Synthesis and Mass Spectral Characterization of Poly(amic methyl ester) Oligomers

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ABSTRACT: A series of monodisperse oligomers of poly(amic methyl ester) were synthesized by a stepwise, convergent-divergent strategy, starting from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA). All of the fully protected, selectively protected, and nonprotected oligomers were studied by MALDI mass spectrometry. The oligomers with protected end groups proved to be stable during MALDI ionization and the possibility of imidization as the result of synthesis or during MALDI experiments was discounted based on mass spectra of imide analogue oligmers. The effect of end groups and oligomer length on the MALDI ionization efficiency was determined. Higher molecular weight oligomers had more intense fragment peaks. MALDI−CID was used to examine the fragmentation patterns of selected oligomers. It was found that the end groups affected the fragmentation of the oligomers. The use of different CID gases (helium, argon, and xenon) had no effect on the fragmentation pattern, but xenon caused more intense fragment peaks in the CID spectra.

Introduction

In recent years, advances in mass spectrometry have led to increased interest in mass spectrometry of polymers. The coupling of electrospray ionization (ESI), matrix-assisted laser desorption/ionization (MALDI), and secondary ion mass spectrometry (SIMS) sources to time-of-flight (TOF) mass analyzers allows the acquisition of high-resolution mass spectra for high mass synthetic polymer oligomers. The molecular weight distribution, including number- and weight-average molecular weights of polymers, can be determined from mass spectra. Additionally, MS/MS can be used to determine fragmentation patterns of polymers and provide insight into the structure and composition of the polymer, including repeat unit, end group, cross-linking, branching, and copolymer structure. Mass spectrometric analysis has been applied to a wide variety of polymers.[1−5] More recently, the combination of size exclusion chromatography (SEC) with MALDI has demonstrated the ability to obtain accurate molecular weight measurements for polydisperse polymers.[6−9]

Aromatic polyimides represent a class of high performance polymers that have a unique combination of physical, chemical, and electrical properties. Their high resitivity, high breakdown voltage, and low dielectric constant make polyimides an excellent choice for use as insulating films on microelectronic chips, wire-wrapping, coatings, and membranes. As with other polymers, the molecular properties of polyimides, i.e., the molecular weight distribution and molecular composition, are critical to the mechanical and electrical properties of polyimides.[10] The polyimide derived from pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) is a polymer developed by DuPont with the trade name Kapton. Like other polyimides, Kapton has physical, electrical, and chemical properties that make it an excellent choice for electronic applications such as encapsulation of IC circuits, an interlayer dielectric, and as a passivation overcoat. The synthesis of the PMDA-ODA polyimide is shown in Figure 1. PMDA (A) is reacted with ODA (B) in a solvent to form a poly(amic acid) (PAA) intermediate (C). Imidization of the amides begins to occur at temperatures of 100 °C and is completed around 300 °C to produce the polyimide (D).

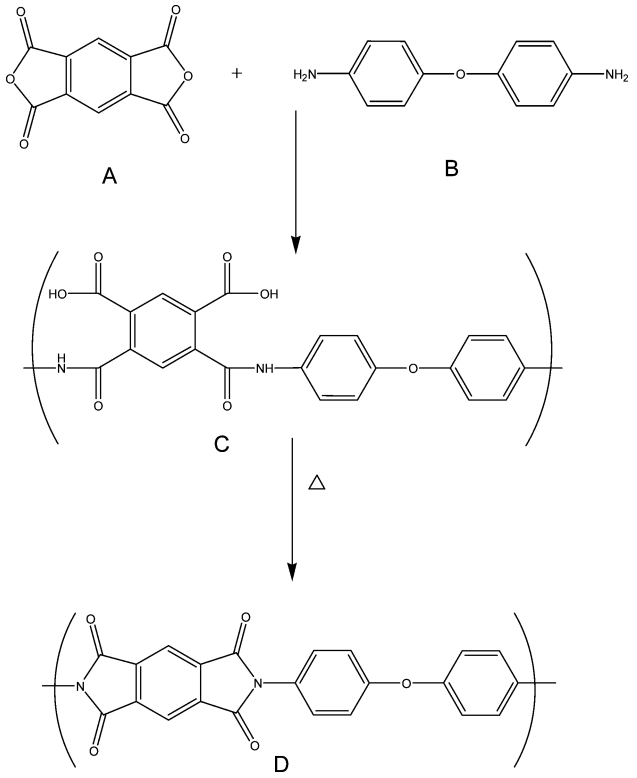

Figure 1. Schematic representation of the reaction of PMDA (A) and ODA (B) to form poly(amic acid) (C). Heat causes imidization of poly(amic acid) to form polyimide (D).

Once polyimides are formed by imidization of PAA, they are difficult to characterize by most analytical techniques because they do not dissolve in common organic solvents. Because of the insolubility of polyimides, PAAs are often characterized in their place. In recent years, poly(amic ester)s

