## Conventional Radical Polymerization and Iodine-Transfer Polymerization of 4'-Nonafluorobutyl styrene: Surface and Thermal Characterizations of the Resulting Poly(fluorostyrene)s

### Flavio Ceretta,<sup>1</sup> Alessandro Zaggia,<sup>1</sup> Lino Conte,<sup>1</sup> Bruno Ameduri<sup>2</sup>

<sup>1</sup>Fluorine Chemistry Laboratory, Dipartimento di Ingegneria Industriale, Università degli Studi di Padova, 35031 Padova, Italy <sup>2</sup>Ingénierie & Architectures Macromoléculaires, Institut Charles Gerhardt, UMR 5253, ENSCM, Montpellier Cedex 34296, France Correspondence to: B. Ameduri (E-mail: bruno.ameduri@enscm.fr)

Received 5 February 2013; accepted 22 March 2013; published online 3 May 2013 DOI: 10.1002/pola.26712

ABSTRACT: 4'-Nonafluorobutylstyrene (3) was synthesized and polymerized by conventional and controlled radical polymerization (iodine transfer polymerization (ITP)). Such an aromatic fluoromonomer was prepared from Ullmann coupling between 1-iodoperfluorobutane and 4-bromoacetophenone followed by a reduction and a dehydration in 50% overall yield. Two radical polymerizations of (3) were initiated by AIBN either under conventional or controlled conditions, with 1-iodoperfluorohexane in 84% monomer conversion and in 50% yield. ITP of (3) featured a fast monomer conversion and a linear evolution of the ln([M]<sub>0</sub>/[M]) versus time. The kinetics of radical homopolymerization of (3) enabled one to assess its square of the propagation rate to the termination rate  $(k_n^2/$  $k_t)$  in ITP conditions (36.2  $\cdot 10^{-2} \ \text{l} \cdot \text{mol}^{-2} \cdot \text{sec}^{-2}$  at 80  $^\circ\text{C})$  from the Tobolsky's kinetic law. Polydispersity index (D) of the fluoropolymer achieved by conventional polymerization was 1.30

**INTRODUCTION** Fluorinated polymers are attractive materials because of their remarkable properties<sup>1,2</sup> such as low polarizability, strong electronegativity, and small Van der Waals radius of the fluorine atom (1.32 Å). The strength of C—F bond (its bond dissociation energy,  $485 \text{ kJ} \cdot \text{mol}^{-1}$ ) implies high thermal and chemical resistance, resistance to oxidation and hydrolytic decomposition, low flammability, low reflective index, and low dielectric constants. One of the more interesting properties achieved by polymers having high density of C-F bonds is the simultaneous hydro- and oleophobicity, low wettability, antisticking properties, low adhesion, and low friction coefficient. When long perfluoroalkyl pendant side chains (more than eight perfluorinated carbon atoms) are incorporated into a polymer backbone, they selfassemble into ordered structures and lead to low-energy surfaces composed of tightly packed --CF3 groups.3-5 The marked rigidity of long perfluoroalkyl chain is responsible while it worthed 1.15 when synthesized by ITP. Thermal stabilities of these oligomers were satisfactory (10% weight loss under air occurred from 305 °C) whereas the melting point was 47 °C. Contact angles and surface energies assessed from spin-coated poly(3) films obtained by conventional (hysteresis =  $18^{\circ}$ , surface energy  $18 \text{ mN.m}^{-1}$ ) and ITP (hysteresis =  $47^{\circ}$ , surface energy  $15 \text{ mN.m}^{-1}$ ) evidenced D values' influence onto surface properties of the synthesized polymers. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 3202–3212

**KEYWORDS**: degree of polymerization (DP); fluoropolymers; 4'nonafluorobutyl styrene; gel permeation chromatography (GPC); heteroatom-containing polymers; iodine transfer polymerization; kinetics; living radical polymerization (LRP); NMR spectroscopy; surface properties; thermal properties

for the formation of stable and highly structured crystalline phases. Conversely, short perfluoroalkyl chain (less than six perfluorinated carbon atoms) at room temperature form isotropic phases without any structuration and leads to poor surface properties.<sup>3</sup>

Because of these outstanding properties and since mid-1950s, fluoropolymers containing long perfluoroalkyl side chains have been extensively used in the synthesis of low surface energy protective coatings of different materials (metals, paper, stone, wood, leather, and textiles, to name a few). In the last decade, concerns about these compounds have been underlined because long-chain perfluorinated telomers<sup>2</sup> satisfy the defining characteristics of persistent organic pollutants. They are toxic, persistent, and resistant to degradation.<sup>6,7</sup> This arises from the too stable perfluorinated chain which cannot degrade under enzymatic or metabolic

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decomposition.<sup>8</sup> In addition, they bioaccumulate and have long half-lives in human blood (3.5 years for perfluorooctanoic acid [PFOA] and 5.4 years for perfluorooctanesulfonic acids).<sup>9</sup> This issue pushed the Environmental Protection Agency to launch the 2010/2015 PFOA Stewardship Program which aims to the complete elimination of long-chain perfluorochemicals by 2015. Consequently, an urging need to find out alternatives has become a real challenge.

