Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Molecular Catalysis A: Chemical 213 (2004) 93–99
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Review

Bio-olefins via condensation metathesis chemistry

T.E. Hopkins*, K.B. Wagener

Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, FL 32611-7200, USA

Abstract

Amino acid based polymers are of interest for a variety of biomaterial applications including drug delivery, proteomics, and tissue engineering. A new class of polymers bearing amino acids and dipeptides has been prepared using acyclic diene metathesis (ADMET) to create copolymers of polyethylene with linear amino alcohol, branched amino acid, or branched peptide substituents termed bio-olefins. Monomers with the amino acid/dipeptide functionality attached through both the N and C-terminus have been prepared, and a discussion on the synthesis of the monomers and a comparison of the thermal properties of the resulting polymers are discussed. The resulting highly functionalized polymers are strong, film-forming materials with moduli in the range of LDPE with molecular weights typical of polycondensation polymers, i.e. Nylon and PET.

Keywords: ADMET; Metathesis; Amino acids; Peptides; Polyolefins; Biologically functionalized surfaces

1. Introduction

Amino acid/peptide incorporation into polymers can give the resulting material interesting physical and structural properties, i.e. enhanced solubility, secondary structure formation, or hydrogen-bonding ability. There are two main ways to attach amino acids/peptides onto a polyolefin by conventional methods. The amino acid can be attached to an acrylic acid derivative through the C-terminus resulting in a polyacrylate or through the N-terminus resulting in a polyacrylamide followed by radical polymerization to yield the amino acid/peptide branched polyolefin [1]. These result in polymers with potential for a variety of biomedical applications such as proteonomics, membranes, artificial surfaces, and drug delivery [1].

Amino acid incorporation into polymers was initially limited in application due to the lack of availability of the enantiopure amino acids. However, modern separation techniques have overcome this problem causing new interest in this area [7], specifically much work has been reported by Morcellot and coworkers [2–7], Endo and coworkers [8–13], North and coworkers [14–16], and most recently Ayres et al. [17]. Recent efforts have even demonstrated the feasibility of using radical [18,19] and ATRP [17] polymerizations to prepare polyacrylates and polyacrylamides bearing peptide substituents.

Recently, metathesis chemistry has demonstrated potential towards the preparation of amino acid/peptide containing polymers, due to the development of new catalyst technology, especially second generation Grubbs' catalyst (**1a**) (tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidine] ruthenium(IV) dichloride) and more recently [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidine] [2-(1-methylethoxy)-phenyl]methylene]ruthenium(IV) dichloride (**1b**) [20] (Fig. 1). Catalyst **1a** has demonstrated a high degree of functional group tolerance, allowing ring opening metathesis (ROMP) chemistry to be used to polymerize norbornene derivatives with amino acid and peptide branches [21–23]. Specifically, Maynard and Grubbs have prepared a polymer bearing the biologically active peptide sequence RGD, which demonstrated cell-binding ability, a property that could make it useful for a variety of biomedical applications [21–24]. In addition, Brezinska et al. have used acyclic diene metathesis (ADMET) along with metal catalyzed, living *N*-carboxyanhydride chemistry to make triblock [25] and most recently pentablock copolymers [26].

Acyclic diene metathesis is a well-defined polycondensation reaction enabling the synthesis of unique polymer architectures by simple monomer design (Fig. 2), [27–30].

* Corresponding author. Tel.: +1-352-392-4666; fax: +1-352-392-9741.
E-mail address: wagener@chem.ufl.edu (T.E. Hopkins).

1381-1169/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2003.11.024

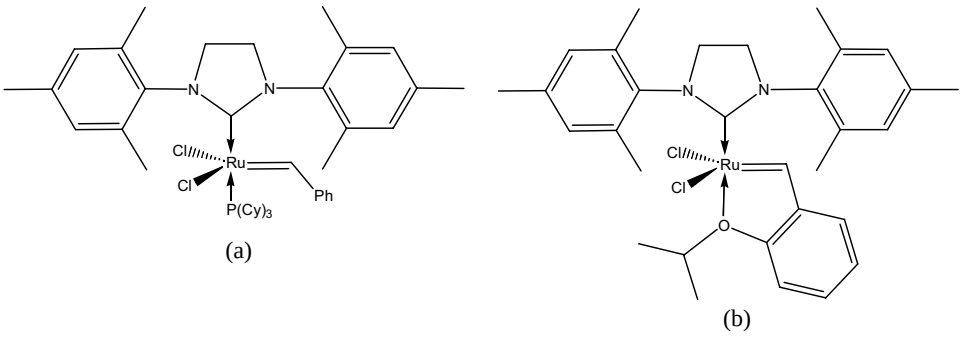


Fig. 1. The second generation Grubbs' Ru catalyst and the Hoveyda version of the second generation Grubbs' catalyst.

