Characterization of synthetic polymers by Matrix assisted laser desorption (MALDI1) is limited by the solubility of different oligomers in a suitable solvent, and the fingerprint of the mass spectrum is affected by the properties of solvents employed (e.g., pH, secondary solvents, evaporation) during sample target preparation. If solvents are not used during sample target preparation, then solvent properties should not play an important role in determining the quality of the MALDI mass spectrum. We report here two solventless approaches for sample target preparation. It was observed that Poly(ethylene glycol) 6000 (PEG) showed the same molecular mass distribution in different modes of sample target preparation. Fluorinated polymer used in these studies was affected by sample target preparation protocol and by target surface. Pyrolysis of PEG oligomers was observed in all the methods of target sample preparation. The desorbed high mass neutral oligomers fragment to give small oligomers which are then cationized by the desolvation of the cationized matrix clusters. Moreover, the origin of the matrix clusters (i.e., formed in the condensed phase or in the gas phase) determines the relative intensities of PEG oligomers cationized by sodium or potassium.

Matrix assisted laser desorption (MALDI) and time-of-flight mass spectrometry (TOF/MS) continues to evolve as an important analytical technique for the characterization of synthetic polymers. A MALDI-TOF mass spectrum gives valuable information1–26 about molecular weight distribution, end groups, and the oligomer repeat unit. Important advantages of this technique are the high speed of analysis, the smaller sample requirement, accurate mass measurement with high resolution and high m/z range. Nevertheless, this technique exhibits significant discrimination against different oligomers, poor reproducibility of the MALDI mass spectrum fingerprint (e.g., ion abundance).

In MALDI experiments it is well established that the sample preparation protocol influences the sensitivity, selectivity, and mass resolution. Many sample preparation techniques for synthetic polymers have been developed in order to improve the mass spectral quality, to characterize complex oligomers, and to rationalize the MALDI desorption/ionization processes. Tanaka et al.27 first demonstrated the potential of MALDI for the characterization of water-soluble polymers. A better dispersion of

the oligomers in the matrix was achieved by the organic solvent approach. This reduced the precipitation of the oligomers during matrix crystallization, and thus many classes of polymers could be analyzed by MALDI efficiently. Because it is easy and simple to practice the “dried droplet method,” is widely employed as the sample preparation technique for the characterization of synthetic polymers. Usually, the polymer sample is dissolved in a few microliters of a suitable solvent (concentration of few micromolar) and diluted with an excess of matrix solution into a homogeneous solution, and about 1 microliter of this solution is crystallized on the target probe. The oligomers are believed to be dispersed in the matrix crystal lattices. The usefulness of the “dried droplet method” is limited to the characterization of synthetic polymers with polydispersities of less than 1.1. In polymers with high polydispersity, the low-mass oligomers appear to readily desorb while the high mass oligomers appear to be suppressed, leading to fingerprint discrimination at higher m/z ratio. Fractionating the highly dispersed polymer sample by size exclusion chromatography and analyzing the individual fractions by MALDI (off-line coupling) gave better molecular weight distribution values and reliable structural information and as well as calibration of the SEC method. In “Electrospray sample deposition,” the matrix and the analyte solution mixture (as practiced for PDMS) is sprayed onto the target surface under the influence of a high-voltage electric field; better shot-to-shot and spot-to-spot reproducibility was reported, due to the formation of homogeneous microcrystals. Chemical derivatization was shown to be another useful approach in which ethoxyethanes were first derivatized with phthalic anhydride and then sample target was prepared by the dried droplet method. This reduced discrimination against low-mass oligomers in MALDI experiments.

Solubility of the polymer in a suitable solvent and miscibility between the polymer and matrix solutions is important for a successful characterization by MALDI. Detergents can be used to enhance or to aid the miscibility of the polymer and matrix solutions. Normally, for synthetic polymers, a mixture of solvents may be required to prepare the analytical deposit. Unfortunately, the presence of secondary solvents or impurities leads to mass discrimination and irreproducible results. On the other hand, Cohen and co-workers demonstrated for biomolecules that changes in pH and matrix solution composition suppressed or favored desorption due to differences in the incorporation of the analytes in the matrix crystals. The Marangoni effect causes the accumulation of the hydrophilic analytes at the periphery of the sample deposit, leading to discrimination.

