Partial Fluorination of Hydroxyl End-Capped Oligoesters Revealed by MALDI−TOF Mass Spectrometry

Weihua Ming,*,† Xianwen Lou,‡
Robert D. van de Grampel,†
Joost L. J. van Dongen,‡ and Rob van der Linde*,†

Department of Polymer Chemistry and Coatings Technology and Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received November 27, 2000

Introduction

Recently, we have shown that polymer films with low surface energy can be readily obtained through the self-stratification in a thermally curable system composed of a partially fluorinated hydroxyl end-capped solventless liquid oligoester (up to 1.5 wt % of fluorine) and a liquid polyisocyanate cross-linker.[1] The fluorine level at the surface is dozens of times higher than that in the bulk, as evidenced from X-ray photoelectron spectroscopy (XPS) investigations. Such a thin layer with low surface energy may introduce many interesting properties to a coating, such as chemical resistance, excellent weatherability, low friction, and so on. However, because of the low extent of fluorination (15−20% of hydroxyls substituted), normal techniques are hardly capable of detecting the partial fluorination, such as NMR (proton, carbon-13, and fluorine-19), size exclusion chromatography (SEC), and elemental analysis. Although these techniques may tell whether there is fluorine in the system or not, it is very hard to know if the fluorinated tail is attached to the oligoester backbone or just exists as a small molecule, like a perfluoroalkyl acid. Neither can these techniques tell how many hydroxyls are substituted in an individual oligoester molecule.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI−TOF MS) has proven to be a powerful technique in determining molecular weights and structures of polymers.[2] MALDI is a “soft” ionization process that allows desorption and ionization of polymers with molecular mass up to hundreds of kilodaltons with very little or no fragmentation.[3] A lot of information, such as molecular weight and its distribution, end group molar mass, and copolymer sequence, can be obtained by MALDI MS,[4−8] together with SEC fractionation for polydisperse polymers.[9,10] A key advantage of MADLI MS is that the absolute molecular weight of individual polymer chains can be determined, instead of obtaining relative average molecular weights by chromatographic techniques. Thus, details of molecular structure may be revealed by MALDI; for instance, the existence of perfluoroalkyl group in a partially fluorinated oligoester can be directly identified. The purpose of the present research is to use MALDI−TOF MS to characterize the molecular structure of a hydroxyl end-capped linear oligoester, polybutylene adipate (PBA), before and after partial fluorination in comparison with some other conventional techniques, like NMR and SEC.

Experimental Section

Materials. Adipic acid (>99%), 1,4-butanediol (>98%), triethylamine, and toluene were purchased from Merck and used as received. A dialkyltin oxide with a trademark of FASCAT 4101 was used as catalyst for direct esterification. Perfluoroalkyl compounds, such as pentadecafluorooctanoic acid (PFOA, 97%) and perfluorooctanoyl chloride (PFOC, 97%), were purchased from Fluorochem and used as received.

Synthesis of Hydroxyl End-Capped Oligoesters. A model linear oligoester (PBA) based on adipic acid and 1,4-butanediol was synthesized by direct esterification as follows.[1] To a 250-mL four-neck flask, equipped with a mechanical stirrer, Dean−Stark trap, reflux condenser, thermometer and nitrogen inlet, were added adipic acid (0.30 mol), 1,4-butanediol (0.40 mol), and FASCAT 4101 (0.1% of total weight). The flask was gradually heated to 140 °C, raised to 200 °C over 3 h, and then kept at 200 °C until the amount of water collected in the Dean−Stark trap reached 95% of the theoretical amount (ca. 0.6 mol). The obtained solid oligoester was dried under vacuum at 50 °C to remove the trace amount of water.