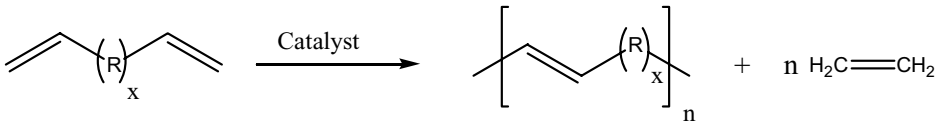


Fig. 2. General ADMET reaction.

Thus, ADMET can be used to prepare macromolecules inaccessible by common polymerization techniques [31,32]. We have recently reported the polymerization of various protected amino acid/peptide branched dienes, yielding polyolefins, termed bio-olefins, as further examples of the functional group tolerance of the second generation Grubbs' catalyst **1a** [33–39]. Further, the molecular weights obtained by ADMET polymerizations resemble those obtained by typical polycondensation reactions e.g. Nylon and PET—molecular weights of only 10–20,000 g/mol are required for good physical properties of these bio-olefins. Indeed, preliminary tensile data give moduli in the same range as LDPE for our amino acid branched dienes. Thus, these materials could be useful for a variety of biomaterial applications including membranes, proteomics, chiral separation media, drug delivery, and surfaces for artificial implants.

Here we report a summary of our efforts to synthesize new biomaterials using ADMET chemistry. We have prepared polymers with protected amino acid and dipeptide branches attached to the polymer backbone through both the N and C-terminus, annotated "N-terminus" and "C-terminus" polymers, respectively. A comparison of the polymerizability of the monomers and thermal data of the resulting polymers are discussed.

2. Results and discussion

2.1. Monomer synthesis

The preparation of amino acid branched polymers requires the synthesis of pre-monomers bearing amine or acid functionality (Fig. 3). The amine and acid branched dienes were chosen so that the amino acids could be attached through either the N or C-terminus, resulting in polymers, once deprotected, with acidic and basic surfaces, respectively. The pre-monomers were synthesized as previously reported using straight-forward, high yielding reactions as shown in Fig. 3, [37,38].

The amino acid/dipeptides were coupled to the corresponding pre-monomers using the well-established 1,3-diisopropylcarbodiimide (DIC)/1-hydroxy benzatriazole (HOBt) peptide coupling method with THF as the solvent at 50 °C. The monomers were purified by recrystallization from ethanol/water or methanol/water or by column chromatography.

2.2. Polymer synthesis

ADMET bio-olefins are prepared using a modified polymerization method since the monomers are solids or become solids after a few couplings. The polymerizations are performed in a 50 ml Schlenk flask using a minimal amount of THF as to assure a homogeneous mixture, and the reactions are stirred at 50 °C for 144 h—an amount of time chosen to allow for complete conversion. To aid in ethylene removal, a continuous purge of argon is passed through the system. The catalyst is then removed by treatment with tris(hydroxymethyl)phosphine (1 M in isopropyl alcohol), extraction, drying over $MgSO_4$, and solvent-casting on a Teflon™ plate.

Fig. 4 demonstrates the wide variety of bio-olefins prepared to date. The amino acids were chosen to determine any limitations, e.g. functionality or size of branch, of this methodology, and to examine the structure property relationships of this new class of macromolecules. Polymers were prepared having alanine, leucine, lysine, cysteine, and arginine branches, amino acids chosen due to their availability and polarity, with a variety of protecting groups. GPC

