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Controlled Radical Polymerization vs Conventional Radical Polymerization: Differences in Surface Properties of 4'-Nonafluorobutyl Styrene Polymers

Falvio Ceretta[a], Alessandro Zaggia*[a], Lino Conte[a], Bruno Ameduri[b]

[a]Dipartimento di Ingegneria Industriale - Università degli Studi di Padova, Via Marzolo 9 35131 Padova, Italy
[b] Ingénierie & Architectures Macromoléculaires, Institut Charles Gherardt, UMR 5253, 8, Rue Ecole Normale 34296 Montpellier , France
alessandro.zaggia@unipd.it

4'-Nonafluorobutyl styrene was synthesized and polymerized by conventional and controlled radical polymerization (CRP) based on iodine transfer polymerization (ITP) technique. The fluorinated monomer was prepared from Ullmann coupling between 1-iodoperfluorobutane and 4'-nonafluorobutyl acetophenone followed by a reduction and a dehydration in overall 50% yield. The radical polymerization of 4'-nonafluorobutyl styrene was initiated by AIBN and controlled by 1-iodoperfluorohexane in 84% monomer conversion and in 50% yield. The benefits of ITP of 4'-nonafluorobutylstyrene featured (i) a fast monomer conversion, monitored by ^{1}H and ^{19}F NMR in the presence of 1,2-dichloroethane as the internal standard, (ii) the evolution of the $\ln([M]_0/[M])$ *versus* time that evidenced a linear behavior. The square of the propagation rate to the termination rate (k_p^2/k_t) of 4'-nonafluorobutyl styrene in ITP conditions was assessed ($3.66 \cdot 10^{-2}$ L · mol^{-1} · s^{-1} at 80 °C) according to the Tobolsky's kinetic law. The polydispersity index of fluoropolymer achieved by conventional polymerization was 1.30 while it was reduced to 1.15 for that synthesized by the controlled way. The thermal stability of these oligomers was satisfactory (the 10% weight loss under air occurred from 305 °C) and the melting point was about 47 °C. Contact angles and surface energies assessed on surface spin-coated polymeric films made of poly(4'-nonafluorobutyl styrene) obtained by conventional (hysteresis = 18° ± 2°, surface energy 18 ± 2 mN/m), and controlled radical polymerization (hysteresis = 47° ± 2°, surface energy 15 ± 2 mN/m) evidenced the influence of the PDI values with the surface properties of the synthesized polymers.

1. Introduction

Fluorinated polymers are attractive materials because of their unique properties (Banks, 1994). One of the more striking property achieved by polymers having high density of C-F bonds is the simultaneous hydro and oleophobicity, low wettability, anti-sticking 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 self-assemble into ordered structures leading to low energy surfaces composed of tightly packed –CF_3 groups (Mao et al., 1997). While the marked rigidity of long perfluoroalkyl chain is responsible for the formation of highly structured crystalline phases short perfluoroalkyl chain (less than six perfluorinated carbon atoms) at room temperature form isotropic phases without any structuration (Wang et al., 1997).

In the last decade, concerns about long-chain perfluorinated compounds are grown because they satisfy the defining characteristics of persistent organic pollutants. They are toxic, persistent and extremely resistant to degradation. As a consequence of the EPA's 2010/2015 PFOA Stewardship Program which aims to the complete elimination of long-chain perfluorochemicals by 2015 an urging need to find out alternatives has become a real challenge.

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Polymers bearing short fluorinated substituents and containing aromatic groups in the side chains (which confer rigidity to the chemical structure) are able to improve the surface properties by the enhanced self-assembly behavior of the semifluorinated side groups containing phenyl rings.

Only a few examples of fluoroalkyl substituted styrene monomers are reported in literature (Wadekar et al., 2010) and most of them were polymerized by conventional radical polymerization. Actually, controlled radical polymerization (CRP) has attracted growing attention due to the ability of this process to control polymer structures and architectures. The present work aims at synthesizing 4'-nonafluorobutyl styrene and at polymerizing it under iodine transfer polymerization in order to assess the influence of the polymerization process on the final surface properties of the polymer itself.

2. Synthesis and Characterization

2.1 Synthesis of 4'-nonafluorobutyl styrene

The synthesis of styrene monomer was achieved in two steps: the reduction of 4'-nonafluorobutylacetophenone (1) and the dehydration of 4'-nonafluorobutyl phenylethanol (2) to 4'-nonafluorobutyl styrene (3) as reported in Scheme 1.

