MALDI-TOF Detection of Olefin Structural Isomerization in Metathesis Chemistry

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Received March 7, 2005; Revised Manuscript Received May 3, 2005

ABSTRACT: MALDI-TOF mass spectrometry has been employed to examine polymers generated via acyclic diene metathesis (ADMET) polymerization using a ruthenium metathesis catalyst at 50 °C, a study which targets the analysis of ADMET polymers having amino acid pendant groups placed at specific positions along the polyolefin backbone. The MALDI spectra clearly delineate olefin isomerization chemistry which competes with propagation when catalyst **2** is employed, the result being loss of precise control of polymer structure. The distribution of peaks in the MALDI spectra matches the distribution pattern of gas chromatography (GC) peaks obtained for other ADMET polymers, leading to the following conclusions. First, structural isomerization and metathesis occur concurrently rather than in any kind of sequence. Second, the relative amount of isomerized chains produced dominates over the amount of nonisomerized products. In contrast to GC, MALDI analysis unequivocally identifies the mass of the oligomeric chains, allowing for increased confidence in assignment of the possible chain structures.

Introduction

Synthesis of polymers with desired properties and morphologies can be achieved through variations in their structural design; precise structural control of macromolecular structure is preferred, of course, but is not easily achieved. For example, chain propagation synthesis of polyethylene leads to chain transfer and formation of randomly branched polymer chains, a result which has been exploited for more than 50 years to generate a large family of polyethylene materials. While random branching can be put to good use, it is of value to systematically study precise branching such that structure/property relationships in polymers can be more carefully identified. Recently, we have embarked on such a study using step polymerization acyclic diene metathesis (ADMET) chemistry rather than chain chemistry, which results in the preparation of polyethylene having branches placed at specific positions along the polymer backbone (Scheme 1).[1,2]

Being a step-growth condensation polymerization, ADMET permits the synthesis of linear and/or branched polyolefins with double bonds and branches placed repeatedly at exact positions along the polymer chain. Precisely branched polyethylene structures with branches placed on every 9th, 11th, 15th, 19th, and 21st carbon have been made, where such structures display different thermal properties from those exhibited for linear and the randomly branched polyolefin analogues. In particular, ADMET polyethylene exhibits sharp, better defined melting and recrystallization peaks in the DSC (differential scanning calorimetry) curves as compared to broad melts in randomly branched copolymers.[3,4] However, ADMET does not always produce precise structural design when olefin isomerization competes with condensation metathesis chemistry, an issue that has been related to catalyst chemistry. As a result, metathesis isomerization has been the subject of extensive research.

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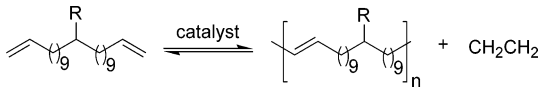
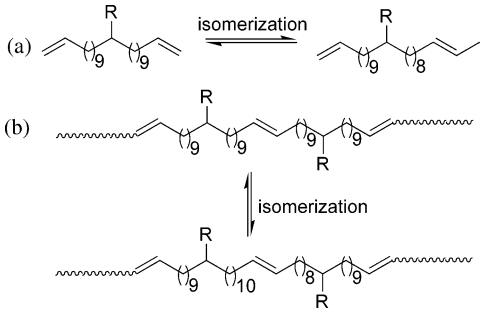
Scheme 1. An Example of the ADMET Equilibrium Reaction



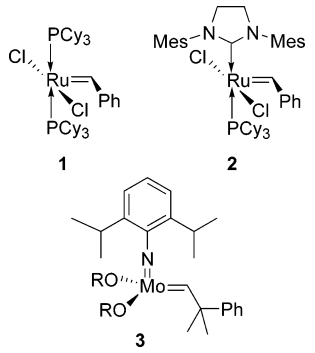
Scheme 2. Structural Isomerization as a Side Reaction (a) in the Monomer and (b) in the Polymer Backbone



Double bonds can migrate (isomerize) along the polymer backbone and/or in the monomer during olefin metathesis chemistry (Scheme 2), and as a result the number of the methylene spacer units separating the branch point on the backbone can become irregular. This process also can affect the precise positioning of any additional functionalities the polyolefin might have, since the distance between them is also determined by the number of the methylene spacers. As a further effect on structural order in ADMET polymerization, isomerization changes not only the regularity of methylene spacing within chains of the same length, but it also changes the length of these chains. For example, dimers with different lengths are produced when isomerized versions of the monomer enter the ADMET polymerization. As a result, the ADMET mechanism leads to release of higher mass molecules like propylene and butylene, instead of just ethylene. The identity of the molecules released relates to the structure of the dimer; that is, isomerized dimers vary in length by multiples

10.1021/ma050480k CCC: $30.25
Published on Web 06/04/2005

Chart 1. Metathesis Catalysts: Mes = 2,4,6-Trimethylphenyl, R = $C(CF_3)_2(CH_3)$



of 14 Da (a methylene group), corresponding to the differences in mass between the olefin molecules released.

