Tetraarylphosphonium Perfluorocyclobutyl Polyelectrolyte with Low Critical Surface Energy, High Thermal Stability, and High Alkaline Resistance

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ABSTRACT: Two tetraarylphosphonium polyelectrolytes having perfluorocyclobutyl units in their backbones have been prepared in which the counteranion is either bromide (**PFP**·Br) or bis(trifluoromethyl)sulfonimide (**PFP**·NTf_2). These polymers exhibit high thermal stability as assessed by thermogravimetric analysis, with a decomposition temperature of 460 °C for **PFP**·NTf_2. Even after heating at 300 °C for 72 h, **PFP**·NTf_2 shows no signs of degradation detectable by nuclear magnetic resonance spectrometry. As is typical for many tetraarylphosphonium species, films of these polymers can be quite resistant to degradation by alkaline solution. Upon alkaline challenge by exposure to 6 *M* NaOH at 65 °C for 24 h, for example, only 16% of the phosphonium centers in **PFP**·NTf_2 are degraded, making **PFP**·NTf_2 one of the most alkaline-stable phosphonium polymers to date. Despite having ionic backbones, **PFP**·Br and **PFP**·NTf_2 exhibit very low critical surface energies of 26.1 and 22.9 mJ m^{-1}, respectively. These values are on par with the values for poly(vinylene fluoride) and dimethylsiloxane. Such low surface energy polycations capable of high alkaline stability may find application as components of alkaline fuel cell membranes. © 2019 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2019**

KEYWORDS: degradation; polyelectrolyte; thermal stability; surface energy

INTRODUCTION Tetraarylphosphonium salts are among the most stable ionic liquids known,[1–5] and their incorporation into polymer backbones has been targeted as a strategy to likewise access polymers with high thermal stability.[6–10] The resistance of tetraarylphosphonium moieties to alkali degradation has also garnered interest in utilizing tetraarylphosphonium polyelectrolytes (TPELs, Scheme 1) as membrane components of alkaline fuel cells and related electrochemical energy technologies. Previously reported TPELs have had relatively high critical surface energies and at least partial attendant solubility in polar solvents such as water and methanol. Unfortunately, such solubility would preclude the applicability of a polyelectrolyte in most fuel cell applications. Some of the most successful membrane polymers for proton-conducting fuel cells are perfluorinated polyelectrolytes having low critical surface energies such as Nafion that not only resist dissolution under fuel cell operating conditions, but also tend to form channels of polar versus nonpolar domains through which ion percolation can occur.[11] Concern for surface wetting has driven the study of low critical surface energy materials in multiblock fuel cell ion-transport materials. For instance, protein-functionalized proton-transport membranes for direct methanol fuel cells were deposited by Langmuir–Blodgett technique on Nafion substrates.[12] In that case, critical surface energy was estimated at 15–18 mJ m^{-2}. Considering these observations, it was hypothesized that low critical surface energy, perfluorinated TPELs might likewise be of interest for alkaline fuel cells.

Some low surface energy phosphonium polymers and salts have already been investigated. Ragogna and coworkers have prepared photopolymerizable tetraalkylphosphonium salts, cleverly designed to incorporate $-C_4F_9$ units rather than longer perfluoroalkyl chains that are persistent ecological threats.[13] Despite the ionic backbone constituents, photopolymerized coatings of these fluorinated phosphonium polymers are quite hydrophobic, attaining water contact angles of up to 101 °C (cf. Teflon, with a 115° water contact angle). The phosphonium units in those polymers were alkylphosphonium salts and would likely not be stable at operating conditions of alkaline fuel cells, however. For this reason, TPELs having low critical surface energies are of interest, yet none have been reported to date.

