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Polymer characterization by laser desorption with multiphoton ionization of end-group chromophores

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Abstract

We have used a combination of laser desorption, separate multiphoton ionization, and mass spectrometry to characterize films of perfluorinated polyethers. Photoionization is achieved through end group chromophores, which are either present in the polymer or chemically attached. The technique provides parent molecular weight distributions without fragmentation. Examples are given of end group analysis, wavelength dependent spectroscopy, analysis of repeat unit distributions in copolymers, and polymer degradation analysis.

1. Introduction

Laser desorption is a powerful tool for surface analysis because it allows for sensitive characterization of organic adsorbates, particularly when combined with soft ionization methods, such as separate photo-ionization, and mass spectrometry [1]. This makes it possible to obtain detailed information about large or fragile molecules on surfaces, which may decompose when analyzed by many other techniques. Here we demonstrate the application to perfluorinated polyether films (PFPEs) by end group photoionization.

Complete characterization of polymers requires absolute molecular weight distributions. Those cannot be obtained by nuclear magnetic resonance (NMR) or by chromatography, which generally only

provide average values or envelopes of the desired distributions [2,3]. In particular in the case of blends or copolymers much more detailed information would be available from complete parent mass distributions. With mass spectrometry the challenge is to obtain results without fragmentation. Conventional polymer mass spectrometry generally measures fragment masses. Secondary ion mass spectrometry (SIMS) has had limited success in obtaining silver cationized species in specific cases [4]. Laser desorption [5–7], particularly in the form of matrix assisted laser desorption and ionization (MALDI) [8,9], has been applied to polymers with some demonstrations of cationized parent mass spectra. The disadvantage is the required sample preparation, which is sample specific. Here we demonstrate an alternative approach for a type of polymer that is particularly hard to ionize, namely perfluorinated polyethers. In earlier work we developed a two laser metal cationization scheme for these molecules [6]. In the present work we employ multiphoton ionization, which is much

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more sensitive and additionally offers the option of wavelength spectroscopy.

The first step is laser desorption which brings molecules into the gas phase in one piece. We have combined this technique with jet cooling and separate multiphoton ionization in order to obtain ions without fragmentation [10]. In the case of perfluorinated polyethers (PFPE's) the neutrals do not absorb light in any useful wavelength range. Multiphoton ionization requires an electronic state in the near UV to absorb the first photon. That condition is not met in the PFPE's. 2 + 1 photon schemes, as demonstrated for ordinary ethers [11], do not work either because the Rydberg state is diffuse [12]. Single photon ionization is not practical because the ionization potential is at least 12 eV and practical light sources for that approach are not available. Here we demonstrate that complete parent mass distributions can still be obtained if the polymers can be functionalized with an end group that contains an aromatic chromophore. We show that multiphoton ionization of such a chromophore results in efficient ionization of the polymer without fragmentation. This allows for complete and accurate mass spectrometry, which permits characterization of this type of molecule with unprecedented detail.

2. Experimental

The laser desorption jet cooling arrangement has been described in detail elsewhere [10], so here a brief outline will suffice. Fig. 1 schematically shows the set-up. The polymers are deposited from solution on a graphite substrate, which is placed on the vacuum side of a pulsed supersonic beam source. Typically Xe at 8 atm expands through a 1 mm diameter hole while the polymers are desorbed with a 532 nm pulse from a doubled ND:YAG laser. The desorbed material is entrained in the jet and intercepted downstream by an ionization laser which is either a 193 nm ArF laser or a YAG pumped, frequency doubled dye laser, tuned to a particular molecular resonance. The ions are extracted into a reflectron time of flight mass spectrometer.

The possible mechanisms of laser desorption have been discussed by various authors [13]. Laser fluences used are less (typically by a few orders of

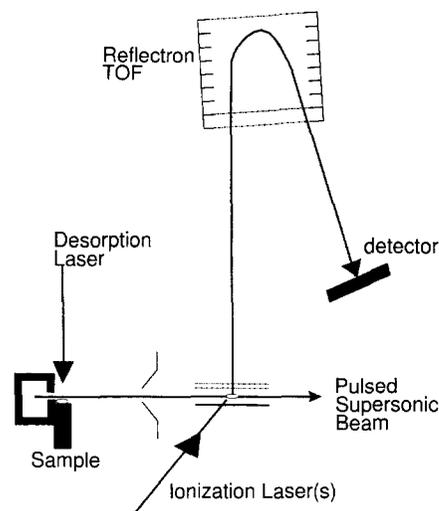
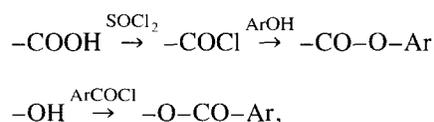