Research suggests that isomerization is promoted by the catalyst used to initiate metathesis.[5−8] Out of the three most common metathesis catalysts (Chart 1), complex **2** is reported to promote significant isomerization, whereas **1** and **3** give little to no isomerization side products.[6,8] In general, catalyst **3** demonstrates the highest activity among the three, but at the same it exhibits high sensitivity to oxygen/moisture and polar functional groups.[9,10] On the other hand, catalysts **1** and **2** show less air sensitivity.[11,12] Among these three catalysts, complex **2** is the most active toward metathesis of functionalized monomers.[13−18] As a result, this catalyst plays an important role in polymerization and ring-closing metathesis reactions, and research efforts are dedicated to elimination of its isomerization activity.

As part of these efforts, Bourgeois et al. reported that proper selection of solvents and additives can eliminate isomerization with Ru-based metathesis catalysts in ring-closing metathesis (RCM).[5] The addition of tricyclohexylphosphine oxide or oxygen inhibits isomerization, whereas using more coordinating solvents favors it. Additional research in this area reports that other types of additives can also enhance or reduce the catalyst activity.[19−21]

Even though additive introduction and careful selection of reaction conditions can provide a degree of control over the catalyst activity, metathesis isomerization with complex **2** remains a challenge. Consequently, a variety of analytical methods have been used to study isomerization, the catalysts that promote it, and the reaction products that result from it. Among the most common techniques are GC, GC-MS, NMR, and X-ray crystallography;[6−8,11] matrix-assisted laser desorption/ionization (MALDI) mass spectrometry has also been applied to study metathesis but not with respect to olefin isomerization.[22−24]

As a "soft" ionization method, MALDI provides a means to transform large, synthetic macromolecules from solution or solid state to a gas phase with little or no fragmentation. Singly charged ions, as opposed to species with multiple charges, are created in the gas phase, which produce easy to interpret mass spectra.[25−27] In contrast to other analytical techniques, such as gel permeation chromatography (GPC), MALDI permits mass measurements and structural characterization of the polymers.[28−31] The spectra give information not only about polymers' molecular weight distribution and polydispersity index (PDI) but also about the nature of their repeat units and end groups.[32,33]

Polymer analysis by MALDI, however, usually is limited to structures having heteroatoms or unsaturated functionalities that can serve as ionization sites, such as poly(ethylene glycol) or polystyrene (even though MALDI analysis of nonfunctionalized polyethylene has also been reported[34,35]). In addition, MALDI does not provide accurate determination of the molecular weight distribution of polydisperse samples since it usually underestimates the molecular weight, as heavier species are harder to vaporize and detect. Coupling chromatography (GPC) and mass spectrometry overcomes this limitation and is widely used for polymer characterization.[27,36−43]

This paper reports MALDI-TOF detection of isomerization found in ADMET polymerization of amino acid bearing diene when using catalyst **2**. The amino acid functionalities make the polymer chains easy to ionize by MALDI and provide mass spectra that not only complement other analytical data used for characterization[17] but also give insight into certain aspects of metathesis isomerization. In the following discussion, the MALDI data are used to confirm the structure of the polymer, relate this structure to the mechanism of ADMET polymerization and isomerization, and compare the conclusions and hypothesis drawn from these data with previously published analysis of metathesis isomerization.

Experimental Section

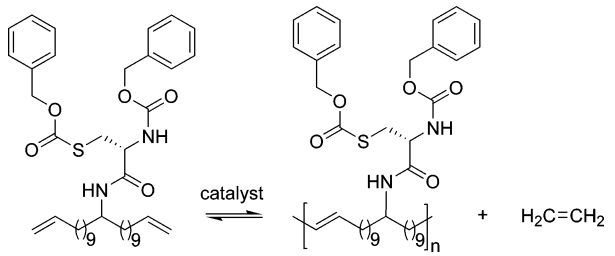
Materials. Dithranol (1,8-dihydroxy-9[10*H*]-anthracenone), HPLC grade, was purchased from Sigma-Aldrich (St. Louis, MO) and used without further purification in MALDI sample preparation. Certified sodium iodide and HPLC grade tetrahydrofuran (THF) were obtained from Fisher Scientific (Fair Lawn, NJ) and used as received. For mass calibration, the standard poly(ethylene glycol) with number-average molecular weights (M_n) of 600, 1500, 2000, 3400, 4600, and 8000 was purchased from Sigma-Aldrich (Milwaukee, WI). Literature reports a variety of procedures for synthesis of polymers having amino acid moieties;[44−47] the procedure for the ADMET synthesis of the analyzed amino acid polymer is previously published as well.[15−17,48]

MALDI Sample Preparation. Solutions of the matrix (dithranol), the polymer, and the ionization salt were prepared in THF as follows: 4 mg/mL matrix solution, 1 mg/mL polymer solution, and 1 mg/mL sodium iodide. Appropriate volumes of the three solutions were mixed to obtain matrix:polymer: ionization salt ratios of 1:1:1, 5:1:1, and 7:1:1. One microliter of each mixture was spotted on a stainless steel plate, and the solvent was allowed to evaporate. The data presented in this paper were obtained from spots having ratio of matrix:polymer: ionization salt 1:1:1 since this ratio produced the best MALDI signal.