TPELs require installation of four aryl groups onto the phosphorus center, and synthetic routes for accomplishing this are limited. The preferred method for preparing TPELs is

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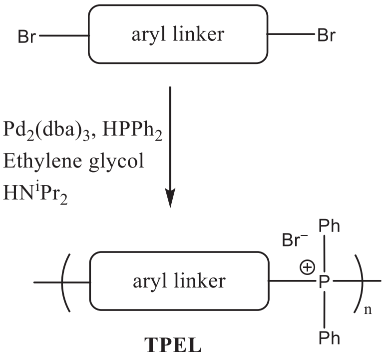


SCHEME 1 Established route to prepare TPELs.

copolymerization of a bifunctional aryl halide or aryl triflate with diphenylphosphine via a Pd-catalyzed P—C bond-forming reaction (Scheme 1).[6,7,10] In selecting potential backbone components for the current study, a perfluorinated moiety having high thermal stability and which could be readily incorporated into the requisite bifunctional aryl comonomer was targeted. The perfluorocyclobutyl (PFCB) unit is an excellent candidate. We previously reported the utility of the PFCB motif to prepare thermally stable polymers supporting fluorescent backbone components within a hydrophobic environment,[14] and many other PFCB polymers having high thermal stability have been reported.[15–20]

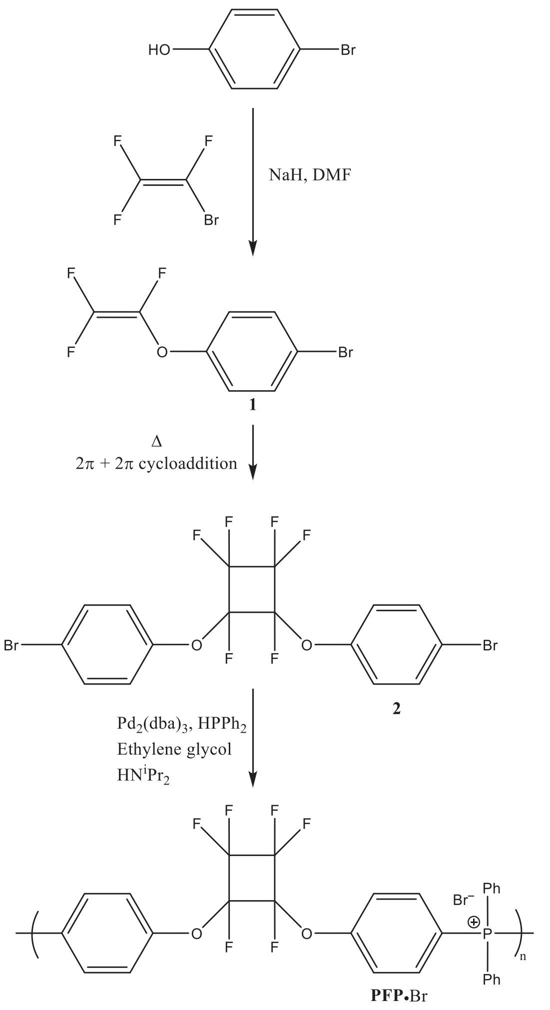
In the current work, we report on the preparation of the first perfluorinated TPELs, **PFP**·Br, and **PFP**·NTf$_2$. These PFCB-incorporating TPELs were assessed for thermal stability, stability of films to alkaline challenge, thin film morphology, and critical surface energy.

RESULTS AND DISCUSSION

Design and Synthesis

The PFCB unit was selected for incorporation into the target tetraarylphosphonium polymer on the basis of its facile preparation and high thermal stability. The requisite monomer, 1,2-bis(4-bromophenoxy) hexafluorocyclobutane (**2**)[21] was thus prepared in two steps from *p*-bromophenol and bromotrifluoroethylene[22] (Scheme 2) via an established methodology. Monomer **2** was reacted with diphenylphosphine via the Pd-catalyzed P—C bond-forming reaction[6] to yield the perfluorinated polyelectrolyte **PFP**·Br.

PFP·Br was readily characterized by multinuclear nuclear magnetic resonance (NMR) spectrometry and elemental microanalysis. The ^{31}P NMR spectrum confirmed the complete consumption of diphenylphosphine (occurring at −41.00 ppm)[23] and the appearance of a major resonance at 22 ppm characteristic of the tetraarylphosphonium unit. The ^{19}F NMR spectrum of the polymer retains the characteristic pattern for the PFCB unit (Fig. 1), confirming its retention under the reaction conditions and broadening of the individual resonances commensurate with the expectation for a polymer.



SCHEME 2 Preparation of **PFP**·Br.