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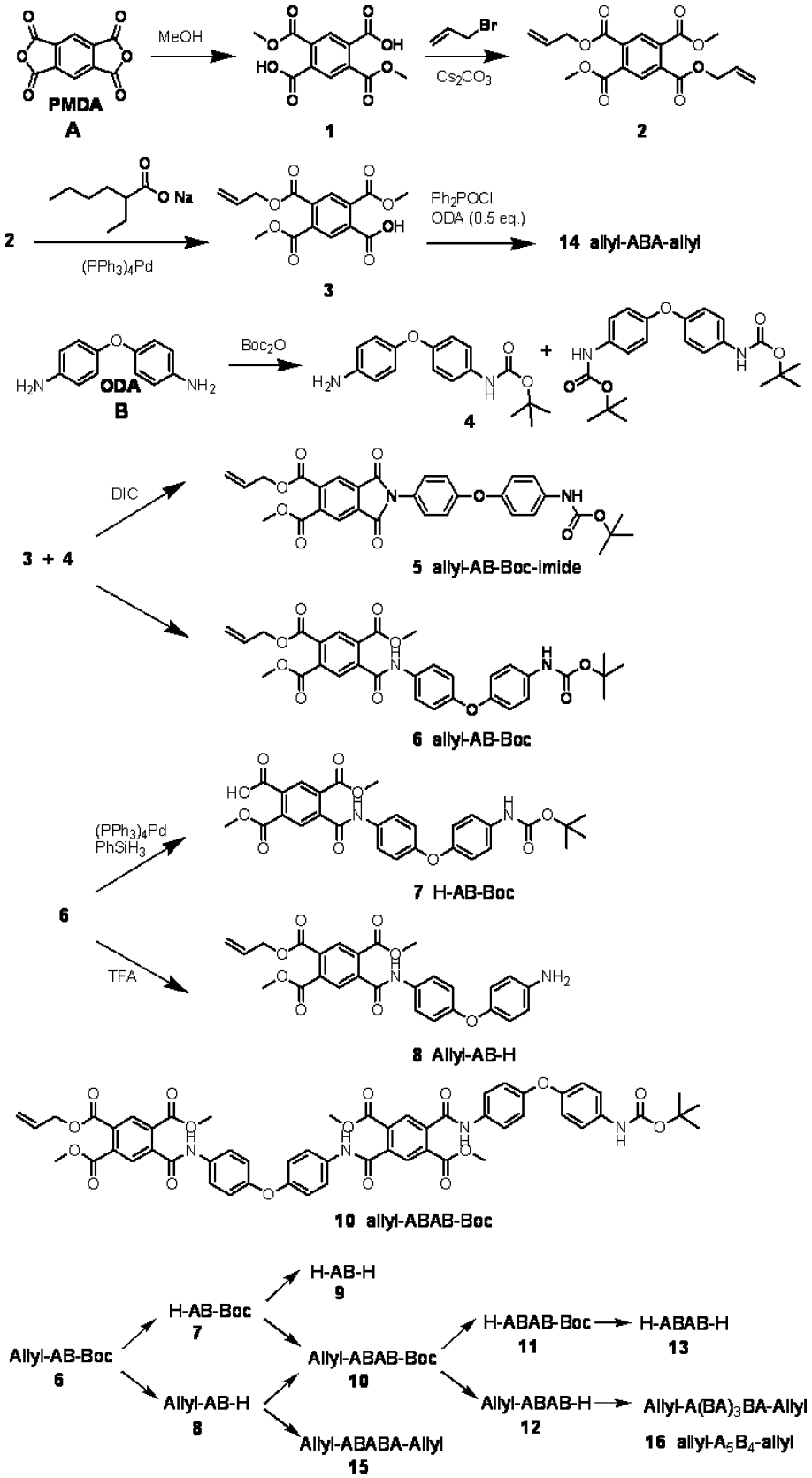

Figure 2. Synthesis scheme of ODA−PMDA model OAMEs.

(PAEs) have been studied in the place of poly(amic acid)s, because PAEs have better solubility and better resistance to hydrolytic degradation.[11−13]

Synthetic routes for PAEs have long been established; however, the preparation and characterization of monodisperse PAE oligomers has not been attempted. Single oligomers have certain advantages over multidispersed samples for use as model compounds;[14] for example, fragmentation patterns can be assigned unambiguously, and the effects of molecular mass and end groups on signal intensity can be elucidated.[15−17] In addition, large oligomers can be used as internal references to adjust for instrument bias.[18] Other variables affecting ionization efficiency,

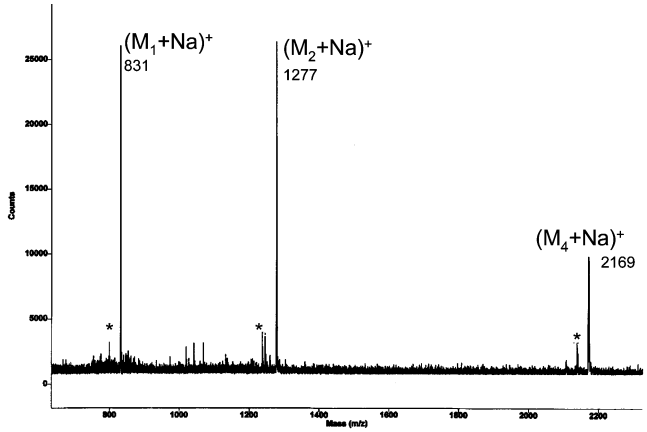

Figure 3. MALDI spectra of allyl−A(AB)$_n$−allyl oligomers (n = 1, 2, 4) in an equal-weight mixture. M is the oligomer, and the peaks marked with asterisks are the $(M - CH_3OH + Na)^+$ ions. Matrix: dithranol. Additive: NaI.

