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Fluorinated poly(acrylates): influence of fluorinated chain length and hydrocarbon spacer on surface properties

A. Zaggia, G. Padoan, L. Conte, A. Morelli
Department of Chemical Processes of Engineering, University of Padua
Via Marzolo, 9 – 35131 Padua
Tel.:+39.049.8272555 – Fax: +39.049.8272557 – e-mail: fluoro@unipd.it

The big concern generated by the discovery that degradation of stain-resistant coatings led to the release of biopersistant perfluorooctanoic acid (PFOA) to the environment urged researchers on developing more environmentally friendly fluorinated compounds maintaining the same surface properties. Polyacrylates with long fluorinated tail (eight fluorinated carbon atoms are well known and apply as surface properties modifiers. The main need is to shorten the fluorinated tail using more effective "spacers" between the polyacrylates backbone and the fluorinated tails. (H. Nakamichi, 1996), (H.S.W. Hu and J.R. Griffith, 1996), (T.F. DeRosa et al., 1994), (V.V. Volkov et al, 1994), (A. Zaggia, 2007).
In this area we developed a family of fluorinated poly(acrylates) containing a short R_F side group (perfluorohexyl) and different type of hydrocarbon "spacers".
These monomers were co-polymerized with other non-fluorinated acrylates (chain extenders) to obtain the corresponding partially fluorinated poly(acrylates).
The surface properties of these new partially fluorinated polymers were then determined through surface tension evaluation and their protection properties on stone were evaluated via specific tests (I.P.A. test and graffiti test).

1. Introduction

Fluorine is a unique element able to impart to a macromolecule outstanding properties which includes low surface energies, low friction, enhanced thermal and chemical stability, extraordinary surface active properties (E. Kissa, 1994), (Y. Morita et al., 1999). Polyacrylates with perfluoroalkyl parts in their side chain are among the most hydrophobic and oleophobic polymers known.
The surface properties of fluorinated poly(acrylates) depends on pendant side perfluoroalkyl groups (R_F). Polymers with short fluorinated chains are not able to form an ordered surface because of high surface molecular mobility (E.F. Hare et al., 1954), (X. Li, et al.,2002). Fluorinated poly(acrylates) with longer R_F groups cause the formation of ordered surface with increased concentration of trifluoromethyl groups in the top layer so that they show high water and oil repellency. For these reasons fluorinated poly(acrylates) with long fluorinated side chains have been widely used for

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surface coatings. The degradation (environmental oxidation) of stain-resistant coatings leads to the release of biopersistant perfluoroctanoic acid (PFOA) to the environment. Toxicity and exposure studies indicate that PFOA can cause developmental issues and other adverse effects in laboratory animals and is a "likely" carcinogen. More research has focused on finding environmentally friendly and nontoxic alternative fluoropolymers to avoid the challenges associated with PFOA. Guo (J. Guo et al., 2008) has synthesized new polymeric materials containing short fluorinated side chains (perfluorobutyl and perfluorohexyl groups) and new "spacers" (i.e. the hydrocarbon group connecting the fluorinated side chain and the functional acrylic group). In these papers we designed, synthesized and characterized new fluorinated poly(acrylates) containing short fluorinated side chains (perfluorohexyl groups) and new hydrocarbon spacers. These fluorinated poly(acrylates) are obtained from new fluorinated alcohols containing double bonds. These materials could avoid the environmental problem caused by PFOA maintaining the same surface properties of long perfluorinated chain compounds.