Fig. 1. Schematic view of the apparatus.

magnitude) than those used for ablation. Under these conditions many large and fragile molecules that are adsorbed on substrates which absorb the light from the laser can be desorbed into the gas phase without fragmentation. In our case we vaporize polymer films from graphite substrates with a desorption laser wavelength (532 nm) for which the polymer film is transparent. The mechanism of laser desorption for this case is not known in detail. Most likely the pulsed heating by absorption of the light at the film/substrate interface generates a shock wave in the film which causes molecules at the film/vacuum boundary to be ejected. This model implies that it is possible to desorb only a small fraction of the material with each laser pulse, which is consistent with the observation that an almost constant signal can be obtained from the same spot of a thick film with 10^2 – 10^3 desorption pulses.

Photoionizable end groups were attached to polymers with –OH or –COOH end groups by esterification, using the following standard reactions:

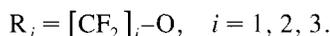


where Ar is an aromatic substituent with a phenyl or phenoxy chromophore. These reactions were carried out with excess reagent in dry $\text{CF}_2\text{Cl-CFCl}_2$ as

solvent, under argon atmosphere at 80°C. After reaction excess ArCOCl was destroyed with 2,5 lutidine in ethanol. Polymer was separated from other reaction products by extraction, using ethanol and perfluorohexanes as solvents. Amounts of polymer converted ranged from 0.02 to 2 mg, using solution volumes of about 1 ml. The amount 0.02 mg of polymer corresponds roughly to the amount of a 1 nm film on a 100 cm² surface. The samples were deposited on graphite in a typically 0.1 cm² area, producing films of 1 to 100 μm thickness.

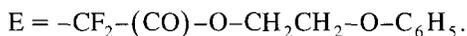
3. Results and discussion

The perfluorinated polyethers investigated in this work have repeat units of the type:



In what follows we will consider homopolymers with repeat units R₃ and co-polymers containing mixtures of R₁ and R₂. End groups can vary as will be discussed below.

Fig. 2 shows the mass spectrum of a monofunctionalized homopolymer with repeat unit R₃ and a functional end group E, consisting of aromatic ester as follows:



The monofunctionalized polymer is of the form:

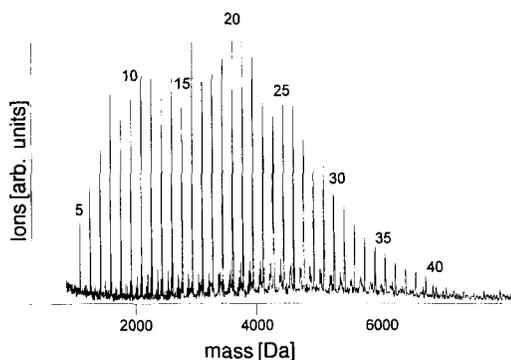
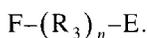
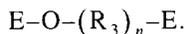


Fig. 2. Laser desorption REMPI time of flight mass spectrum of Demnum-SP[®]. Ionization wavelength 193 nm. Major peaks represent parent masses, separated by the 166 Da mass of a repeat unit: $[\text{CF}_2]_3\text{-O}$. The numbers of units are indicated for some paths.

Bifunctional polymers have the form:



The monofunctional material is commercially available under the brand name Demnum-SP[®]. We performed two-photon ionizations with 193 nm and obtained the mass spectrum shown in Fig. 2. All major peaks correspond to parent ions and are spaced apart by 166 Da, the mass of a repeat unit. They range from polymers with $n = 5$ ($m/z = 1114$ Da) to $n = 40$ ($m/z = 6924$ Da). Values of n are indicated with selected peaks. This mass spectrum qualitatively shows the distribution of chain lengths in the sample. The measured distribution may be affected by mass dependencies in the experiment, such as transmission, detector response and entrainment efficiency. However the average of this distribution is consistent with NMR measurements in this laboratory. Minor peaks in the spectrum are due to (a) bifunctionalized polymers that are present in this sample as an impurity and (b) polymers missing a CF₂ in one of their repeat units or their end unit. We note that the presence of bifunctional polymers cannot be observed by either NMR or size exclusion chromatography, and in fact would lead to an erroneous assignment of the average chain length distribution in the case of NMR.