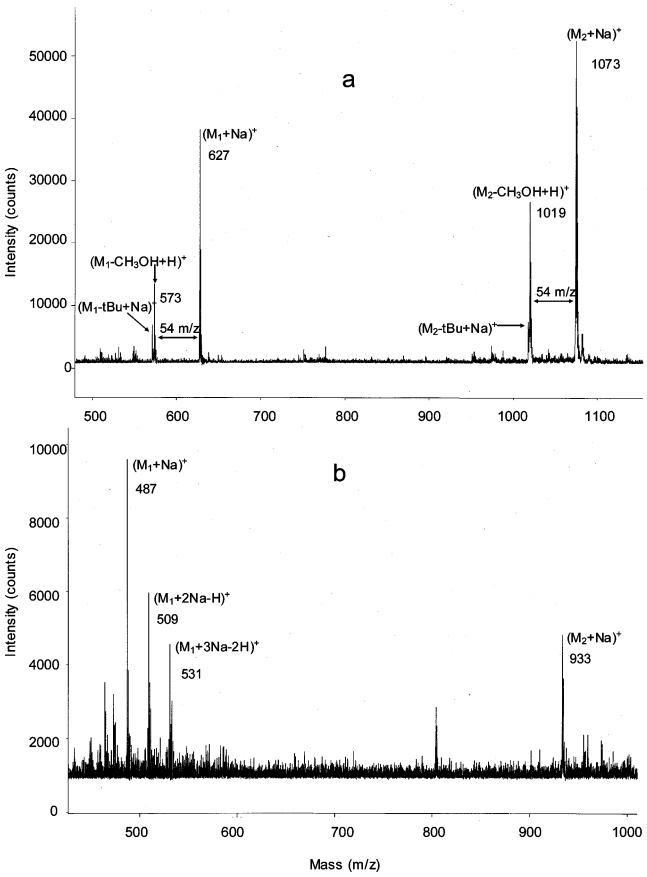

Figure 4. MALDI spectra of homooligomers as mixtures. Panel a: allyl−(AB)$_n$−Boc, n = 1 (M_1), 2 (M_2). Panel b: H−(AB)$_n$−H, n = 1 (M_1), 2 (M_2).

such as selecting a matrix or cationization agent for matrix-assisted laser desorption/ionization (MALDI) mass spectrometry, can also be examined.

The present study addresses the MALDI mass spectrometric characterization of the ionization conditions and fragmentation patterns of monodispersed oligo(amic methyl ester)s (OAMEs) model compounds based on OMDA and PMDA.

Experimental Section

Synthesis. Detailed synthetic procedures as well as NMR characterization are found in the Supporting Information. Figure 2 is a scheme which outlines of the synthetic strategy used to synthesize the OAME oligomers.

Sample Preparation. A stock solution of 1.0 mg/mL for each of the analytes was prepared in acetone for all studies. Samples for MS study were purified by precipitation in different solvent systems, such as acetone/ether, methanol/water, or ethyl acetate/hexane. Preparative TLC (silica gel) was performed for appropriate compounds.

Mass Spectrometry. MALDI mass spectra were acquired using an Applied Biosystems Voyager DE STR mass spectrometer equipped with a nitrogen laser source (337 nm). The reflectron mode was chosen for the TOF analyzer for better resolution; 128 scans were conducted for data acquisition. The preparation of MALDI-MS samples involved mixing 100 μL of dithranol solution (10 mg/mL in acetone), 100 μL of NaI solution (4 mg/mL in acetone), and 2 or 20 μL of sample stock solutions (1 mg/mL in acetone) except for allyl−A_5B_4−Boc (0.5 mg/mL in 6:4 DMF/acetone, 4 or 40 μL), followed by dried droplet deposition.

MALDI−CID spectra were acquired with a Voyager DE STR using the delayed extraction mode; the acceleration voltage was 25 kV, and the grid voltage was 67% of the acceleration voltage. The laser intensity was set to provide maximum signal intensity of the precursor ion without saturating the detector. The CID cell pressure was adjusted to attenuate the precursor ion signal to 50% of its maximum intensity. Air, xenon, argon, or helium were used as the collision gas, and the gate width was set at 6 mm of the total 1126.5 mm flight length to the reflector. The source pressure for CID experiments was about 3×10^{-6} Torr. Each composite CID spectrum was the sum of nine fragment spectra acquired with different reflectron mirror voltages. About 200 laser shots were averaged to obtain each fragment spectrum. All CID data were processed using the Applied Biosystems Data Explorer 4.0 software.

Results and Discussion

Synthesis Strategy. A convergent synthetic strategy was chosen which can yield high molecular weight (MW) single oligomers quickly as detailed in Figure 2.[19] There are three major issues for the development of a valid synthetic route: selection of protecting groups for acid and amine functionalities, respectively, production of monoprotected diacid (**3**) and diamine (**4**) on a large scale, and the choice of coupling reagent for amide formation.

To protect the carboxyl group(s) of 2,5-dicarboxyl-1,4-dimethylbenzoate (**1**), the yields of both coupling and removal of various protecting groups such as benzyl, trimethylsilylethyl, carboxamidomethyl, (trimethylsilyl)ethoxymethyl, and allyl were compared, and the allyl group was selected. Then the *tert*-butyloxycarbonyl (Boc) group was chosen to protect the amino group(s) of ODA; thus, the two protecting groups can be removed without cross-reaction.

Practically, large-scale synthesis of monoprotected diacid or diamine can only be achieved by finding an effective way to isolate the monoprotected compound from a mixture of non-protected and diprotected compounds based on their different solubilities. In this study, the mono-Boc-protected ODA (4) was separated from the di-Boc-protected byproduct and unreacted ODA after reaction of ODA with the optimum amount of $(Boc)_2O$ (0.8 eqv.). Separation was achieved based on the solubility of (4) in acidified water/ethanol cosolvent, in which the di-Boc−ODA is not soluble, and its insolubility in a DMF−water mixture, in which ODA is soluble. On the other hand, the mono-allyl-protected pyromellitic dimethyl ester (3) was prepared by controlled deprotection of the diallyl benzoate (2). Isolation took place during the reaction process; compound 2 was precipitated from the solution before the second allyl group could be cleaved by the palladium-catalyzed reaction. Careful choice of the solvent system is essential. A three-component solvent system (toluene−methanol−water) was used to separate compound **3** from **1** (overly deprotected product).