The ionic nature of polyelectrolytes leads to high affinity to gel permeation chromatography (GPC) columns. Although some success has been observed in acquiring GPC data for polyelectrolytes in solvents such as formic acid, a simpler method for determining the M_n of TPELs has been reported.[24–26] Specifically, since a slight excess of diphenylphosphine monomer was used in the synthesis, end groups will be comprised of phosphine groups that are subsequently oxidized to the phosphine oxides. NMR end-group analysis comparing main chain phosphonium to end-group phosphine oxide units was employed to determine a M_n of 31.8 kDa, corresponding to a degree of polymerization of 52. This degree of polymerization is similar to the reported values for TPELs prepared by Pd-catalysis.[6,7] Although ^{31}P NMR integrations are not accurate in a typically acquired spectrum, a 10 s delay between scans was employed and triphenylphosphine was added as an external standard after acquiring spectra of the polymer alone to further validate the calculation following the reported procedure.[6]

Somewhat surprisingly, **PFP**·Br can be solubilized in methanol despite the presence of PFCB units. To increase both the hydrophobicity and thermal stability of **PFP**·Br, the bromide counterions were exchanged for bis(trifluoromethyl) sulfonimide ($[NTf_2]^-$)

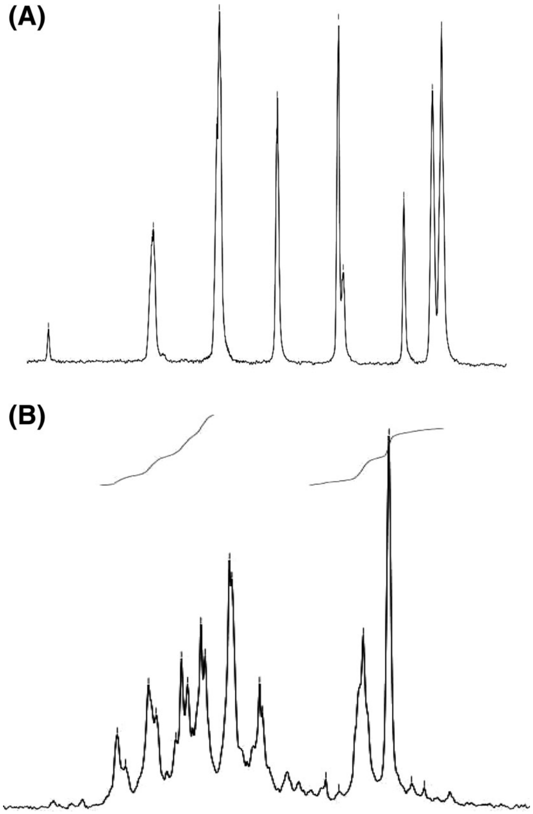


FIGURE 1 The ^{19}F NMR spectrum for monomer **2** (A) and polymer **PFP**·Br and (B) demonstrating the characteristic pattern for the PFCB ring and the broadening of the signals in the polymer.

counteranions. This was readily accomplished by dropwise addition of a LiNTf$_2$ solution to a vigorously stirred solution of **PFP**·Br, upon which **PFP**·NTf$_2$ precipitated. Elemental analysis and integration of ^{19}F NMR signals for [NTf$_2$]$^-$ fluorine atoms versus those in the polymer backbone PFCB unit confirmed the quantitative exchange of bromide for [NTf$_2$]$^-$counteranions by this method.

Thermal and Alkaline Stability

Tetraarylphosphonium salts are among the most thermally stable ionic liquids known, and the PFCB moiety is likewise thermally robust. Polymers **PFP**·Br and **PFP**·NTf$_2$ were thus subjected to thermogravimetric analysis (TGA) to assess their thermal stability, whereas the decomposition temperatures (T_d) for **PFP**·Br is unimpressive at 235 °C, T_d for **PFP**·NTf$_2$ (460 °C), is quite good and on par with reported values for some of the more thermally stable ionic liquids. It has been pointed out in the literature that TGA analysis under a nitrogen atmosphere is not necessarily a good indicator of long-term thermal stability of a material as may be required in a real-world application setting.[5] A sample of **PFP**·NTf$_2$ was thus held at a temperature of 300 °C open to the air for 72 h. Over this time, the sample color changed only slightly from pale tan to slightly darker tan. After the sample was cooled, it was fully soluble and its NMR spectra matched those of the as-synthesized material, suggesting that **PFP**·NTf$_2$ may be a good candidate for practical high temperature applications.