Solutions of the PEG standards in deionized water were prepared as follows: 1 μL/mL PEG 600, 1 mg/mL PEG 1500, 1 mg/mL PEG 2000, 1 mg/mL PEG 3400, 2 mg/mL PEG 4600, and 3 mg/mL PEG 8000. A mixture of each standard PEG solution with 4 mg/mL dithranol water solution was prepared in the matrix:PEG ratio of 10:1; 1 μL of each mixture was spotted on a MALDI plate.

MALDI−TOF Analysis. All spectra were acquired with a Bruker Reflex II MALDI-TOF (Billerica, MA) instrument retrofitted with delayed extraction and a nitrogen laser emitting at 337 nm. All ions produced—from the analyte and the PEG standards—were sodiated. We speculate that the sodiated ions of the PEGs are due to impurities possibly present in the matrix, the solvents, or the glassware. The positive ions were detected in linear mode with acceleration voltage of 20 kV after 100 laser shots were summed for every spot. Analyte detection in reflectron mode was also attempted but with no success. External calibration with PEG standards

Scheme 3. ADMET Conversion of the Cysteine Diene to Polymer P_1



having molecular weights covering the mass range of interest provided a mass accuracy of 0.1% in linear mode. All data processing and theoretical mass calculations were done with Bruker Xmass software.

Results and Discussion

The ADMET polymer **P_1** (Scheme 3) is designed to have precisely placed amino acid branches along the polymer backbone, where the protected amino acid (cysteine in this case) induces polymer chirality.[17] A zoom into the first three oligomeric peaks [$n = 1$ (dimer), $n = 2$ (trimer), $n = 3$ (tetramer)] of the MALDI spectrum of the polymer (Figure 1b) shows that every oligomeric peak consists of a cluster of peaks separated by 14 Da, corresponding to a methylene group.

Were isomerization not to occur, the MALDI spectrum would consist only of single peaks representing the oligomeric chains of the dimer, the trimer, or the tetramer, etc., with masses 1409, 2088, and 2767 (Table 1). Obviously, more chemistry is occurring than just ADMET polymerization.

The balance of the peaks in Figure 1 results from olefin structural isomerization (olefin migration) occurring along with ADMET polymerization, which leads to formation of oligomers having the same number of monomer units attached, but yet, a different chain length. This translates into having a cluster of peaks for each oligomer in the MALDI mass spectrum. For example, the dimer of the polymer is represented not only by the peak at *m/z* 1409 at the MALDI spectrum but also by the peaks at *m/z* 1339, 1352, 1366, 1380, 1395, and 1423.

When olefin isomerization occurs only at one site **1I**, that is, the double bond moves one position away from its original place in the nonisomerized product **NI**, the isomerized product formed (*m/z* 1395, 2074, 2753, etc.) could have a structure such as the one shown in Table 2. To confirm, the experimental masses from the MALDI spectrum are shown to match the theoretical masses calculated on the basis of the proposed structure.

The isomerized product **1I** has one methylene group less in the polymer backbone compared to the nonisomerized product **NI**, which in the MALDI mass spectrum shows as a difference of 14 Da. Likewise, olefin isomerization that occurs at more than one site forms products (**2I**, **3I**, **4I,** ...), each having masses lower than the mass of the nonisomerized product by multiples of 14.

In addition, every oligomeric cluster of peaks in the spectrum also has peaks with masses higher than the mass of the nonisomerized product by multiples of fourteen. The mechanism of ADMET polymerization[19,49] can be used to explain the formation of all products observed in the MALDI spectrum (Scheme 4) when considering the presence of olefin bond migration. Apparently, three major types of products form during polymerization—main metathesis products (**NI**), "light products" having mass lower than the mass of the corresponding main products, and "heavy products" with mass higher than the mass of the corresponding main metathesis products. Three pathways, all consistent with the ADMET mechanism, play a role in the observed metathesis polymerization: productive metathesis (**M**), olefin isomerization followed by productive (condensation) metathesis (**I** + **M**), and olefin isomerization followed by nonproductive (trans metathesis) pathways (**I** + **NP**). The MALDI-TOF data clearly can discern each one of them.