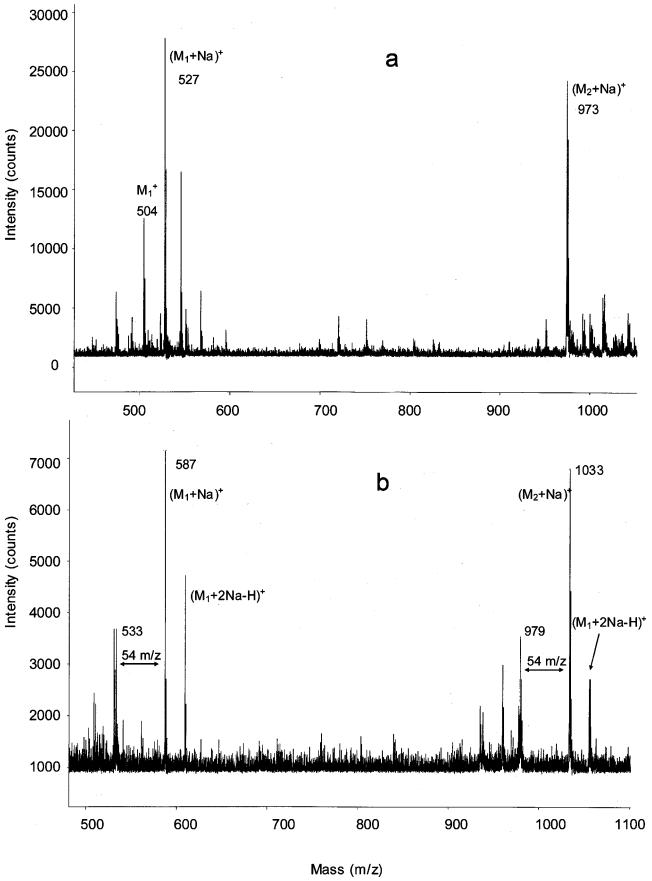

Figure 5. MALDI spectra of homooligomers as mixtures. Panel a: allyl−$(AB)_n$−H, $n = 1$ (M1), 2 (M2). Panel b: H−$(AB)_n$−Boc, $n = 1$ (M_1), 2 (M_2). $(M + Na)^+$ peaks are labeled.

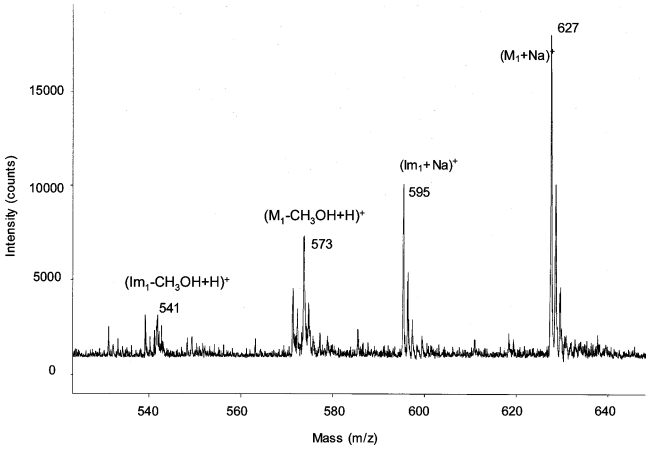

Figure 6. MALDI spectra of homooligomers as mixtures, allyl−AB−Boc (M_1) and allyl−AB−Boc−imide (Im_1). Matrix: dithranol. Additive: NaI.

The major difficulty with high MW oligomer synthesis resides in the interplay of three intrinsic aspects of this system: (1) low solubility of high MW oligomers; (2) spontaneous imidization; (3) purification. First of all, the solubility of oligomers in organic solvents decreases dramatically with an increase in MW. Meanwhile, the OAME oligomers inevitably imidize in solution over a long period of time, and they can do so quickly in the presence of certain bases or nucleophiles. In fact, the 2-ethyl hexanoate sodium salt caused complete imidization in an attempt to convert 6 to 7, even at 0 °C and only 0.5 h reaction time. Because it is important to have amide formation outpace imidization as much as possible, achieving a high concentration of reactants in an appropriate solvent system favorable for the bimolecular coupling is a critical aspect (heating is not an option). Ultimately, as the yield of the desired products decreased along with an increase in MW, purification became more difficult. Recrystallization is not very useful for high MW OAMEs, because heating causes partial imidization within the backbone chain which is hard to remove. Column chromatography is problematic because high MW oligomers (e.g., allyl−A_5B_4−Boc) do not appear to elute on either normal phase or reverse phase chromatographic gels. Thus, precipitation with two-solvent systems was the major method adopted for most of the product purifications. Note, the terminology used here is A for the acid component (PMDA) and B for the base component (ODA).