Additional information can be obtained by varying the wavelength of the ionizing laser while monitoring specific parent masses. As described in more detail elsewhere [14], we have obtained the resonance enhanced multiphoton ionization (REMPI) spectra of these molecules at the S₀₋₀ transition. Fig. 3 shows the mass spectra at two different wavelengths of a sample of the same polymer with a narrower molecular weight distribution and containing both mono- and bifunctional polymers. Fig. 3a was obtained at an ionization wavelength of 273.5 nm. This is the resonant wavelength for the S₀₋₀ transition of the monofunctional polymers. Fig. 3b shows a mass spectrum of the same sample obtained at a wavelength of 274.8 nm. This wavelength is not resonant for the monofunctional species and its parent peaks (solid circles) are reduced in intensity. Instead, this wavelength is resonant with two other species in the beam simultaneously. The open circles mark peaks corresponding to dimers of the monofunctional polymers, while the crosses mark peaks

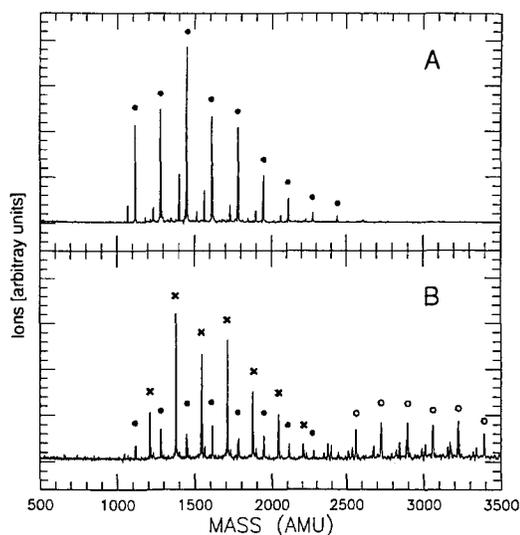
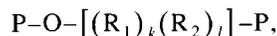


Fig. 3. Laser desorption REMPI time of flight mass spectra of a sample of Demnum-SP[®] with a narrow molecular weight distribution. Ionization wavelength (a) 273.5 nm, (b) 274.8 nm. (●) monofunctional polymers, (○) dimers of monofunctional polymers, (×) bifunctional monomers. The repeat unit is $[\text{CF}_2]_3\text{-O}$. The functional end group is: $-\text{CF}_2-(\text{CO})-\text{O}-\text{CH}_2\text{CH}_2-\text{O}-\text{C}_6\text{H}_5$. The non-functional end group is $-\text{O}-\text{CF}_2\text{CF}_2\text{CF}_3$.

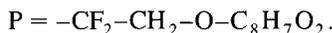
corresponding to bifunctional polymers. This assignment is based on the mass of each individual peak. The 1.3 nm wavelength difference between the two spectra corresponds to the van der Waals dimer shift, resulting from interaction between two phenoxy groups [15,16]. From the fact that the bifunctional polymers are resonant at the same shifted wavelength as the monofunctional dimers we can deduce that both represent van der Waals complexes linked at the phenoxy groups. We conclude that the bifunctional polymer forms internal dimers as it explores phase space in the supersonic expansion, implying that for these molecules the van der Waals forces between the end groups are larger than the barriers for internal rotation.

We note that to our knowledge these are the first examples of REMPI spectroscopy of molecules of molecular weights of several 1000 Da.

Fig. 4a shows the mass spectrum of a co-polymer of the type:



where P represents an end-group containing a piperonyl chromophore:



This material is commercially available under the name AM-2001[®]. Ionization was done with 193 nm. Every peak in this mass spectrum corresponds to a parent mass with one of the possible combinations of k and l . Information contained in this mass spectrum goes beyond the distribution of chain lengths. The ability to distinguish the abundances of individual (k , l) combinations provides for a much more refined characterization of co-polymers, as will be further discussed below.

From an analytical perspective there is the limitation that the molecule needs to have a chromophore in order to be detected by REMPI. We have ex-

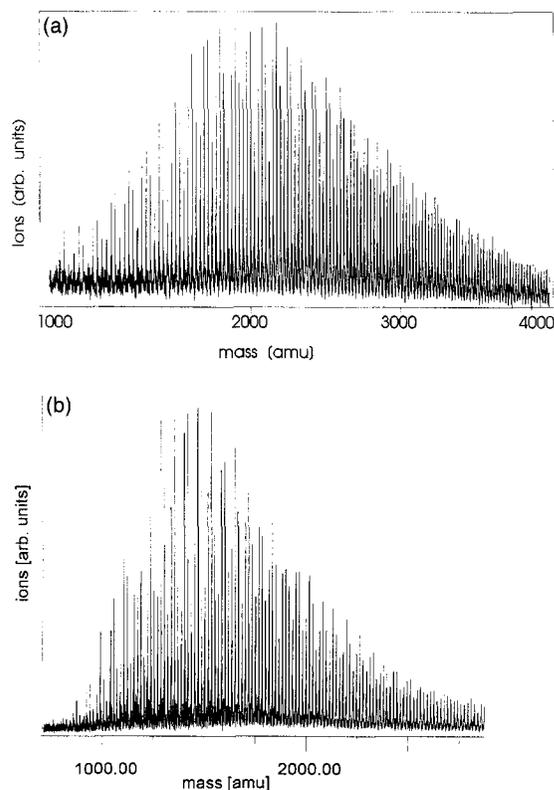
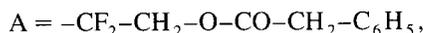
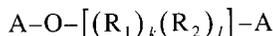


