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Collision-Induced Dissociation Studies of Poly(vinylidene) Fluoride Telomers in an Electrospray-Ion Trap Mass Spectrometer

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Although fluorinated polymers are widely used in different applications, they are rarely investigated by "soft ionization" techniques such as matrix-assisted laser desorption/ionization and electrospray ionization (ESI). We report here, the desorption and fragmentation of poly(vinylidene) fluoride (PVDF) telomers in an ion trap mass spectrometer coupled to an ESI source. Protonated and lithiated telomers under collision-induced dissociation resonant excitation show mainly HF losses. Fragmentation of protonated telomers can be rationalized by a double proton-transfer mechanism and that of lithiated and anionic telomers by an ion−dipole mechanism. Both mechanisms predict the formation of a stable aromatic or a linear conjugated species, respectively. For lithiated telomers, we could determine the degree of polymerization (*n*) from the product ion abundance in MS^2 experiments. The nature of the end group plays a substantial role in orienting the fragmentation of the PVDF ions. It is interesting to note that, in MS^2 experiments, Li^+ and F^- act as catalysts in the fragmentation of PVDF telomers. Fragmentation of the PVDF telomer backbone was not observed under any experimental conditions.

Mass spectrometry is an important technique for characterizing synthetic polymers.[1] Generally, mass spectra reveal information about end groups, repeating unit of the polymer, degree of polymerization (*n*), and molecular weight distribution (if the polydispersivity is <1.2), all of which determine the important physical and chemical properties of the polymer.[2] Soft ionization techniques such as matrix-assisted laser desorption/ionization (MALDI)[3] and electrospray ionization (ESI)[4] are used for generating intact protonated/cationized molecules stable in the gas phase, from which useful structural information can be obtained. MALDI combined with a time-of-flight mass analyzer (TOFMS) is widely used for characterizing synthetic polymers.[5−20] Sometimes, interpretation of MALDI mass spectra is confusing due to pyrolysis, discrimination, and reproducibility phenomena that are associated with the desorption/ionization mechanism.[21−24] Also, desorption/

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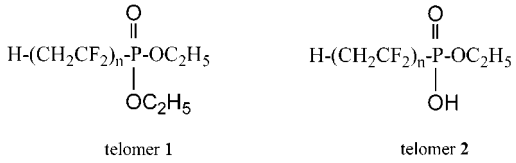
ionization of poly(vinylidene) fluoride (PVDF) oligomers is difficult in MALDI experiments, and in addition, modification of the terminal groups is often obseved.[25] Though an ESI source coupled to an ion trap mass spectrometer (ITMS)[26] is not widely used to characterize synthetic oligomers, it has been successfully applied to analyze polymers with low molecular weight distribution[18,27,28] and to study the structure of dendrimers.[29] Generally, under ESI conditions, synthetic polymers are desorbed as multiply charged oligomers and the overlap of different charge-state distributions renders the mass spectrum uninterpretable.[30] Another drawback of ITMS for synthetic polymer analysis is its limited m/z range as encountered in the case of quadrupole mass filters.

Additional information about the structure and gas-phase chemistry of the oligomers can be obtained from tandem MS/MS experiments.[31,32] In MALDI-TOFMS, some of the quasi-molecular ions formed possess enough internal energy to fragment either promptly in the source (termed "in-source decay" (ISD))[33] or after acceleration into the field-free region of the flight tube (termed "postsource decay" (PSD))[34] by metastable processes that are characterized by lower rate constants. PSD can be employed to gain useful structural information about the oligomers;[35−37] but most of the synthetic oligomers form stable quasi-molecular ions with metal cations such as Na^+ and K^+ and do not readily fragment by PSD. Therefore, important data about oligomer structure and gas-phase fragmentation are not accessible. The multiple-stage MS^n capability offered by the ITMS analyzer might be advantageously used to study the fragmentation pathways of ionized polymers. In sequential MS^n experiments, a single parent ion is isolated and its resonant excitation leads to fragmentations[38] (termed an MS^2 experiment). If the product ions formed in the MS^2 step are sufficiently abundant then, they can be selectively isolated and made to undergo collision-induced dissociation (CID) to fragment further (i.e., sequential MS^3 experiment) and so on. It should be noted here that the fragmentation of the selected ions takes place under low-energy conditions (i.e., a few eV)[39] due to kinetic energy relaxation by multiple collisions with helium present in ion trap.