The hydrophobicity can be attributable to the tightly packed structure of the fluorinated side chains both in the bulk and at the surface of the polymer.<sup>3–5</sup> Polymers bearing fluorinated substituents that contain aromatic groups in the side chains are able to improve the surface properties by the enhanced self-assembly behavior of the semifluorinated side groups containing phenyl rings.<sup>10</sup>

Among polymers, polystyrenes exhibit several advantages such as satisfactory light transmittance, easy processing, good transparency, and low cost.<sup>11</sup> For these reasons, polystyrenes can be appropriate candidates for optical device materials, as evidenced by Boner and Hagemann<sup>12</sup> who reported that the  $T_g$  value is higher for a polystyrene that bears an ortho-substituted CF<sub>3</sub> group ( $T_g = 175$  °C) than those substituted in meta ( $T_g = 63$  °C) and para ( $T_g = 101$  °C) positions.

Regarding the synthetic aspect, the literature reports only a few examples of fluoroalkyl-substituted styrene mono- $\rm mers^{13}$  and most of them have been polymerized by conventional  $^{14-16}$  or controlled  $^{17-21}$  radical polymerization (Table 1). Indeed, controlled radical polymerization (CRP) has attracted a growing interest owing to the ability of this process to control the polymeric structures and architectures,<sup>22,23</sup> to predict molar masses, and to get narrow polydispersities.<sup>22-24</sup> Examples of different methods that lead to the controlled free-radical polymerization are as follows: nitroxide-mediated radical polymerization (i) (NMP),<sup>25,26</sup> (ii) atom-transfer radical polymerization (ATRP),<sup>27-29</sup> (iii) iodine-transfer polymerization (ITP),<sup>30-40</sup> (iv) reversed addition-fragmentation chain transfer,<sup>41,42</sup> (v) macromolecular design by interchange of xanthate,43 and (vi) organometallic radical polymerization,<sup>44,45</sup> including organocobalt-mediated radical polymerization, based on (Co(acac)<sub>2</sub>),<sup>46</sup> and CRP controlled by boron derivatives.<sup>47-53</sup> The literature reports a few studies on the CRP of fluorinated monomers<sup>23,31-40,45</sup> compared to those of hydrogenated styrenic and methacrylic monomers. This article aims at synthesizing a new poly(fluoroalkyl styrene) by controlled free radical polymerization. To the best of our knowledge, scarce fluorinated styrene monomers, for example 2,3,4,5,6pentafluorostyrene, have been polymerized by radical controlled conditions, either by ATRP<sup>17,54,55</sup> or by NMP,<sup>19-21</sup> only. However, to the best of our knowledge, no fluorinated styrene has been polymerized under degenerative transfer. Hence, this article deals with the synthesis of 4'-nonafluorobutyl styrene, its radical polymerization under conventional or controlled conditions (by ITP), and the comparison of the surface and thermal properties on both the resulting polymers.

### **EXPERIMENTAL**

### Materials

2,2'-Azobisisobutyronitrile (AIBN), tetrahydrofuran (THF), methanol, acetonitrile, potassium hydrogen sulfate, sodium borohydride, diiodomethane, and toluene were purchased from Aldrich Chemical. 1-Iodoperfluorohexane was a gift from Elf Atochem. 4'-Nonafluorobutylacetophenone (**1**) was synthesized as in the previously published study<sup>56</sup> from the crosscoupling reaction of 1-iodoperfluorobutane with 4'bromoacetophenone. Deuterated solvents were purchased at Eurisop-Top (Grenoble, France). All the solvents and reactants were used with a purity of 98–99%. AIBN was purified by recrystallization from methanol and dried under vacuum prior to use.

### Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 400 instrument, using deuterated chloroform as the solvent and tetramethylsilane (or CFCl<sub>3</sub>) as the reference for <sup>1</sup>H (or <sup>19</sup>F) nuclei. Coupling constants and chemical shifts are given in hertz (Hz) and parts per million (ppm), respectively. The experimental conditions for recording <sup>1</sup>H (or <sup>19</sup>F) NMR spectra were as follows: flip angle: 90° (or 30°), acquisition time: 4.5 s (or 0.7 s), pulse delay: 2 s, number of scans: 128, and pulse width: 5  $\mu$ s for <sup>19</sup>F NMR. In the details of NMR characterization, s, d, t, q, and m stand for singlet, doublet, triplet, quinted, and multiplet, respectively.

Size exclusion analyses were performed using a Spectra-Physics apparatus equipped with a set of two PLgel 5  $\mu m$  MIXED-C columns from Polymer Laboratories. The eluent was pure THF at a flow rate of 0.8 mL min^{-1}. The calibration curve was established using monodispersed PS standards from Polymer Laboratories (now Agilent).

Thermogravimetric analyses (TGAs) were carried out with a TGA 51 apparatus from TA instruments, under air, at the heating rate of 10 °C min<sup>-1</sup> from room temperature up to a maximum of 500 °C. The sample size was 15 mg.

GC/MS spectra were measured on a Carlo Erba Instrument MFC 500/QMD1000 using a silica-fused capillary PS264 column (30 m  $\times$  0.25 mm) on a Finnigan Mat TSQ7000 (capillary column, 30 m  $\times$  0.32 mm). Typical conditions were as follows: temperature program is 60 °C for 2 min, heating at 10 °C min<sup>-1</sup> up to 280 °C. Helium was used as the gas carrier (1 mL min<sup>-1</sup>).