A suitable coupling reagent that causes minimal imidization in synthesis is crucial. For the coupling of ortho-substituted acids and aniline-type amines, various combinations of reagents and solvents were attempted for the synthesis of Allyl−AB−Boc (**6**). *N*,*N*′-Dicyclohexylcarbodiimide (DCC) or *N*,*N*′-diisopropylcarbodiimide (DIC) coupling of the acid and amine in various solvents led to reasonable yields (ca. 50%), but imidization was significant or predominant in methylene chloride as the solvent. *N*,*N*-(Dimethylamino)pyridine (DMAP) was tried as a catalyst but was not successful. Using benzotriazo-1-yloxytris(pyrrolidinophosphonium hexafluorophosphate) (PyBOP) gave comparable yields to DCC but imidization was still significant. Catechoborane activation of the carboxylic acid failed to give the amide product. Making active esters (pentafluorophenyl or *N*-hydroxysuccinyl) of the acid before coupling with the amine was also attempted but failed. A third way was to convert the acid to the acid chloride under neutral conditions (the imidization goes easily under basic or strongly acidic conditions) for amide formation. However, the salt of H−AB−Boc (**7**) reacting with oxalyl chloride causes the Boc group to fall off. Using PPh_3/$CBrCl_3$/pyridine as coupling reagents in methylene chloride gave reasonable yields (49%) without appreciable production of the imide. Also, the use of diphenylphosphinic chloride/pyridine in methylene chloride gave a comparable yield, but the workup was less cumbersome. Thus, the latter was chosen as the coupling reagent for synthesis of high MW oligomers.

All of these problems being solved, compounds **6** and **10** were made as shown in Figure 2. The coupling-splitting-deprotection sequence was repeated in each cycle, and thus the molecular weight was grossly doubled. It was also found that reaction of the diacid chloride of compound 1 and allyl−$(AB)_n$−H ($n = 1, 2$) gave high MW single oligomers in reasonable yield. Thus, compounds 15 and 16 were prepared accordingly.

MALDI—MS. A variety of matrices and salts/additives were screened for MALDI ionization of the OAMEs. It was found that 1,8,9-anthracenetriol (dithranol) with addition of NaI worked better than other matrices such as α-CHCA, THAP, DHB, IAA, and anthranilic acid with NaI. 9-Aminoacridine showed promise as a matrix for the negative ion mode. Interestingly, it was observed that the PAAs and PAMEs (prepared by methylation of the acid group of PAA) seem to promote the formation of matrix clusters up to 2000 mass units. Since the proton was found to be a very weak ionization promoter, the addition of NaI is important. The sodiated molecular ion peaks were present as base peaks in all MALDI spectra in this study.

Oligomers with different end groups showed different fragmentation and/or clustering patterns. For the allyl−$A(BA)_n$−allyl series ($n = 1, 2, 4$; Figure 3), only $(M + Na)^+$ and $(M +$

Table 1. Relative Signal Intensities of Oligomers[a] (Ratio of Signal Intensities of the Sums of All Identified Sodiated Peaks, Molecular Ions and Fragment Ions for a Given Oligomer)

mixture components/ratio	M_2/M_1	M_3/M_1	M_4/M_1
compounds **14** (M_1), **15** (M_2), and **16** (M_3)	1.8 (2.9)[b]	1.3 (3.5)	
compounds **6** (M_1) and **10** (M_2)	6.2 (11)		
compounds **6** (M_1), **7** (M_2), **8** (M_3), and **9** (M_4)	0.57 (0.53)	1.0 (0.83)	0.24 (0.18)
compounds **10** (M_1), **11** (M_2), **12** (M_3) and **13** (M_4)	.57 (0.49)	0.69 (0.62)	0.24 (0.23)

[a] Each analyte in the mixture has the same amount by weight (54.5 ng per MALDI sample spot). [b] Converted to equal moles of samples (ratio of peak area/nanomole).

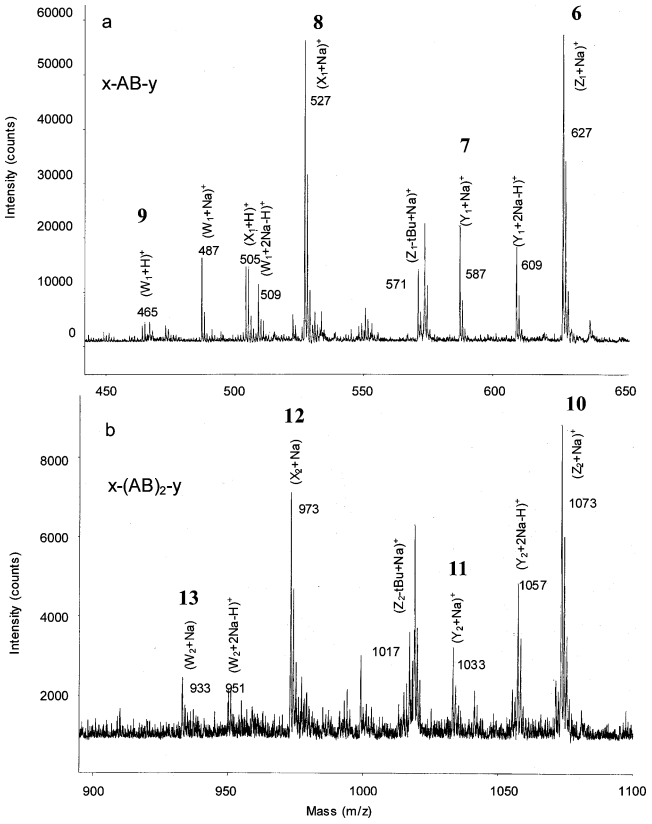

Figure 7. MALDI spectra of four-component mixture of equal weight: (a) x−AB−y; (b) x−$(AB)_2$−y. Matrix: dithranol. Additive: NaI. Spectrum a is of x−AB−y oligomers with different end groups defined below, and spectrum b is of x−$(AB)_2$−y with different end groups defined as follows. W: x = H, y = H. X: x = allyl, y = H. Y: x = H, y = Boc. Z: x = allyl, y = Boc.