Synthesis of 4'-nonafluorobutyl phenylethanol (2). 4'-Nonafluorobutyl acetophenone (1) (15.5 g, 45.8 mmol), sodium borohydride (1.8 g, 47.7 mmol), and THF (50 ml) as the solvent were stirring 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 hours under heating after being stirred for 30 minutes at room temperature. Methanol was removed by distillation. Water was added to the ether solution and the ether layer was taken out. The ether was removed by rotavapor and 14.4 g of colorless oil (b.p. 60-65 °C/0.2 mmHg) were obtained (yield: 90%).

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 hours in a 100 ml round flask connected to a reflux condenser. The reaction was monitored by gas-chromatography. 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%).

Radical polymerizations of 4'-nonafluorobutyl styrene

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 13.6 mg ($1.01 \cdot 10^{-2}$ mol·L^{-1}) of AIBN, 2.00 g (1.01 mol·L^{-1}) of 4'-nonafluorobutyl styrene, 153.7 mg (0.25 mol·L^{-1}) of 1,2-dichloroethane and 4 ml of acetonitrile. The flask was evacuated and backfilled with argon for 20 minutes and 5 thaw-freeze cycles were applied prior to the polymerization. The reaction mixture was then placed in an oil bath, pre-heated at 80 °C for 270 minutes. 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 (yield 50%) of a white powder was obtained.

Iodine transfer polymerization of 4'-nonafluorobutyl styrene was carried out in the same conditions as above. The mixture was composed of 13.6 mg ($1.01 \cdot 10^{-2}$ mol·L^{-1}) of AIBN, 2.00 g (1.01 mol·L^{-1}) of 4'-nonafluorobutyl styrene,138.0 mg ($5.05 \cdot 10^{-2}$ mol·L^{-1}) of 1-iodoperfluorohexane, 153.7 mg (0.25 mol·L^{-1}) of 1,2-dichloroethane and 4 ml of acetonitrile. After bubbling argon for 20 minutes, and 5 thaw-freeze cycles were applied, the reactant mixture was placed for 270 minutes in a oil bath pre-heated at 80 °C. The same purification procedure was adopted as above. The precipitated product was dried in vacuum oven at 60 °C for 15 h, 1.01 g (yield 50%) of white polymer was obtained.

Samples were periodically withdrawn from the medium during the polymerization in order to monitor the monomer conversion by ^{1}H and ^{19}F NMR spectroscopy.

3. Results and discussion

The synthesis of 4'-nonafluorobutyl styrene was achieved into two steps (Figure 1).

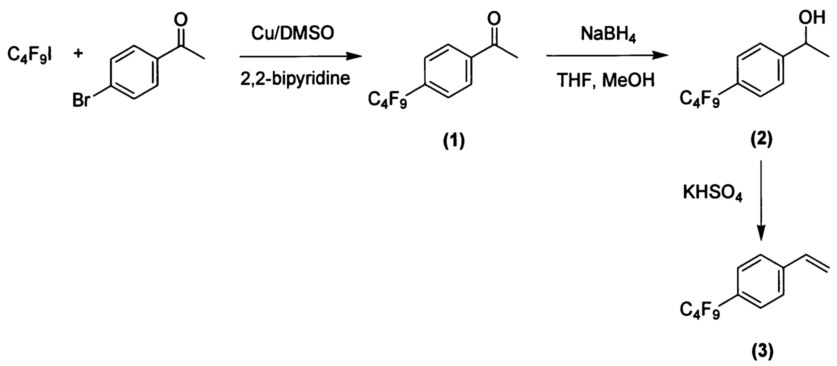

Figure 1: Synthetic route for the preparation of 4'-nonafluorobutyl styrene (3).

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.

Second, in iodine transfer polymerization of monomer (**3**), the initiator was required together with the iodine chain transfer agent (in the present case 1-iodoperfluorohexane was chosen) (Figure 2).

