

# Desorption Behavior and Distributions of Fluorinated Polymers in MALDI and Electrospray Ionization Mass Spectrometry

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**Matrix-assisted laser desorption/ionization (MALDI) and electrospray ionization (ESI) have been used to desorb fluorinated polymers for mass spectrometric analyses. Compounds with high fluorine content are insoluble or only sparingly soluble in conventional solvent systems, making them difficult candidates for mass spectrometry studies. Among 11 tested MALDI matrixes, 2,5-dihydroxybenzoic acid produced the highest ion yield for a model fluorinated analyte at a matrix/analyte molar ratio of 1000. Use of this matrix allowed determination of repeat units and the polymer distribution parameters:  $M_n$ ,  $M_w$ , and  $D$ . In MALDI, solubility requirements for a fluorinated polymer may be incompatible with those of the matrix, potentially leading to inhomogeneous crystallization which may influence the observed distribution of oligomers. In ESI, when precipitation was not an overriding factor, a minimal aqueous content in the employed solvent vastly improved fluorinated polymer signal intensities compared to purely organic solvent systems. Dilution with small amounts of higher polarity solvents could promote the desorption of longer chain fluorocarbons, presumably due to augmented solvophobicity. However, a very high aqueous content (high polarity) may disfavor the desorption of longer chain fluorocarbons, especially at higher polymer concentrations. This latter observation has been attributed to preferential intermolecular aggregation of longer fluorocarbon chains. The presence of fluorinated groups offers the advantage of inductive stabilization of anionic charge sites for improved signals in negative ion MALDI and ESI, while low molecular weight halogenated solvents used for dissolution of fluorinated polymers can suppress the tendency toward discharge in negative ion ESI.**

Matrix-assisted laser desorption/ionization (MALDI) time-of-flight mass spectrometry (TOF/MS) and electrospray ionization (ESI) mass spectrometry are techniques that have been increasingly applied to the characterization of dissolved macromolecules. Now applicable to a wide variety of polymers, these techniques can provide information complementary to traditional methods of polymer analysis such as size exclusion chromatography,<sup>1</sup> infrared spectroscopy,<sup>2</sup> and nuclear magnetic resonance.<sup>3</sup>

Since the 1970s, lasers have been used to desorb ions from samples deposited on metallic surfaces. This approach coupled with mass spectrometric detection permitted the observation of ions derived from small organic and inorganic compounds (up to ~9000 u),<sup>4</sup> most often accompanied by high levels of fragmentation. The development of MALDI methods<sup>5,6</sup> permitted the detection of intact molecules of substantially higher masses, while minimizing fragmentation. A few years after its introduction, Hillenkamp and co-workers<sup>7</sup> applied the MALDI method to the characterization of synthetic polymers [e.g., poly(ethylene glycol) (PEG), poly(propylene glycol) (PPG), poly(methyl methacrylate) (PMMA), and polystyrene (PS)] having molecular weights between 1000 and 70 000. Salts were added to the matrixes to increase the yields of cationized species. Later MALDI experiments have demonstrated the ability to desorb and analyze intact polymers having molecular weights as high as 1,500,000.<sup>8</sup>

Electrospray is an ionization technique originally introduced by Dole et al. in 1968<sup>9</sup> to investigate solutions of polystyrene. Developed by Fenn and co-workers<sup>10</sup> during the 1980s, it has been used extensively to desorb biomolecules dissolved in polar solvents. In 1988, Fenn and co-workers demonstrated the ability of ESI to desorb poly(ethylene glycol) polymers,<sup>11</sup> including those having molecular weights in the region of 5 000 000<sup>12</sup>. The ability to extensively multiply charge the polymer originally dissolved in a water/methanol (1:1) mixture allowed the viewing of overlapping (unresolved) peaks, on a quadrupole mass spectrometer having a mass range extending only to  $m/z$  1500.<sup>12</sup>

The power of the soft ionization methods MALDI and ESI for polymer analyses lies in the fact that an indication of oligomer

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distribution parameters (including average molecular weights) can be obtained from direct mixture analysis of less than 1 nmol of polymeric material in a very short time (e.g., 10 min). Moreover, precise molecular weight data for each oligomer obtained from desorbed intact molecules can offer much information concerning details of polymer structure (e.g., sequence of repeat unit, end groups), and information regarding polymer additives and/or impurities present. MALDI and ESI have now been used to analyze a wide variety of polymers, such as polyacrylates,<sup>7,13–15</sup> polyamines,<sup>16</sup> polysiloxanes,<sup>17–19</sup> polyoxides,<sup>20</sup> and polyesters.<sup>21–27</sup>

Of particular interest in the current study are fluorinated polymers, which are useful industrially owing to the hydrophobic and oleophobic properties that they confer onto various supports (e.g., walls, clothes, cooking utensils, etc.). Very thin coatings of fluorinated polymers on such surfaces can afford decreased adhesion, facility in cleaning, and waterproofing to the surface. These beneficial properties come about with often easy application of very low quantities of the fluorinated polymer to the support. Moreover, many of the physical qualities that the support possessed prior to the application may be retained. Because of some unique properties, principally their limited solubility in all but the very lowest polarity solvents, analyses of these polymers can be problematic. For example, because complete dissolution of larger perfluorinated polymers may only be possible in halo-carbon solvents, the use of size exclusion chromatography is impractical because such solvents can degrade the column packing.

Small perfluorinated organic molecules have been used as calibration standards for mass spectrometry for many years, but specific protocols for characterization of intact larger fluorinated polymers by MALDI and ESI have not yet appeared. Because fluorocarbons are poor nucleophiles, they are often poor candidates for the capture of protons or other cations in positive ion mass spectrometry. Nonetheless, a few reports of successful

analyses of fluorinated polymers have appeared, notably those employing secondary ion mass spectrometry (SIMS).<sup>28–31</sup>

In this report, MALDI and ESI are used to study the desorption/ionization of fluorinated polymers<sup>32</sup> and have been applied to the characterization of such compounds. In a first step, the influence of different experimental parameters on the appearance of the mass spectrum and the polymer distribution have been investigated by employing a model fluorinated compound, a fluorinated phosphazene,<sup>33,34</sup> that contains perfluorinated repeat units. In MALDI, target preparation (solvent, matrix, and additives) and laser irradiance were systematically varied. In ESI, the effect of solvent utilized and the temperature in the spray region were investigated. Optimized protocols were then applied to two types of industrial fluorinated polymers which contain either a perfluorinated repeat unit or a perfluorinated end group of varying chain length.