Chart 1. Structure of Diester **1** and Monoester **2** of PVDF Telomers

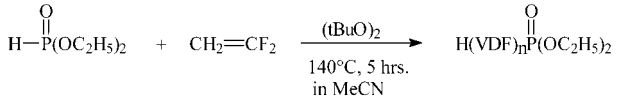


telomer **1** telomer **2**

Increasing consumption and diverse applications of fluorinated polymers[40] demand fast and reliable analytical techniques to characterize them without ambiguity. Fluorinated derivatives bearing phosphorus atoms are known for their applications in the field of surfactants, lubricants, oleophobic textile treatment, fire fighting agents, insecticides, complexing agents, and electrolytes. No report exists in the literature on the characterization of such PVDF telomers[41] desorbed under MALDI or ESI conditions. Telomers are functional oligomers that contatin a functional group and exhibits a high transfer rate constant. The structures of the PVDF telomers that were synthesized and studied (telomers **1** and **2**) using MALDI-TOFMS and ESI-ITMS are shown in Chart 1. This report focuses in detail only on the fragmentation of **1** in ESI-ITMS. Mass spectral acquisitions and resonant excitation experiments were carried out both in the positive and in the negative ionization modes, and the results of these experiments are discussed here.

EXPERIMENTAL SECTION

Synthesis of PVDF Telomers. (i) Telomer 1. The synthesis of the telomers used in this study is described elsewhere.[42] Briefly, the first adducts of the telomerization of VDF with diethyl hydrogenphosphonate (DEHP) were synthesized in a 1-L autoclave by using di-*tert*-butyl peroxide as the initiatior (1 mol % as the ratio of VDF/"C_0" = $[(tBuO)_2]_0/[VDF]_0 = 0.01$) and acetonitrile as the solvent using an equimolar amount of VDF and DEHP (defined as $R_0 = [DEHP]_0/[VDF]_0 = 1.0$).



The overall VDF conversion was ~91%, according to the released VDF, after the reaction. The average cumulated degree of the polymerization in number DP_{ncum} of these telomers has been determined to be 15 by assuming that each adduct has the following formulas: $H(VDF)_nP(O)(OEt)_2$. The first four adducts of the telomeriation reaction were isolated by distillation and characterized without any ambiguity by elemental analysis and by ^1H, ^{19}F, ^{13}C, and ^{31}P NMR spectroscopies.

(ii) Telomer 2. A mixture containing 3.0 g of $H(VDF)_nP(O)(OEt)_2$ and 1 mL of HCl (36 N) in 20 mL of toluene was refluxed for 24 h. The organic layer after decantation contained waxy particles (2.1 g) which were solublized in acetone and precipitated

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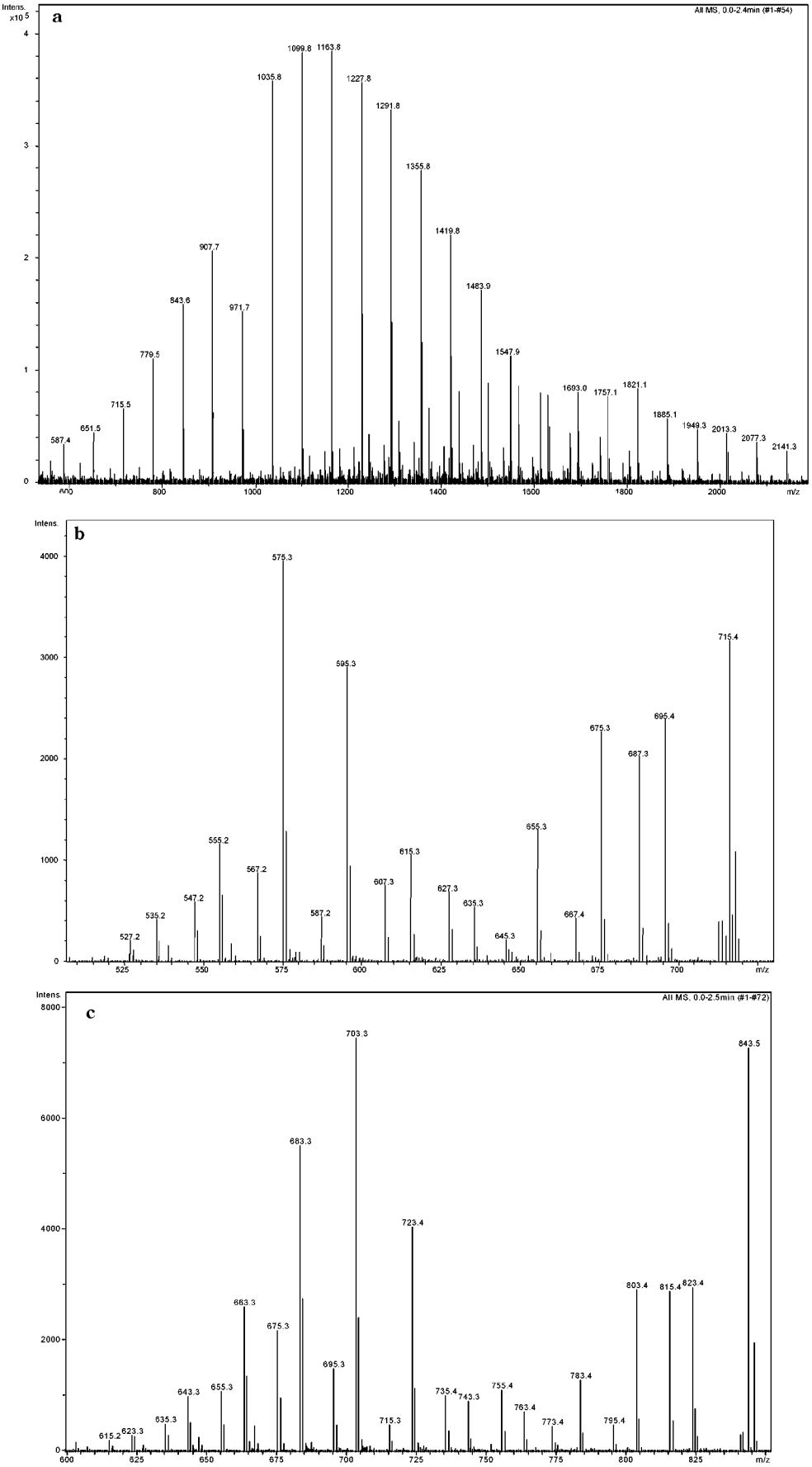