PFP·NTf$_2$ was then tested for its stability to alkaline conditions. The alkaline challenge conditions involved exposure of a thin film of the polymer to a 6 *M* NaOH(*aq*) solution at either room temperature (ca. 21 °C) or 65 °C. These conditions were selected to simulate potential operating conditions of an alkaline fuel cell. At room temperature, **PFP**·NTf$_2$ shows no sign of degradation even after 4 days of exposure. At 65 °C, however, 16% of the phosphonium moieties are decomposed to phosphine oxides (presumably via air oxidation of an intermediately formed phosphine) after 24 h. The stability of **PFP**·NTf$_2$ is thus on par with the most alkaline-resistant TPELs, and it is more alkaline-resistant under these conditions than phosphonium polyelectrolytes that have been successfully incorporated into operational alkaline fuel cells.[27]

Thin Film Surface Energy and Morphology

The critical surface energies (γ_c) for previously reported phosphonium polymer dip-cast films ranged from 35.0 to 73.6 mJ m^{-1}. γ_c values for **PFP**·Br and **PFP**·NTf$_2$ were expected to be quite low by merit of the PFCB moieties in the backbone. γ_c values were thus determined by the method of Zisman[28] whereby contact angles (θ_c) are measured between the film and a series of test liquids having known surface tension values. The Zisman plots of these data are provided in Figure 2. γ_c values for **PFP**·Br and **PFP**·NTf$_2$ from this method were found to be 26.1 and 22.9 mJ m^{-1}, respectively. The contact angles with water for **PFP**·Br and **PFP**·NTf$_2$ were correspondingly high at 63 and 76°, respectively. These contact angles with water are significantly lower than those achieved by the aforementioned fluorinated phosphonium polymers reported by Ragogna and coworkers (up to 101°).[13] Despite their ionic nature,

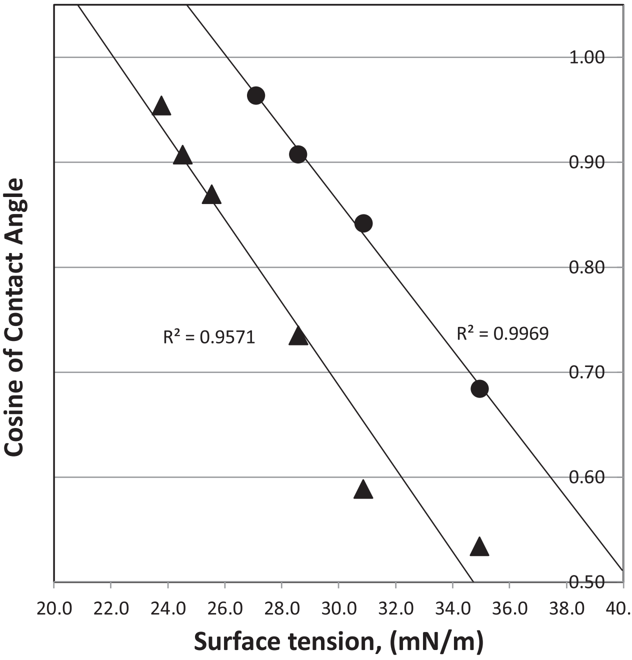


FIGURE 2 Zisman plots from contact angle data for **PFP**·Br and **PFP**·NTf$_2$ polymers.

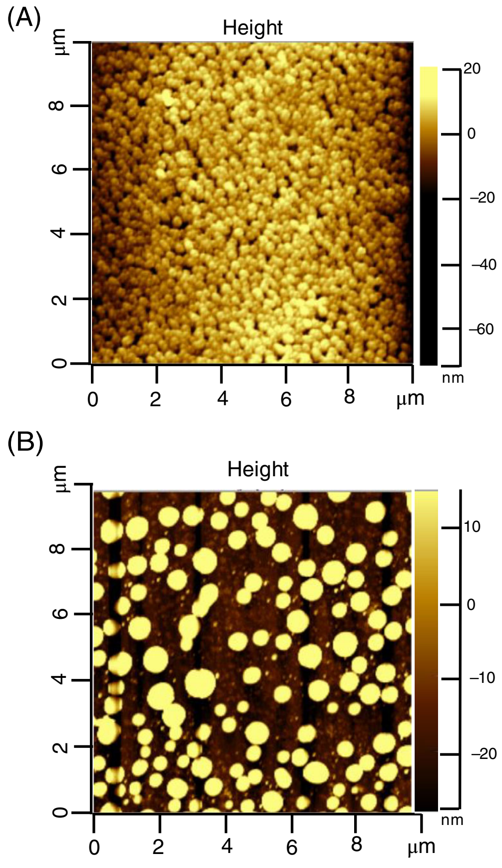


FIGURE 3 AFM height images for **PFP**·Br (A) and **PFP**·NTf_2 and (B) films cast from acetone. [Color figure can be viewed at wileyonlinelibrary.com]