Differential scanning calorimetry (DSC) measurements were conducted using a Pyris 1 apparatus from Perkin-Elmer Scans were recorded at a heating rate of 20 °C min<sup>-1</sup> from -100 to +150 °C and values of  $T_{\rm g}$  and  $T_{\rm m}$  were assessed from the second cycle. The sample weight was 10 mg.

The static, advancing, and receding contact angles were assessed using a KRÜSS GmbH *EasyDrop*, Drop Shape Analysis System, with a measuring range of  $1-180^{\circ}$ , volume of one drop of water: 5  $\mu$ L, volume of one drop of diiodomethane: 2  $\mu$ L, with a monochrome interline CCD, 25/30 fps camera

Monomer	Polymerization	<i>M</i> <sub>n</sub>	$M_{\rm w}/M_{\rm n}$	<i>T</i> g (°C)	<i>T</i> <sub>d</sub> (°C)	Ref.
F F F F	CONV.	470,000	1.83	107	420	Lou et al. <sup>15</sup>
	ATRP	11,400	1.21	95	436	Jankova and Hvilsted <sup>17</sup>
	NMP	3,500	1.03	-	-	Remzi et al. <sup>19</sup>
F F F CF <sub>3</sub>	CONV.	390,000	2.20	112	-	Lou et al. <sup>15</sup>
CF3	CONV.	59,700	3.23	165	382	Teng et al. <sup>16</sup>
CF <sub>3</sub>	CONV.	88,800	3.00	160	366	Teng et al. <sup>16</sup>

**TABLE 1** Methods of Radical Polymerization, Molecular Weights, and Thermal Properties of Several Fluorinated and Fluoroalkyl styrene-based Polymers<sup>a</sup>

<sup>a</sup> CONV., ATRP, and NMP stand for conventional, atom-transfer radical polymerization, and nitroxide-mediated polymerization, respectively.

with halogen lamp. The contact angles were determined using KRÜSS DSA1 v1.91 program. The values mentioned in this article were obtained from the average of 10 measurements.

The polymer film obtained for the contact angle assessments was formed using the spin coater (Karl Suss Technique SA apparatus, CT60 model). A solution of 20 mg of 4'-nonafluor-obutyl styrene in 2 mL of THF was placed on a 20 mm  $\times$  20 mm  $\times$  1 mm of quartz substrate. The substrate surface was covered using a pipette and followed by spinning at 1000 rpm for 3 min to spread and form a uniform thin film over the substrate.

During the static contact angle determination, the size of the drop did not alter during the measurement. For the assessments of the advancing angle, the syringe needle remained in the drop. Advancing and receding contact angles were determined by the sessile drop method, also carried out on the same polymer samples using a stainless steel needle connected with an automatically microliter syringe (diameter of the needle, 0.5 mm). Further, the difference between advancing and receding contact angles represents the hysteresis which is the result of the surface reorganization and mobility of the outer most atom groups. The water introduction and its withdrawal were monitored by a video camera that recorded the profile during the process. All calculation methods were based on the sessile drop method, whereas the surface energies calculation were assessed by the Owens-Wendt method.57 Further experiments were carried out with the same apparatus as follows: a drop of testing liquid was deposited on the

polymer surface by a syringe until a drop volume of 5  $\mu$ L is reached. Then, the test liquid was withdrawn from the surface until the liquid was completely removed. During this process, the instrument automatically recorded the contact angles with a preset speed of 25 frames per second. Each frame was then acquired at a specific time which corresponds to a specific drop volume. This event recorded by the instrument, which is called "run number," is associated to a specific contact angle measurement. Alternatively to run number, the *x*-axis could be converted in time and expressed in seconds.

### Synthesis of 4'-Nonafluorobutyl styrene Monomer (3)

The synthesis of 4'-nonafluorobutyl styrene monomer was achieved in two steps: the reduction of 4'-nonafluorobutyl acetophenone (1) followed by the dehydration of the resulting 4'-nonafluorobutyl phenylethanol (2) into 4'-nonafluorobutyl styrene (3) as shown in Scheme 1.

### Synthesis of 4'-Nonafluorobutyl phenylethanol (2)

4'-Nonafluorobutyl acetophenone (1) (15.5 g, 45.8 mmol), sodium borohydride (1.802 g, 47.7 mmol), and THF (50 mL) as the solvent were stirred into a 100-mL round-bottom flask in an ice bath. Methanol (50 mL) was slowly added drop-wise into the flask and the mixture was refluxed for 2 h under heating after being stirred for 30 min at room temperature. Then, methanol was removed by distillation. Water was added to the ether solution and the ether layer was separated from the aqueous one. The ether was removed by rotavapor and 14.4 g of colorless oil was distilled (b.p., 60–65 °C/0.2 mmHg; yield, 90%).



SCHEME 1 Synthetic route for the preparation of 4'-nonafluorobutyl styrene (3).

<sup>1</sup>H NMR of 4'-nonafluorobutyl phenylethanol (**2**) (Supporting Information Fig. S1),  $\delta$  (in CDCl<sub>3</sub>): 1.48 (d, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, CH<sub>3</sub>, 3H); 2.29 (s, -OH, 1H); 4.93 (m, CH, 1H); 7.50 (dd, <sup>3</sup>J<sub>HH</sub> = 16 Hz, <sup>4</sup>J<sub>HH</sub> = 8 Hz, protons form phenyl ring, 4H). <sup>19</sup>F NMR spectrum of 4'-nonafluorobutyl phenylethanol (Supporting Information Fig. S2)  $\delta$ : -81.1 (CF<sub>3</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub></sub>

### Synthesis of 4'-Nonafluorobutyl styrene (3)

A mixture composed of 4'-nonafluorobutyl phenylethanol **(2)** (14.41 g, 42.3 mmol), toluene (50 mL), and potassium hydrogen sulfate (4.02 g, 29.5 mmol) was heated under stirring at 100 °C for 48 h in a 100-mL round flask connected to a reflux condenser. The reaction was monitored by GC. After reaction, the mixture was distilled under vacuum to led to 9.35 g of a colorless liquid (b.p., 66–69 °C/0.39 mmHg; yield, 77%).