During productive metathesis (**M**) (Scheme 4, middle rectangle), monomer **A** first reacts with the catalyst to form the cyclobutane intermediate **B**, which later rearranges to **C**. Upon the addition of another monomer molecule to **C**, the cyclobutane intermediate **D** is formed. In the next step, the productive ADMET mechanism releases the polymer's dimer **NI** (*m/z* 1409) with a structure corresponding to a nonisomerized, main metathesis product (also see Table 1). Next, another monomer molecule forms the cyclobutane **E** with the modified version of the catalyst followed by release of ethylene gas. The catalytic cycle repeats in the same manner to produce the trimer (*m/z* 2088), tetramer (*m/z* 2767), etc.

When isomerization occurs (Scheme 4, last rectangle, red), isomerized versions of the monomer **A** (such as **A1** and **A2**) take part in the metathesis cycle; these events could be described by the second major process occurring during polymerization—isomerization followed by productive metathesis (**I** + **M**). In this case, the metathesis cycle maintains the same course, but the produced intermediate **D1** differs from the intermediate **D** created in the cycle that forms the nonisomerized products. As a result, instead of release of ethylene during the metal carbene reaction with an olefin, the catalytic cycle releases propylene and produces a dimer **1I** (*m/z* 1395) with one methylene group less in the chain. As the cycle repeats, the corresponding trimer (*m/z* 2074), tetramer (*m/z* 2753), etc., are produced ("light products"). Similarly, with the isomerized monomer **A2**, the catalytic cycle releases butylene and produces a dimer **2I** (*m/z* 1380) with two methylene groups less in the backbone.

The third pathway (Scheme 4, first rectangle, blue), isomerization followed by nonproductive (trans metathesis) chemistry (**I** + **NP**), is initiated by the same isomerized versions of the monomer as the second pathway (**I** + **M**); in essence, these two pathways represent different consequences caused by the same olefin isomerization event. The difference arises from the alternate way the starting materials arrange to form a cyclobutane intermediate during productive and nonproductive metathesis. For example, when the isomerized monomer **A1** and **C** react, they can form a cyclobutane intermediate in several ways. If they arrange to intermediate **D1**, productive metathesis follows isomerization and an isomerized dimer forms (*m/z* 1395). However, if they arrange to form **D2**, instead of forming a dimer, the intermediate breaks in two to form structures **A3** and **C**1, a process referred to as nonproductive metathesis that results in no net reaction when nonisomerized molecules are reacting. This nonproductive reaction is similar to interchange reactions which accompany all polycondensation chemistry, thus the term

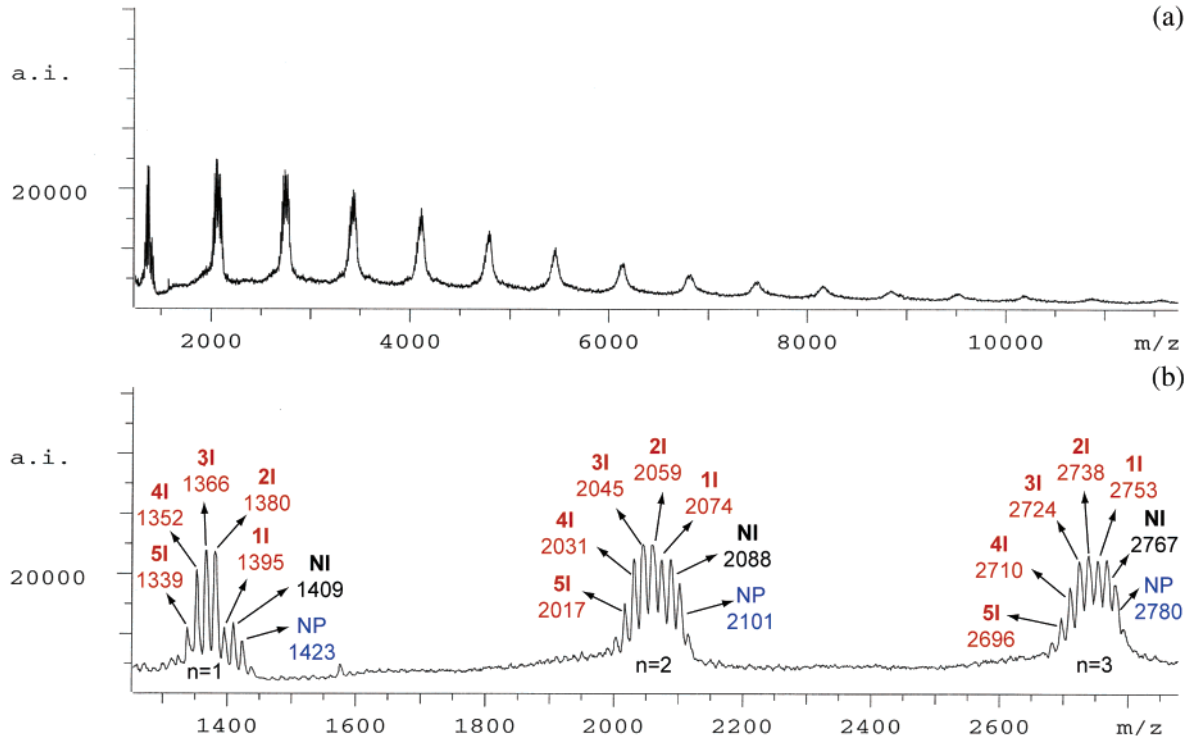
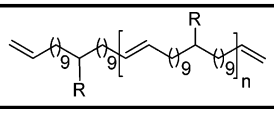