however, the critical surface energies of **PFP**·Br and **PFP**·NTf_2 are significantly lower than those of familiar polymers such as polystyrene (γ_c = 34 mJ m^{-2}), poly(methyl methacrylate) (γ_c = 37.5 mJ m^{-2}) and polyethylene terephthalate (γ_c = 39 mJ m^{-2}) and on par with the values for well-known hydrophobic polymers like poly(vinylene fluoride) (25 mJ m^{-1}) and polydimethylsiloxane (23 mJ m^{-1}).[29–31]

Atomic force microscopy (AFM) was used to further analyze the film morphology of **PFP**·Br and **PFP**·NTf_2. Although both polymers fully coat the glass slide upon dip casting from an acetone solution, there are notable differences in the size of nanoaggregates at the film surface (Fig. 3). The surface of the **PFP**·Br film is comprised of a dense layer of polydisperse nanoaggregates with an average diameter of about 350 nm. In contrast, the surface of the **PFP**·NTf_2 film is much more sparsely populated with larger, still polydisperse, aggregates having an average size of about 750 nm. The collapse of polymers to form aggregates may be attributable to incompatibility of polar acetone solvent with the PFCB moieties.

CONCLUSIONS

The first perfluorinated TPEL has been prepared. **PFP**·NTf_2 is quite thermally stable, even to heating at 300 °C for 72 h open to the air. **PFP**·NTf_2 also resists degradation upon exposure to 6 *M* NaOH(*aq*) at 65 °C for 24 h with 16% loss of phosphonium functional groups, making it one of the two most stable of phosphonium polymers under these conditions. The low surface energies of **PFP**·Br and **PFP**·NTf_2 place them as the most hydrophobic of TPELs for which surface energies are reported. The combination of thermal/alkaline stability and low critical surface energy suggest potential utility of these and related perfluorinated TPELs in alkaline fuel cell and related applications. Efforts are underway to prepare an expanded suite of perfluorinated TPELs for testing in electrochemical energy generation contexts.

EXPERIMENTAL

General Considerations

All air-sensitive reactions were performed in an MBRAUN UNILab glovebox under nitrogen. Anhydrous solvents were dried and degassed using an MBRAUN solvent purifier. Chemicals were used without further purification after purchased. All the NMR spectra were collected on a Joel ECX-300 MHz spectrometer operating at 300 and 121.4 MHz for ^{1}H and ^{31}P, respectively. TGA was performed on TA Instruments SDT Q600 (Newcastle, Delaware, USA) from 25 to 800 °C with a heating rate of 20 °C min^{-1}. To assure that the ^{31}P nuclei were fully relaxed between scans and thus provide accurate integrations, the spectra with 2, 4, 8, and 10 s delay were compared. Integration of resonances in spectra collected with a 10 s delay is identical to those collected with an 8 s delay. As a result, ^{31}P NMR spectra provided here were collected with a 10 s relaxation delay. To assure the accuracy of the chemical shift values, PPh_3 was added as an internal standard.

Synthesis of Compound 2

4-Bromo(trifluorovinyloxy)benzene (2.00 g, 7.90 mmol) was heated up to 180 °C in 25 mL round-bottom flask for 24 h under nitrogen atmosphere. The reaction mixture was then purified via silica-gel chromatograph by using *n*-hexane/ethyl acetate = 10:1 as fluent phase to yield colorless liquid (1.41 g, 2.79 mmol, 70.5%). ^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.40–7.50 (m, 4H), 6.96–7.09 (m, 4H), ^{19}F NMR (282 MHz) δ: −131.35, −131.25, −130.90, −130.10, −129.37, −128.68, −127.86.