<sup>1</sup>H NMR of 4'-nonafluorobutyl styrene (**3**), δ (in CDCl<sub>3</sub>, Supporting Information Fig. S3): 5.39 (d, cis =CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 10.0 Hz, 1H); 5.87 (trans =CH<sub>2</sub>, <sup>3</sup>J<sub>HH</sub> = 17.5 Hz, 1H), 6.71-6.82 (dd, <sup>3</sup>J<sub>HH</sub> = 17.5 Hz, <sup>3</sup>J<sub>HH</sub> = 10 Hz, =CH, 1H); 7.52 (d, <sup>3</sup>J<sub>HH</sub> = 10.0 Hz, *m*-protons about C<sub>4</sub>F<sub>9</sub>, 2H), 7.56 (2H, d, <sup>3</sup>J<sub>HH</sub> = 10.0 Hz, *o*-protons about C<sub>4</sub>F<sub>9</sub>). <sup>19</sup>F NMR, δ (in CDCl<sub>3</sub>, Supporting Information Fig. S4): -81.1 (CF<sub>3</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>

# Radical Polymerizations of 4'-Nonafluorobutyl styrene (3)

The conventional radical polymerization of 4'-nonafluorobutyl styrene was carried out in a 50-mL two-necked round flask equipped with a magnet bar, a rubber septum, and a condenser connected to argon source, and containing 10.1 mg ( $1.02 \times \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ) of AIBN, 1.210 g (1.03

 $mol \cdot L^{-1}$ ) of 4'-nonafluorobutyl styrene, and 4 mL of acetonitrile. The flask was evacuated and backfilled with argon for 20 min and five thaw-freeze cycles were applied prior to the polymerization. The reaction mixture was then placed in a preheated oil bath at 80 °C for 270 min. Then, the solvent was removed by rotavapor, the residue was solubilized in minimum of THF, and precipitated from a large excess of cold methanol. After filtration, the precipitated product was dried in a vacuum oven at 60 °C for 15 h and 1.00 g (50% yield) of a white powder was obtained.

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ITP of 4'-nonafluorobutyl styrene was carried out by using the same conditions mentioned above. The mixture was composed of 10.1 mg ( $1.02 \times \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ) of AIBN, 2.002 g ( $1.03 \text{ mol} \cdot \text{L}^{-1}$ ) of 4'-nonafluorobutyl styrene, 138.0 mg ( $5.15 \times \cdot 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ) of 1-iodoperfluorohexane, 153.7 mg ( $0.26 \text{ mol} \cdot \text{L}^{-1}$ ) of 1,2-dichloroethane, and 4 mL of acetonitrile. After bubbling argon for 20 min, five thaw-freeze cycles were applied and then the mixture was placed in a preheated oil bath at 80 °C. The same purification procedure was adopted as mentioned above. For the kinetics, samples were periodically withdrawn from the medium during the polymerization to monitor the monomer conversion by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy. The precipitated product was dried in vacuum oven at 60 °C for 15 h, leading to 1.01 g (yield 50%) of a white powder ( $T_{\rm m} = 47$  °C, the DSC thermogram is shown in Supporting Information Fig. S9).

### **RESULTS AND DISCUSSION**

### Synthesis of 4'-Nonafluorobutyl styrene

The preparation of 4'-nonafluorobutyl styrene was achieved into two steps (Scheme 1): (i) first, a reduction of 4'-nona-fluorobutyl acetophenone (**1** that was optimized in the previous study<sup>56</sup>) in the presence of NaBH<sub>4</sub> as the reducing agent, leading to the formation of alcohol (**2**); (ii) the dehydration of the latter, in the presence of KHSO<sub>4</sub>, enabled us to synthesize monomer (**3**) in good yields (77%).<sup>58</sup>

<sup>1</sup>H (Supporting Information Fig. S3) and <sup>19</sup>F (Supporting Information Fig. S4) NMR spectra of 4'-nonafluorobutyl styrene are reported in the Supporting Information material and





**SCHEME 2** ITP of 4'-nonafluorobutyl styrene (**3**) in the presence of 1-iodoperfluorohexane as the chain-transfer agent, initiated by AIBN.

show the characteristic signals assigned to ethylenic (range, 5.39–6.82 ppm) and aromatic protons (7.50–7.58 ppm), and to  $CF_3$  (-81.1 ppm) and to  $C_3F_7$  (from -126.5 to -111.1 ppm) groups, respectively.

**Radical Polymerization of** 4'**-Nonafluorobutyl styrene (3)** Both the conventional and the controlled free radical polymerizations of 4'-perfluorobutyl styrene (3) have been investigated in this article in *quasi*-similar conditions; except for the second method that involves  $C_6F_{13}I$  as the chain-transfer agent.