It is clear that co-crystallization of the matrix and oligomers from the condensed phase exhibits sensitivity, selectivity, reproducibility, and, unfortunately, discrimination problems. Since synthetic polymers possess different functional groups and a different chemical unit structure, chain length, and polydispersity, it is necessary to develop new complementary sample target preparation protocols to characterize them by MALDI. If solvents are avoided in the sample preparation step, then polymer solubility, pH of the analyte and matrix solutions, crystallization temperature, and secondary solvent effects should not play an important role in determining the quality of the MALDI mass spectrum fingerprint. Also, this might give new insights about the applicability of MALDI to synthetic polymer analysis and the multistep mechanism of the desorption/ionization process.

In the present work, MALDI compatible sample targets were prepared without utilizing solvents, and the potential of these methods for the characterization of synthetic polymers is evaluated. PEG 6000 analyzed by these methods was used to study the efficiency of the new sample preparation methods and the desorption/ionization of a hydrophobic fluoropolymer was also investigated. Fluoropolymers are industrially and commercially important due to their special chemical and physical properties, such as thermal stability, chemical inertness, good oil and water repellence, and valuable electrical properties. Some important applications are in paints and coatings, bio-materials, high-performance resins, functional materials for photoresists, and optical fibers and thermostable polymers for aerospace applications.

**EXPERIMENTAL SECTION:**

**Materials.** Poly(ethylene glycol) 6000 was purchased from Fluka (Saint Quentin Fallavier, France). Dithranol was obtained from Sigma (Saint Quentin Fallavier, France) and 2,5-dihydroxy Benzoic acid (DHB) from Aldrich Chimie (Saint Quentin Fallavier, France). Samples of fluorinated polymer were received from Atochim (Lyon, France). Carbon disks were obtained from Agar (France). These are small circular conducting scotch which can be fixed on both the sides. One side is pasted on the MALDI target and on the other side the sample (powder or crystals) can be fixed. All the solvents used (dichloromethane, butyl acetate) were of HPLC grade. All the materials and reagents were used as such without further purification.

**Sample Target Preparation.**

(a) Dried Droplet Method. About 2 mg of PEG 6000 was dissolved in 500 μL of dichloromethane, and 1 μL of this solution was diluted with 100 μL of dithranol in dichloromethane (3.5 × 10⁻² M). One microliter of this was applied to the sample target and air-dried. About 2 mg of fluoropolymer in 500 μL of butyl acetate was warmed to 60 °C to solubilize the polymer. Further dilution and sample target preparation was done using DHB in butyl acetate (9.2 × 10⁻² M) as described for PEG 6000.

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(b) Fusion Mode. About 2 mg of PEG 6000 was ground with 10 mg of dithranol and was maintained at about 85 °C for about 10 minutes and rapidly cooled. This was ground again, and a little quantity of the powder was spread uniformly on a conducting carbon disk fixed on the sample target. The same procedure was adopted for investigating desorption/ionization of the fluorinated polymers with DHB as the matrix.

(c) Matrix Vapor Deposition Method. About 2 mg of polymer and 1 mg of matrix mixture was ground to a fine powder and it was spread on the outer side of the coldfinger of a sublimation apparatus (the inner tube through which water is circulated). The matrix was placed inside the sidearm test tube and heated to about 100 °C using a silicone oil bath. The matrix slowly sublimed and deposited on the coldfinger. The deposit was removed crushed, and a little quantity was applied over the conducting carbon disk.

(d) Matrix Vapor Deposition on Teflon Surface. A small piece of Teflon was stretched a little and fixed on the coldfinger of the sublimation apparatus. Analyte solutions were deposited on the membrane and allowed to dry. Matrix vapors were then deposited as described above, and the intact membrane was removed and fixed on the sample target.

(e) Mass Spectrum Recording. MALDI-TOF mass spectra were recorded using a perSeptive Biosystems Inc. Voyager Elite (Framingham, MA) time-of-flight mass spectrometer. A nitrogen laser (337 nm, 3-ns pulse width) was used to desorb the sample ions. All the spectra were recorded in reflectron delayed-extraction mode with an accelerating voltage of 20 KV and a delay time of 225 ns. A Tektronix TDS 520A digitizing oscilloscope was used to acquire raw spectral data. The spectral data were treated using GRAMS/386 software. Each spectrum was the average of 256 laser shots. The mass spectra shown here for polymers were the average of 10 such spectra. This was necessary to characterize the low-mass oligomers formed by pyrolysis and to increase the S/N ratio.