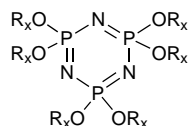
## EXPERIMENTAL SECTION

**MALDI Instrument.** Positive or negative MALDI mass spectra were recorded using a built in-house linear TOF mass spectrometer. Light from a pulsed nitrogen laser (VSL 337 ND, Laser Science Inc., Cambridge, MA; 337 nm, 3 ns pulse, 250  $\mu$ J/pulse) was focused by a quartz lens onto the target. The laser energy was set using neutral filters. Secondary ions were accelerated to 20 or 28 keV kinetic energy and drifted through a field-free flight tube (1.36 m) before being detected with a "Venetian-blind" electron multiplier (EM643, Thorn EMI, Ruislip, Middlesex, U.K.). The output signal of the detector was digitized by a digital oscilloscope (LeCroy 9450, Chestnut Ridge, NY), and the data were transferred to a Mac-IIci computer (Apple Computer Inc., Cupertino, CA) for spectrum summation, mass calibration, and storage. Presented mass spectra represent the average of 25 or 50 laser shots. The pressure in the TOF mass spectrometer was  $2 \times 10^{-7}$  Torr.

**MALDI Sample Preparation.** Polymer solution (1 or 2  $\mu$ L) mixed with a matrix solution ( $10^{-1}$  M) was deposited onto polished stainless steel substrates (5 mm in diameter) and allowed to dry in air. Matrix compounds: 2,5-dihydroxybenzoic acid<sup>7,35</sup> (2,5-DHB), *trans*-3 indoleacrylic acid<sup>36</sup> (IAA), 2-(4-hydroxyphenylazo)-benzoic acid<sup>27</sup> (HABA), 2-nitrophenyl octyl ether<sup>7,35</sup> (NPOE), 2,4,6-trihydroxyacetophenone,<sup>37</sup> 2,4-bis(trifluoromethyl)benzoic acid (TFMBA), sinapinic acid,<sup>38,39</sup> and 5-chlorosalicylic acid<sup>17</sup> (5-CSA) were purchased from Aldrich Chimie (Saint Quentin Fallavier, France).  $\alpha$ -Cyano 4-hydroxycinnamic acid<sup>36</sup> (HCCA) and dithra-

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<sup>a</sup> Where  $R_x = \text{CH}_2(\text{CF}_2)_x\text{H}$  and  $x = 2, 4, \text{ or } 6$ .

not<sup>40,41</sup> were obtained from Sigma (Saint Quentin Fallavier, France), and pentafluorobenzoic acid was from Acros (Noisy le Grand, France). All were used without further purification.

**ESI-MS Instrument.** Positive or negative ion ESI mass spectra were acquired by directly infusing polymer solutions into the Analytica of Branford (Quad Service, Poissy, France) modified ESI ion source coupled to a Nermag R10-10 quadrupole mass spectrometer with a  $m/z$  range of 2000. The entry capillary voltage was held just above the onset potential for electrospray for each investigated sample. The skimmer voltage was adjusted to minimize fragmentation. A Harvard 11 syringe pump (Cambridge, MA) delivered the sample solution at a flow rate of 2  $\mu\text{L}/\text{min}$ . Mass calibration was achieved by using a mixture of PPG 500 and PPG 1000, giving calibration peaks over the full mass range.<sup>24</sup>

**Chemicals.** The employed solvents chloroform, methanol, and acetonitrile were obtained from Prolabo (Paris, France), water was from Millipore (France), and trichlorotrifluoroethane (Forane 113) was from Elf-Atochem (France); all were used without further purification. A fluorinated phosphazine (Ultramark 1621, from PCR Inc., Gainesville, FL), (Chart 1) containing six perfluorinated side chains has been used as a calibration compound for FAB and electrospray,<sup>33,34</sup> and has served in this study as a model compound whose different forms correspond directly to species comprised of varying lengths of fluorocarbon chains. However, this analyte bears basic sites, so it can easily be protonated. The average number of fluorocarbon chains ( $\bar{R}_f$ ) present can easily be quantified from the mass spectrum.

This compound is soluble in acetonitrile and low molecular weight halocarbons such as trichlorotrifluoroethane, but it precipitates in solutions having a high content of water or methanol. To quantify the distribution of perfluorinated chains in mass spectra of the fluorinated phosphazine,  $\bar{R}_f$  (defined below) was used as an indicator of the average number of  $(\text{CF}_2)_x$  units present:

$$\bar{R}_f = \frac{\sum x N_x}{\sum N_x}$$

where  $N_x$  is the mass spectral intensity of the peak representing the protonated oligomer with  $x$  repeat units

For the industrial polymers analyzed, number-average molecular weight ( $M_n$ ), weight-average molecular weight ( $M_w$ ), and polydispersity index ( $D$ ) were calculated from both MALDI and ESI mass spectra according to the following equations:

$$M_n = \frac{\sum_{i=1}^{\infty} M_i N_i}{\sum_{i=1}^{\infty} N_i} \quad M_w = \frac{\sum_{i=1}^{\infty} M_i^2 N_i}{\sum_{i=1}^{\infty} M_i N_i} \quad D = \frac{M_w}{M_n}$$

where  $i$  is the degree of polymerization (number of repeat units);  $M_i$  is the molecular weight of a linear oligomer with  $n = i$  repeat units; and  $N_i$  in ESI, corresponds to the mass spectral intensity of the peak representing the cationized oligomer and in MALDI corresponds to the integrated area under the peak. If an oligomer appears as the adduct of several different cations, the sum of the adduct peaks was used.

## RESULTS AND DISCUSSION

**MALDI.** MALDI is a soft ionization technique that permits desorption/ionization of a wide range of molecules, but mechanisms involved in the production of large intact gaseous molecular ions are still not well understood. Of the experimental factors influencing this process, the nature of the matrix is very important because it plays a fundamental role in the transfer of the laser photon energy to the solid, which is related to both the extinction coefficient of the matrix material and the crystallographic structure of the target. In particular, the kinetic and internal energies of the desorbed species (responsible respectively for mass dispersion and fragmentation processes), as well as ionization reactions through collisions in the very dense initial plume of ablated material, strongly depend on the nature of the matrix<sup>42,43</sup> and on the laser irradiance.<sup>44</sup> The sample preparation method,<sup>45</sup> which involves the choice of solvents,<sup>46</sup> the concentration and the matrix/analyte molar ratio,<sup>47</sup> the pH,<sup>48</sup> the presence of metal salts,<sup>49,50</sup> the deposition protocol, etc., also plays an important role in the crystal growth and therefore in the homogeneity of the target. These factors can considerably affect the ion yield and can introduce mass discrimination effects. Such considerations are particularly important for polymers bearing very hydrophobic groups, such as fluorinated polymers, because most matrices used in the past were rather polar compounds. Thus, in order to optimize analysis of this type of polymer, the matrix composition, the laser irradiance, and the solvents were systematically varied.