First, the conventional radical polymerization was initiated by AIBN with an initial  $[3]_0/[AIBN]_0$  molar ratio of 100, using acetonitrile as the solvent. The resulting poly(4'-nonafluorobutyl styrene) was characterized by NMR spectroscopy (Supporting Information Figs. S6 and S7), which shows the absence of the ethylenic signals of monomer (3), and by size exclusion chromatography (SEC) (Supporting Information Fig. S8) from which the polydispersity value (D) of 1.3 was obtained.

Second, the ITP of monomer (3) required both the initiator and the iodine chain-transfer agent (in the present case, 1iodoperfluorohexane was chosen) (Scheme 2).

CRP was carried out in similar experimental conditions as mentioned above, but with the presence of 1-iodoperfluorohexane as the chain-transfer agent, with  $[3]_0/[C_6F_{13}I]_0/$ [AIBN]<sub>0</sub> initial molar ratio of 10:5:1. This reaction was simply carried out at atmospheric pressure and, after purification, the resulting poly(4'-nonafluorobutyl styrene) was characterized by NMR spectroscopy (Supporting Information Fig. S7) and SEC (Supporting Information Fig. S9).

The average number of monomer units present in the final polymer was calculated by <sup>19</sup>F NMR. In the case of ITP, the <sup>19</sup>F NMR spectrum (Fig. 1) of the produced polymer exhibits an overlapping between the signals assigned to  $CF_2$  of the perfluorobutyl chain, resulting from the monomer units and the signals of perfluorohexyl group which belongs to the chain-transfer moiety. However, the  $CF_3$  end groups were the only ones to be distinguished by two different signals: one peak is centered at -82.14 ppm (signal *a*) assigned to the perfluorobutyl chain arising from the pendant styrene, whereas that the other located at -82.44 ppm (signal *m*) attributed to  $CF_3$  group results from the perfluorohexyl group of the chain-transfer agent. Hence, the integrals of these signals obtained from the <sup>19</sup>F NMR spectrum enabled



**FIGURE 1** <sup>19</sup>F NMR spectrum of poly(4'-nonafluorobutyl styrene) (4) synthesized by ITP (recorded in d-THF, from  $[3]_0:[C_6F_{13}I]_0:[AIBN]_0 = 100:5:1)$ .



**FIGURE 2** TGA thermograms of the poly(4'-nonafluorobutyl styrene) (under air) obtained by conventional radical polymerization and ITP of 4'-nonafluorobutyl styrene (**3**).

us to assess the average monomer units in the polymer, as  $DP_n$  (eq 1).

DP<sub>n</sub>

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$$\frac{\left(\int_{\text{Styrene}} CF_3 - \int_{C_6F_{13}} CF_3\right) + \sum \left(\int_{\text{Styrene}} CF_2 - \int_{C_6F_{13}} CF_2\right)}{\text{Number of fluorine atoms for each monomer unit (9)}}$$
(1)

where  $\int_x CF_t$  stands for the integral of the NMR signal assigned to  $CF_t$  in *x*-unit (monomer or CTA).

Subtracting the values of the integrals of signals assigned to the fluorinated moiety in the pendant chains  $(\int_{\text{Styrene}} CF_3)$  from the integral of the peaks corresponding to the chain-transfer agent  $(\int_{C_6F_{13}} CF_3)$  enabled us to obtain an average  $DP_n$  value of 8 monomeric units.

The values of polydispersity indices (Ds) are 1.30 (Supporting Information Fig. S7) for the conventional polymerization



### Kinetics of ITP of 4'-Nonafluorobutyl styrene

The kinetics of radical homopolymerization of monomer (3) by ITP was monitored by <sup>1</sup>H NMR spectroscopy (Fig. 3) from the calculation of the integrals of the characteristic signals of 4'-nonafluorobutyl styrene. 19F NMR spectra are also supplied (Supporting Information Fig. S10) but are not convincing for that kinetics. Thus, <sup>1</sup>H NMR spectroscopy enabled one to assess the conversion  $(\chi)$  of monomer (3) using 1,2dichloroethane as the internal standard (which exhibits a singlet centered at 3.66 ppm assigned to four equivalent protons). When the polymerization reaction was carried out in the presence of acetonitrile as the solvent, the NMR spectrum did not exhibit any signals attributed to the polymer but only those of the monomer, because the polymer precipitated when it was formed. However, these NMR spectra (Fig. 4) permitted to monitor fluorinated styrene (3) conversion ( $\chi$ ) versus time during ITP of 4'-nonafluorobutyl styrene.

4'-Nonafluorobutyl styrene conversion ( $\chi$ ) is calculated from eq 2.

$$\chi = \frac{[M]_0 - [M]}{[M]_0} \times 100$$
 (2)

where  $[M]_0$  and [M] represent the initial concentration of monomer (**3**) and the monomer concentration at time *t*, respectively. Values of  $\chi$  were assessed from the integrals of the signals of 4'-nonafluorobutyl styrene deduced from the <sup>1</sup>H NMR spectra (eq 3).

$$\chi = 100 \times \frac{\left(\int_{7.3 \text{ppm}}^{7.4 \text{ppm}} C_6 H_4 + \int_{6.6 \text{ppm}}^{6.7 \text{ppm}} C H_+ \int_{5.3 \text{ppm}}^{5.8 \text{ppm}} C H_2\right)_{t=0} - \left(\int_{7.3 \text{ppm}}^{7.4 \text{ppm}} C_6 H_4 + \int_{6.6 \text{ppm}}^{6.7 \text{ppm}} C H_+ \int_{5.3 \text{ppm}}^{5.8 \text{ppm}} C H_2\right)_t}{\left(\int_{7.3 \text{ppm}}^{7.4 \text{ppm}} C_6 H_4 + \int_{6.6 \text{ppm}}^{6.7 \text{ppm}} C H_+ \int_{5.3 \text{ppm}}^{5.8 \text{ppm}} C H_2\right)_{t=0}}$$
(3)

Values of 4'-nonafluorobutyl styrene conversion ( $\chi$ ) are listed in Table 3. The maximum of  $\chi$  value was reached at 84% after 270 min.