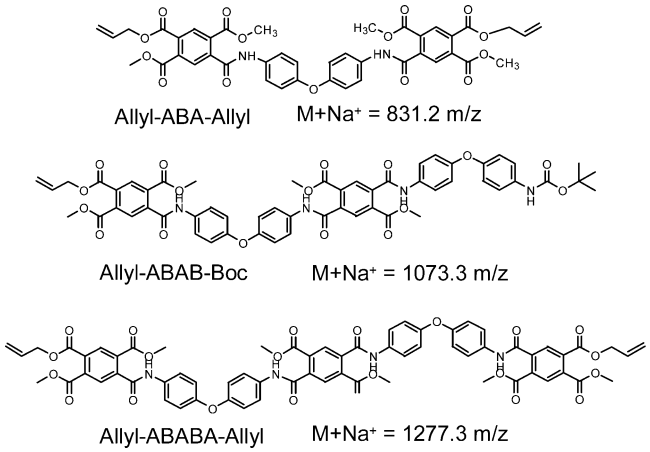

Figure 8. PAME oligomers for MALDI−CID.

$Na - CH_3OH)^+$ (marked with *) were observed in the MALDI spectra. Loss of CH_3OH indicates that either imidization of one amide link between A and B occurred or methanol was eliminated from an allyl end group during the MALDI sample preparation or experiment. The lack of additional peaks in the mass spectrum is desirable for ionizing and determining the MW of PAME samples. It is also noteworthy that the degree of fragmentation increases with increasing oligomer size.

For allyl−AB−Boc and allyl−ABAB−Boc (Figure 4a), the dominant peaks are $(M + Na)^+$ and $(M + H - CH_3OH)^+$. A third weak peak (at *m*/*z* 571 and 1017, respectively) is probably $(M + Na - t\text{Bu} + H)^+$, not $(M + H - CH_3OH - H_2)^+$. The peaks could also be from loss of an isobutene neutral (loss of 56 *m*/*z*) which was previously reported as a fragment of *tert*-butyl esters of PMDA/ODA polyamic acid by Houlihan et al.[20] The same fragment ion peak is seen in the spectra of H−$(AB)_n$−Boc and allyl−$(AB)_n$−Boc, but does not appear in spectra of the other oliogmers without a Boc end group, i.e., H−$(AB)_n$−H, allyl−$(AB)_n$−H, or allyl−A$(AB)_n$−allyl, which indicates that the fragment is *t*Bu from the Boc end group. Ions corresponding to $(M + Na - Boc + H)^+$ and $(M + \text{dithranol} + H)^+$ sometimes appeared in spectra depending on the instrument conditions used. On the other hand, spectra of H−AB−H and H−ABAB−H (Figure 4b) have $(M + Na)^+$ and $(M + 2Na - H)^+$ as the major peaks in the spectra. The peak at *m*/*z* 531 for H−AB−H is due to $(M + 3Na - 2H)^+$.

For allyl−AB−H and allyl−ABAB−H, like the allyl−A$(BA)_n$−allyl series, only $(M + Na)^+$ along with a minor $M^{\bullet+}$ peak (*m*/*z* 504 and 950, respectively) was observed (Figure 5a). Finally, $(M + Na)^+$, $(M + 2Na - H)^+$, and $(M + H - CH_3OH)^+$ (*m*/*z* 533, 979) were observed for H−AB−Boc and H−ABAB−Boc (Figure 5b). Peaks observed in these spectra at M − 33 *m*/*z* probably come from loss of 2-methyl-1-propylene from the sodiated molecular ion $(M + Na - t\text{Bu} + H)^+$. The $(M + H - CH_3OH)^+$ peaks (Figures 4a and 5b) are derived from imidization or the loss of methanol from the terminal methoxycarbonyl group during ionization rather than from imide contaminants present in the solution. To demonstrate this, a 1:1 (w/w) mixture of allyl−AB−Boc and allyl−AB−Boc-imide was measured under the same MALDI conditions. It was found that the $(\text{allyl−AB−Boc} + Na)^+$ peak (*m*/*z* 627) has about twice the intensity of $(\text{allyl−AB−Boc−imide} + Na)^+$ (*m*/*z* 595) (Figure 6). This observation rules out the possibility that a trace amount of imide impurity in the allyl−AB−Boc sample gave a disproportionally high instrument response in Figures 4a and 5b. Furthermore, no evidence of imide contaminants were seen in the oligomer samples in TLC or NMR (Supporting Information). Imidization during sample deposition onto the MALDI plate is also unlikely, as the M-54 peak is much less intense in spectra from Figure 3 in which the samples were prepared under the same conditions. Therefore, the only plausible source of the M_1-54 peaks in Figures 4a and Figure 5b is from ionization and/or gas-phase elimination of a methanol molecule. Noticeably, the mass spectrum of allyl−AB−Boc−imide also has a M_2-54 peak, for which the only possibility is the loss of methanol from the terminal methoxycarbonyl group (plus a proton) and not imidization.