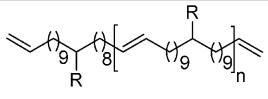
Figure 1. (a) MALDI-TOF spectrum of polymer $\mathbf{P}_1$. (b) A zoom into the first three oligomeric peaks of the spectrum. **NI**: nonisomerized product; **1I**, **2I**, **3I**, **4I**, **5I**: products with isomerization at one, two, three, etc., sites—"light products" (red). **NP**: products resulting from isomerization with nonproductive metathesis-like reactions—"heavy products" (blue).

Table 1. Theoretical and Experimental Average Masses of the Dimer (n = 1), Trimer (n = 2), and the Tetramer (n = 3) of Polymer $\mathbf{P}_1$

n	Average Mass Theoretical (Da)	Average Mass Experimental [b] (Da)	Corresponding Ions	Non-isomerized Product (**NI**) [a]
1	1409.01	1409	$[C_{82}H_{120}S_2O_{10}N_4+Na]^+$	
2	2087.99	2088	$[C_{122}H_{178}S_3O_{15}N_6+Na]^+$	
3	2766.97	2767	$[C_{162}H_{236}S_4O_{20}N_8+Na]^+$	

[a] R stands for the amino acid branches. [b] 0.1% accuracy for a linear TOF analyzer.

Table 2. Theoretical and Experimental Average Masses of Isomerized at One Site (1I) Dimer (n = 1), Trimer (n = 2), and Tetramer (n = 3) of Polymer $\mathbf{P}_1$

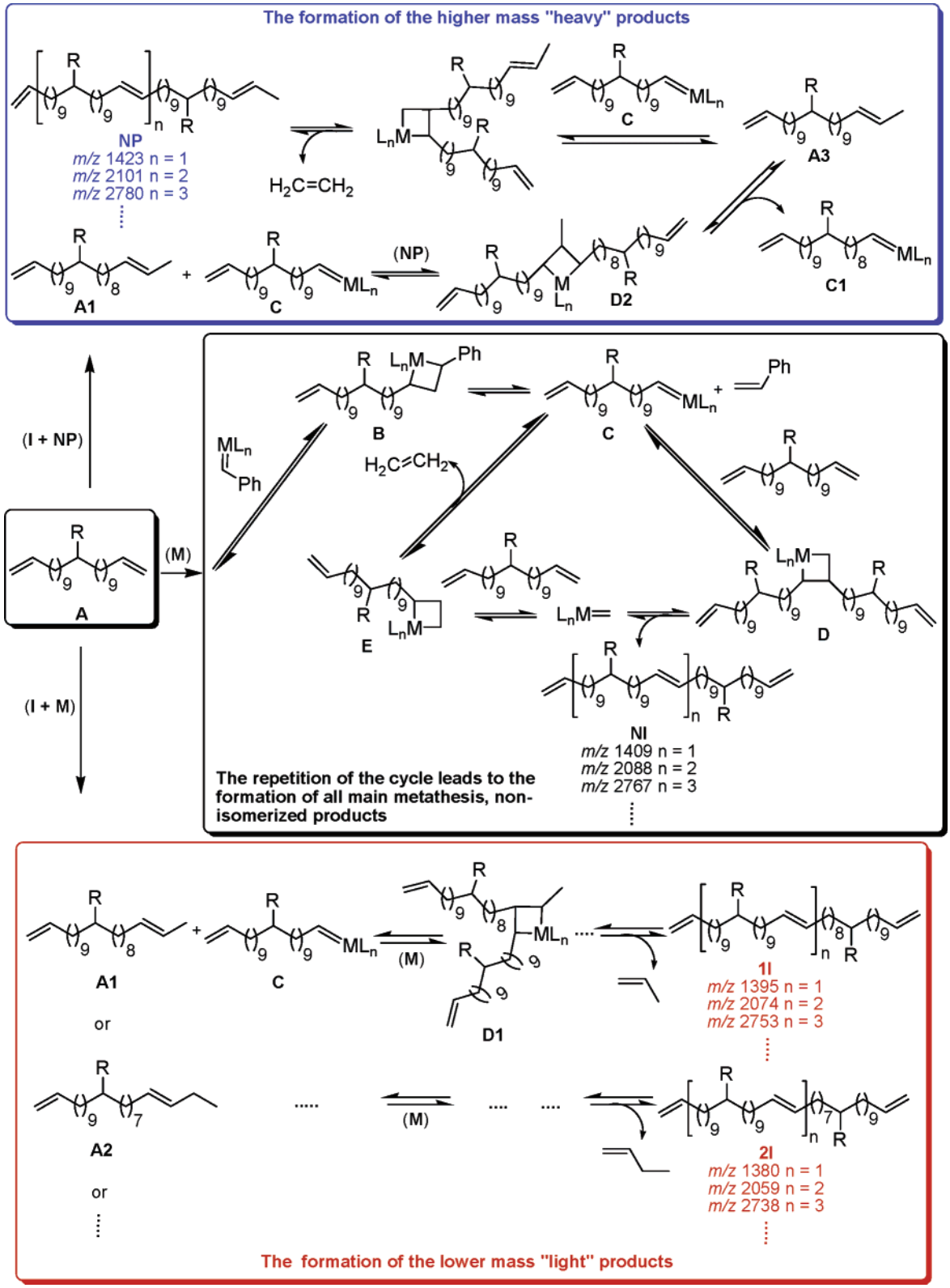
n	Average Mass Theoretical (Da)	Average Mass Experimental [b] (Da)	Corresponding Ions	Isomerized Product (**1I**) [a]
1	1394.98	1395	$[C_{81}H_{118}S_2O_{10}N_4+Na]^+$	
2	2073.96	2074	$[C_{121}H_{176}S_3O_{15}N_6+Na]^+$	
3	2752.94	2753	$[C_{161}H_{234}S_4O_{20}N_8+Na]^+$	