Values of  $ln([M]_0/[M])$  versus time are plotted in Figure 4 and show a linear tendency.

The mechanism of free radical polymerization<sup>59,60</sup> requires that the polymerization rate to be of first order with respect to the monomer and of half-order with respect to the initiator concentration. Using the Tobolsky's equation<sup>61</sup>:

**TABLE 2** Values of the Average Molecular Weight ( $M_n$ ), Polydispersity Index (D) Assessed by SEC, and Temperature of the Thermal Stability After 10% Weight Loss (Under Air) of the Polymer Obtained by Conventional Radical Polymerization and ITP of 4'-Nonafluorobutyl Styrene (**3**) With [3]<sub>0</sub>:[C<sub>6</sub>F<sub>13</sub>]<sub>0</sub>:[AIBN]<sub>0</sub> = 100:5:1 Initial Molar Ratio

Method of radical Polymerization	<i>M</i> <sub>n</sub>	Ð	<i>T</i> <sub>d</sub> (10%)
Conventional	7,400	1.30	305
Controlled (ITP)	7,500	1.15	305





**FIGURE 3** <sup>1</sup>H NMR spectra of samples from the CRP of 4'-nonafluorobutyl styrene in the presence of  $C_6F_{13}I$  after 40 (bottom), 60, 120, 180, and 270 min (top) of reaction (recorded in CDCI<sub>3</sub>).

$$\ln\left(\frac{[M]_{0}}{[M]}\right) = 2k_{p}\sqrt{\frac{f[I]_{0}}{k_{d}k_{t}}}(1 - e^{-\frac{k_{d}t}{2}})$$
(4)

and plotting the experimental values of ln([M]<sub>0</sub>/[M]) *versus*  $(1-e^{-\frac{k_d t}{2}})$  enabled to assess the square of the propagation rate to the termination rate,  $k_p^2/k_t$ , (Fig. 5) from the slope of the straight line,<sup>62</sup> considering the rate of decomposition of the initiator,<sup>63</sup>  $k_d$  (AIBN in acetonitrile at 80 °C) as  $1.25 \times \cdot 10^{-4} \text{ s}^{-1}$ , whereas the efficiency of the initiator<sup>61</sup> (f) was 0.6.

The  $k_p^2/k_t$  value of 4'-nonafluorobutyl styrene obtained is  $3.62 \times 10^{-2}$  at 80 °C. Table 4 lists the different  $k_p^2/k_t$  values of several styrenic monomers. However, it is difficult to



**FIGURE 4** Ln([M]<sub>0</sub>/[M]) versus time for the CRP of 4'-nonafluorobutyl styrene (**3**) in the presence of 1-iodoperfluorohexane as the chain-transfer agent ([monomer **3**]<sub>0</sub>:[ $C_6F_{13}I$ ]<sub>0</sub>:[AIBN]<sub>0</sub> = 100:5:1) at 80 °C.

compare  $k_p^2/k_t$  values assessed from different surveys because the results can be influenced by temperature, the nature of the solvent, and the initiator (as evidenced by the first three values reported from the polymerization of styrene, Table 4). Monomer (3) was found to exhibit the highest  $k_p^2/k_t$  value with respect to those of the other styrenic monomers.

### **Contact Angle Assessment**

The surface morphology of the polymers affects their surface property.<sup>68–71</sup> Besides the chemical inertness and the thermal stability, one of the most relevant properties of fluoropolymers is the hydro- and oleophobicity<sup>1,2,72</sup> which can be assessed by contact angle measurements between solid and liquid interfaces. Spontaneous spreading of a solvent (water and diiodomethane as polar and apolar solvents, respectively) onto the surface of a polymer film has been studied with the sessile drop method. Three different types of contact angles can be measured: (i) the static contact angle,  $\theta_s$ 

**TABLE 3** Evolution of the 4'-Nonafluorobutyl Styrene Conversion ( $\chi$ ) Monitored by <sup>1</sup>H NMR Spectroscopy ([3]<sub>0</sub>:[AIBN]<sub>0</sub>:[C<sub>6</sub>F<sub>13</sub>I] = 100:1:5 at 80 °C).

Time (min)	[M]/[M] <sub>0</sub>	In([M] <sub>0</sub> /[M])	$1 - \exp(-k_{ m d}  imes t/2)$	χ (%)
0	1.000	0	0	0.0
40	0.9929	0.0072	0.1393	0.7
60	0.9200	0.0834	0.2015	8.0
120	0.5071	0.6790	0.3624	49.3
180	0.2100	1.5606	0.4908	79.0
270	0.1514	1.8876	0.6367	84.9



**FIGURE 5** Ln([M]<sub>0</sub>/[M]) versus  $1 - \exp(-k_d \times t/2)$  for the CRP of 4'-nonafluorobutyl styrene initiated by AIBN at 80 °C in the presence of C<sub>6</sub>F<sub>13</sub>I (slope = 2.664).