Synthesis of Partially Fluorinated Liquid Oligoesters. A partially fluorinated oligoester was prepared by reacting the previously synthesized oligoester (in large excess) with a perfluoroalkyl acid chloride (e.g., PFOC) in dried toluene in the presence of dried triethylamine. For instance, 5.0 g of linear oligoester (about 1.45×10^{-2} mol OH) and 0.34 g of triethylamine (3.2×10^{-3} mol) were first dissolved in 20 mL of toluene. 1.25 g of PFOC (2.9×10^{-3} mol, $^1/_5$ of OH amount) was then added dropwise under an ice bath. The temperature was raised to ambient and the reaction remained overnight. The produced salt, $(CH_3CH_2)_3HN^+Cl^-$, was removed by filtration and the solution was distilled under reduced pressure to remove toluene and the left triethylamine. After being dried under vacuum at 50 °C for 24 h, the partially fluorinated oligoester, a white solid, was then obtained.

Conventional Characterization Techniques. NMR spectra were recorded on a Varian 400 spectrometer at 25 °C, operating at 400.162 MHz for ^1H, 100.630 MHz for ^{13}C, and 376.487 MHz for ^{19}F, respectively. $CDCl_3$ was used as a solvent and as an internal standard for ^1H and ^{13}C. SEC analyses were carried out using four PLgel (Mixed-C) columns (Polymer Laboratories) at 40 °C with a Waters 510 pump. The injection volume was 100 μL, and THF was used as eluent at a flow rate of 1 mL/min. A Waters 410 differential refractometer was applied for detection. Narrowly distributed polystyrene standards (Polymer Laboratories) with molecular weights ranging from 580 to 7.1×10^6 were used to calibrate the SEC setup.

MALDI−TOF MS. MALDI−TOF MS measurements were performed on a Voyager-DE Pro (PerSpective Biosystems, Framingham, MA) instrument equipped with a 337 nm nitrogen laser. Positive-ion spectra were acquired in reflectron mode. α-Cyano-4-hydroxycinnamic acid was chosen as the matrix. Oligomer samples were dissolved in tetrahydrofuran (THF) at 2 mg/mL and the matrix at 20 mg/mL; matrix and oligomer solutions were mixed afterward. The MALDI system was calibrated with polythiophene oligomer standards of known molecular mass. The mass accuracy is within ±0.05%. It was found unnecessary to add extra sodium or potassium salts for the formation of the corresponding oligomeric ion adducts.

Results and Discussions

In our previous study, we used a mixture of three diacids during esterification in order to decrease the

---

* Corresponding authors: Fax: 31-40-2463966. E-mail addresses: W.Ming@tue.nl and R.van.der.Linde@tue.nl.
† Department of Polymer Chemistry and Coatings Technology, Eindhoven University of Technology.
‡ Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology.

10.1021/ma002016f CCC: $20.00

oligoester crystallinity and to obtain solventless liquid oligoesters.[1] Besides 1,4-butanediol, we also introduced a triol, 1,1,1-trimethyloylpropane, to prepare a three-armed oligoester to increase the functionality. Partial fluorination was then performed. However, since only one of five to six hydroxyls was substituted, it is very difficult for normal techniques like SEC and NMR to characterize this low extent of fluorination. In addition, the existence of three diacids and a triol further complicated the analysis. To simplify the analysis, a model linear oligoester, polybutylene adipate (PBA), based on adipic acid and 1,4-butanediol was synthesized, with both chain ends being hydroxyls. One out of five hydroxyls was then replaced by a perfluoroacyl group [$CF_3(CF_2)_6CO-$].

Characterizations by Conventional Techniques. Since both chain ends are hydroxyls, the number-average molecular weight (M_n) of PBA can be simply calculated from the OH number.[1] Before partial fluorination, the OH number is 128 mg KOH/g (the acid value was found to be negligible), and the M_n is therefore 878. After the partial fluorination, the OH number drops to 88 mg KOH/g, indicative of some extent of substitution of hydroxyl.

M_n can be also derived from proton NMR, based on the ratio of the peak area of two different methylene hydrogens: one next to an ester group (H_β, 4.1 ppm, in Figure 1b) and the other adjacent to a hydroxyl group (H_α, 3.7 ppm).[1] The number-average molecular weight for the oligoester before partial fluorination is 914, which agrees well with the titration result.