Fig. 4. Laser desorption REMPI time of flight mass spectrum of (a) AM-2001[®]: $\text{P-O}-[(\text{CF}_2-\text{O})_k(\text{C}_2\text{F}_4-\text{O})_l]\text{P}$, with $\text{P} = -\text{CF}_2-\text{CH}_2-\text{O}-\text{C}_8\text{H}_7\text{O}_2$, (b) Z-Dol[®] with esterified end-groups: $\text{A-O}-[(\text{CF}_2-\text{O})_k(\text{C}_2\text{F}_4-\text{O})_l]-\text{A}$ with $\text{A} = -\text{CF}_2-\text{CH}_2-\text{O}-\text{CO}-\text{CH}_2-\text{C}_6\text{H}_5$. Ionization wavelength 193 nm.

tended the applicability of the technique by chemically attaching chromophores to a number of commercial PFPEs that do not have chromophores, particularly those with alcohol and acid end groups.

Fig. 4b shows the mass spectrum of a co-polymer of the type:



where A takes the place of the alcohol end group of the original polymer and was obtained by esterifying it with phenyl acetyl chloride. The alcohol polymer is commercially available under the name Z-Dol[®]. Ionization was at 193 nm. The difference between this material and that in Fig. 4a is that in the case of AM-2001 the end-group is itself a chromophore, while in the case of Z-Dol the chromophore first had to be attached. Furthermore our analysis shows that the distribution of repeat units as a function of chain length is different in the two cases, as discussed below.

To demonstrate the increased level of detail which is available because parent molecules can be detected without fragmentation for individual (k , l) combinations, we have plotted the relative abundances in a different way. Fig. 5 shows relative peak integrals plotted in a grid of k and l . Fig. 5a is for the AM-2001; Fig. 5b is for the Z-Dol. For comparison Fig. 5c shows a plot for a model distribution, which assumes a purely random copolymer. This takes the form of a binomial distribution, with $I_{k,l}$ denoting the relative abundance of a polymer with repeat unit combination (k , l) as follows:

$$I_{k,l} = \binom{k+l}{l} p_1^k p_2^l$$

$$p_1 + p_2 = 1.$$

p_1 and p_2 represent the relative probabilities of adding either an R_1 or a R_2 unit as the chain is being built up during the polymerization. The ratio $f = p_1/p_2$ is the only free parameter in the model. Furthermore we have restricted the overall chain length by multiplying the distribution with an envelope function which was taken from the actual molecular weight distribution. We cannot completely reproduce the actual distributions of Fig. 5a or b with any single value of f . In the model the line of