(a drop is produced before the measurements and has a constant volume during the experiment), (ii) the advancing contact angle,  $\theta_a$  (the mean of the contact angle measurements during the advancing of the liquid boundary over a dry clean surface), and (iii) the receding contact angle,  $\theta_r$  (the mean of the contact angle values determined during the retreating of the liquid boundary over a previously wetted surface). The contact angle hysteresis is defined as the difference between the advancing and the receding angles ( $\Delta \theta = \theta_a - \theta_r$ ).<sup>73,74</sup>

The values of static contact angles were calculated for water and diiodomethane drops on the surface of a glass spin-coated with poly(4'-nonafluorobutyl styrene) (Fig. 6), to assess the surface tension of the solid. Measurements were achieved onto polymeric coatings produced from both conventional radical polymerization and CRP of 4'-nonafluorobutyl styrene and are listed in Table 5. Poly(4'-nonafluorobutyl styrene) achieved by CRP displayed a water and diiodomethane static contact angles of  $110 \pm 1$  and  $85 \pm 1^{\circ}$ , respectively, higher than that obtained by the conventional method that led to static contact angles of  $103 \pm 1$  and  $84 \pm 1^{\circ}$ , respectively.

Static contact angles of a surface spin-coated with poly (4'-nonafluorobutyl styrene) are comparable to those

reported by Takahara's team for a coating made of poly(2-perfluorooctyl-ethyl acrylate).<sup>75</sup> Yet, this latter polymer has four CF<sub>2</sub> units more than poly(4'-nonafluorobutyl) styrene. The total surface energy of poly(4'-nonafluorobutyl styrene) calculated by the Owens and Wendt equation<sup>57</sup> synthesized by conventional radical polymerization is about  $18 \pm 2$  mN m<sup>-1</sup>. Interestingly, the surface energy value of the polymer obtained by ITP is  $15 \pm 2$  mN m<sup>-1</sup>.

These results underline that ITP process improves not only the D-value but also the hydro- and oleophobicity of the polymer. Yamaguchi et al.<sup>75</sup> compared the surface properties poly(2-perfluorooctyl-ethyl acrylate) of with broad (D = 1.86) and narrow (D = 1.05) polydispersity indices synthesized by surface-initiated ATRP on a flat silicon substrate. These authors found that the contact angle hysteresis strongly depended on the D-values of such fluoropolymers. Conversely, no significant difference was noted between static contact angles assessed on poly(2-perfluorooctyl-ethyl acrylate) with broad and narrow *D*-values. The difference on contact angle hysteresis recorded for low and high D polymers can be probably explained by the different surface orientations of fluorinated chains on the polymer surfaces. Takahara<sup>75</sup> performed GI-WAXD experiments on poly(2-perfluorooctyl)ethyl acrylates having low and high D-values. This study nicely revealed that, in the polymers with high Dvalues, the Rf groups formed hexagonal packing states with a direction normal to the air/polymer interface and thus reducing the surface free energy. In contrast, the Rf density at the outermost surface of the brush with low D would be high enough to stretch the polymer backbone in the perpendicular direction. As a consequence, Rf groups lay parallel to the surface and thus decreasing their contribution to the surface energy reduction. Though we did not deeply characterize the polymeric layer by SAXS or GI-WAXD techniques, the relationship between D-values and surface-free energy for poly(4'-nonafluorobutyl styrene) is in agreement with that obtained by Takahara's team for poly(2-perfluorooctylethyl acrylate) (Table 6).

Values of advancing and receding water contact angles are shown in Figure 7 which represents the advancing and receding contact angle values versus the progressive number

**TABLE 4** Values of  $k_p^2/k_t$  for Different Styrenic and Fluorinated Styrenic Monomers

Monomer	$k_{\rm p}^2/k_{\rm t}$ (L mol <sup>-1</sup> s <sup>-1</sup> )	<i>T</i> (°C)	Initiator	Ref.
Styrene	$8.37  imes 10^{-3}$	100	AIBN	Tobolsky <sup>61</sup>
Styrene	$3.84 \times 10^{-3}$	80	DTBP <sup>a</sup>	Pryor et al. <sup>64</sup>
Styrene	$1.11 \times 10^{-3}$	60	DTBP <sup>a</sup>	Pryor et al. <sup>64</sup>
Pentafluorostyrene	$2.96 \times 10^{-3}$	60	AIBN	Pryor and Huang <sup>65</sup>
4'-Nonafluorobutyl styrene (3)	$36.20  imes 10^{-3}$	80	AIBN	This study
Vinylbenzyl chloride	$3.40 imes10^{-3}$	80	AIBN	Couture and Ameduri <sup>66</sup>
<i>p</i> -Chlorostyrene	$0.29 \times 10^{-3}$	30	AIBN	Boyer et al. <sup>67</sup>
<i>p</i> -Methylstyrene	$0.17 \times 10^{-3}$	30	AIBN	Boyer et al. <sup>67</sup>

<sup>a</sup> DTBP stands for di *t*-butyl peroxide.





