arranged in such a manner to avoid reconstruction (which is considered one important disadvantage of such materials). Such a behavior is possible if the side chain phase separates from the polymer backbone in which it is attached

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on. In most of the cases, surface molecular composition is not uniform (exhibiting exclusively -CF_3 sidegroups), but instead a mixture of hydrocarbon and fluorocarbon groups (-CH_2- and –CF_2-) is most commonly observed.[14,15] Better surface organization and increased surface stability is exhibited when fluorocarbon side groups are bonded to the initial block copolymer. The use of materials such as copolymers with polystyrene (PS) segments enhanced the solubility of the material in organic solvents. With increased solubility and adhesion the surface chemistry can be prominently understood and controlled.[16]

The major scope of this manuscript is to evaluate hydrophobicity of a fluorinated modified diblock copolymer and to study the topography of the surface through various techniques such as SEM, AFM and contact angle measurements.

Experimental Part

Materials

PS-b-$PB_{1,2}$ (approximately 100% $PB_{1,2}$) was synthesized via anionic polymerization[17] and was modified with pentadecafluorooctanoyl chloride in the side groups, in order to prepare a semifluorinated PB block. Its modification, synthesis and molecular characteristics (GPC & ^{1}H-NMR) have already been reported in the literature.[16] It was very crucial to obtain almost exclusively 1,2-microstructure in the PB segment, since it is necessary to achieve the maximum modification with fluorocarbon groups.

Molecular Characterization

For thermal evaluation, a thermogravimetric analysis (TGA) instrument from Mettler Toledo Company, TGA/SDTA 851^e was used at air atmosphere. Also ^{13}C-NMR (carbon nuclear magnetic resonance) and ^{13}C-NMR-DEPT (carbon nuclear magnetic resonance-distortionless enhancement by polarization transfer) spectroscopies were also used in order to further justify the structure of SBF in $CDCl_3$ at room temperature.

Structural Characterization

Contact angle measurements were performed with HPLC water (Scharlaw), using a contact angle system OCA from Dataphysics. Atomic force microscopy (AFM) was performed by using a scanning probe microscope (NanoScope IIIa) from Digital Instruments. Finally, scanning electron microscopy (SEM) was also used in order to collect additional information of the surfaces.

Results and Discussion

Carbon Nuclear Magnetic Resonance (^{13}C-NMR) Spectroscopy

Even though, the molecular characterization of SBF was carried out in a previous manuscript,[16] ^{13}C-NMR experiments were performed in order to fully verify the chemical structure of the finally modified material. In Figure 1 the ^{13}C-NMR spectra for SBF can be observed. By identifying specific chemical shifts the successful modification from the SB initial diblock copolymer to SBF can be actually verified. Table 1 summarizes specific chemical shifts for the SBF sample, with the most important being those for carbon atoms of -CF_2-, -CF_3 and -OC(O)- groups which are exhibited at 110–120 ppm and are attributed at carbon atoms bonded with F atoms and 150 ppm for the C atoms connecting the PB segment with fluoro-side groups respectively.[14]

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was used to evaluate the thermal degradation of SB and SBF block copolymers. Figure 2 exhibits the relative TGA scans for both cases, from which it is evident that SBF and SB have similar thermal stability. It can be concluded that the modification reaction maintained the thermal stability of the material even at high temperatures, leading to a thermo stable semifluorinated copolymer.

Contact Angle Measurements

Hydrophobic surfaces are considered to exhibit low surface energy and contact angles higher than 90 °. Table 2 exhibits the

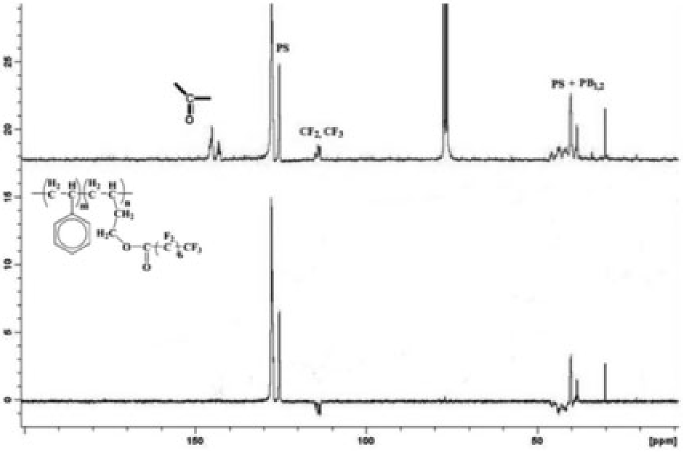

Figure 1.
^{13}C-NMR (up) and ^{13}C-NMR-DEPT (bottom) spectra for modified SBF, with characteristic chemical groups.

