



# Superhydrophobic fluorinated acrylonitrile coatings via electrospaying



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## ABSTRACT

The electrospaying of copolymers containing fluorinated acrylate and acrylonitrile with different composition ratios was performed. Copolymers of 3,5-bis(perfluorobenzyloxy)benzyl acrylate (FM) monomer with acrylonitrile (AN) were synthesized via free radical polymerization at 75 °C in dimethylformamide (DMF) using 2,2'-azobisisobutyronitrile (AIBN) as the initiator. Extended Kelen-Tüdös (EKT) method was utilized to calculate the monomer reactivity ratios. For the used monomer pair  $r_1$  was found as 0.11 for AN and  $r_2$  was found as 0.93 for FM. The result of  $r_1 \cdot r_2 < 1$  indicates that the reaction went forward as random copolymerization. Molecular weights of the obtained copolymers were determined by gel permeation chromatography (GPC). <sup>1</sup>H NMR spectroscopy is used for the characterization of the copolymers. The thermal behaviors of the copolymers were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Copolymers showed one glass-transition temperature changing on the copolymer composition which indicated that copolymers were amorphous. Contact angle values of ethylene glycol and water on the films which were prepared by electrospaying process indicated superhydrophobic character. The crystallinity and surface morphology of the copolymers were described by X-ray diffraction (XRD) and scanning electron microscope (SEM) respectively.

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## 1. Introduction

Since it has numerous practical applications superhydrophobicity has drawn considerable attention. The development of several excellent production techniques make possible to combine micro and nano levels into one structure.

Electrospinning or electrospaying of polymers are convenient techniques for the generation of polymeric nanofibers and mats [1–7]. A powerful electrical field is employed on. By this method in this process, polymer nanofibers can be obtained by the employment of a powerful electrical area on an earthed-point and a sample material solvent mixture that is exerted from a storage chamber through a small capillary orifice. Electrospinning of hydrophobic materials is very useful technique to generate a superhydrophobic covering in fiber structure with a simple procedure method. The surface that displays significantly large water contact angle by bigger than 150° can be specified as superhydrophobic

surface. A good number of techniques are practised to produce superhydrophobic surfaces [8].

The classical models [9–11], experimental [12] and theoretical studies [13,14] have revealed that surface morphology and roughness on the micro or nano rate cause a serious impact in the investigation of superhydrophobic coatings. Superhydrophobic surfaces can be formed from different hydrophobic materials by using electrospinning technique in a one step process. Jiang et al. [15] used electrospinning technique to generate hydrophobic surface and produced polystyrene fibers with a contact angle of 139°. Also several superhydrophobic surfaces can be obtained by consolidation of electrospaying and electrospinning techniques [16]. Fluorinated hydrocarbons are extensively distinguished substances due to they have very low surface energy and high hydrophobicity.

It is definitely expressed that fluorine containing structures prefer to retain at the polymer surface which cause reduction of the surface energy [17]. The reason for this property is fluorine has extremely small atomic radius and high electronegativity generating stable covalent bonds, remarkably increasing the hydrophobicity [18]. Hydrophobic surface coating applications has enhanced concern for fluorocarbon materials [19–22]. Beside in view of the fact that the specific features of fluorinated sub-

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stances these materials represent repelling features and could be employed as coverings with dirt-free or self-cleaning activity [23]. A variety of semifluorinated polymer structures are found in the literature, from homopolymers to block, random, graft and star-like polymers. Semifluorinated polymers can be prepared with copolymerization of fluorinated and non-fluorinated monomers via conventional free radical polymerization [24–29]. Various alkylic or aromatic perfluorinated monomers were polymerized successfully [30–34]. In another study copolymers of perfluoroalkyl ethyl methacrylate were synthesized in supercritical CO<sub>2</sub> [35]. Fluorinated copolymers having well-defined structural units utilized for the formation of low-energy surfaces by using atom transfer radical polymerization [36–40]. Fluorinated surfaces have also application in medicine, in systems where protein repellency is needed. Fluorinated films, for which fluorinated end-capped poly-*n*-alkyl methacrylate polymers were synthesized [41]. Surface energy of fluorine-containing monomers and their methyl methacrylate copolymer coatings were investigated by Van de Grampel et al. [42]. Generation of fluorine containing hydrophobic surfaces by electrospinning/electrospraying polymers was realized [15,43–50]. Electrospun fibers of acrylonitrile copolymers were produced and a water contact angle of 156° was obtained for the fibers [51]. Fibers of a fluorinated polymer were electrospun by Allcock and coworkers using different concentrations of polymer solutions [52,53].

Electrospun fiber mats were produced from copolymers of pentafluorostyrene samples and obtained that introduction of little amount of pentafluorostyrene into the styrene polymer gaved superhydrophobicity [20]. In another study several new synthesis methods of fluorinated carbon nanofibres were investigated and examined with the direct fluorination using undiluted fluorine gas [54].

We recently have indicated the generation of fluorinated acrylate monomer and its methyl methacrylate (MMA) copolymers [55]. The fluorinated monomer which showed low surface energy had a propensity to accumulate toward the film surface. For the fluorinated content of 90% in the copolymer, the water contact angle was obtained to 104° for the films which spin cast on a smooth glass substrates.