Figure 1. (a) ESI mass spectrum (positive ion mode) of **1** in DMSO with NH_4NO_3. (b) and (c) CID spectrum (MS^2) of protonated 9- (*m*/*z* 715) and 11-mer (*m*/*z* 843) of **1** (excitation amplitudes were 0.85 and 1.0 V, respectively). All the spectra (both MS and CID) were recorded using smart parameter of 1000 and stability and trap drive values of 100%.

from hexane. The telomers obtained were characterized by ^1H and ^{31}P spectroscopies.

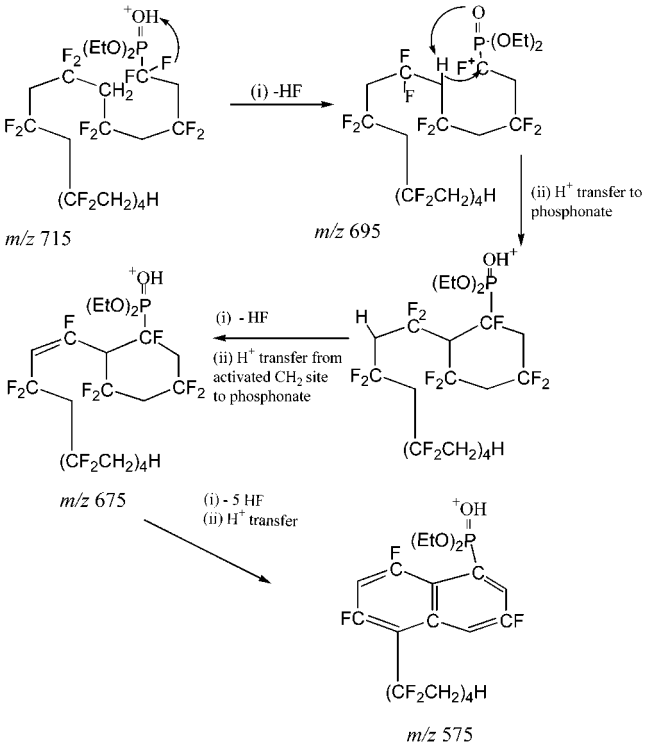
Mass Spectral Acquisitions. Mass spectral recording and CID resonant experiments were carried out using an ESI-ITMS (Esquire 3000 supplied by Bruker, Wissembourg, France). Samples were introduced by "infusion" into the ESI source at a rate of 120 μL/h. The capillary voltage was −4 kV, the flow rate of the dry gas (nitrogen) was 6 L/min, and the nebulizer pressure was 7 psi. For operating in the negative mode, a capillary voltage of +3 kV was applied. The "smart" parameter setting was 1000, the "stability " and the "trap drive" values were 100%, and the other trap parameters were automatically selected by the acquisition software. The spectra were treated using Bruker data analysis software (version 2.0).

Sample solutions were prepared using HPLC grade dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF). About 2 mg of each sample was dissolved in ∼500 μL of DMSO, and ∼10 μL of this solution was further diluted to 1 mL with DMSO (working solution). Aqueous salt solutions of lithium chloride, ammonium nitrate, ammonium acetate (NH_4OAc), and ammonium chloride solutions of a concentration of ∼10 ppm were prepared separately in "Millipore" water. About 10 μL of the salt solutions was added separately to the working solution and the resultant mixtures were electrosprayed. To obtain ESI mass spectra in negative mode, the samples were dissolved in THF and were electrosprayed without any salts.