RESULTS AND DISCUSSION
1. Fusion Mode of Sample Preparation and PEG 6000. Polyglycols [127,42,43] have been used as model polymers to develop new analytical methods for characterizing synthetic polymers by MALDI-TOF/MS. Figure 1a shows a MALDI mass spectrum of PEG 6000 cocrystallized with dithranol matrix using the dichloromethane solvent system (dried droplet preparation). Figure 1b shows a MALDI mass spectrum of PEG 6000 obtained by the

Assignment of the end groups to different oligomers found in the low m/z ratio is difficult due to the superimposition of the isobaric series such as the Na⁺ cationized PEG (N) and K⁺ cationized dPEG (M₂) ions. Furthermore, limited resolution may hinder the assignment especially at higher m/z ratio range (i.e. around 2 000 Th). For instance, the mass spectrum shows the presence of minor series and major series separated by ZTh (Figure 1c.). The overlap of the monoisotopic peak distribution of the major series with the isotopic distribution of the minor ion peak is exemplified by the series shown in Table 2.

An important point to note here is that the above discussion rules out the eventual decomposition of a cationized oligomer in the gas phase as proposed earlier. Indeed, Lattimer et al. demonstrated that, under the high collision energy regime, Na⁺ cationized PEG oligomers fragment to give vinyloxy and aldehyde-terminated oligomers in high abundance, while methoxy-terminated oligomers seemed to be less abundant. On the other hand, under the low-energy regime, much less fragmentation with an intense Na⁺ is observed. Thus, herein prompt dissociations of the cationized PEG oligomers possessing high internal energy due to laser desorption/ionization must be ruled out because of the presence of intense sodium-cationized mMPEG and dPEG product ions rather than oligomers with vinyloxy or aldehyde end groups. In addition, the intensity of the pyrolysis products increases with increasing laser fluence, substantiating further the phenomenon of pyrolysis in MALDI.

2. Matrix Vapor Deposition and Desorption of PEG 6000.

Figure 2a shows the mass spectrum recorded by vapor deposition of the matrix over the polymer. The MWD is centered at ~7000 Th, and mass discrimination due to sample preparation is not evident. The pyrolyzed products discussed in the fusion mode are also seen in the low m/z mass region.

Though the signal intensity of the oligomers varies in different modes of sample preparation, a correlation between the analyte/matrix ratio and the signal intensity was not attempted. For a successful MALDI experiment, cocrystallization of the polymer and the analyte is required. But results from these experiments point out that it may not be a general requirement.

A careful examination of the three mass spectra (Figures 1a,b and 2a) reveals that the relative abundance of [M + K⁺]⁻ and [M + Na⁺] ions vary according to the sample target preparation protocol, which merits further examination; therefore, we studied the variation of [M + Na⁺] and [M + K⁺] intensities with laser fluence. Interestingly, the intensity of [M + Na⁺] increased and decreased after reaching a maximum value, while that of [M + K⁺] decreased (Figure 2b). Many reports have noted the presence of intense Na⁺ cationized quasi-molecular ions in contrast to less intense K⁺ cationized quasi-molecular ions in MALDI mass spectrum, but a detailed explanation for this "natural effect" is lacking. To explain this observed phenomenon two assumptions are made:

(i) Quick stabilization of the desorbed Na⁺ in the short-lived, highly dense plume occurs due to multiple solvation by matrix (m) molecules.

(a) Note here that the fragmentation of the neutral high-mass oligomers gives different low-mass products which may be cationized or undergo further elimination and cationization.

“fusion mode” of target preparation. Both MALDI mass spectra display molecular weight distributions (MWD) centered approximately at 7000 u. Compared with the dried droplet method, the fusion mode shows relatively intense pyrolysis products (discussed below), giving small errors in M and M WD calculations.