2. Experimental

2.1 Analysis

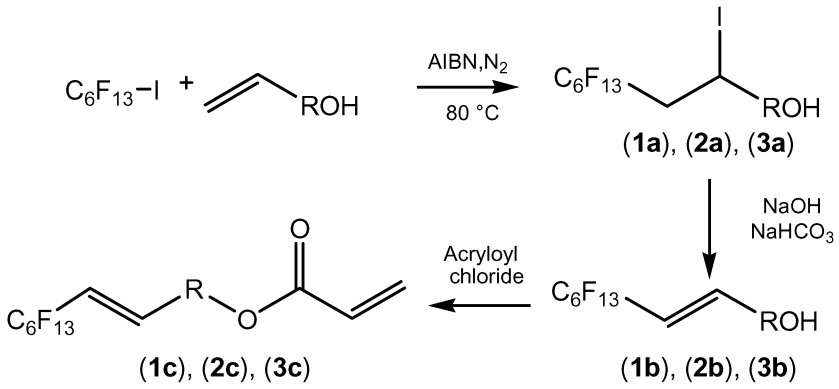
GLC analyses were performed using a DANI GC1000 instrument (15 m x 0.25 mm silica fused capillary column, PS264 stationary phase). GC/MS spectra were measured on a CARLO ERBA MFC 500/QMD1000. FTIR spectra were measured using a Nicolet Avatar 330 FT-IR spectrophotometer. Surface free-energies were determined using a Kruss G10/DSA10 goniometer interfaced to image-capture software.

2.2 Synthesis and characterization of the fluorinated monomers

The fluorinated acrylates synthesized were *n*-$C_6F_{13}CH{=}CHCH_2OCOCH{=}CH_2$ (**1c**), *n*-$C_6F_{13}CH{=}CHCH_2OCH_2CH_2OCOCH{=}CH_2$ (**2c**) and $C_6F_{13}CH{=}CHCH_2$-$(OCH_2CH_2CH_2)_{1.6}$-$OCOCH{=}CH_2$ (**3c**) (Scheme 1).

2.2.1. General procedure

n-$C_6F_{13}I$ (350 mmol) was added to a 22% aqueous solution of $Na_2S_2O_5$ (120 mL) then heated at 60 °C and flushed with nitrogen. After addition of AIBN (10 mmol) the corresponding alcohol (500 mmol) was added dropwise. After the slow addition (1 h) was completed the reaction mixture was stirred for 2 h and the temperature slowly increased until 80 °C. The reaction was monitored by GC. When disappearance of perfluorohexyl iodide was observed the alcohol excess was distilled off under vaccum. The mixture was warmed to room temperature and the adduct formed as a white solid was separated by filtration and washed with water to give (**1a**), (**2a**) and (**3a**). The obtained products (250 mmol) were dissolved in acetone (200 mL) and, under stirring, 200 mL of an aqueous solution of NaOH (60.0 g) and $NaHCO_3$ (36 g). The mixture was stirred at room temperature for 3 hours, after which the reaction mixture was dried under vacuum. GC/MS analyses confirmed the formation of products (**1b**), (**2b**) and (**3b**).



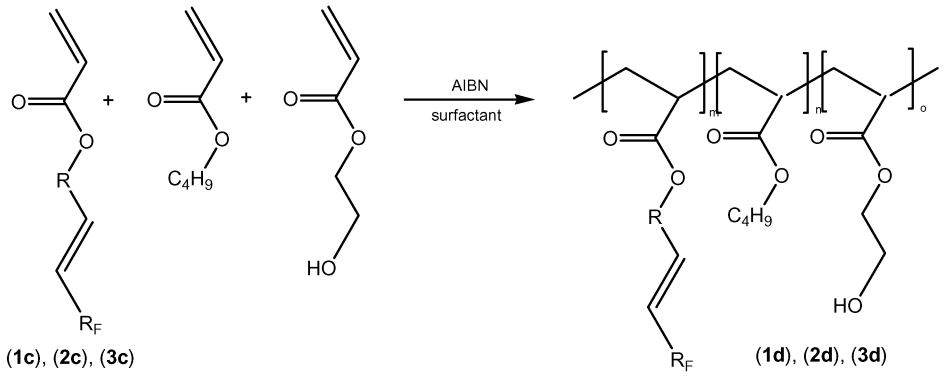
*Scheme 1. Synthesis of monomer (**1c**).*