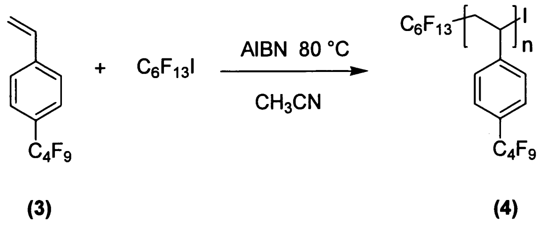

Figure 2: Iodine transfer polymerization of 4'-nonafluorobutyl styrene (3) in the presence of 1-iodoperfluorohexane as the chain transfer agent, initiated by AIBN.

Controlled radical polymerization was carried out in similar experimental conditions, but with the presence of 1-iodoperfluorohexane as the chain transfer, with $[3]_0/[AIBN]_0$ and $[3]_0/[C_6F_{13}I]_0$ initial molar ratios of 100 and 20, respectively. The average number of monomer units present in the final polymer was calculated by ^{19}F NMR. In the case of iodine transfer polymerization, the ^{19}F NMR spectrum exhibits an overlapping between the signals assigned to CF_2 of the perfluorobutyl chain resulting from the monomer units and the signals of perfluorohexyl that belong to the chain transfer ($C_6F_{13}I$) moiety. The integrals of these signals of CF_3 groups obtained from the ^{19}F NMR spectrum enabled us to assess the average monomer units present in the polymer, as DP_n (eq 1).

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

Where $\int_x CF_i$ stands for the integral of signal of CF_i in x unit (monomer or CTA).

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

The values of polydispersity indices (PDIs) are 1.30 for the conventional polymerization and 1.15 for the iodine transfer polymerization (ITP). The thermal stability of the polymers was satisfactory (the 10% of the weight loss under air was achieved from 305 °C, Table 1 and the melting point (T_m) was about 50 °C.

Table 1: Values of the average molecular weight (M_n), polydispersity index (PDI) measured by SEC, and temperature of the thermal stability after 10% of the loss of the polymer obtained by conventional and controlled radical polymerization of 4'-nonafluorobutyl styrene.

	M_n	PDI	T_d (10 %)
conventional	7400	1.30	305
controlled (ITP)	7500	1.15	305

Kinetics of iodine transfer polymerization of 4'-nonafluorobutyl styrene

The kinetics of radical homopolymerization of monomer (3) by ITP was monitored from the calculation of the integrals assessed from the ^{1}H NMR spectrum of 4'-nonafluorobutyl styrene. ^{1}H NMR spectroscopy was used to monitor the conversion (χ) using 1,2-dichloroethane as the internal standard. In fact, 1,2-dichloroethane was added to the reaction mixture as it exhibits a singlet at 3.66 ppm assigned to four equivalent protons.

When the polymerization reaction was carried out in the presence of acetonitrile as solvent, the NMR spectrum does not exhibit the signals characteristic of the polymer but only those of the monomer, because the polymer precipitates when it is formed. However, these NMR spectra (Figure 4) enabled to monitor the fluorostyrene conversion *versus* time during ITP of 4'-nonafluorobutyl styrene.

4'-Nonafluorobutyl styrene conversion (χ) was calculated according to Eq 2.

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

Where $[M]_0$ and $[M]$ represent the initial concentration of (3) monomer and the concentration of the monomer at time t, respectively. Values of χ were assessed from the integrals of the signals of 4'-nonafluorobutyl styrene deduced from the ^{1}H NMR measurements (Equation 3).

$$\chi = 100 \cdot \frac{\left(\int_{7.3\,ppm}^{7.4\,ppm} C_6H_4 + \int_{6.6\,ppm}^{6.7\,ppm} CH + \int_{5.3\,ppm}^{5.8\,ppm} CH_2\right)_{t=0} - \left(\int_{7.3\,ppm}^{7.4\,ppm} C_6H_4 + \int_{6.6\,ppm}^{6.7\,ppm} CH + \int_{5.3\,ppm}^{5.8\,ppm} CH_2\right)_t}{\left(\int_{7.3\,ppm}^{7.4\,ppm} C_6H_4 + \int_{6.6\,ppm}^{6.7\,ppm} CH + \int_{5.3\,ppm}^{5.8\,ppm} CH_2\right)_{t=0}} \qquad (3)$$

The results of the calculation of χ are reported in Table 2. The maximum of 4'-nonafluorobutyl styrene conversion was reached at 84 % after 270 minutes.

Table 2: Evolution of the 4'-nonafluorobutyl styrene conversion monitored by ^{1}H NMR spectroscopy ($[monomer]_0 : [AIBN]_0 : [C_6F_{13}I] = 100 : 1 : 5$ at 80 °C).