When the ground mixture of PEG 6000 and dithranol is heated (see Experimental Section), the solid polymer transforms into a viscous liquid. This phase modification might facilitate the movement of the oligomers between the matrix particles; upon rapid cooling, the oligomers might form a noncrystalline film over the matrix molecules. Though MALDI is considered as a soft ionization technique, the phenomenon of pyrolysis cannot be excluded during desorption and prior to gas-phase ionization. Then, different oligomers cationized by Na⁺ and K⁺ dominating the low m/z range region in the MALDI mass spectum could be considered as formed by pyrolysis. In fact, these are formed in a two-step reaction: first, pyrolysis of neutral PEG oligomers takes place, and second, this is followed by cationization of the neutral pyrolysis products by matrix clusters (Scheme 1).

Pyrolysis by direct and consecutive thermal 1,5 H shift processes can be envisaged giving rise to Na⁺ and K⁺ cationized quasi-molecular ion series such as (i) monomethylated PEG (mPEG, M₁), dimethylated PEG (dPEG, M₂), and/or (ii) monovinyl PEG (mVPEG, V₁) and divinyl PEG (dVPEG, V₂). The K⁺ cationized series are marked as M₁', M₂', V₁', and V₂', respectively (Figure 1c). The two series appear in addition to the cationized intact PEG (N and N'). First, formaldehyde elimination occurs (Scheme 1) from the neutral oligomers concomitant with the formation of both mMPEG and mVPEG complementary neutrals according to the six-membered mechanism in Scheme 1. In the following consecutive decompositions, cationized mVPEG and dPEG are formed as minor products and dVPEG ions are formed in trace amounts. The different pyrolysis products can be represented as shown in Table 1.

| Conditiona | Scheme 1. Fragmentation Pathway of the High-Mass PEG Oligomers under MALDI Conditionsa |

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Thermal Cleavage</th>
<th>Pyrolysis Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH-(CH₂-CH₂-O)ₙ-CH₂</td>
<td>H</td>
<td>CH₂-O⁻-(CH₂-CH₂-O)ₘ⁻H</td>
</tr>
<tr>
<td>CH₂=CHO-(CH₂-CH₂-O)ₘ⁻H</td>
<td>-CH₂O</td>
<td>CH₂=CHO-(CH₂-CH₂-O)ₙ⁺</td>
</tr>
<tr>
<td>CH₃O-(CH₂-CH₂-O)₁⁻CH₂</td>
<td>-CH₂O</td>
<td>CH₃O-(CH₂-CH₂-O)₁⁻CH₂</td>
</tr>
<tr>
<td>CH₂=CHO-(CH₂-CH₂-O)ₙ⁻z⁺CH=CH₂</td>
<td>-CH₂O</td>
<td>CH₂=CHO-(CH₂-CH₂-O)ₙ⁻z⁺CH=CH₂</td>
</tr>
<tr>
<td>dMPEG</td>
<td>-CH₂O</td>
<td>dVPEG</td>
</tr>
<tr>
<td>CH₃O-(CH₂-CH₂-O)₁⁻CH₂</td>
<td>-CH₂O</td>
<td>CH₃O-(CH₂-CH₂-O)₁⁻CH₂</td>
</tr>
<tr>
<td>CH₂=CHO-(CH₂-CH₂-O)ₙ⁻z⁺CH=CH₂</td>
<td>-CH₂O</td>
<td>CH₂=CHO-(CH₂-CH₂-O)ₙ⁻z⁺CH=CH₂</td>
</tr>
<tr>
<td>dMPEG</td>
<td>-CH₂O</td>
<td>dVPEG</td>
</tr>
</tbody>
</table>

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(i) Quick stabilization of the desorbed Na⁺ in the short-lived, highly dense plume occurs due to multiple solvation by matrix (m) molecules.

Table 1. K⁺ and Na⁺ Cationized Ion Series Observed at Lower m/z Range (i.e., from 2000 Th to 2300 Th) in MALDI Mass Spectrum of PEG

<table>
<thead>
<tr>
<th>n</th>
<th>intact PEG(N) [44n + 18 + 23]⁺</th>
<th>mVPEG(V₁)² [44n₋₁ + 18 + 5]⁺</th>
<th>mMPEG(M₂)⁻ [44n₋₁ + 18 + 7]⁻</th>
<th>dMPEG(M₂)⁺ [44n₋₁ + 18 + 7]⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>45</td>
<td>2021</td>
<td>2047</td>
<td>2035</td>
<td>2049</td>
</tr>
<tr>
<td>46</td>
<td>2065</td>
<td>2091</td>
<td>2079</td>
<td>2093</td>
</tr>
<tr>
<td>47</td>
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<td>2135</td>
<td>2123</td>
<td>2137</td>
</tr>
<tr>
<td>48</td>
<td>2153</td>
<td>2179</td>
<td>2167</td>
<td>2181</td>
</tr>
<tr>
<td>49</td>
<td>2197</td>
<td>2223</td>
<td>2211</td>
<td>2225</td>
</tr>
<tr>
<td>50</td>
<td>2241</td>
<td>2267</td>
<td>2255</td>
<td>2269</td>
</tr>
</tbody>
</table>