**MALDI Matrix.** The typical matrix used for MALDI is a low molecular weight organic compound that absorbs at the wavelength of the pulsed UV laser.<sup>51</sup> For an optimum analyte ion

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Table 1. Influence of the MALDI Matrix on the Total Oligomer Signal Intensity for the Fluorinated Phosphazine

matrix	oligomer signal <sup>a</sup>	$M_n$ <sup>b</sup>	oligomers detected
dithranol	++	1500	$\bar{R}f12-\bar{R}f34$
PFBA	+	nc	
TFMBA	+	nc	
5-CSA	++	1520	$\bar{R}f14-\bar{R}f34$
NPOE	—	nc	
2,5-DHB	+++	1470	$\bar{R}f12-\bar{R}f36$
HABA	+	nc	$\bar{R}f16-\bar{R}f30$
THAP	++	1490	$\bar{R}f14-\bar{R}f34$
IAA	+	nc	$\bar{R}f12-\bar{R}f34$
sinapinic acid	++	1480	$\bar{R}f12-\bar{R}f36$
HCCA	++	1460	$\bar{R}f14-\bar{R}f36$

<sup>a</sup> —, not observed; +, weak; ++, medium; +++, strong. <sup>b</sup> nc, not calculated.

signal, the matrix is usually present in a large molar excess over the analyte, typically 2–4 orders of magnitude. To select the optimum matrix, 11 candidate matrixes proposed for polymer analyses were tested (Table 1). Each matrix is soluble in THF, except the fluorinated matrixes (PFBA, TFMBA) which were dissolved in trichlorotrifluoroethane, and NPOE, which was used without solvent. No cationizing agents were added. Oligomer signals corresponding to protonated molecules of the employed model fluorinated compound (Chart 1) were obtained from all of these matrixes, with the exception of NPOE where no signal was obtained. Of the matrixes tested, 2,5-dihydroxybenzoic acid offered the highest intensity peaks, corresponding to protonated oligomers (Table 1). Interpretation of the improved response obtained with 2,5-DHB is not straightforward. Availability of protons, derived from photoionization or electronically excited matrix molecules for transfer to the analyte, is probably not the limiting factor in the case of other matrixes. It has been shown for instance that sinapinic acid or  $\alpha$ -cyano-4-hydroxycinnamic acid has comparable or higher “protonating powers” than 2,5-DHB for different peptides.<sup>52</sup> Considerations including the incorporation of the polymer into the matrix crystals, as well as some specific chemical interactions (e.g., hydrogen bonding) with the matrix molecules, could be involved in improving the signal level.<sup>52</sup>

The positive ion MALDI mass spectrum of the fluorinated phosphazine with 2,5-DHB as matrix appears in Figure 1a. Each peak is separated by 100 u corresponding to the difference in mass of two  $CF_2$  repeat units. The oligomer distribution extended from 922 (12 repeat units,  $\bar{R}f12$ ) to 2122 u (36 repeat units,  $\bar{R}f36$ ). The mass range of detected oligomers for a given sample is quite similar for all matrixes, and matrix choice had only a subtle influence on oligomer distributions (Table 1). The number-average molecular weight ( $M_n$ ) did not vary significantly with the nature of the matrix.

**MALDI Target Preparation.** Four solvent systems presented in decreasing polarity order were used to prepare the target using 2,5-DHB as the matrix: (i) water/acetonitrile (1:1, v/v) for analyte and matrix; (ii) THF for matrix, acetonitrile for analyte; (iii) THF for analyte and matrix, (iv) THF for matrix, trichlorotrifluoroethane for analyte.

No premature precipitation of analyte and matrix occurred with these systems. The most polar solvent system [water/acetonitrile

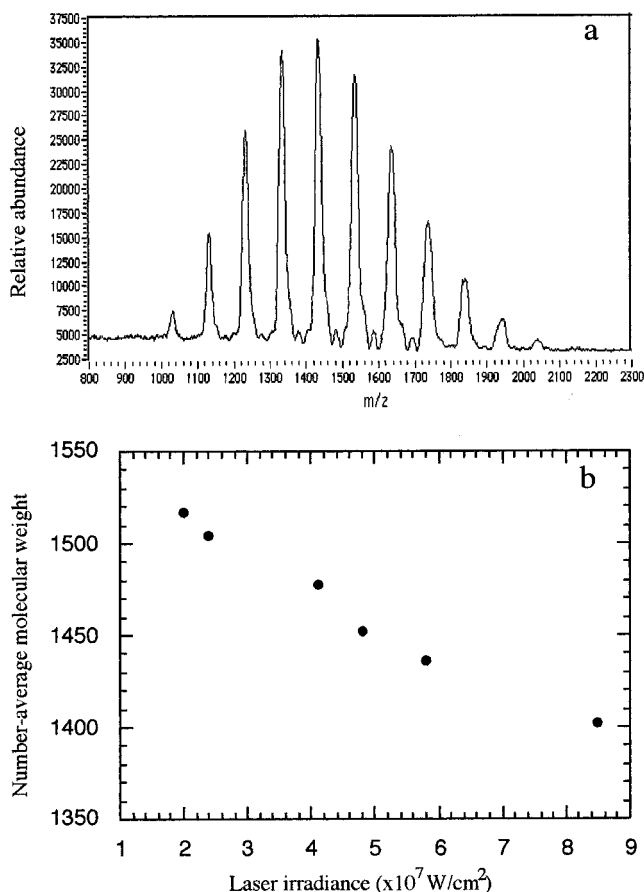


Figure 1. (a) MALDI mass spectrum of the model fluorinated compound, a fluorinated phosphazine, dissolved in acetonitrile. The matrix is 2,5-DHB initially in THF. Peaks observed represent protonated oligomers. Conditions: matrix/analyte molar ratio 1000; laser irradiance  $4.8 \times 10^7$  W/cm<sup>2</sup>. (b) Number-average molecular weight ( $M_n$ ) vs laser irradiance. Standard deviations of  $\pm 20$  (RSD = 1.4%) and  $\pm 18$  (RSD 1.3%) were calculated for laser irradiances of  $4.8 \times 10^7$  and  $5.8 \times 10^7$  W/cm<sup>2</sup>, respectively.