The technique for coating the surface is also very important that affect the final coating morphologies. For the generation of electronic and photonic devices it is required to produce superhydrophobic well-aligned architectures. Electrospun nanofiber mats are very beneficial to produce sensors, filters or protective coatings in consequence of their high surface area and increasing number of scientists are employ electrospun nanofiber mats as scaffolds for culturing cells [56]. Carbon nanofibers can be obtained from sort of initial materials such as polyacrylonitrile (PAN), pitch, rayon, polybenzimidazole and lignin [57,58].

In the present work, fluorine containing acrylate monomer was introduced into acrylonitrile copolymers and their well-distributed coatings with outstanding hydrophobic properties were successfully prepared by electrospraying process to obtain superhydrophobic surfaces. Acrylonitrile was chosen as second monomer for the copolymerization as the spinnable polymers could be obtained for the semifluorinated superhydrophobic surfaces.

## 2. Experimental

### 2.1. Materials

Solvents such as dichloromethane, acetone, toluene, tetrahydrofuran were purified and dried by standard techniques before use. *N,N*-Dimethylformamide (Reagent Plus, ≥99.9% Sigma-Aldrich), triethylamine (99% Acros), acryloylchloride (97% Aldrich), pentafluoro-

orobenzyl bromide (98% Alfa Aesar), 3,5-dihydroxybenzyl alcohol (99% Aldrich), 18-crown-6 (99% Merck), 2,2'-azobisisobutyronitrile (99% Aldrich) and acrylonitrile (99.5% Aldrich) were used as received without further purification.

### 2.2. Characterization and analysis

<sup>1</sup>H NMR analysis was realized with Bruker AC spectrometer at 250 MHz using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as internal standard. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with a set up consisting of the Agilent pump and refractive-index detector and three Agilent Zorbax PSM 1000S, 300S and 60S columns (6.2 × 250 mm, 5 μ) measuring in the range of 10<sup>4</sup> – 10<sup>6</sup>, 3 × 10<sup>3</sup> – 3 × 10<sup>5</sup>, 5 × 10<sup>2</sup> – 10<sup>4</sup> respectively. Mobile phase was THF at a flow rate of 0,5 mL/min at 30 °C. Differential scanning calorimeter (TA, DSC Q10) in a flowing nitrogen atmosphere from 30 °C at scanning rate of 10 °C/min and thermogravimetric analyzer TA Q50 were used to measure the thermal properties of obtained polymers. In TGA measurements samples were run from 30 to 800 °C with heating rate of 20 °C/min. Scanning Electron Microscope (SEM) imaging of the films were performed on Zeiss/Leo Supra 35 VP instrument. All the samples were coated with Palladium (Pd) as preparation to SEM analyses in order to avoid electron dissipation from the sample surface due to the electrically insulative character of polymeric material.

KSV Attension Theta Lite contact angle instrument was used to measure contact angle surface free energy. Deionized water and ethylene glycol drops (4–6 μL) were dispensed from a 1000 μL syringe. Geometric-mean approximations were utilized to calculate the dispersive and non-dispersive contributions to the total surface energy. Surface energy of a given solid can be calculated by using an equation applied to two liquids according to Owens and Wendt [57].

### 2.3. Synthesis of 3,5-bis(perfluorobenzoyloxy)benzyl acrylate (FM)

3,5-Bis(perfluorobenzoyloxy)benzyl acrylate (FM) was synthesized which had previously been synthesized by our group [21,55] in the presence of acryloylchloride, 3,5-bis(perfluorobenzoyloxy)benzyl alcohol (FOH) [36], triethylamine and tetrahydrofuran. After addition of all reagents the reaction was stirred at room temperature for determined time. At the end of the reaction, obtained mixture was washed with acid and base solutions. The product was further purified by column chromatography on silica (eluent; hexane: ethylacetate, 4:1) to give pure monomer. Yield: 77%, m.p: 50.8 °C. FT-IR  $\nu$  (cm<sup>-1</sup>): 2930,1722, 1656, 1598, 1286, 1159, 937; <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 6.7 (m, 2H), 6.5 (m, 1H), 6.4 (m, 1H), 6.2 (m, 1H), 5.8 (m,1H), 5.1 (m,2H), 5.0 (m,4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$  (ppm): 166.0, 159.4, 147.0, 140.1, 138.7, 131.8, 128.2, 109.8, 106.9, 102.0, 65.8, 57.4. <sup>19</sup>F NMR (CDCl<sub>3</sub>)  $\delta$  = -145.2 (m, 4F), -155.2 (m, 2F), -164.5 (m, 4F) ppm.

### 2.4. Synthesis of AN-FM copolymers

The polymerizations were realized in a dry Schlenk tube which was charged with determined amount of 3,5-bis(perfluorobenzoyloxy)benzyl acrylate and acrylonitrile monomers, specified amount of DMF and 2,2'-azobisisobutyronitrile. Freze-pump-thaw cycles were applied to remove the oxygen by vacuum and backfilling with nitrogen. Polymerization solution was placed into a silicon oil bath preheated to 75 °C. After the specified time the tube was picked up from the bath and let to cool down to ambient temperature. For the dilution of polymer solution tetrahydrofuran was added into the reaction mixture. Before the yields were determined gravimet-

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