Table 1.
Chemical shifts for various carbons of SBF from ^{13}C-NMR.

Chemical shift (ppm)	Chemical group
20–50	PS and $PB_{1,2}$ aliphatic carbons
110–120	$-\underline{\mathbf{C}}F_2$-, -$\underline{\mathbf{C}}F_3$
120–130	PS aromatic carbons
140	PS aromatic carbon
150	–O$\underline{\mathbf{C}}$(O)-

Table 2.
Contact angle results for neat and SBF copolymers.

Copolymer	Contact angle (°)	γ_s(mN/m)[a]
SB	106.1	9.51
SBF	113.6	6.54

[a] $\gamma_S = \frac{\gamma_L}{4}(1+\cos\theta)^2$, with $\gamma_L(H_2O) = 72.8$ mN/m[18,19].

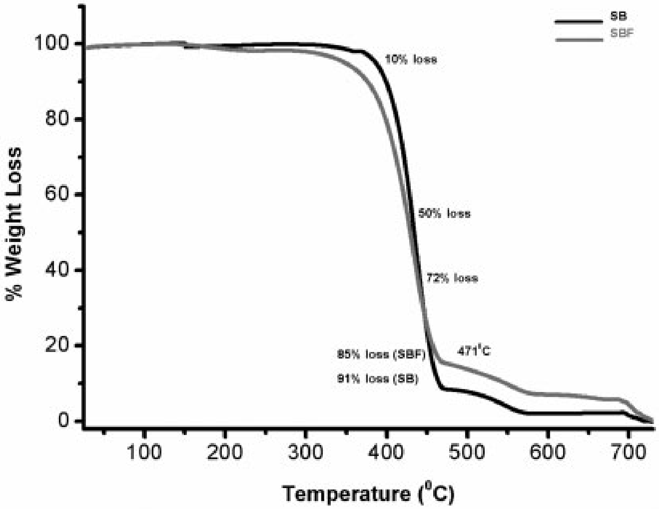

Figure 2.
TGA scans for neat SB and SBF copolymers.

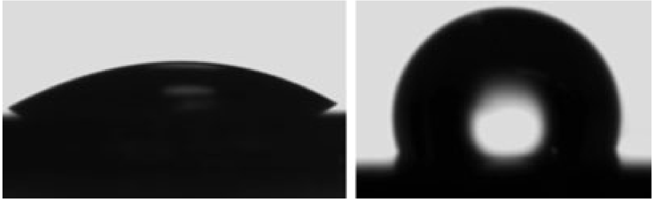

Figure 3.
Photographs of contact angles for Si (left) and SBF (right) copolymer at ambient conditions.

results for both the precursor and the modified copolymer, respectively. Images of contact angles for Si substrates (without any copolymer) and the SBF samples can be observed in Figure 3.

As can be observed from Table 2 the SBF copolymer shows higher hydrophobicity than the corresponding PS-b-$PB_{1,2}$. The F atoms incorporation critically affects hydrophobicity. Side groups, -CF_2- and -CF_3 can easily orient in the surface exhibiting high affinity with air and immiscibility with the copolymer backbone.[3,6,14,20–22] Fluorocarbon groups can migrate onto the surface, creating a surface fully occupied by F atoms. From contact angle measurements SBF showed a contact angle of 113.6° higher than that of its precursor $SB_{1,2}$ (106.1°).

Scanning Electron Microscopy (SEM)

As can be seen in Figure 4, from the SEM images for the surfaces of $SB_{1,2}$ and SBF copolymers, different topographies were observed. Therefore, we may conclude that the F atoms affect the texture, due to hydrogen bonding and the manner the side groups orient towards the surface, eventually leads to a more sponge-like structure for the SBF sample.

Atomic Force Microscopy (AFM)

For AFM analysis, films prepared from 5% w/w solutions of the neat and the modified copolymer was used. AFM images for SB and SBF show significant differences in the topography since after modification, the PB segment has a different molecular weight (attached fluorocarbon side group), which eventually alters the ratio of molecular weights between segments. In Figure 5 the morphologies for SB and SBF can be seen, where SB and SBF exhibit spherical and cylindrical morphology respectively at R.T.

Groups of -CF_3 can orient vertically (or at an angle) at the interface between polymer and air. This hexagonal orientation is possible due to immiscibility and affinity parameters.[3,6,14,20–22] It should be noted that the length and nature of the fluorocarbon chain can change the orientation of the -CF_3 groups.