Table 2. Influence of the MALDI Solvent on the Number-Average Molecular Weight for the Fluorinated Phosphazine<sup>a</sup>

matrix/analyte solvent system	$M_n$
water/acetonitrile (1:1)	$1410 \pm 20$
THF/acetonitrile <sup>b</sup>	$1460 \pm 20$
THF	$1480 \pm 20$
THF/forane <sup>c</sup>	$1470 \pm 10$

<sup>a</sup> Matrix, 2,5-DHB, laser irradiance,  $4.8 \times 10^7$  W/cm<sup>2</sup>. <sup>b</sup> Matrix dissolved in THF, analyte dissolved in acetonitrile. <sup>c</sup> Matrix dissolved in THF; analyte dissolved in trichlorotrifluoroethane.

(i)] yielded larger crystals as viewed by an optical microscope. The best signal intensity was obtained for a matrix/analyte molar ratio of  $\sim 1000$ . Obtained oligomer distributions for systems ii, iii, and iv were virtually indistinguishable, but that obtained using the more polar solvent system [water/acetonitrile (i)] yielded a slightly lower value ( $\sim 5\%$ ) for the number-average molecular weight (Table 2). This difference suggests that higher mass oligomers were not well included in the matrix crystals; hence, ion yields for these species were diminished slightly, relative to lower mass oligomers.

**MALDI Laser Irradiance.** The signal level depended strongly on laser beam irradiance, with a tendency for the signal to increase

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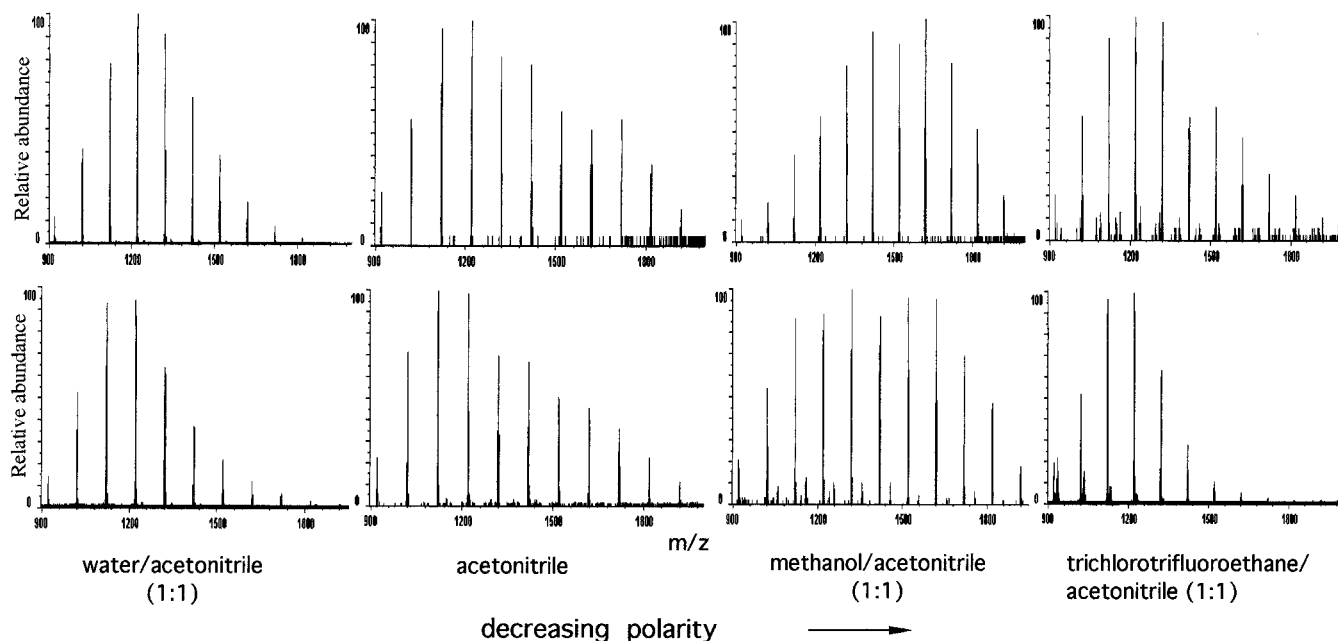


Figure 2. ESI mass spectra of the fluorinated phosphazine ( $10^{-3}$  M) dissolved in four different solvent systems, presented in order of decreasing polarity. Acetic acid (1.7% v/v) was added to each solution. In the top row, drying gas temperature and flow rate were  $\sim 90$  °C and  $\sim 5$  L/min, respectively. In the bottom row, these values were  $\sim 105$  °C and  $\sim 6$  L/min, respectively.

rapidly above the ionization threshold of  $\sim 2 \times 10^7$  W/cm<sup>2</sup>, reaching a maximum at  $\sim 7 \times 10^7$  W/cm<sup>2</sup>. At the same time, the mass resolution ( $m/\Delta m$ ) decreased, as generally reported in the literature.<sup>53</sup> For solvent system ii, employing the 2,5-DHB matrix, Figure 1b shows that the number-average molecular weight decreased with increasing laser irradiance above the ionization threshold. The decrease in the number-average molecular weight could be rationalized by considering that higher mass fluorinated oligomers were not well included in the matrix crystals. At higher irradiances, where the depth of ejected material increases, the desorption of lower mass oligomers preferentially incorporated in the bulk matrix crystals could be favored. In addition, pyrolysis processes cannot be totally excluded.

For solvent system iv employing the 2,5-DHB matrix, a very high laser irradiance favored the formation of protonated dimers and trimers of the oligomers. The number-average molecular weight of the dimers corresponded to  $2M_n$  monomers, while those of the trimers corresponded to  $3M_n$ . Use of this low-polarity solvent can apparently lead to augmented intermolecular interactions between oligomers on the prepared sample.

**Electrospray Ionization.** In ESI-MS, experimental parameters such as the choice of solvent employed, and the temperature (and flow velocity) of the bath gas (e.g., N<sub>2</sub>) can often influence the success of the ESI-MS experiment. In order to optimize experimental conditions for fluorinated polymer analysis, these two parameters were systematically studied.

**ESI Solvent.** Solution parameters such as polarity,<sup>54–56</sup> viscosity,<sup>57</sup> surface tension,<sup>55,57–59</sup> and conductivity<sup>57–59</sup> are known to

affect spray stability, and to have bearing on the appearance of obtained mass spectra. In order to prepare compounds with a high degree of fluorocarbon character for electrospray analysis, the use of low-polarity solvents (rarely used for ESI-MS of more polar species) may be necessary. The essence of the difficulty of solvent choice for analyzing highly fluorinated species by ESI-MS is that a compromise must be found between enabling analyte dissolution (restricting solvent choice to those of quite low polarity) and achieving electrospray stability and analyte charging (requiring a minimum solvent polarity).