RESULTS AND DISCUSSION

MH^+ Protonated Telomers: Competitive Decompositions. To form even-electron noncovalent adduct ions of the PVDF telomers, solutions of NH_4Cl, $NH_4(OAc)$, and NH_4NO_3 were separately added to the sample solutions and were electrosprayed; a stable, intense signal was obtained from the solution containing NH_4NO_3, and the recorded ESI mass spectrum is shown in Figure 1a. An intense singly charged protonated telomer distribution, starting from the 7-mer, centered approximately at the 16-mer [i.e., $(16 \times 64) + 139 = 1163$ Th[43]] is observed in the ESI mass spectrum of **1**. At higher mass, the $[M + NH_4]^+$ adduct ion distribution centered approximately at 1600 Th (i.e., 22-mer) is detected. The MH^+ ions might be partially formed by the dissociation of the $[M + NH_4]^+$ adduct ions induced by collision with the residual gas present in the capillary−skimmer interface region.[44] The presence of the $[M + NH_4]^+$ distribution in the higher m/z range compared to that of the MH^+ ions may be explained by considering the oligomer size. Indeed, the larger the size of the adduct ion, the lower the desolvation rate constant due to the internal energy distribution throughout all the oscillators of the telomers. Separation between two adjacent peaks of the main distribution in the mass spectrum is 64 Th, which corresponds to the mass of (CH_2CF_2), the expected repeating unit of the PVDF telomers. To obtain complementary information, sequential MS^2 experiments were carried out for the protonated telomer from 7-mer (m/z 587) through 14-mer (m/z 1035). The CID spectra of the protonated 9- (m/z 715) and 11-mer (m/z 843) are shown in Figure 1b and c, respectively.

Scheme 1. Fragmentation Mechanism of Protonated PVDF Telomers under Low-Energy CID Conditions. Formation of a Stable Naphthalene-like Aromatic System by the Consecutive Losses of Seven HFs



Two product ion series are noticed in the CID spectra. The most intense series (main series) corresponds to the consecutive losses of 20 u from the parent ion, i.e., consecutive elimination of HF. Chen et al,[45] reported multiple HF losses from fluorinated isocyanate oligomers in desorption chemical ionization-tandem mass spectrometry experiments. One interesting observation in the CID spectra is that the product ion corresponding to the consecutive loss of seven HF from MH^+ is always relatively intense. This phenomenon is independent of the telomer chain length. The assumed fragmentation mechanism of the MH^+ telomers is shown in Scheme 1. We consider here that the protonation takes place at the phosphonate group, which induces the elimination of one HF from the activated CF_2 position (step i, Scheme 1), and this is followed by the double proton transfer to the departing fluorine group (step ii, Scheme 1); subsequent elimination of HF is the favored fragmentation pathway rather than a 1,2 HF elimination. Very likely, the double proton transfer should have a higher rate constant. In the mechanism, we note that the loss of the first HF molecule leads to the formation of a reactive carbocation intermediate and gives rise to the formation of a six-membered ring. Consecutive loss of seven HFs from the MH^+ precursor ions leads to the formation of a stable naphthalene-like aromatic system explaining why the seven HF losses are favored from MH^+. However, loss of HF by a 1,2 elimination pathway that is characterized by a low rate constant is not ruled out when the double proton transfer is not sterically favored due to the telomer