The fluorinated alcholos (**1b**), (**2b**) and (**3b**) (80 mmol dissolved in 100 mL of diethyl ether) were converted to the corresponding acrylate by reaction with acrylic acid chloride in presence of thriethylamine (160 mmol). In a typical esterification, the resulting mixture was first flushed with nitrogen and then heated to 30-32 °C. Acrylic acid chloride (160 mmol) and catalytic amounts of hydroquinone (polymerization inhibitor) were added dropwise over a period of 40 minutes. The reaction mixture was filtered, washed with water and dried under vacuum. GC/MS analyses and spectroscopic data confirmed the formation of (**1c**) n-$C_6F_{13}CH{=}CHCH_2OCOCH{=}CH_2$,, (**2c**) n-$C_6F_{13}CH{=}CHCH_2OCH_2CH_2OCOCH{=}CH_2$ or (**3c**) n-$C_6F_{13}CH{=}CHCH_2$-$(OCH_2CH_2CH_2)_{1.6}$-$OCOCH{=}CH_2$. In particular, infrared spectra showed for all compounds both absorption at 1050-1100 cm^{-1} (typical for –C(O)-O-C- stretching) and the shift of C=O stretching absorption of acryloyl chloride from 1780 cm^{-1} to 1730 cm^{-1}.

2.3 Polymerization

The emulsion polymerization was chosen for co-polymerization as outlined in Scheme 2. A mixture composed by a fluorinated acrylate (**1c**), (**2c**), or (**3c**) (23 mmol), *n*-butyl acrylate (230 mmol), 2-hydroxylethyl acrylate (5 mmol), distillated water (150mL) and sodium lauryl sulfate (0.2 mmol) were added into a flask and stirred for 4.5 h at 70 °C. Finally 1-hexanethiol (0. 1 mmol) was added and the reaction mixture was stirred at 70 °C for a further 1 h. The resulting mixture was than washed with distilled water and the solid products were recovered by filtration and dried under vacuum to give polymers (**1d**), (**2d**), or (**3d**). The synthesized polymers were characterized by Fourier transform infrared (FTIR) analyses. The characteristic absorption of O-H stretching (3400-3500 cm^{-1}), C=O (1740 cm^{-1}), aliphatic stretching (2960-2980 cm^{-1}) and C-F stretching (1200-1245 cm^{-1}) were clearly visible. Meanwhile the characteristic stretching of acrylic double bond at frequencies of ν=1630 cm^{-1} disappeared, this confirmed that monomers had been polymerized.

Polymers (**1d**), (**2d**), or (**3d**) were dissolved in *n*-butyl acetate to obtain a 50% (vol/vol) solution.



Scheme 2. Polymerization of monomers.

2.4 Coating formulation and stone treatment

In a beaker 10 mL of a 50% (vol/vol) *n*-butyl acetate solution of polymers (**1d**), (**2d**), or (**3d**) were mixed with 5 mL of a 10 % *n*-butyl acetate solution of hexamethylene diisocianate. The solution was manually stirred for 1 minutes obtaining latexes (**1e**), (**2e**) and (**3e**). On the upper face of a concrete sample (3 cm x 15 cm x 0.5 cm squares) a thin layer of latexe was applied using a brush. Samples were then dried at 80 °C for 10 minutes. A reference sample was treated with Foraperle® 321 (DuPont Company) a product available on the market and based on C_8 fluorinated tails.

2.5 Wetting properties and water, oil and stain repellency tests

The surface properties of the coatings were characterized by static contact angle measurements using a Kruss G10/DSA10 goniometer interfaced to an image-capture software.

Water, oil and stain repellency were characterized by two specific tests: IPA test and graffiti test.

2.5.1. IPA test

A 10 μl drop of a solution of rhodamine in 2-propanol (1 : 99 vol : vol) is applied on the concrete sample. After 5 minutes the drop is removed with blotting paper by capillarity. The grading system is based on the following judgments: good (no stain), fair (weak stain), poor (marked stain); no resistance (surface completely wetted).

2.5.2. Graffiti test

With a felt-tip a straight line (5 cm in length, 0.5 cm in width) is drawn on the sample surface. After 5 minutes the stain is removed with a cotton wool soaked in ethanol. The grading system is based on the following judgments: good (70%-100% of the stain removed); fair (40%-70% of the stain removed); poor (10%-40% of the stain removed); 0 (<10% of the stain removed).

Surface free energies, IPA test results and Graffiti test results for latexes (**1e**), (**2e**) and (**3e**) are reported on Table 1.