The relative signal intensities of homologous oligomers having different numbers of repeat units were studied to

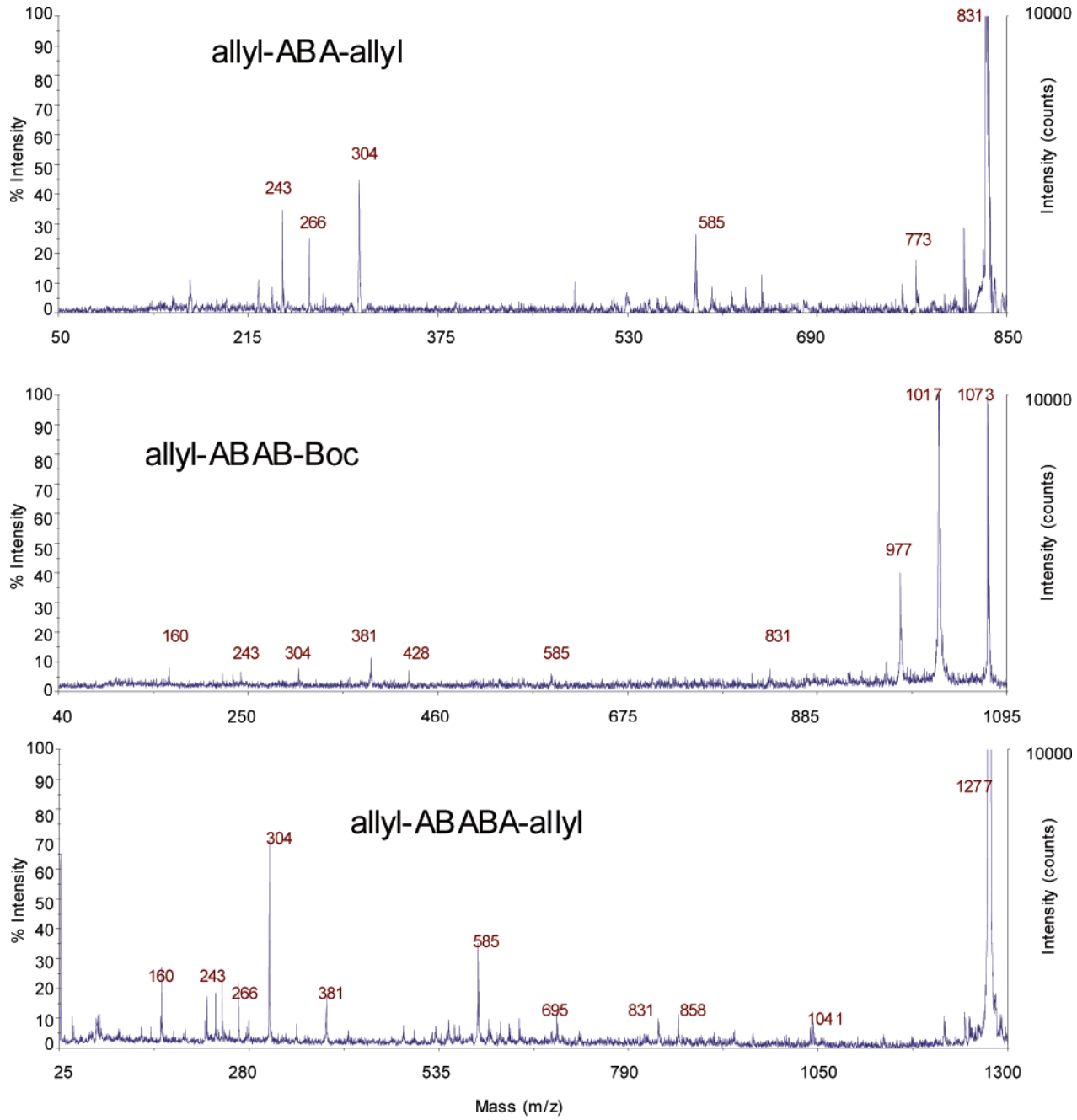

Figure 9. MALDI−CID spectra of OAME oligomers. The *y* axis is normalized to 10 000 counts in each spectrum.

determine whether significant suppression effects were observed for monomer−dimer mixtures. The relative signal intensities for analytes in various mixture combinations are summarized in Table 1. For the allyl−$(AB)_n$−A−allyl series of oligomers, the intensity per mole is much higher for the large ones (**15**, **16**) than for the small one (**14**). The same was observed for compounds **10** and **6**. These results probably indicate suppression effects, because when the same analytes were tested individually, the signal/noise ratios were comparable based on equal molar quantities in the samples.

The end groups (Boc, allyl) affect the relative signal intensities significantly, both for single components and for mixtures. A set of MALDI experiments on equal-weight mixtures of comparably sized oligomers was carried out as shown in Figure 7. The intensities of allyl−$(AB)_n$−Boc (Z) and allyl−$(AB)_n$−H (X) are typically several times higher than those for H−$(AB)_n$−H (W) and H−$(AB)_n$−Boc (Y) having the same number of repeat units ($n = 1, 2$; see Table 1). Furthermore, allyl−AB−Boc and allyl−AB−Boc−imide have similar fragmentation patterns; about 2:1 relative ionization efficiencies can be estimated from the spectra shown in Figure 6. The implication of these measurements is that the state of derivatization of the polar functional groups (COOH and NH_2), or nature of the linkage (amide vs imide) have a significant effect on ionization efficiency. This correlates well with an earlier study of the MALDI ionization of a commercial polyamic acid (PAA) sample.[21] Our results are also supported an earlier study which found different ion efficiencies of polymers based on end groups.[22]

MALDI—CID. Fragmentation of a series of PAME oligomers was investigated using MALDI−CID. The structures of the oligomers and the molecular weights for each oligomer with hydrogen and sodium are shown in Figure 8. The oligomers include allyl−ABA−allyl (**14**), allyl−ABAB−Boc (**10**), and allyl−ABABA−allyl (**15**). The purpose of the CID experiments was to determine the effects of oligomer size and end groups