Proton NMR spectra for PBA and its partially fluorinated counterpart are shown in Figure 1, parts b and a. These two spectra appear to be quite similar except the varying ratio of peak area for two hydrogens (H_α and H_β) due to some H_α being converted into H_β during partial fluorination. This is again an indication of the substitution of some hydroxyls. The small peak at 4.4 ppm (Figure 1a) may be assigned to the hydrogen in $-C\boldsymbol{H}_2-O-CO-C_7F_{15}$. ^{13}C NMR measurements were also performed for both samples, but no significant difference was observed between them. Furthermore, the fluorocarbons that are supposed to appear at 100−120 ppm did not show up after over 5000 scans in the 400 MHz instrument. This is reasonable because of the multiple coupling among fluorocarbons and the low fluorine content. We also compared ^{19}F NMR spectra between partially fluorinated PBA (Figure 1c) and a perfluoroalkyl acid, pentadecafluorooctanoic acid (PFOA, Figure 1d). For both of them, major peaks due to seven kinds of fluorine were found at almost the same positions, as marked in the figure, except that peak *g* (the fluorine next to the carbonyl) shifts slightly from −119.2 in PFOA to −118.8 ppm in the fluorinated PBA. In PFOA the perfluoroalkyl is next to an acid group, while in fluorinated PBA the perfluoroalkyl is connected with an ester group to the PBA backbone. A close look was taken at the peak (*g*), but the peak splitting appears to be exactly the same. On the other hand, there is a new small peak, *i*, in Figure 1c, for partially fluorinated PBA; it is not yet clear where it is from. Despite the slight difference in the ^{19}F NMR spectra, the influence of PBA backbone on the perfluoroalkyl group is not very pronounced.

We also used SEC to measure the molecular weight of oligoesters before and after the partial fluorination. The molecular weights determined by SEC are apparent values relative to a PS calibration curve. Because of the significant difference in polarity and likely difference in conformational characteristics and excluded volume effects between hydroxyl end-capped PBA and polystyrene standards, the molecular weights from SEC may deviate considerably from those determined by NMR and titration. Since SEC chromatograms (Figure 2) are multimodal, the attention will be paid on the major peak value (M_p). As can be seen in Figure 2, M_p slightly shifts from 3100 to 3440 after the partial fluorination. This may be another indication of the partial fluorination. However, due to the uncertainty in the molecular weight determination of the oligoesters, it would be inappropriate to draw any firm conclusion from SEC.

So far a few conventional techniques have been employed to examine the difference for PBA before and after partial fluorination. Despite some minor differences in SEC and NMR spectra (^1H and ^{19}F), almost no details about the molecular structure of the fluorinated oligomers have been revealed. MALDI−TOF MS is capable of accurately determining the molecular weight of individual chains, which may be used to show the fluorinated species distinctively.

MALDI MS Analysis. A typical full positive-ion MALDI mass spectrum for PBA before partial fluorination is shown in Figure 3a. The sets of signals are separated by 200 Da, characteristic of the butylene adipate (BA) repeating unit. The molecular weights of individual main peaks correspond to the expected structure: $[HO-(CH_2)_4-O-(CO(CH_2)_4CO-O-(CH_2)_4-O)_n-H + Na]^+$. The molecular weight for PBA of different degrees of condensation (n) is $MW_{BA-unit} \times n + MW_{diol}$. For example, for $n = 5$ species, the molecular weight was determined to be 1091.21 Da (after subtracting 22.98 for sodium), very comparable to the theoretical value of 1090.29. For species with a degree of condensation greater than 5, neither cyclic oligoesters nor monocarboxyl-terminated esters reported by Hercules et al.[6,7] were found. But at lower molecular weight region, very small peaks at 423, 623, and 823 Da can be seen, corresponding to the cyclic oligoesters with a degree of condensation of 2, 3, and 4, respectively. Although the cyclic structure may affect the molecular weight determination by titration, the effect would be very small since the intensity of these peaks is about 2 orders of magnitude lower than the major peaks.