**FIGURE 6** Drops of water (left,  $\theta = 110 \pm 1^{\circ}$ ) and diiodomethane (right,  $\theta = 85 \pm 1^{\circ}$ ) deposited on a surface treated with a poly(4'-nonafluorobutyl styrene) polymerized by ITP.

of measurements acquired by the instrument (run number). In the case of broad *D*-value of poly(4'-nonafluorobutyl styrene), the mean advancing contact angle ( $\theta_a$ ) was  $102 \pm 1^{\circ}$ , whereas the average receding contact angle ( $\theta_r$ ) was  $84 \pm 1^{\circ}$  with a hysteresis of  $18 \pm 2^{\circ}$ . Instead, in the case of narrow *D*, the mean advancing contact angle ( $\theta_a$ ) of poly(4'-nona-fluorobutyl styrene) reached  $113 \pm 1^{\circ}$ , whereas mean receding contact angle ( $\theta_a$ ) was  $66 \pm 1^{\circ}$  with an hysteresis of  $47 \pm 2^{\circ}$ . This observation features that water repellency of poly(4'-nonafluorobutyl styrene) is strongly influenced by the *D*-value. Similar to the study reported by other authors,<sup>75,76</sup> the relationship between the aggregation state of the fluorinated chains and the *D*-values should deserve to be further investigated.

#### CONCLUSIONS

For the first time, ITP of 4'-nonafluorobutyl styrene controlled by 1-iodoperfluorohexane has been reported and compared to the conventional radical polymerization. As expected, polymers obtained by ITP displayed more narrow polydispersity index (D = 1.15) than those synthesized by conventional radical polymerization (D = 1.30). The thermal stability of the polymers was satisfactory with a 10% weight loss under air noted at 305 °C. Though the molar masses-conversion linear relationship was not investigated, the kinetics of radical homopolymerization enabled to assess the  $k_p^2/k_t$  value ( $3.62 \times 10^{-2}$  L mol<sup>-1</sup> s<sup>-1</sup> at 80 °C). Static water and diiodomethane contact angles and dynamic water contact angles were determined from surfaces spin-coated

with poly(4'-nonafluorobutyl styrene) achieved from both strategies. Values of contact angles evidenced the satisfactory hydro- and oleophobicity of the synthesized polymers, and no significant difference was noted for the static contact angles between the polymer synthesized by both techniques with a surface tension of  $15 \pm 2$  and  $18 \pm 2$  mN·m<sup>-1</sup>, respectively. Conversely, an increase of the hysteresis in polymer with lower polydispersity ( $47 \pm 2^{\circ}$ ) compared to those with higher  $\mathcal{D}$  ( $18 \pm 2^{\circ}$ ) was observed. These obtained results suggest a strong correlation between  $\mathcal{D}$ -values and surface properties of poly(4'-nonafluorobutyl styrene). These preliminary results deserve to be extended to higher-molecular-weight polymers and to further polymerizations (also in

**TABLE 6** Comparison Between the Dynamic Water ContactAngle Measurements of Poly(4'-nonafluorobutylstyrene) andPoly(2-perfluorooctylethyl acrylate) with Narrow and Broad Polydispersity (D)

	Ð	θa <sup>a</sup> (°)	$ heta_{r}^{\;b}$ (°)	Hysteresis <sup>c</sup> (°)
Poly(4'-nonafluorobutyl	1.30	$102\pm1$	$84\pm1$	$18\pm2$
styrene)	1.15	$113\pm1$	$66 \pm 1$	$47 \pm 2$
Poly(2-perfluorooctyl-	1.86	128	105	23
ethyl acrylate) <sup>74</sup>	1.05	115	80	35

<sup>a</sup>  $\theta_{a}$ , advancing contact angle.

<sup>b</sup>  $\theta_{\rm r}$ , receding contact angle.

<sup>c</sup> Hysteresis =  $\theta_a - \theta_r$ .

**TABLE 5** Comparison Between the Static Contact Angle Measurements and Surface Tension of Poly(4'-nonafluorobutyl styrene) and Poly(2-perfluorooctylethyl acrylate)<sup>75</sup> with Broad And Narrow D, achieved by Conventional Radical Polymerization and CRP, respectively

	Đ	Water Contact Angle (°)	CH <sub>2</sub> I <sub>2</sub> Contact Angle (°)	Polar Part (mN m <sup>-1</sup> )	Dispersive Part (mN m <sup>-1</sup> )	Surface Tension (mN m <sup>-1</sup> )
Poly(4'-nonafluorobutyl styrene)	1.30	$103\pm1$	$84\pm1$	$3\pm1$	$15\pm1$	$18\pm2$
	1.15	$110\pm1$	$85\pm1$	$1\pm1$	$14\pm1$	$15\pm2$
Poly(2-perfluorooctyl-ethyl acrylate) <sup>75</sup>	1.86	122	99	-	-	7.7
	1.05	115	103	-	-	9.4



FIGURE 7 Advancing and receding water contact angles assessed with water drop on surface spin-coated with poly(4'-nonafluorobutyl styrene) polymer synthesized by conventional radical polymerization (left) and ITP (right).

the presence of  $\alpha, \omega$ -diiodoperfluoroalkanes, under progress). The influence of *D*-values onto the molecular aggregation state and the fluorinated groups should also be investigated.

### ACKNOWLEDGMENT

The authors thank Elf Atochem Company for providing of 1iodoperfluorohexane free sample and Institut de Chimie of CNRS for financial support.

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