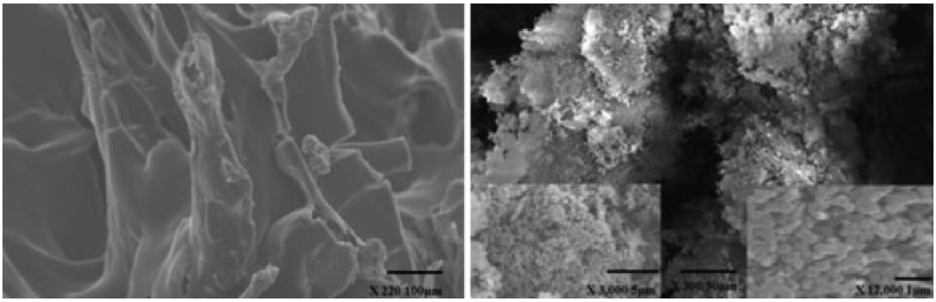

Figure 4.
SEM micrographs for: a) SB (left) and b) SBF (right) copolymers, at different magnifications.

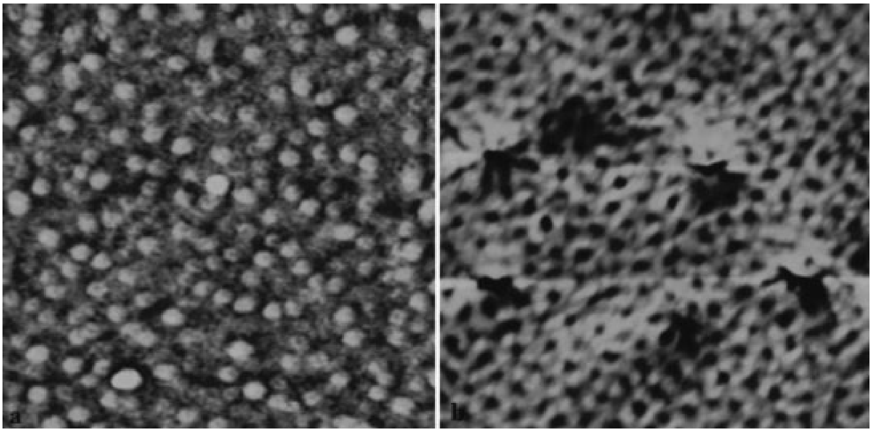

Figure 5.
AFM images for: a) SB and b) SBF copolymers, at R.T casted from toluene and THF respectively (1 μm × 1 μm).

Table 3.
Results from phase and height AFM images.

Sample	Phase				Height			
	Peak Range (°)	Max Peak (°)	(%) Max Peak	Roughness (°)	Peak Range (nm)	Max Peak (nm)	(%) Max Peak	Roughness (nm)
SB	12–28	22.5	7	1.81	1–21	17.1	4	1.89
SBF	6–47	21	10	3.86	1–76	23.1	7	8.19

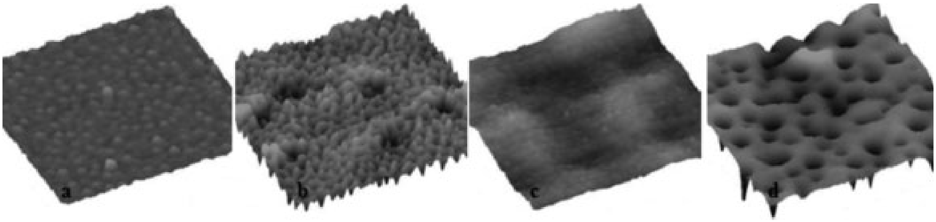

Figure 6.
AFM 3D images for: a) SB, b) SBF copolymers at 1 μm × 1 μm and c) SB, d) SBF copolymers at 3 μm × 3 μm.

Finally, from the results in Table 3 it is clear that SBF exhibits enhanced roughness when compared with the precursor SB. The peak range for SBF as well as the maximum peak is considerably higher than SB. In Figure 6 the 3D images for SB and SBF at different magnitude are exhibited. The synergy of the orientation for the fluorocarbon side groups and the enhanced roughness can lead to enhanced hydrophobicity as already was shown through the contact angle measurements.

Conclusion

SBF was found to exhibit better thermal stability than its precursor SB after the proper modification reaction was accomplished. The hydrophobicity of the modified copolymer was proven by conducting contact angle measurements, where SBF exhibited higher contact angle and lower surface energy than SB. From SEM images it is clear that after the modification, the SBF surface was altered leading to a sponge-like morphology (due to different electrostatic forces from the F atoms on the SBF). Finally, from the 3D AFM images it was found that roughness was relatively enhanced when compared with the SB precursor and the morphology was changed due to different ratio between the molecular weights for the two different systems (as it is explained before). It is clear that the SBF enhanced hydrophobicity was due to orientation of the fluorocarbon groups on the interface air-polymer and its increased roughness. Therefore, SBF can be used as a hydrophobic material at relatively high temperatures.

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