The mass spectrum (Figure 3b) after partial fluorination looks quite similar to that of normal PBA (Figure 3a): major peaks are located at the exactly same positions. Only when carefully examined a small but very important difference is noticeable: some small peaks neighboring to those major peaks emerge, as pointed out by the arrows in the inset of Figure 3b. It is these small peaks that count for the fluorinated species.

Some details of the mass spectra are shown in Figure 4. Figure 4a gives the spectra of PBA before and after partial fluorination in the m/z region of 1100−1150. Before fluorination, two series of peaks at 1114.19 and 1130.16 Da with $n = 5$ are shown, corresponding to the sodium and potassium adducts, respectively. The observed isotope distribution (from C, H, and O) is in a very good agreement with the simulated one as calculated by the instrument (Voyager-DE Pro) software. On the other hand, after partial fluorination the major peaks at 1114 (A_5-F^0, in Figure 4a) and 1130 Da remain the same, indicating a large amount of hydroxyl end-

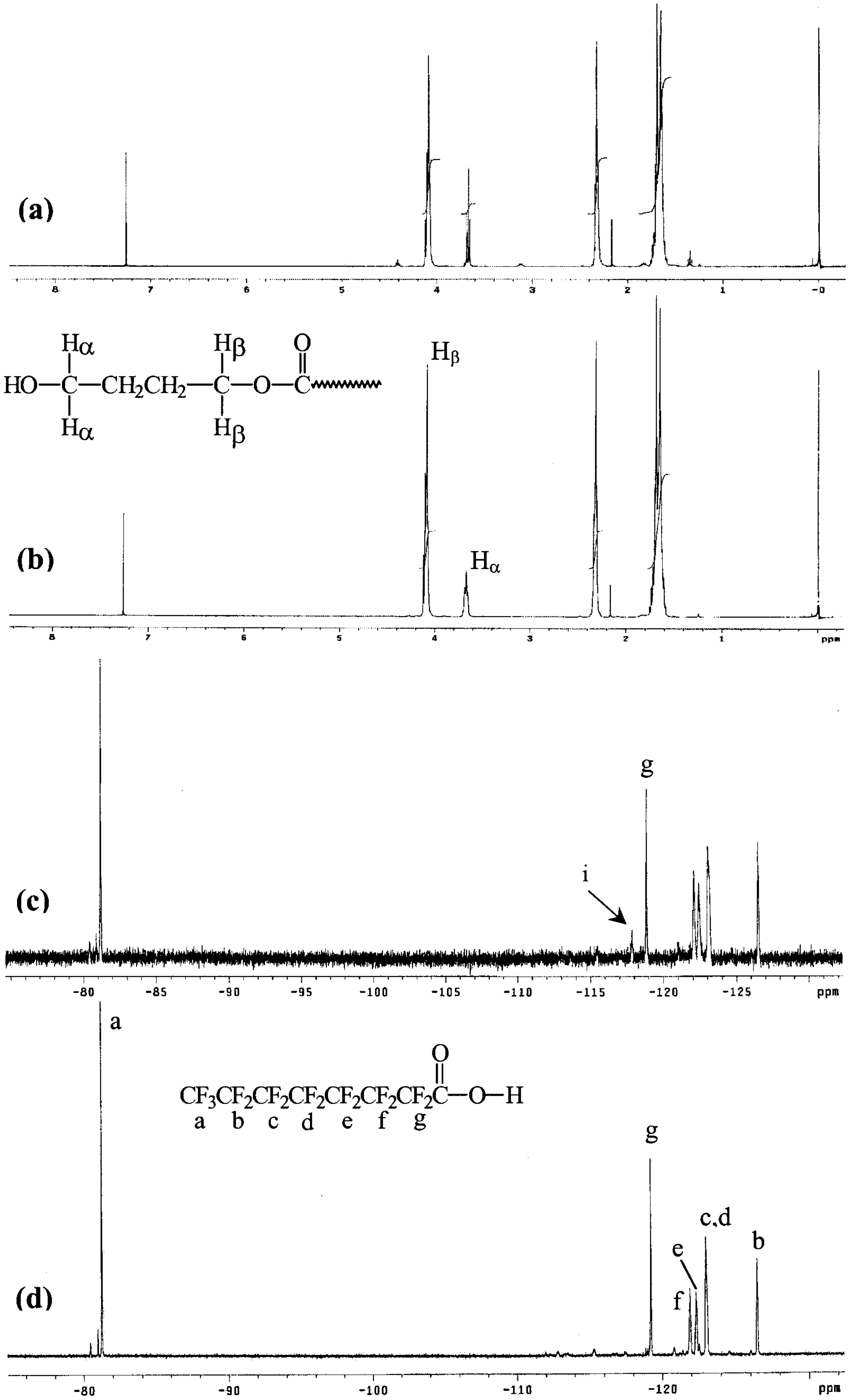

Figure 1. NMR spectra for PBA: proton spectra before (b) and after (a) partial fluorination, (c) ^{19}F spectrum for fluorinated PBA, and (d) ^{19}F spectrum for PFOA. Peak assignments for ^{19}F follow the literature.[11]

capped PBA remains unsubstituted. But a few more peaks due to fluorinated species show up. The peak at 1109.77 Da (A_3-F^1) results from the monosubstituted perfluoroalkyl oligoester with the following structure of a lower degree of condensation ($n = 3$): $[HO-(CH_2)_4-O-(CO(CH_2)_4CO-O-(CH_2)_4-O)_3-CO-C_7F_{15} + Na]^+$. The theoretical molecular weight for this species is 1109.33 Da. A corresponding potassium adduct can be

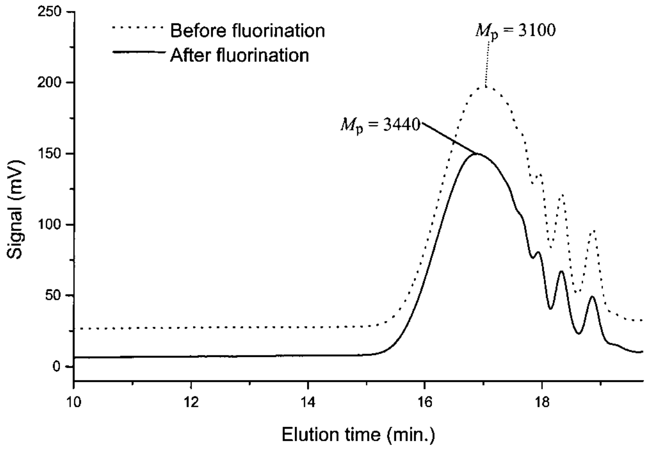

Figure 2. Size exclusion chromatograms of PBA before and after partial fluorination.

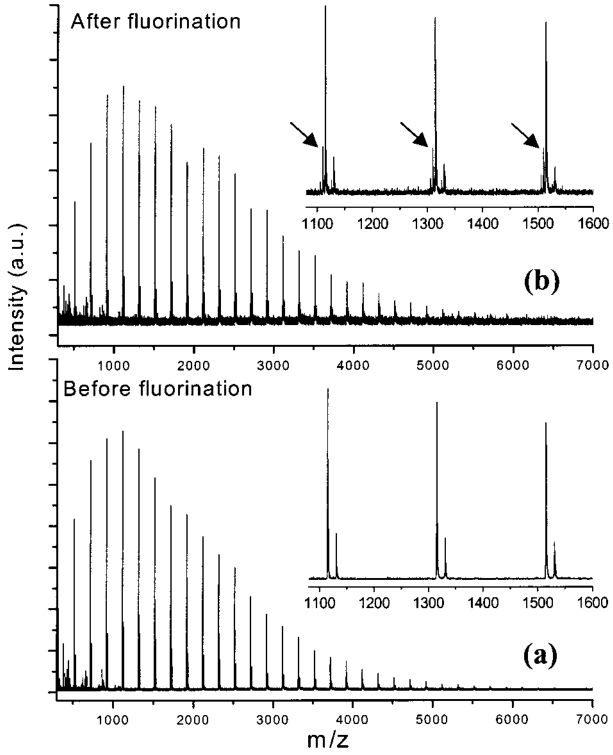

Figure 3. Full MALDI mass spectra for PBA before (a) and after (b) partial fluorination. Peaks indicated by arrows are from fluorinated PBA.