² The values tabulated are average m/z. ³ 44n + 18 - 1 + 27 + 23. ⁴ 44n + 18 - 1 + 15 + 23. ⁵ 44n + 18 - 2 + 15 + 23.

Table 2. Series Exemplifying the Overlap of the Monoisotopic Peak Distribution of the Major Series with the Isotopic Distribution of the Minor Ion Peak

cation | Na⁺ | K⁺ |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(M₂)</td>
<td>[44n + 18 + 7]⁺ and (M₁⁻) [44n + 18 + 9]⁺</td>
<td></td>
</tr>
<tr>
<td>(M₁⁻)</td>
<td>[44n + 18 - 7]⁺ and (N⁻) [44n + 18 + 39]⁺</td>
<td></td>
</tr>
<tr>
<td>(N)</td>
<td>[44n + 18 + 23]⁺ and (V₁⁻) [44n + 18 + 21]⁺</td>
<td></td>
</tr>
</tbody>
</table>

(ii) Desorption of the preferentially solvated K⁺ ions by matrix in the condensed phase (in preference to Na⁺) occurs during sample target preparation.

The attachment of cations (Cat⁺) to the oligomers (P) then must proceed in the gas phase by a multistep desolvation (which constitutes an endothermic process) of the solvated cation clusters followed by numerous endothemic ion–molecule reactions as represented below:

\[
[m_n, \text{Cat}^+] \rightarrow [m_{n-x} \text{Cat}^+]^x + x \text{m} \quad \Delta H_f^0 > 0
\]

\[
[m_n-x, \text{Cat}^+] + P \rightarrow [m_{n-x} \text{Cat}^+ + P]^x \rightarrow [P-\text{Cat}^+] + (n - x)\text{m} \quad \Delta H_f^0 > 0
\]

The efficiency of these consecutive process depends on: the internal energy relaxation of the excited cluster ions and the exothermicity of the ion attachment, which is intimately related to the cation affinity of the matrix cluster mₙ₋x, and the sample and to the presence of an intrinsic barrier (entropy effect).

Direct attachment of the cation with oligomers is highly improbable since the concentration of P is very low (compared with matrix m). Moreover, cooling of [P + Cat⁺] cluster formed by the substrate is unfavorable because of its low density. On the other hand, the \([m_{n-x} \text{Cat}^+ + P]^x\) complex can be relaxed by multiple low-energy collisions, and its dissociation leads to stable cationized oligomers. Also, on increasing the matrix/polymer molar ratio gradually (in our experiments from 77 to 3080) the absolute intensity of \([P + K]^+\) evolves and sometimes exceeds the intensity of \([P + Na]^+\). This observation points out that, in condensed-phase, preferential solvation of K⁺ ion by the matrix molecules takes place (i.e. mₙK⁺) over the formation of mₙNa⁺. Consequently, during laser desorption, two cationizing mₙK⁺ and Na⁺ species are ejected in the plume. An increase in matrix concentration raises the density of mₙK⁺ (relative to mₙNa⁺), and in the gas-phase cationization of P takes place very rapidly by the desolvation of the readily available solvated K⁺. These experiments demonstrate that matrix clusters play an important role in the cationization of the PEG oligomers. The number and stability of the species ejected into the gas phase depend on the sample target preparation protocol and Laser fluence, which in turn affect the cationization process, altering the intensity of \([P + Na]^+\) and \([P + K]^+\) in different experiments. Another important observation is that the relative intensity of the oligomers cationized by Na⁺ and K⁺ is not dependent on the oligomer chain length.

3. Desorption of Fluorinated Polymers. Fluorinated polymers are hydrophobic and are insoluble in common organic solvents. Despite their useful properties and wide applications, few reports exist on their characterization by MALDI-TOF/MS. Figure 3a shows the MALDI mass spectrum obtained by the dried droplet method for an industrial fluorinated polymer in its earlier stages of development. DHB is an efficient matrix for the desorption of this class of polymers. MALDI mass spectra in Figure 3 parts b and c were recorded from sample targets prepared by fusion mode and by matrix vapor deposit, respectively.