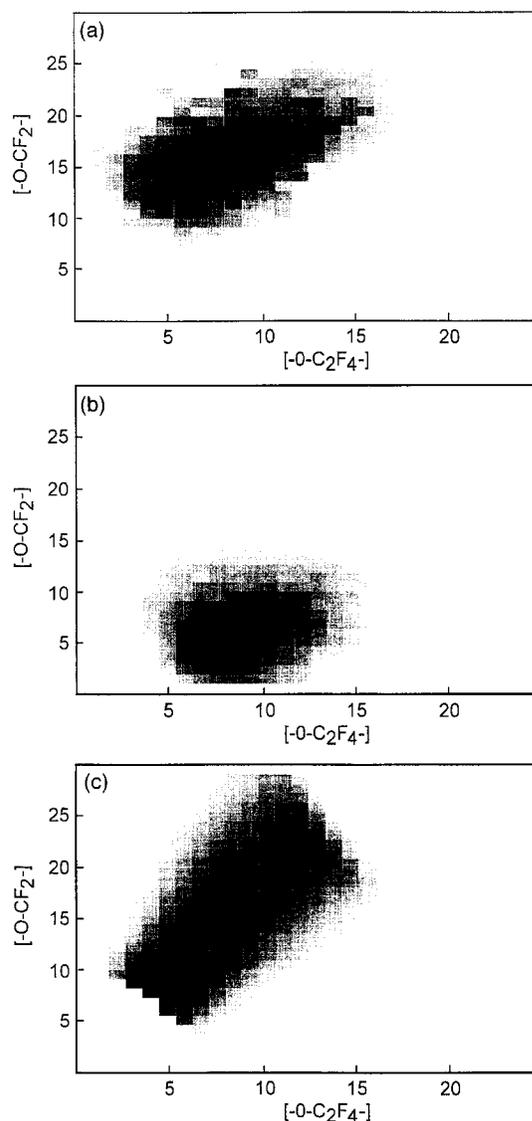


Fig. 5. Relative abundances of copolymers of type $A-O-[(CF_2-O)_k(C_2F_4-O)_l]-A$, plotted as a function of k and l . (a) AM-2001[®], (b) Z-Dol[®], (c) model calculation for a random copolymer.

maximum abundance must pass through the origin for any f while for the actual polymers this is not the case. We find f to be different depending on the overall length of the polymer chain. For Z-Dol the smaller polymers tend to have relatively more single carbon repeat units, while the larger ones on average have somewhat more two carbon repeat units. For

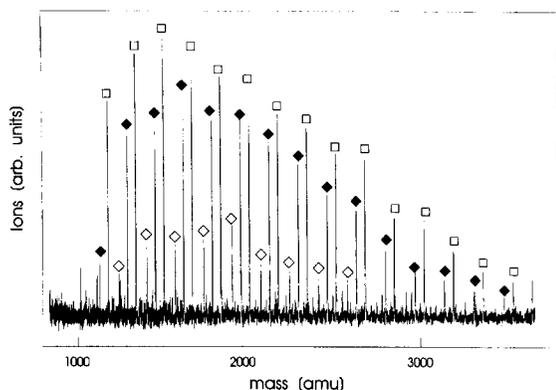
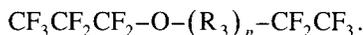


Fig. 6. Laser desorption REMPI time of flight mass spectrum of degradation products of Demnum-S65[®] after frictional wear. The spectrum is obtained by esterification of fragments that have acid end groups. Ionization wavelength 193 nm. The symbols differentiate three different series of fragments, as described in the text.

AM2001 this trend appears to be inverted. This phenomenon must be related to the detailed kinetics of the polymerization reactions that formed these polymers.

Attachment of chromophore end groups can also be used as a labeling technique. We have used it to investigate degradation by friction of a non-functionalized, commercial PFPE polymer, Demnum-S65[®] with the structure:



Friction tends to break this polymer randomly at the ether linkages, producing carbonyl fluoride and new C₃ end groups. The effect is similar to that of electron attachment [6] although the mechanism may be different. In the presence of water the carbonyl fluoride is transformed into carboxylic acid which we selectively labeled with a phenoxy group. The resulting laser desorption REMPI mass spectrum of the labeled acid fragments is shown in Fig. 6. It exhibits a molecular weight distribution which peaks around 1500 Da and averages about 2000 Da, while that of the original polymer peaks around 3800 Da and averages 4600 Da [6]. Fragmentation is evident in the pattern of major peaks which occur in pairs 50 Da apart: The labeled acid group appears with either the -CF₂CF₂CF₃ or the -CF₂CF₃ end group of the original polymer, labeled □ and ◆ respectively. Peaks with the former end group are stronger since

additional C₃ end groups are formed during fragmentation, and these products may fragment again. There is a third set of peaks 50 Da below those with the -CF₂CF₃ end group, labeled ◇. Two possible explanations for this set are (1) loss of C₂F₄ from a radical intermediate of the fragmentation process or (2) preferential chain breaking at R₂ repeat units which are present in minor amounts, as mentioned above.

4. Conclusion

We have demonstrated the application of laser desorption jet cooling with separate multiphoton ionization to obtain parent molecular weight distributions of perfluorinated polyether films. The technique can directly be applied to polymers that have aromatic end groups. In the case of acid or alcohol end groups we have chemically attached aromatic chromophores. The importance of obtaining unfragmented parent molecular weight distributions is demonstrated with copolymers, where we obtained maps of the statistical distribution of all possible combinations of repeat units. For homopolymers we distinguished mono- and bifunctional species in the same sample. The chromophore attachment can also be used as a labeling technique as demonstrated by a study of polymer degradation. These details are unavailable by conventional techniques. Furthermore we have varied the ionization wavelength in order to obtain REMPI spectra of the first excited electronic state of these polymers and their internal and external van der Waals dimers.

Acknowledgements

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