To examine the influence of solvent choice on the desorption behavior of fluorinated species, four solvent systems were investigated, listed here in order of decreasing polarity using the fluorinated phosphazine as the test analyte in the presence of 1.7% (v/v) acetic acid: (i) water/acetonitrile (1:1); (ii) acetonitrile; (iii) methanol/acetonitrile (1:1); and (iv) trichlorotrifluoroethane/acetonitrile (1:1). Shown in Figure 2 are the positive ion ESI mass spectra obtained in each solvent at two different bath gas conditions. In each case, singly protonated oligomers were observed with no multiply charged species detected. Adjacent peaks are separated by 100  $m/z$  units corresponding to the mass of two CF<sub>2</sub> repeat units. The distribution of molecular weights of fluorinated phosphazine species (see Chart 1) varied from 922 (12 repeat units,  $\bar{R}_f$  12) to 1922 (32 repeat units,  $\bar{R}_f$  32). As shown in Figures 3a and 4a, total peak intensities increased markedly with addition of minor quantities of water to the solvent system, presumably because of the polarity increase. The highest signal response was obtained using 40% water (Figure 4a).

Another spectral characteristic that was monitored as a function of solvent choice was the average fluorinated chain length ( $\bar{R}_f$ , defined in the Experimental Section). As shown in Figure 3b, when a solvent of intermediate polarity (e.g., acetonitrile, or 1:1 acetonitrile/methanol) was employed, the  $\bar{R}_f$  value was in the

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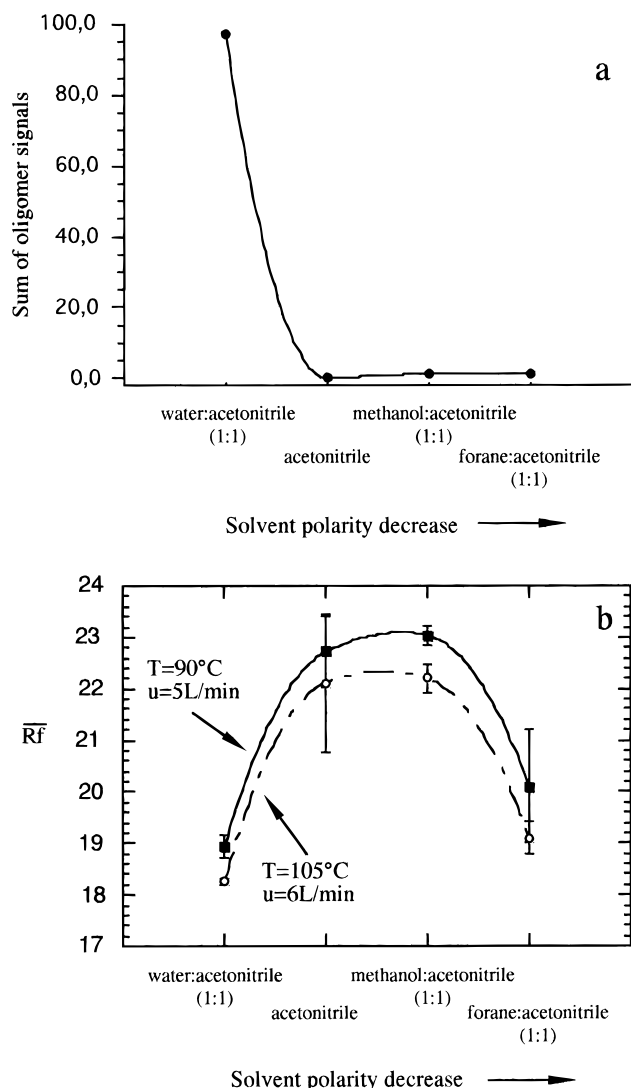


Figure 3. Data from ESI mass spectra obtained from the fluorinated phosphazine dissolved in different solvent systems, listed in order of decreasing polarity. (a) The total of all oligomer signals; (b) the average number of fluorocarbon ( $\text{CF}_2$ ) repeat units ( $\bar{R}_f$ ), as defined in the Experimental Section.

range of 22.4–23.2 (low bath gas temperature and flow). When the solvent polarity was either lowered (trichlorotrifluoroethane/acetonitrile, 1:1) or raised (water/acetonitrile, 1:1) relative to the intermediate situations, in each case, the oligomer distribution shifted toward lower masses, indicative of a favored desorption of species containing shorter perfluorinated chains. This shift in the desorption profile can be rationalized by considering that when the solvent polarity was decreased (trichlorotrifluoroethane/acetonitrile), species bearing the longest perfluorinated chains were better solvated in the interior of the charged droplets. This implies that species bearing shorter perfluorinated chains were more solvophobic and, hence, had a higher tendency to move to the droplet's surface. Consequently, they desorbed more readily from the droplet, yielding higher signal intensities.

When solvent polarity was markedly increased (water/acetonitrile 1:1), highly perfluorinated chain oligomers were also observed to desorb in lower abundances relative to the intermediate situation (acetonitrile, or 1:1 acetonitrile/methanol) (Figure 3b). In the water/acetonitrile mixture, the oligomers experienced a marked reduction in solubility. Van der Waals intermolecular

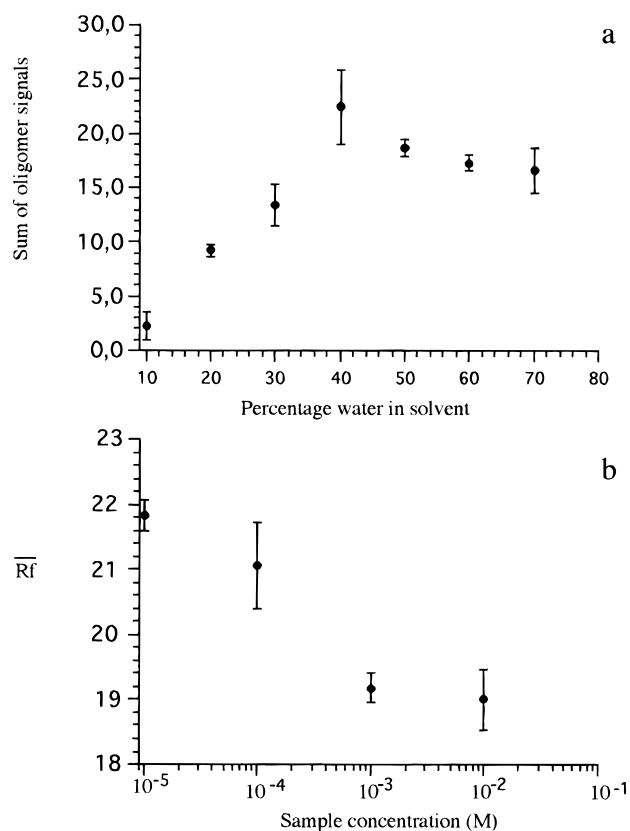


Figure 4. (a) Sum of oligomer signals obtained from the fluorinated phosphazine ( $\sim 10^{-4}$  M) dissolved in water/acetonitrile mixtures of varying aqueous content, with addition of 1.7% (v/v) acetic acid. (b) Average number of fluorocarbon ( $\text{CF}_2$ ) repeat units ( $\bar{R}_f$ ) vs fluorinated phosphazine concentration in water/acetonitrile (1:1) with 1.7% (v/v) acetic acid.