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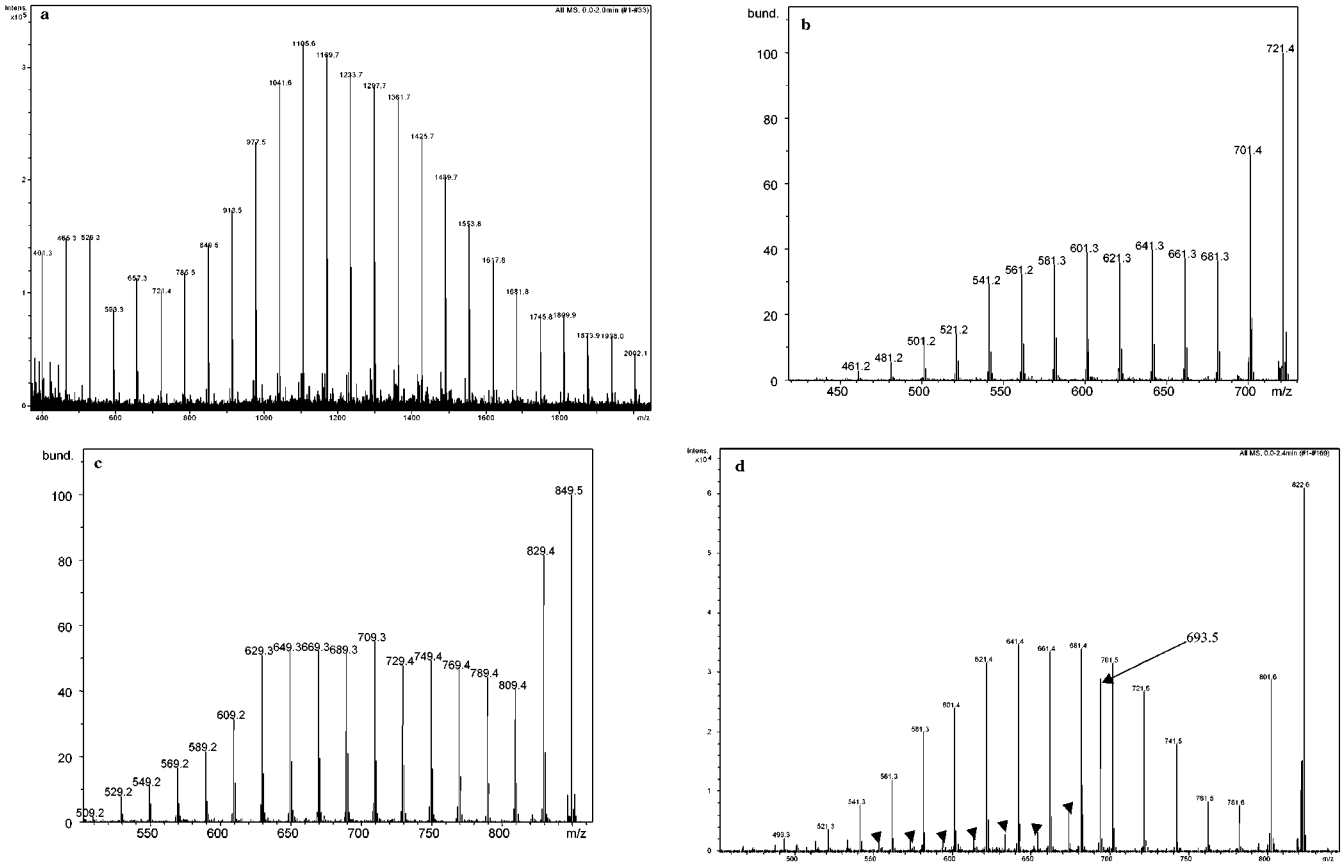

Figure 2. (a) ESI mass spectrum (positive ion mode) of **1** in DMSO with LiCl. (b) and (c) CID spectrum of lithiated 9- (*m*/*z* 721) and 11-mer (*m*/*z* 849) (excitation amplitudes were 0.92 and 1.1 V, respectively) (d) lithiated 11-mer (*m*/*z* 822) of **2** (excitation amplitude was 0.02 V). The peak at *m*/*z* 693 corresponds to the $[MLi - HF - PO_2(OEt)]^+$ ion, which loses HF consecutively to give the series marked by ▼.

chain length (i.e., phosphonate group is far away from the migrating proton).

In addition to the loss of the first HF, the MH^+ ions can competitively lose a C_2H_4 molecule (28 u) from the phosphonyl terminal group. Consecutive loss of HF from the resulting ion gives rise to the less intense second product ion series. This primary loss of the C_2H_4 molecule from an activated phosphonyl ester containing the ethoxy groups was reported earlier, and a mechanism was also proposed for this loss.[46] Loss of C_2H_4 takes place due to the activation of the (P═O) site of the phosphonyl terminal group by its protonation [i.e., due to the partial charge (ä+) acquired by the phosphorus atom]. Note that the cleavage of the CH_2─CF_2 backbone from PVDF has been observed in secondary ion mass spectrometry experiments in both the negative and positive ion modes.[47] This is very likely due to the relatively high internal energy acquired by the quasimolecular oligomers of small chain length.

It is interesting to note that in the case of lithiated telomers (discussed in the next section) loss of ethylene is entirely hindered due to the stronger localization of the charge at Li^+, and consequently, the (P═O) site stays inactivated. The CID spectra of **2** showed similar fragmentation patterns, i.e., competitive losses of HF and C_2H_4 from the parent ion. Although oligomers containing heteroatoms in their backbone have been shown to fragment under resonant CID conditions,[48] the absence of such fragmentation in the case of PVDF telomers is not surprising, because the C−C bonds in PVDF telomers are characterized by strong bond dissociation energy values due to the presence of fluorine atoms.