[a] R stands for the amino acid branches. [b] 0.1% accuracy for a linear TOF analyzer.

"trans-metathesis". Compared to the original monomer **A**, **A3** has a methyl group in place of one of the hydrogens of the terminal olefin, which corresponds to a mass increase of 14 Da (methylene unit). If the new monomer-like structure **A3** enters the productive catalytic cycle with another molecule of **C**, then a dimer having an additional methylene group on the chain forms (*m/z* 1423). The repetition of the cycle forms the corresponding trimer (*m/z* 2101), tetramer (*m/z* 2780), etc., the so-called "heavy products". All products formed by the (**I** + **NP**) pathway are referred for short as nonproductive metathesis products **NP**, as they are in Figure 1.

While Scheme 4 shows rationalizations made about the possible mechanistic pathways leading to the formation of the products observed in the MALDI spectrum, it does not represent all the possibilities. For instance, apart from the examples given in Scheme 4, numerous combinations of different monomers, formed either by isomerization (**I**) or by isomerization followed by nonproductive metathesis (**I** + **NP**), may be paired to produce dimers through metathesis (Scheme 5a). Of course, some structures in Scheme 5a are more probable to occur than others. The point, however, is that every monomer shown in the schematic (as well as countless others) may undergo metathesis with another monomer of either the same or a different kind. As a result, dimer chains with different numbers of methylene groups are generated which lead to the first cluster of peaks in the MALDI spectrum with masses ranging from *m/z* 1339 to *m/z* 1423 (Scheme 5b). At the same time, each peak within every cluster in the spectrum represents a

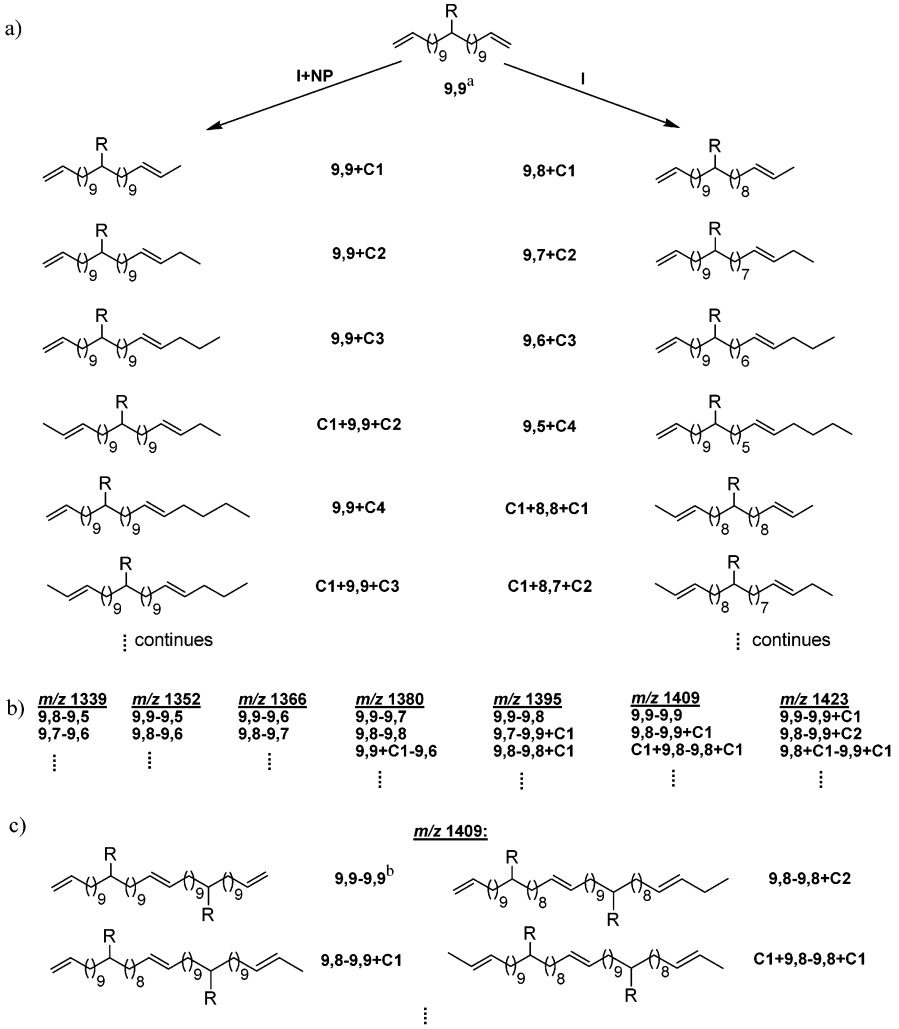
Scheme 4. Some Possible Mechanistic Pathways for the Formation of the Metathesis (NI), Isomerization (I), and Nonproductive Metathesis (NP) Products