interactions between perfluorocarbon chains were likely augmented, possibly resulting in aggregation of perfluorinated portions of adjacent molecules. Higher relative desorption of lower mass species could arise if such aggregation was more prevalent for species bearing longer perfluorocarbon chains. These species might desorb with lower relative efficiencies and appear in lower relative abundances in ESI mass spectra.

This reasoning is in agreement with previous observations by Fenn<sup>60</sup> wherein the ion abundances of various quaternary alkyl amines, present at fixed concentrations, increased with alkyl chain length up to a certain limit. Fenn argued that, in polar solvent, the solvophobicity of the tetraalkyl amines increased with increasing alkyl chain length. Longer chain species were considered to take on increased prominence on the surface of the droplet, favoring increased desorption and higher ESI-MS signals. However, when alkyl chains became too long, signals decreased abruptly, presumably because they are so solvophobic that a "film" was formed on the droplet surface, with only the hydrophilic (or charge-bearing) portion of the molecule bound to the "substrate" liquid.<sup>60</sup> Such films, which comprehend a high degree of hydrophobic interaction, reduce the possibilities for desorption of species into the gas phase.

To further test these hypotheses, the concentration of the fluorinated phosphazine was varied over the range  $10^{-5}$ – $10^{-2}$  M in water/acetonitrile (1:1) with acetic acid [1.7% (v/v)]. As shown in Figure 4b, as the analyte concentration was raised, the  $\bar{R}_f$  value

(60) Fenn, J. B. *J. Am. Soc. Mass Spectrom.* **1993**, *4*, 524–535.

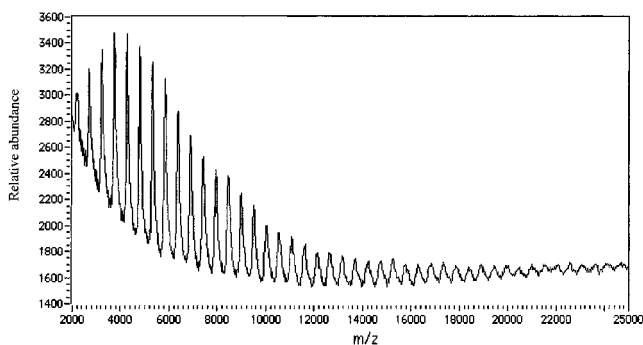


Figure 5. Positive ion MALDI mass spectrum of a poly(perfluorooctadecyl)acrylate polymer dissolved in trichlorotrifluoroethane. The matrix was 2,5-DHB in THF and the laser irradiance was  $4.8 \times 10^7$  W/cm<sup>2</sup>. Peaks represent sodium cationized oligomers.

decreased, indicating that desorption of shorter length fluorocarbon species was progressively favored over the longer chain species. This is consistent with the reasoning that, in this rather

polar solvent, aggregation of the longer fluorocarbon chains is occurring preferentially, leading to a lower desorption efficiency. This phenomenon apparently becomes increasingly prevalent as the concentration of fluorinated species is increased.

Corroborative evidence for the important role of solvophobicity and aggregation in the ESI desorption of perfluorocarbons was obtained from experiments wherein the percentage of water (highest polarity component in the solvent) was systematically varied (Figure 4a). Signal intensity was observed to steadily increase as the percentage of water was raised up to ~40%. The fluorocarbon portion can be considered to be progressively more solvophobic in solutions containing increasing percentages of water. The improved desorption can be rationalized on the basis of this higher solvophobicity. At water percentages above 40%, signal intensity leveled off, likely indicative of a droplet surface rich in fluorocarbon species.

**ESI Drying Gas Temperature and Flow Rate.** Results obtained at elevated drying gas temperature and augmented drying gas flow rate (Figure 3b, dashed line) provide additional