Each oligomer distribution is complex (about 15 peaks are present) and the difference of 644 Th between two successive distributions corresponds to the following repeating unit

\[
R = C_{15}F_{32}(CH_2)_{10}OCO.
\]

Similar to PEG, the oligomers appear predominantly as \([M + Na]^+\). In contrast to PEG, the signal intensity of the fluorinated oligomers changes remarkably with sample preparation methodology, i.e., it decreases rapidly beyond m/z 5000 in Figure 2b and it decreases gradually after m/z 7000 in Figure 2c. It seems that the gas-phase cationization of PEG by Na⁺ is not very much affected by the sample target preparation protocol. Whereas, it seems that the gas-phase cationization of fluorinated high-mass oligomers is dependent on the sample preparation target prepara-

tion. One possible explanation is the different hydrophobicity and gas-phase cation affinity of fluoro polymers (which influence the ion–molecule reaction efficiency) and or the dispersion of the oligomers in the matrix is not sufficient.

The scanning electron microscopy study of DHB crystals in the presence and absence of fluoro polymer (samples obtained by fusion and matrix vapor deposition) showed that the presence of oligomers drastically alters the shape and size of the matrix crystals (images not shown here) as reported for the dried droplet method of sample preparation. In both the cases, the matrix and the polymer coexist as agglomerates. The size of the agglomerates is larger in the samples obtained by fusion mode compared with that of the samples prepared by matrix vapor deposition. It can be inferred that the extent of dispersion of the oligomers in the matrix should also be an important factor that determines the accessible mass range for fluoropolymers.

Figure 2. (a) MALDI mass spectrum of PEG 6000 obtained by the matrix vapor deposition method on a sample target preparation. Dithranol was used as the matrix (b) Variation in ion abundances of Na⁺ and K⁺ cationized PEG 6000 oligomers with laser fluence.
Matrix vapor (DHB) was deposited on the Teflon membrane containing PEG as described in the Experimental Section. The mass spectrum obtained in this case showed slightly less metastable decompositions of the oligomers compared with the spectrum obtained from dried droplet preparation, suggesting that ions carry less internal energy under these conditions. Fluoropolymer could not be desorbed from the Teflon membrane surface by any mode of sample preparation, illustrating the importance of the sample target surface for desorbing fluoro polymers by MALDI.

CONCLUSION

We investigated new methods of sample preparation for the characterization of synthetic polymers by MALDI. Matrix vapor deposition is found to be an interesting method of sample target preparation when the cocrystallization of the matrix and polymers from the condensed phase is difficult. The absence of solvents during the sample target shows that the extent of dispersion of the oligomers in the matrix required for MALDI depends on the nature of the analyte itself. Furthermore, solvent properties should be critical only when better dispersion of the analyte in the matrix is required. Under MALDI conditions, pyrolysis of neutral high-mass PEG oligomers and the subsequent cationization of the products of pyrolysis give rise to the ion signals at low-mass range in the mass spectrum. Another important observation is the origin and role of the matrix clusters in the cationization of the oligomers.

Experiments with PEG show that the desolvation of the cationized matrix clusters in the gas phase leads to the cationization of the oligomers, and their formation in the condensed phase or in the gas phase determines the intensity of the Na$^+$ or K$^+$ cationized oligomers. Unlike PEG, the success of MALDI experiments for the characterization of fluorinated polymer depends on the distribution of oligomers in the matrix and on the nature of the sample target surface preparation. Further work is on progress to find a method to dope the polymers with cations to suppress the quasi molecular ions formed due to the presence of adventitious cations. Characterization of fluorinated polyethers will also be undertaken to make a better comparison with PEG. A better understanding of the role of different factors will enable us to develop new analytical approaches for the characterization of hydrophobic fluoro polymers by MALDI-TOF/MS.

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Figure 3. MALDI mass spectrum of a fluorinated polymer (a) obtained by dried droplet method using DHB and butyl acetate solvent, (b) obtained by the fusion mode of sample target preparation, and (c) obtained by the matrix vapor deposition mode of sample target preparation.