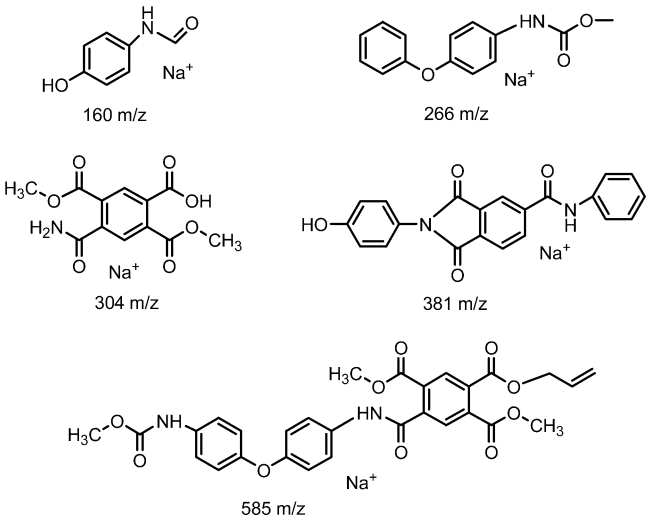

Figure 10. Possible CID fragment structures of OAME oligomers.

on the CID spectra. MALDI−CID spectra of the oligomers acquired under the same conditions are shown in Figure 9. Air was used as the collision gas in the CID experiments. Fragment ion peaks at *m*/*z* 160, 243, 304, and 585 were present in each of the CID spectra. The fragments *m*/*z* 266 and 381 were present in two of the three CID spectra. The presence of a regular set of fragment ions in the different oligomers suggests the same CID fragments ions form for each oligomer. Possible structures of the fragment ions are shown in Figure 10. The fragment ion *m*/*z* 243 is likely the *m*/*z* 266 without sodium cationization. The formation of these fragments involves rearrangement reactions instead of simple chain depolymerization. Interestingly, the allyl−ABAB−Boc fragment ions are much less intense than those from the allyl−ABA−allyl and the allyl−ABABA−allyl oligomers. The difference might be attributed to the presence of the Boc end group, which may stabilize the oligomer ions and hinder fragmentation.

The effect of collision gas on the CID spectrum of allyl−ABA−allyl was tested. Figure 11 shows CID spectra of the allyl−ABA−allyl oligomer with helium, argon, and xenon as the collision gases. The fragment ions in each of the CID spectra are the same regardless of the collision gas. The main differences in the spectra are the intensities of the fragment ion peaks. The collision gas xenon, the heaviest gas of the three tested, seemed to cause more intense *m*/*z* 304 and 585 fragment ion peaks. The noise level in the spectra with the noble collision gases was lower than for the CID spectra with air as the collision gas.

Conclusions

Oligo(amic methyl ester) model oligomers provide an interesting test of MALDI ionization efficiency and fragmentation for small oligomers with different end groups. Mass spectra of allyl−A(BA)$_n$−allyl showed only sodium-ionized molecular ion peaks and fragment ion peaks of $(M + Na - CH_3OH)^+$. Spectra of allyl−(AB)$_n$−Boc oligomers showed molecular ion peaks along with fragment ion peaks of $(M - tBu + Na)^+$ and $(M + Na - CH_3OH)^+$. Fragment ions increased in intensity in the mass spectra with increasing mass of the oligomer. Other than fragmentation of the *tert*-butyl group from the Boc end group or methanol from the allyl-terminated oligomers, no other fragmentation was seen in the mass spectra. In mixtures of oligomers, the end groups affected the relative signal intensities of the ion peaks. In MALDI−CID studies, spectra of allyl-terminated ABA and ABABA oligomers had much more intense fragment ion peaks than the allyl−ABAB−Boc CID spectrum. Xenon proved to be the most effective collision gas for OAME oligomers in CID experiments.

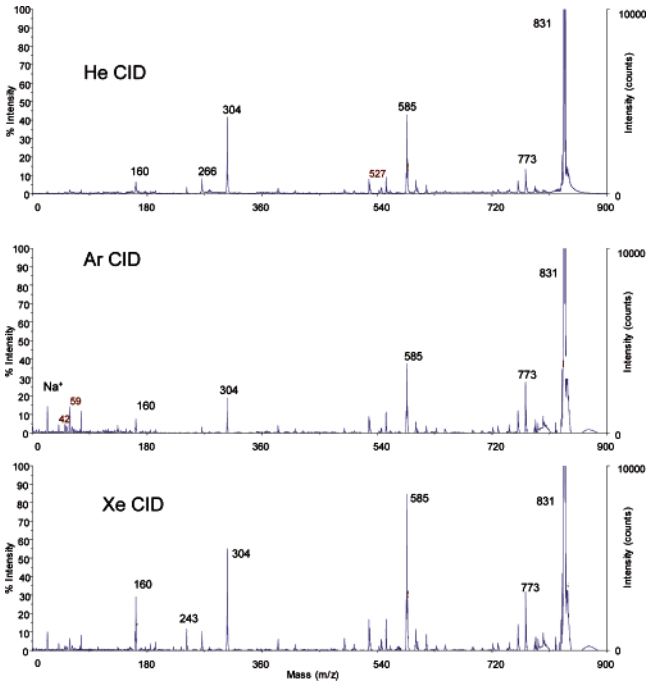

Figure 11. CID spectra of allyl−ABA−allyl acquired with different collision gases.

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Supporting Information Available: Text giving detailed synthesis procedures of the poly(amic methyl ester) oligomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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