$(M + Li)^+$ Quasi-Molecular Species. The PVDF telomers formed abundant cationized molecules with lithium, and oligomers from $n = 4$ to $n = 30$ were observed in ESI mass spectrum of **1**. Compared to the mass spectrum in Figure 1a, the quasi-molecular ions formed here are shifted by six Th, confirming the attachment of a single lithium ion to the telomers (Figure 2a). Lithiated oligomers were shown to fragment efficiently in sequential MS^2 experiments compared to protonated or sodiated oligomers.[49] In our study, CID by resonant excitation of $(M + Li)^+$ species was carried out for telomers from $n = 4$ (m/z 401) through $n = 13$ (m/z 977). In all the cases, only one series of daughter ions was formed by the consecutive losses of HF from the $(M + Li)^+$ ion as discussed previously for the MH^+ species. However, compared to the CID spectra of the protonated species, the CID spectra of these ions displayed remarkable differences in the number of HF molecules lost and in the distribution of the product ion abundance. Panels b and c of Figure 2 show the CID spectra of oligomers $n = 9$ (m/z 721) and $n = 11$(m/z 849), respectively. Examination of the CID spectra in Figure 2b shows that the intensity of the product ions diminishes remarkably after the

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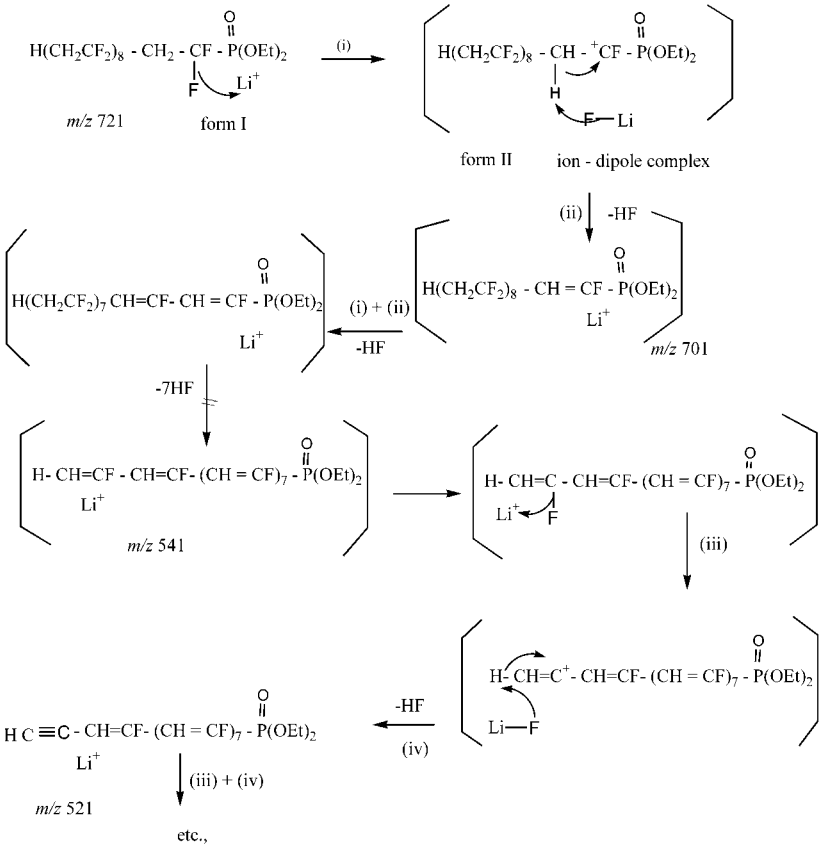
Scheme 2. Fragmentation Mechanism of Lithiated PVDF Oligomers under Low-Energy CID Conditions[a]



[a] HF losses from the parent ion leads to the formation of a conjugated diene system.

consecutive losses of 9 HFs, and in Figure 2c, this decrease is noticed after the consecutive 11 HF losses. In general, the abundance of the product ions decreases after the loss of "*n*" number of HF molecules from the cationized *n*-mers. The change in the product ion abundance can aid to confirm the degree of polymerization of the telomer under investigation.

The possible fragmentation mechanism of the $(M + Li)^+$ ions is shown in Scheme 2. The important aspect of the assumed mechanism is the formation of an ion−dipole complex between the LiF salt and the charged *n*-mer (e.g., form II) in contrast with the double proton-transfer fragmentation mechanism of the protonated telomers (Scheme 1). Formation of LiF is favored due to the fact that Li^+ can be considered a hard acid and F^- a hard base in the gas phase, respectively.[50] In the ion−dipole complex, we can possibly consider the attachement of the H^+ or the Li^+ to the P═O site of the phosphonyl diester (form II, Scheme 2). If the attachment of the H^+ takes place, then it should be evidenced by the diagnostic loss of C_2H_4 (vide supra) observed in the spectra of MH^+, which is not the case here. If proton migration does not take place then a fortiori, the Li^+ attachment must be less favored (for instance, proton affinity of diethyl methyl phosphonate is ∼216 kcal/mol while its lithium cation affinity is ∼52.6 kcal/mol).[51−53] Thus, the Li^+ reagent must be more labile and must induce the removal of F^- by forming LiF salt as shown in the ion−dipole complex (i.e., form II). The formal H^+/Li^+ exchange (i.e., LiF + $H^+ \rightarrow$ HF + Li^+) is strongly exothermic by more than 233 kcal/mol, and thus, HF elimination can take place by charge-promoted dissociation in the ion−dipole complex.