Time (min)	$[M]/[M]_0$	$\ln [M]_0/[M]$	$1-\exp(-k_d{*}t/2)$	χ (%)
0	1	0	0	0.0
40	0.9929	0.0031	0.1393	0.7
60	0.9200	0.0362	0.2015	8.0
120	0.5071	0.2949	0.3624	49.3
180	0.2100	0.6778	0.4908	79.0
270	0.1514	0.8198	0.6367	84.9

The mechanism of free-radical polymerization requires that the polymerization rate be of first order with respect to the monomer and of half-order with respect to initiator concentration. Using the Tobolsky's equation:

$$\ln\left(\frac{[M]_0}{[M]}\right) = 2k_p\sqrt{\frac{f[I]_0}{k_d k_t}}\left(1 - e^{-\frac{k_d t}{2}}\right) \qquad (4)$$

and plotting the experimental values of $ln\left(\frac{[M]_0}{[M]}\right)$ *versus* $\left(1-e^{-\frac{k_d t}{2}}\right)$ enabled us to assess the value of the square of the propagation rate to the termination rate, k_p^2/k_t, from the slope of the straight line
The k_p^2/k_t value of 4'-nonafluorobutyl styrene obtained is 3.66 10^{-2} at 80 °C. Table 3 lists different k_p^2/k_t values for different styrenic monomers. Considering that is difficult to compare k_p^2/k_t values calculated from different surveys because the results can be influenced by temperature, the solvent and the initiator (as evidenced by the first three values obtained the polymerization of styrene), it is found a higher k_p^2/k_t values with respect to that of the others monomers.

Table 3: Values of k_p^2/k_t for different styrenic and fluorinated styrenic monomers.

Monomer	k_p^2/k_t (l mol^{-1} s^{-1})	T(°C)	initiator
Styrene	$8.37 \cdot 10^{-3}$	100	AIBN
Styrene	$3.84 \cdot 10^{-3}$	80	DTBP*
Styrene	$1.11 \cdot 10^{-3}$	60	DTBP*
Pentafluorostyrene	$2.96 \cdot 10^{-3}$	60	AIBN
4'-nonafluorobutyl styrene (3)	$3.66 \cdot 10^{-2}$	80	AIBN
Vinylbenzyl chloride	$3.40 \cdot 10^{-3}$	80	AIBN
p-chlorostyrene	$2.92 \cdot 10^{-4}$	30	AIBN
p-methylstyrene	$1.70 \cdot 10^{-4}$	30	AIBN

**DTBP stands for di t-butyl peroxide.*

3.1 Contact angle determination

Measurements of static and dynamic contact angles were achieved onto coatings of polymers obtained both by conventional and by controlled radical polymerization of 4'-nonafluorobutyl styrene (Figure 3). Polymers achieved by controlled radical polymerization showed water and diiodomethane static contact angle of 110° ± 1° and 85° ± 1°, while for that obtained by conventional method, the static contact angles were 103° ± 1° and 84° ± 1°, respectively.

The total surface energy of poly(4'-nonafluorobutyl styrene) calculated by the Owens and Wendt equation synthesized by conventional radical polymerization worth 18 ± 2 mN/m. Conversely for the polymer obtained by ITP, the surface energy value is 15 ± 2 mN/m.

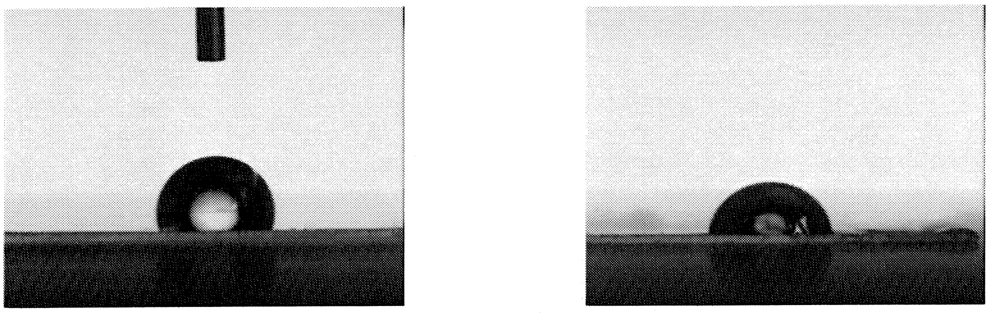

Figure 3: Drops of water (left, θ = 110° ÷ 1°) and diiodomethane (right, θ = 85° ÷ 1°) deposited on a surface treated with a poly (4'-nonafluorobutyl styrene) polymerized by ITP.