*Table 1 Water, oil and stain repellency of concrete treated with Foraperle® 321 and latexes (**1e**)-(**3e**).*

Samples	θ_{H2O} (°)	θ_{CH2I2} (°)	γ_C ($mN \cdot m^{-1}$)	IPA test	Graffiti test
Untreated	No resistance	No resistance	-	No resistance	No resistance
Foraperle 321	150	120	12	Good	Good
(**1e**)	90	75	26	Poor	Poor/No resistance
(**2e**)	115	110	18	Good	Fair
(**3e**)	98	80	21	Fair	Fair

Image of contact angles for concrete samples treated with Foraperle® 321 (reference sample) and with latex (**2e**) are reported in Figure 1.
Figure 2 shows photographs of IPA test performances for untreated and treated specimen. (A) Untreated specimen. (B) Treated with (**2e**). (C) Treated with Foraperle® 321.

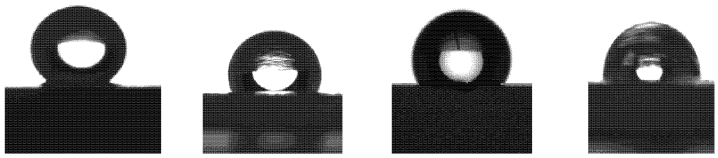


*Figure 1. (**A**) Foraperle® 321 water drop; (**B**) Foraperle® 321 diiodomethane drop; (**C**) Latex (**2e**) water drop; (**D**) Latex (**2e**) diiodomethane drop.*

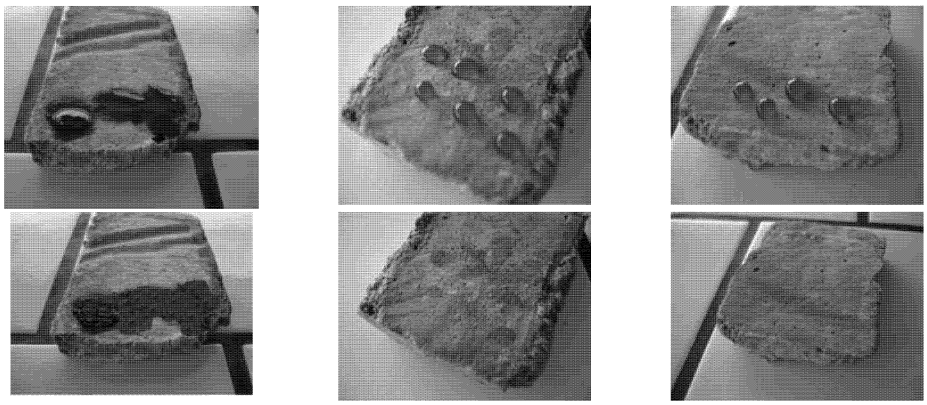


*Figure 2. Photographs of IPA test performances of the untreated and treated specimen. (A). Untreated specimen; (B) Treated with (**2e**); (C) Treated with Foraperle® 321.*

3. Conclusion

Although the measurements of contact angles, IPA test and graffiti test showed that Foraperle® 321 provided concrete samples with good water, oil and stain repellency, this type of polymer is persistent in the environment and may be bio-accumulated owing to the long perfluoroalkyl chain. The best results were obtain with latex (**2e**) containing the acrylate n-$C_6F_{13}CH{=}CHCH_2OCH_2CH_2OCOCH{=}CH_2$. This product provided concrete samples with good water repellency and fair oil and stain repellency. Latex (**1e**) showed only poor water repellency and practically no oil and stain repellency. Latex (**3e**) had fair water, oil and stain repellency.

As expected the shortening of the fluorinated tail involved a decrease in surface properties but the structure of the hydrocarbon spacer probably allowed a tighter packaging of the fluorinated side chains. The properties of the polymers were tuned by varying the length and the structure of the hydrocarbon spacer.

The different surface behavior of latexes (**1e**), (**2e**) and (**3e**) is attributed to the different ways segregation of side chains takes place owing to the different length and structure of the hydrocarbon spacer.

Probably the use of products without double bond allow a best mobility of the fluorinated tail and can be increased the surface performance of the obtained product. This will be the progress of the research.

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