The ion−dipole complex formed can be considered to be mobile throughout the telomer skeleton favoring the loss of one HF from each repeating unit present in the *n*-mer. The comparable intensity of the product ions in the CID spectrum of $(M + Li)^+$ ion indicates that loss of HF does not lead to a particular stable structure (as seen in the case of protonated telomer), but rather, one can imagine the formation of a conjugated diene system (Scheme 2). Additional losses of HF molecules are also observed from the diene intermediate ions, which might lead to the formation of activated allylic bonds; however, this is not the major fragmentation pathway. Lithium adducts of the telomer **2** showed only consecutive HF losses in CID experiments, but the product ion intensity distribution was different, i.e., a Gaussian-like distribution is observed (Figure 2d). Rather an unexpected result was that the $(M + Li)^+$ ions of **2**, after losing one HF, could lose the terminal phosphonyl group (peak at *m*/*z* 693.5, Figure 2d). The resulting PVDF chain then undergoes consecutive HF losses. Note that the telomers **1** and **2** formed intense sodiated molecules with Na^+, but under CID resonance excitation conditions, the sodium adducts did not induce any useful fragmentations. Very

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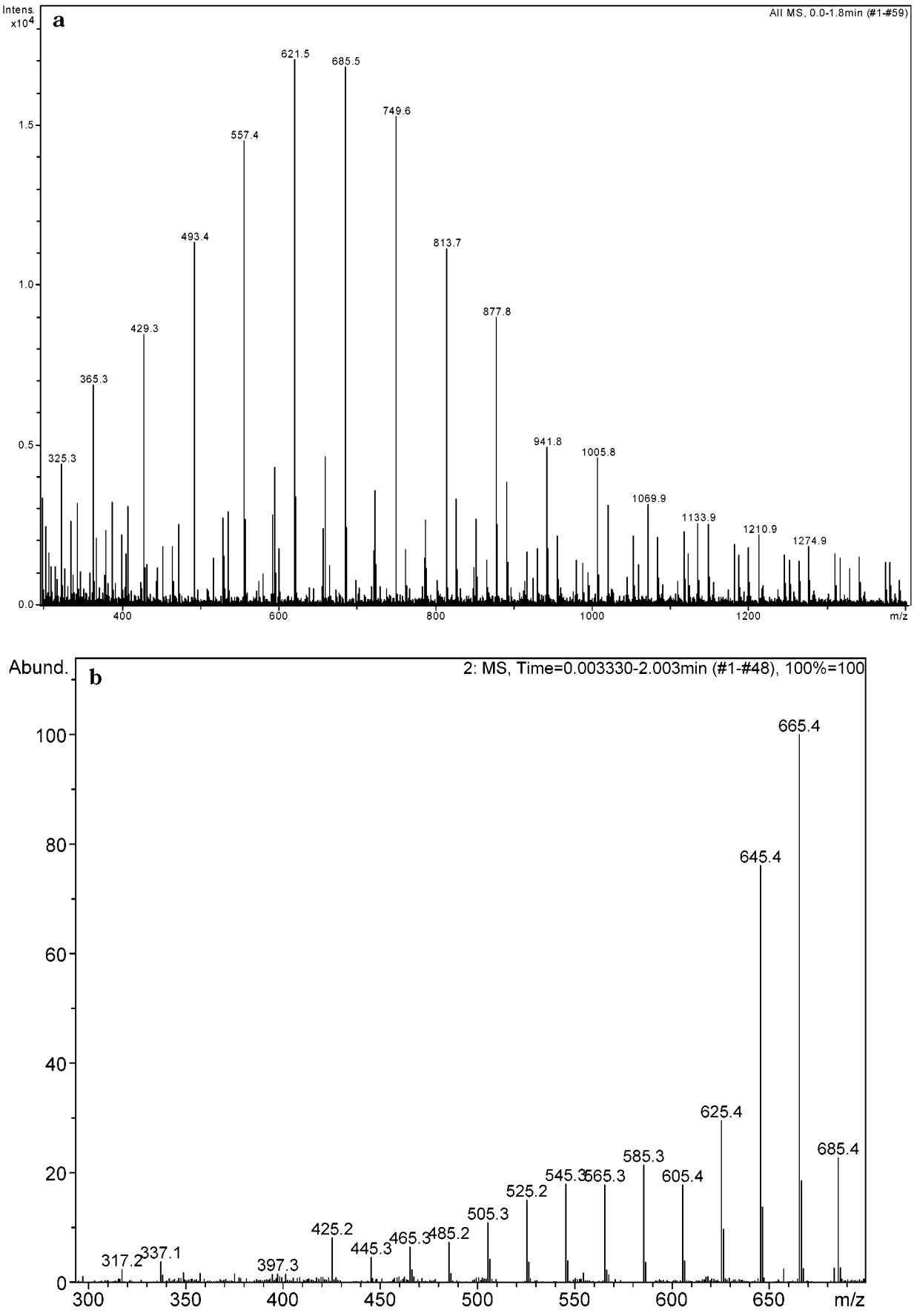
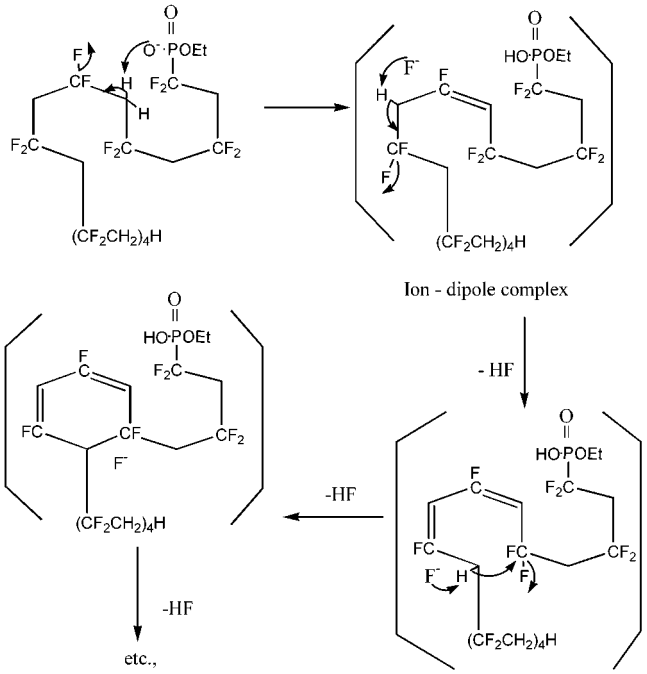