also found at 1125.77 Da. More interestingly, an even smaller peak at 1105.46 Da (A_1–F^2) becomes visible, which comes from a bisubstituted perfluoroalkyl oligoester with $n = 1$ as follows: $[C_7F_{15}-CO-O-(CH_2)_4-O-(CO(CH_2)_4CO-O-(CH_2)_4-O)_1-CO-C_7F_{15} + Na]^+$. This unambiguously shows that a bisubstituted species can be obtained even when a reaction starts at an acid chloride/hydroxyl ratio of 1/5, which is, though, not surprising as far as the statistical possibility is concerned. This is the reason that in our practical systems[1] we also introduced a triol to start the oligoester synthesis to keep the hydroxyl functionality of at least 1–2 for individual oligomers after partial fluorination. The hydroxyls were used for further cross-linking with a polyisocyanate agent.

In general, both mono- and bisubstituted perfluoroalkyl oligoesters can be seen for species with an $n = 1-10$, while only monosubstituted perfluoroalkyl oligoester can be found when $n = 11-14$. When n is greater than 14, no substituted species is visible because of the small amount of high molecular weight species. For instance, in the m/z region between 900 and 950 (Figure 4b), besides the unsubstituted species at 913.95 Da ($n = 4$), a peak at 909.68 Da is due to a monosubstituted PBA with an $n = 2$. Furthermore, in the low molecular weight region, no peaks were found at either 509 Da for $[HO(CH_2)_4O-CO-C_7F_{15} + Na]^+$ or 437 Da for $[C_7F_{15}COOH + Na]^+$, suggesting no small fluorinated molecules are present after partial fluorination. This is very important to the investigation of surface segregation of fluorinated species, and clearly indicates that the low surface energy of the film does not come from small fluorinated molecules in our previous study.[1]

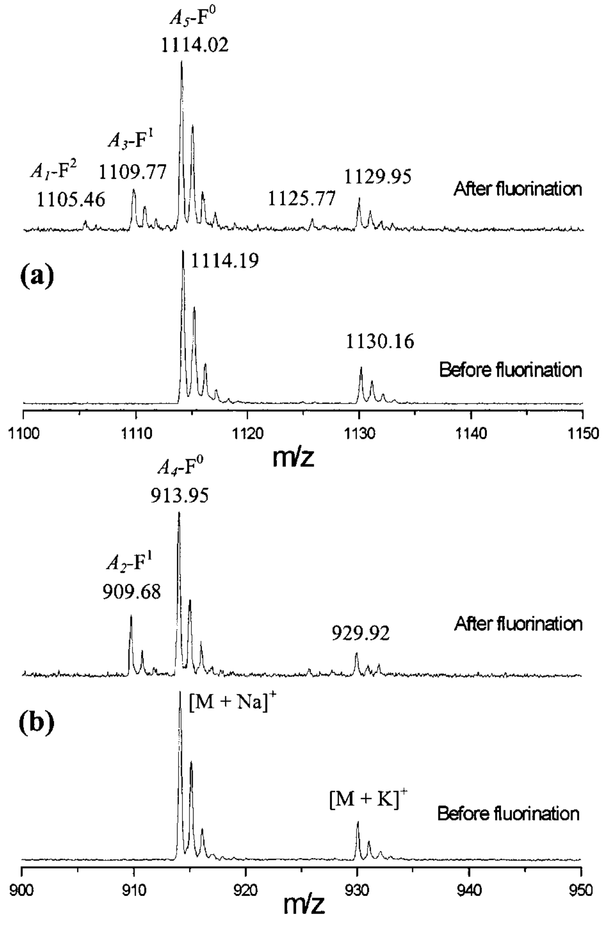

Figure 4. Enlarged MALDI mass spectra for PBA before and after partial fluorination: (a) m/z between 1100 and 1150; (b) m/z between 900 and 950. Symbol A_n–F^m represents an oligomer with a degree of condensation of n and a degree of fluorination of m ($m = 0-2$).