certain number of isomerization events that have occurred. Consequently, several possible molecular configurations could be assigned to a single mass. Note that even the peak that represents a nonisomerized structure **NI** (*m/z* 1409 in the case of dimer) also corresponds to several isomerized structures that have the same mass (Scheme 5c). Even though the probability of formation for every isomer is different, the information and the data available so far do not allow for elimination of any of the possible structures. Consequently, every possibility should be considered (Scheme 5b,c).

In addition, Schemes 4 and 5 represent the possible pathways of oligomeric chains formation based on the assumption that isomerization occurs prior to metathesis of the monomer. However, previous studies[6,8] and the MALDI data presented here indicate that isomer-

Scheme 5. Formation of the Polymer's Dimers: (a) Monomers Available for Metathesis; (b) Dimers Formed during Metathesis of These Monomers, Arranged by Their Mass; (c) Dimer Structures Corresponding to *m/z* 1409



[a] Refers to a non-isomerized, nine-spacer monomer [b] Refers to a non-isomerized, nine-spacer dimer. All other abbreviations are made based on the same principle. Any added carbons refer to additional methylene groups in the monomer produced during non-productive metathesis-like reactions

ization occurs concurrently with metathesis. This idea is supported by the peak distribution pattern that emerges in every oligomeric cluster in the MALDI spectrum (Figures 1 and 2). Just like in the gas chromatograms,[8] the MALDI peaks in every cluster are not distributed evenly around the peak corresponding to the nonisomerized product (**NI**); in other words, the peaks representing the nonisomerized products (**NI**) are not centered within the distributions. Had any such order been observed, the data would imply that metathesis occurs prior to isomerization. Instead, the nonisomerized peaks (**NI**) are shifted to the right of the center in each distribution. Even though no attempts for quantitative analyses were made to determine the relative abundance of the different chains, in general, the MALDI data allow for following conclusions. First, regardless of the degree of polymerization, the amount of isomerized chains produced (**1I**, **2I**, **3I**, **4I**, etc.) dominates over the amount of nonisomerized (**NI**) products for each type of oligomer. Second, the amount of "heavy products" produced is relatively low.

The information that MALDI gives about isomerization is similar to and yet different from the data received by gas chromatography.[6,8] In both cases, a certain pattern of GC or MALDI peaks reveals the presence of isomerization; however, while every GC peak indicates the number of carbon atoms associated with the structure corresponding to the peak, every MALDI peak indicates the average mass of the structure corresponding to that peak. As a result, MALDI provides valuable information about the possible structure of the oligomeric chains, and in particular, about the possible structure of the polymer's end groups, information not accessible by gas chromatography.