Figure 3. (a) Negative ion ESI mass spectrum of **1** in THF. (b) CID spectrum of anionic 9-mer of telomer **1** (excitation amplitude was 0.98 V).

Scheme 3. Fragmentation Mechanism of Anionic Telomer by Loss of HF after Isomerization into an Ion−Dipole Complex



likely, the fragmentation results in the liberation of Na^+, which is not observed in the CID spectra due to its unstable position in the stability diagram of the ion trap.

Anionic Telomers. To obtain an improved ESI mass spectrum in the negative mode, THF was used instead of DMSO as solvent without any added salts. The mass spectrum of **1** showed telomeric distribution centered approximately at 900 Th, i.e., at low-m/z range compared to the ESI mass spectrum obtained in the positive mode (Figure 3a). The species detected in the negative mode are due to loss of C_2H_5 from the terminal phosphonyl group either by an E_2 or by an SN_2 mechanism induced by the nucleophilic ions originating from solvent such as the open form of THF ($C_4H_7O^-$). Similar to the lithiated ions, the CID of telomers **1** and **2** showed only HF losses.

The CID spectrum (Figure 3b) of the 9-mer (m/z 685) of **1** shows the product ions corresponding to the first and second HF losses in abundance and in lesser abundance the other product ions. Under high-energy conditions in negative chemical ionization mass spectrometry, it has been shown[54] that the odd-electron molecular ion of pentafluroalkyl ketones of fatty acids could lose all the 5HF probably by a mechanism that involves long-distance hydrogen transfer. However, no C−C cleavage was observed. The fragmentation of the anionic oligomers **1** could also be explained by an ion−dipole mechanism that is similar to the one proposed for the lithiated ions as shown in Scheme 3. In this mechanism, it is the F^- ion that is mobile throughout the telomer chain.

The PVDF telomers studied here did not show any backbone fragmentation and also did not give any additional information about the telomer structure.

CONCLUSION

The usefulness of the ESI-ITMS technique to analyze PVDF telomers was demonstrated. The ESI mass spectrum obtained can be used to gain information about the repeating unit and end groups of fluorinated telomers. CID by resonant excitation of different telomer ions under low-energy conditions showed that the backbone cleavage does not take place and instead consecutive losses of HF are favored. From the different fragmentation mechanisms (that are unique), we identify that HF losses from the telomer ions lead preferentially to the formation of either a stable aromatic or conjugated system. A correlation between the number of HFs lost and the degree of polymerization can be obtained for the lithiated telomers of PVDF diphosphonate ester. It seems that the end group substituents play a considerable role in determining the orientation of the fragmentation pathways and the product ion intensities. Interestingly, Li^+ and F^- ions act as catalysts in the fragmentation of PVDF telomers. One more important observation is that the loss of one HF molecule from each repeating unit is the principal fragmentation pathway. Contrary to high-energy CID experiments, the fragmentation of the PVDF telomers under CID resonant excitation in an ESI-ITMS is not a charge-remote process[55] as expected. Under a high-energy regime, these telomers might lead to the fragmentations of the backbone, and thus, additional structural information may be obtained.

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