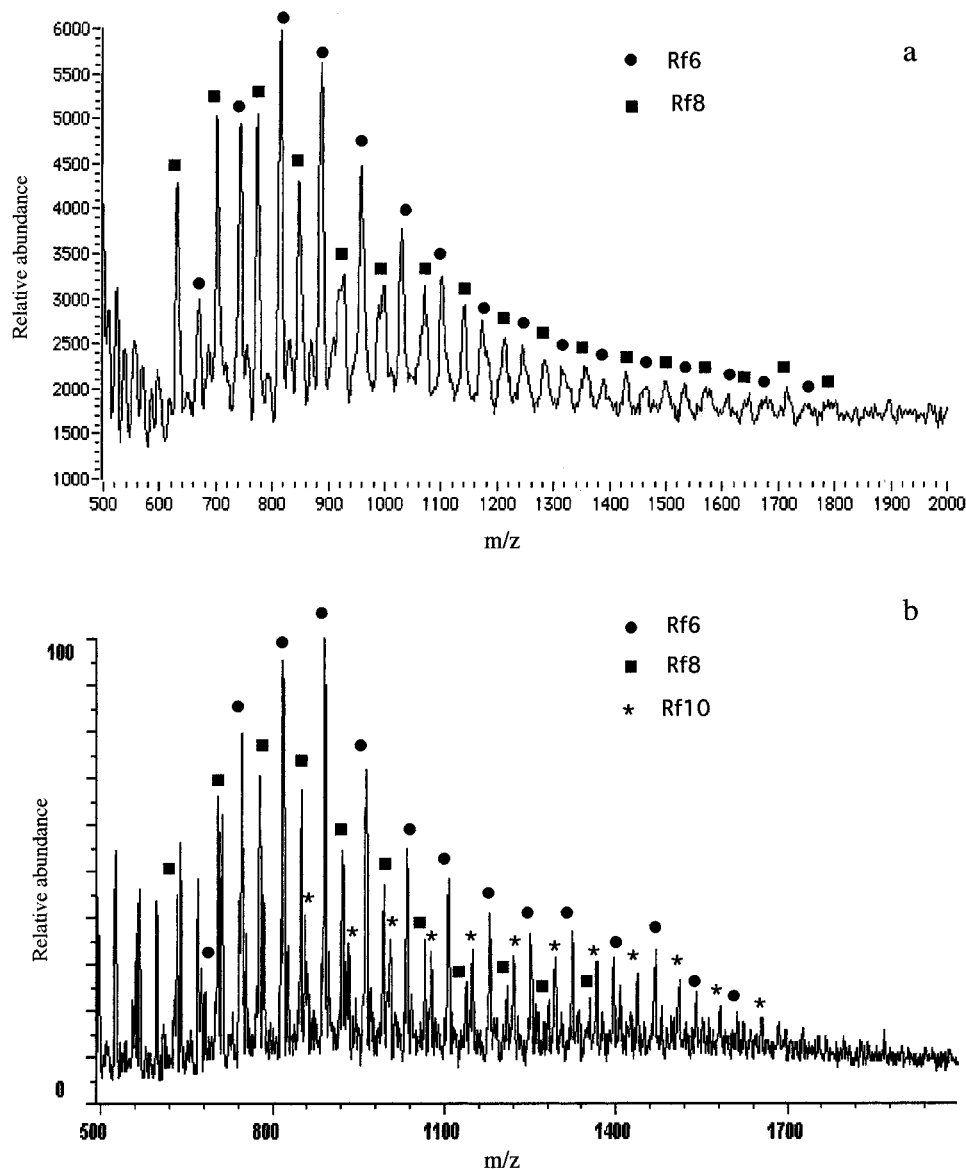


Figure 6. Negative ion mass spectra of a poly(acrylic acid) polymer containing a perfluorinated carbon chain end group. (a) MALDI analysis, the polymer and the matrix (2,5-DHB) were dissolved in THF in a matrix/analyte molar ratio of ~1000; (b) ESI analysis. The polymer was dissolved in CH<sub>3</sub>OH/H<sub>2</sub>O/CHCl<sub>3</sub> (3:1:1) with 2% triethylamine. Each labeled series corresponds to a specific perfluorinated end group chain length: Rf6, Rf8, or Rf10.

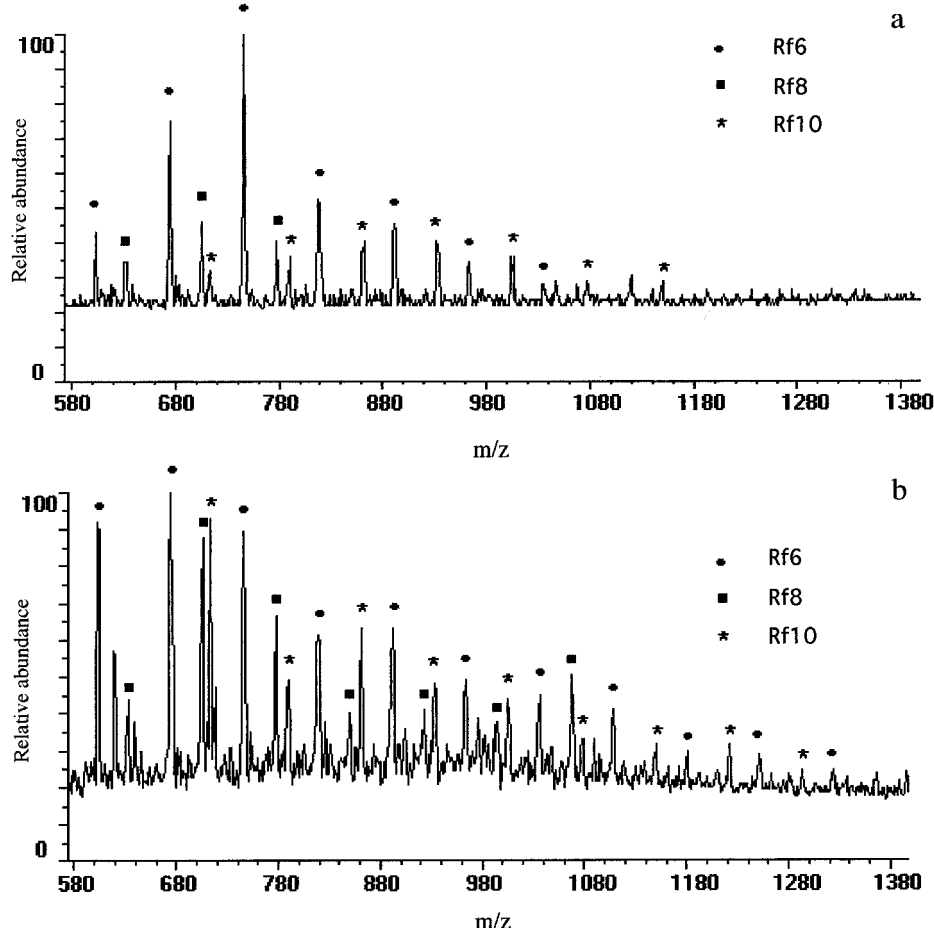


Figure 7. Negative ion ESI mass spectra of a poly(acrylic acid) polymer with perfluorinated carbon chain end group of varying length. Initial solution  $\text{CH}_3\text{OH}/\text{H}_2\text{O}/\text{CHCl}_3$  (3:1:1) with 2% triethylamine, diluted 1:1 with (a)  $\text{CHCl}_3$  and (b) 50% aqueous methanol.

evidence of the aggregation of fluorinated carbon chains. Under these more severe drying conditions, the  $\bar{R}_f$  was shifted toward lower values in each solvent (Figure 3b), indicating that longer chain fluorocarbon oligomers were desorbing less efficiently relative to their shorter chain counterparts. This effect can be rationalized by considering that, at higher temperatures and flow rates, charged droplets containing the various oligomers were desolvating at a faster rate; hence, increased aggregation of fluorinated chains (Van der Waals type interactions) may have been occurring. As previously postulated, a higher level of aggregation could preferentially impede efficient desorption of the higher mass oligomers.

**Desorption of Fluorinated Polymers.** The preceding results have shown the feasibility of studying compounds bearing hydrophobic perfluorinated chains by MALDI and ESI, under particular experimental conditions. Using these previously obtained conditions as a point of departure, two types of industrial fluorinated polymers have been investigated. The first is a polyacrylate containing a perfluorinated carbon chain in the repeat unit [poly(perfluorooctadecyl)acrylate, polymer A], while the second is a poly(acrylic acid) bearing a perfluorinated carbon chain end group of varying length [poly(acrylic acid) polymer with perfluorinated end group, polymer B].