As has been clearly shown in this Note, MALDI–TOF MS is especially powerful at identifying the partially fluorinated oligoesters, either mono- or bisubstituted, even at quite low extent of substitution (ca. 1/5), which cannot be accomplished by some conventional techniques, such as NMR and SEC. Though, up to now the quantification based on MALDI MS remains somehow a problem. For example, we are unable to know the quantity of monosubstituted and bisubstituted species in the fluorinated oligoesters. Other techniques may be required to obtain more quantitative information on the extent of fluorination. The observed general structures in the neighborhood of the m/z of $(MW_{BA-unit} \times n + MW_{diol} + MW_{Na})$ for a partially fluorinated PBA with different degrees of condensation (*n*) can be summarized as follows.

(I) Unsubstituted series (the majority): $HO-(CH_2)_4-O-(CO(CH_2)_4CO-O-(CH_2)_4-O)_n-H$.

(II) Monosubstituted series (4 Da less than series I): $HO-(CH_2)_4-O-(CO(CH_2)_4CO-O-(CH_2)_4-O)_{n-2}-CO-C_7F_{15}$.

(III) Bisubstituted series (8 Da less than series I, in a very small amount): $C_7F_{15}-CO-O-(CH_2)_4-O-(CO(CH_2)_4CO-O-(CH_2)_4-O)_{n-4}-CO-C_7F_{15}$.

The accurate determination of the structure of the fluorinated species may be of help in gaining better understandings on the segregation mechanism of the low surface energy species in the previously reported systems,[1] where a polymeric film with low surface energy was obtained based on partially fluorinated hydroxyl end-capped solventless liquid oligoesters and a polyisocyanate cross-linker.

Acknowledgment. We are grateful to Mr. Wieb Kingma for SEC analysis and Dr. Marcel van Genderen for the discussion on NMR investigations. We acknowledge the financial support from CW-PPM in The Netherlands.

References and Notes

(1) Ming, W.; Laven, J.; van der Linde, R. *Macromolecules* **2000**, *33*, 6886.
(2) Wu, K. J.; Odom, R. W. *Anal. Chem.* **1998**, *70*, 456A.
(3) Schriemer, D. C.; Li, L. *Anal. Chem.* **1996**, *68*, 2721.
(4) Gooden, J. K.; Gross, M. L.; Mueller, A.; Stefanescu, A. D.; Wooley, K. L. *J. Am. Chem. Soc.* **1998**, *120*, 10180.
(5) Bu, L.; Nonidez, W.; Mays, J. W.; Tan, N. B. *Macromolecules* **2000**, *33*, 4445.
(6) Williams, J. B.; Gusev, A. I.; Hercules, D. M. *Macromolecules* **1997**, *30*, 3781.
(7) Mehl, J. T.; Murgasova, R.; Dong, X.; Hercules, D. M. *Anal. Chem.* **2000**, *72*, 2490.
(8) Montaudo, G.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *J. Polym. Sci.: Polym. Chem.* **1996**, *34*, 439.
(9) Montaudo, G.; Garozzo, D.; Montaudo, M. S.; Puglisi, C.; Samperi, F. *Macromolecules* **1995**, *28*, 7983.
(10) Lou, X.; van Dongen, J. L. J.; Meijer, E. W. *J. Chromatogr. A* **2000**, *896*, 19.
(11) Ameduri, B.; Boutevin, B.; Kostov, G. K.; Petrova, P. *J. Fluorine Chem.* **1998**, *92*, 77.

MA002016F