Synthesis of PFP·Br

In a glovebox, PFCBPPh2Br2 (0.500 g, 0.99 mmol), diphenylphosphine (0.193 g, 1.04 mmol), and diisoproplyamine (1.05 g, 1.04 mmol) were mixed together in a 15 mL heavy-wall pressure reaction tube. A sample of $Pd_2(dba)_3$ (0.010 g, 0.01 mmol) and 1.5 mL anhydrous ethylene glycol were then added, and the tube was screwed on with a Teflon screw cap equipped with a Viton O-ring. The sealed reaction system was heated at 145 °C with stirring for 24 h to yield dark yellow liquid. After cooling down to room temperature, the reaction tube was opened to air and 50 mL dichloromethane (DCM) was added to dissolve all components of the reaction mixture. The DCM solution was washed by 25 mL 1 *M* NaBr solution twice and dried over anhydrous Na_2SO_4. After concentrating to 10 mL by vacuum evaporation, the DCM solution was added to 200 mL diethyl ether with vigorous stirring to yield white cloudy precipitation. The solid was separated by centrifuge and washed with 20 mL diethyl ether twice, and then dried in vacuum oven overnight to obtain pure white powder product (0.466 g, 75.0%). ^{1}H-NMR (300 MHz, CD_3CN) δ: 7.50–8.05 (br m, 18H). ^{19}F NMR (282 MHz, CD_3CN) δ: −134.11, −133.43, −130.74, −130.67, −129.93, −129.87, −129.22, −129.11, −128.76, −128.59, −128.44, −127.92, −127.72, −127.10, −126.89. ^{31}P NMR (121.4 MHz, CD_3CN) δ: 22.01. anal. calcd for monomer formula $C_{28}H_{18}BrF_{12}O_2PS_2$ (ignoring end groups): C, 55.01; H, 2.97; found: C, 57.17; H, 3.47%.

Anion Exchange to Prepare PFP·NTf$_2$

PFP·Br (0.100 g, 0.16 mmol) solid was dissolved in 20 mL H_2O/MeOH (1:1), and then 10 mL bis(trifluoromethyl)sulfonimide lithium (0.150 g, 0.53 mmol) H_2O solution was added dropwise with vigorous stirring to form a pale yellow flocculent precipitate. The solid was separated by centrifuge and washed by deionized water twice. The purified solid was dried in vacuum oven overnight to yield a pale tan colored solid. ^{1}H-NMR (300 MHz, $(CD_3)_2CO$) δ: 7.57–8.05 (br m, 18H). ^{19}F NMR (282 MHz, $(CD_3)_2CO$) δ: −134.37, −133.90, −131.06, −130.76, −130.67, −129.93, −129.89, −129.26, −129.20, −128.81, −128.68, −127.97, −127.87, −127.14, −127.02, −126.86, −79.87. ^{31}P NMR (121.4 MHz, $(CD_3)_2CO$) δ: 22.86. Anal. calc'd for monomer formula $C_{30}H_{18}F_{12}NO_6PS_2$ (ignoring end groups): C, 44.40; H, 2.24; N, 1.73%; found: C, 44.36; H, 2.43; N, 1.75%.

Alkaline Stability Testing

To a 50 mL round-bottom flask, 20 mg of the polymer dissolved in 1 mL DCM was slowly evaporated so that the polymer thin film was coated homogeneously on the bottom of the flask. The film was soaked in 25 mL NaOH (6 *M*) over 24 h at room temperature or 65 °C, and then collected by dissolving in 0.5 mL $CDCl_3$ to collect phosphorus-31 NMR spectra.

Contact Angle and Critical Surface Energy Testing

Silane-coated glass slides from electron microscopy science were used as received. Dip-cast samples were prepared using a machine-controlled linear rate of 50 mm s^{-1} and allowed to dry overnight in a 45 °C oven. Samples were placed directly in capped vials. A Krüss DSA 10 Mk2 Instrument was used with automatic dosing and a 0.5 mm diameter needle to dispense an 8 μL (average) volume drop. The contact angle was measured by circle fitting method within 30 s of drop placement in ambient air with an average temperature of 22.5 °C. Test liquids were prepared with varying concentrations of 2-propanol and water drawn from a Millipore Milli-Q Instrument with resistivity measured at 18.2 MΩ cm^{-1}. Isopropanol was used as received from Beantown Chemicals with purity of 99.8% as recorded on the manufacturer analysis report. Surface tension of the various binary mixtures of isopropanol and water were interpolated to account for actual laboratory temperatures at the time of measurement.[32]

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