Two possible mechanisms explain isomerization occurring during transition-metal-catalyzed reactions.[50] Both mechanisms suggest that isomerization proceeds through the formation of metal−hydride complexes of the metathesis catalyst. In the case of ruthenium-catalyzed metathesis reactions, research indicates that ruthenium−hydride species formed during metathesis serve as a catalyst that initiates isomerization. The source and the formation of the hydride species are unclear. Some reports assume that isomerization might result during purification of the final metathesis product by distillation;[51] others suggest that impurities in the metathesis catalyst lead to isomerization.[52] A lot of data also implies that ruthenium−hydride species might form during heating of the ruthenium metathesis catalyst.[11,53−57] One such species was obtained during

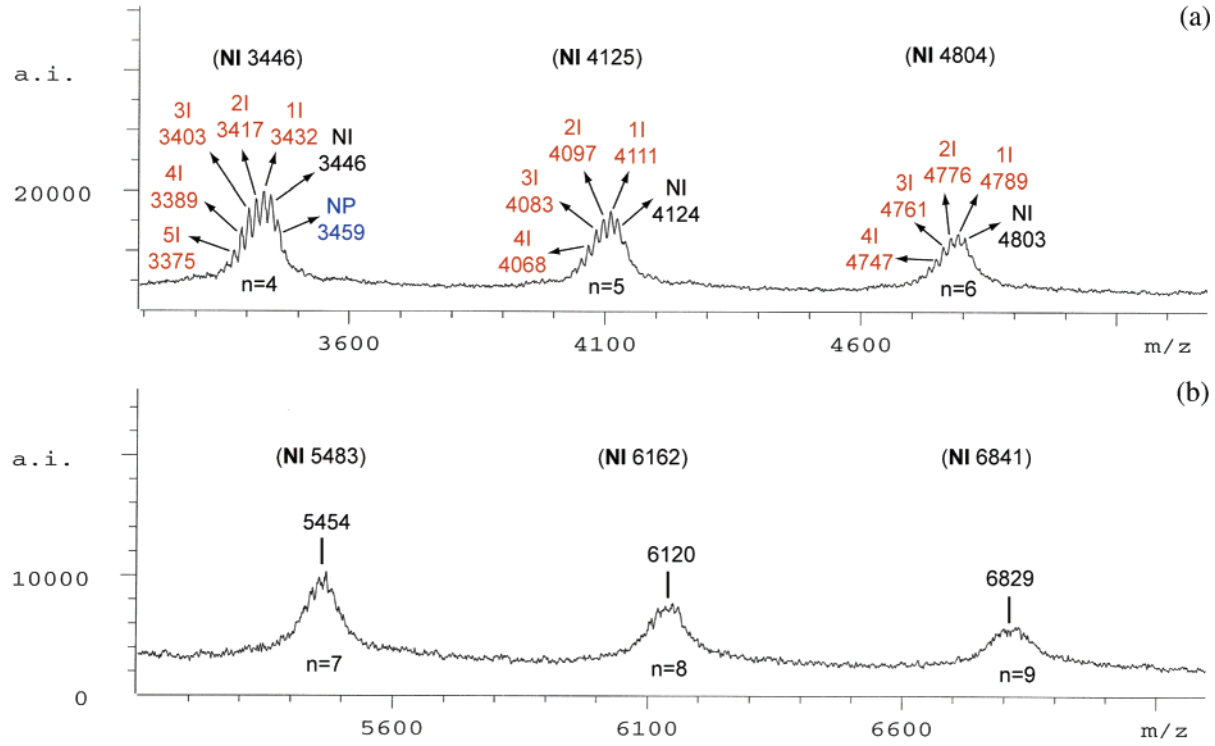


Figure 2. A MALDI−TOF spectrum of polymer $\mathbf{P}_1$. (a) A zoom into the second three oligomeric peaks of the spectrum. (b) A zoom into the third three oligomeric peaks of the spectrum.

heating at 55 °C of an N-heterocyclic-based ruthenium metathesis catalyst in benzene; the crystal structure confirmed the formation of a hydride complex of the catalyst that was proven to initiate metathesis isomerization.[7] Since the ADMET polymer analyzed in our study was formed at about the same temperature with a similar catalyst, it is possible that analogous decomposition species of the catalyst is responsible for the isomerization observed during ADMET conditions.

Conclusions

MALDI analysis of an amino acid ADMET polymer complements and confirms previous analytical data about olefin isomerization in metathesis chemistry. It confirms the presence of isomerization in metathesis polymerization when using complex **2** at elevated temperature, and it complements previous GC data by giving the mass of the polymer chains rather than just the number of carbon atoms corresponding to each peak. Consequently, these mass spectrometry data increase the level of certainty when assessing the possible chemical structure of the polymer chains corresponding to each peak. Current and future work includes coupling GPC and MALDI to obtain more reliable data about the polymer's molecular weight distribution and polydispersity index. Fourier transform ion cyclotron resonance (MALDI-FTICR) analysis is also being investigated due to its higher resolution and mass accuracy to obtain the exact mass of the oligomeric chains.

Acknowledgment. The authors thank Dr. Phil Price from Dow Chemical for his help in data processing and calibration. Thanks to Dr. Garrett W. Oakley and Dr. Danielle Dickinson for their help in the preparation of this manuscript, Abbott labs for the donation of the MALDI-TOF mass spectrometer, and the National Science Foundation and the Army Research Office for financial support.

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MA050480K