**(1) MALDI.** Because the best signal response for the fluorinated phosphazine was obtained using 2,5-DHB as the matrix in solvents of varying polarity, this matrix was again employed for the study of fluorinated polymers A and B. Owing to its high fluorine content, the poly(perfluorooctadecyl)acrylate polymer A

required trichlorotrifluoroethane for dissolution, while the matrix 2,5-DHB was dissolved in THF. Polymer and matrix solution were mixed to give a final matrix/analyte molar ratio of 1000:1. The positive MALDI mass spectrum exhibited a broad distribution of sodium cationized oligomers extending above 25 000 u (Figure 5). No addition of sodium salt was necessary. The distribution parameters  $M_n = 7360$  and  $M_w = 10\,080$  and the polydispersity index  $D = 1.37$  determined from the MALDI mass spectrum are probably underestimated as generally observed for polydisperse polymers exhibiting high  $D$  values.<sup>17,61</sup>

The poly(acrylic acid) polymer with perfluorinated end group (polymer B), containing a lower percentage of fluorine, was soluble in THF, as was 2,5-DHB. Polymer and matrix solutions in THF were mixed to give a final matrix/analyte molar ratio of 1000:1. The negative ion MALDI mass spectrum (Figure 6a) exhibited two series of peaks attributed to deprotonated oligomers bearing  $\bar{R}_f6$  or  $\bar{R}_f8$  end groups, without additives to promote deprotonation. Distribution parameters  $M_n = 920$  and  $M_w = 980$  and the polydispersity index  $D = 1.06$  were determined from the MALDI mass spectrum.

**(2) Electrospray Ionization.** The propensity for multiple charging in ESI is known to diminish in nonpolar solvents.<sup>54–56</sup> The poly(perfluorooctadecyl)acrylate polymer (A) required a high percentage of trichlorotrifluoroethane to enable dissolution. The decreased tendency toward formation of multiply charged species in this low-polarity solvent combined with the limited mass range

(61) Lehrle, R. S.; Sarson, D. S. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 91–92.



( $m/z$  2000) of the employed quadrupole mass spectrometer rendered this polymer an unsuitable candidate for study.

The poly(acrylic acid) polymer with perfluorinated end group (polymer B) responded well in the negative ion mode. An intermediate polarity solvent [methanol/water/chloroform (3:1:1) with 2% triethylamine to promote deprotonation] gave the optimum signal (Figure 6b). Use of chloroform solvent is known to improve stability of ESI operation in the negative ion mode due to discharge suppression via dissociative electron capture.<sup>54</sup> Three series of oligomers could be identified corresponding to different length perfluorinated end groups ( $\bar{R}f6$ ,  $\bar{R}f8$ , or  $\bar{R}f10$ ). Notably, the  $\bar{R}f10$  oligomers observed in Figure 6b had not been identified in the negative ion MALDI mass spectrum (Figure 6a) because they were poorly resolved from neighboring peaks.

To investigate the effect of solvent polarity on the ESI signals of the poly(acrylic acid) polymer with perfluorinated end group (polymer B), a concentrated polymer solution prepared as above [methanol/water/chloroform (3:1:1) with 2% triethylamine] was diluted 1:1 with (a) chloroform (thus reducing the polarity) or (b) 50% aqueous methanol (thus increasing the polarity). Mass spectra obtained with these solvent systems are shown in parts a and b of Figure 7, respectively. The signal responses decreased in each of these solvents relative to that obtainable with the optimized mixture used to generate Figure 6b. Most noteworthy, however, is the distinct contrast in the desorption profiles obtained in the two solvent systems shown in Figure 7. In Figure 7a, the shortest chain  $\bar{R}f6$  oligomers dominate the mass spectrum, while the longer chain  $\bar{R}f8$  and  $\bar{R}f10$  oligomers are present in significantly lower abundances. In clear contrast, in Figure 7b the abundances of the longest chain  $\bar{R}f10$  oligomers are strongly augmented, while the abundances of the  $\bar{R}f8$  oligomers are also raised, relative to the  $\bar{R}f6$  oligomers. This augmented propensity for desorption of longer chain fluorocarbon oligomers relative to the shorter chain counterparts in solvent of increased polarity can be rationalized by considering that the longer chain species are more solvophobic in higher polarity solutions. Corroborating the previous discussion pertaining to the fluorinated phosphazine, a higher solvophobicity can lead to preferential occupation of sites near the droplet surface by longer chain fluorocarbon oligomers, augmenting desorption and mass spectrometric signals of these species (Figure 7b). By the same argument, in the lowest polarity solvent, the longest chain fluorocarbon oligomers ( $\bar{R}f10$ ) are more highly solvated in the interior of the droplet, leaving the shorter chain fluorocarbon oligomers ( $\bar{R}f6$ ) to be preferentially detected (Figure 7a).

## CONCLUSION

The specific dissolution requirements of fluorinated polymers make them difficult candidates for mass spectrometric analyses. Short-chain fluorocarbons initially used for polymer dissolution may be diluted with more polar, miscible solvents in preparation for MALDI or ESI analyses. In MALDI, provided that a minimum solubility was achieved, detection of ions representative of intact oligomers was possible. In certain cases, solubility considerations related to the matrix may be at odds with those concerning the analyte, leading to peculiarities in crystallization such as preferential segregation of species with longer fluorocarbon chains on the exterior of the crystals, potentially resulting in alteration of the observed oligomer distribution. In ESI, very low polarity solvents, which may offer optimum solubility to highly fluorinated polymers, impede the droplet charging process (and the tendency toward multiple charging) while demanding extremely high ESI operating voltages, thus creating a very unstable spray condition. Dilution with small quantities of polar, yet miscible, electrolyte solutions can rectify this situation and vastly augment analyte signals. As the solution polarity is raised, however, preferential aggregation of longer chain fluorinated oligomers may occur, especially at higher analyte concentrations, thereby favoring desorption of lower mass oligomers.

Fluorinated polymers, especially those bearing acidic sites, have distinct advantages for negative ion mass spectrometric analyses. Fluorine atoms contained in analyte molecules inductively stabilize anionic charge sites, which can augment signals in both MALDI and ESI. In addition, owing to their notable electron-capturing ability, employed short-chain fluorinated or chlorinated solvents used for dissolution can help to suppress the tendency toward discharge in negative ion ESI.

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