4. Conclusions

These results underline that ITP process improves not only the PDI but also the hydro- and oleophobicity of the polymer. Yamaguchi et al. (2012) compared the surface properties of poly(2-perfluorooctyl-ethyl acrylate) with broad (M_w/M_n = 1.86) and narrow (M_w/M_n = 1.05) polydispersity indices synthesized by surface-initiated ATRP on a flat silicon substrate. These authors found that contact angle hysteresis strongly depended on the PDI of such fluoropolymers. Conversely, no significant differences were noted between static contact angles assessed on poly(2-perfluorooctyl-ethyl acrylate) with broad and narrow PDI. The relationship between PDI values and surface free energy for poly(4'-nonafluorobutyl styrene) is in agreement with that obtained by Takahara's group for poly(2-perfluorooctyl-ethyl acrylate) (Table 4).

Values of advancing and receding water contact angles are reported in Figure 4. In the case of broad PDI of poly(4'-nonafluorobutyl styrene), the mean advancing contact angle (θ_a) was 102° ± 1°, while the average receding contact angle (θ_r) was 84° ± 1° with a hysteresis of 18° ± 2°. Instead, in the case of narrow PDI the poly(4'-nonafluorobutyl styrene) mean advancing contact angle (θ_a) reached 113° ± 1°, while mean receding contact angle (θ_a) was 66° ± 1° with an hysteresis of 47° ± 2°. In conclusion, water repellency of poly(4'-nonafluorobutyl styrene) is strongly influenced by the PDI value. In analogy with the work reported by other authors, the relationship between the aggregation state of the fluorinated chains and PDI should deserve to be further investigated.

Table 4: Comparison between the dynamic water contact angle measurements of poly(4'-nonafluorobutylstyrene) and poly(FA-C8) with narrow and broad PDI.

	PDI	**θ_a[a] (degree)**	**θ_r[b] (degree)**	**hysteresis[c] (degree)**
poly(4'-nonafluorobutyl styrene)	1.30	102 ± 1	84 ± 1	18° ± 2
	1.15	113 ± 1	66 ± 1	47° ± 2
poly(2-perfluorooctyl-ethyl acrylate)[58]	1.86	128	105	23
	1.05	115	80	35

[a] θ_a = advancing contact angle, [b] θ_r = reciding contact angle, [c] hysteresis = θ_a-θ_r.

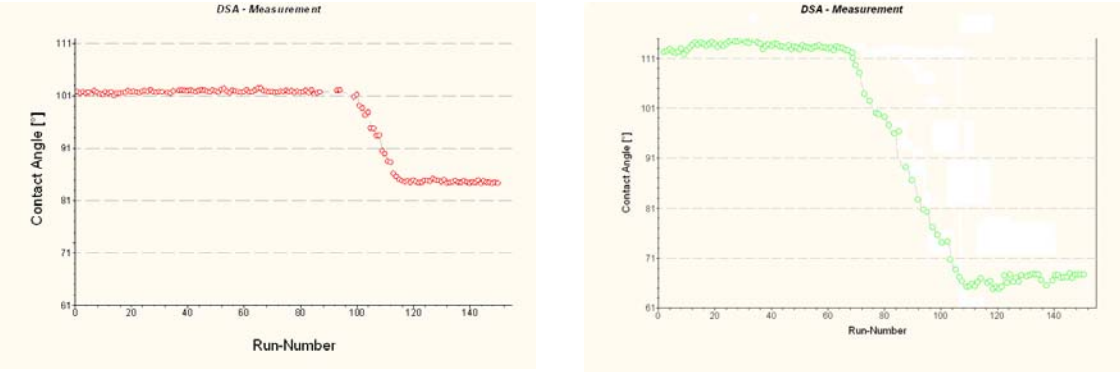

Figure 4: Advancing and receding water contact angle values assessed with water drop on surface spin-coated with poly(4'-nonafluorobutyl styrene) surface synthesized by conventional radical (left) and iodine transfer polymerization (right).

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