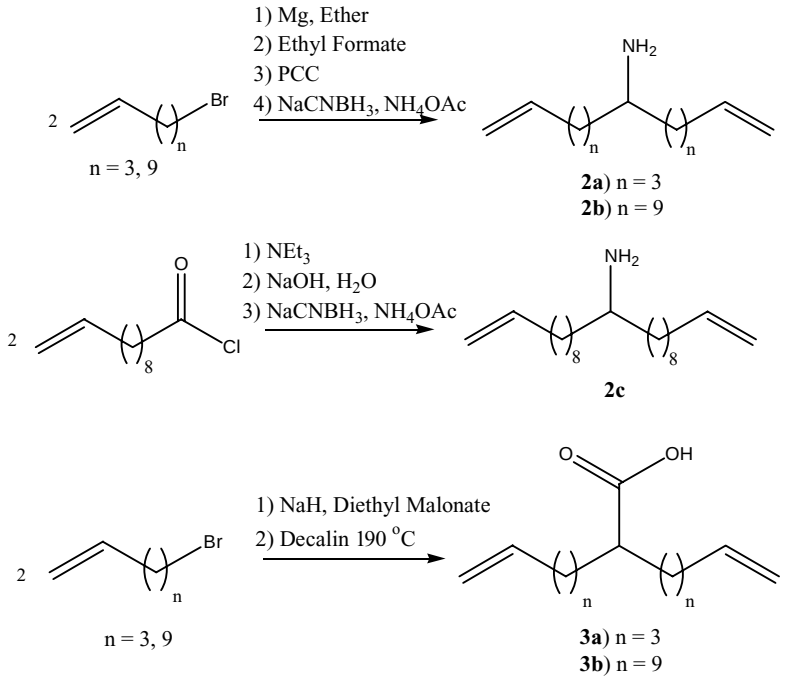


Fig. 3. Synthesis of the amine and acid branched premonomers.

and differential scanning calorimetry (DSC) were run on the polymers, and the data is given in Tables 1–3.

To investigate the polymerizability of amino acid branched monomers, the smallest chiral amino acid (alanine) branched dienes were prepared first [33,37,38]. To our delight, all of the alanine branched polymers (**9a**–**9f**) were prepared in high molecular weight (Table 1). Previously we reported that monomer **4c**, which has an alanine branch three methylenes away from the branch point, yields only oligomers upon polymerization with catalyst **1a** [37]; however, polymerization with the Hoveyda catalyst **1b** yields a high molecular weight polymer. The reason for the lack of activity with catalyst **1a** is believed to be due to intramolecular complexation between the catalyst and the monomer functionality. In the ADMET mechanism, the active catalyst for metathesis is the same for both **1a** and **1b**, which suggests that the catalyst binds to the functionality prior to activation by dissociation of the labile ligand, a property much faster for **1b** than **1a** [39]. At this point there is no clear explanation for why the two catalysts give drastically different results. Also, it is worth noting the differences in reactivity of the "N-terminus" monomer **4a** and "C-terminus" monomer **4c**; the first forms high polymer when polymerized with catalyst **1a** and the latter only forms oligomers.

The thermal data for the alanine branched polymers reveals that regardless of the points of attachment the benzyl

Table 1
Molecular weight and thermal data for the alanine branched bio-olefins

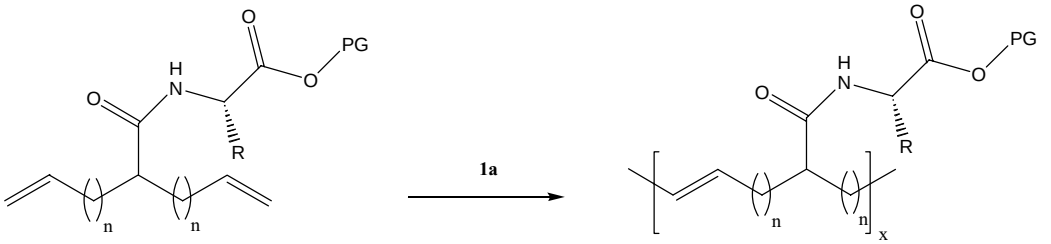
Polymer	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	PDI	T_m (°C)[c]	T_g (°C)[c]
9a	26,000[a]	17,000[a]	1.54	N/A[d]	28
9b	21,000[a]	13,000[a]	1.62	38[f]	−21
9c	18,000[b]	12,000[b]	1.50	N/A[d]	N/A[e]
9d	68,000[b]	37,000[b]	1.85	N/A[d]	7
9e	40,000[b]	21,000[b]	1.89	46[f]	N/A[e]
9f	27,000[b]	13,000[b]	2.11	N/A[d]	18

[a] $\bar{M}_w$ values were calculated by GPC using LALLS.
[b] $\bar{M}_n$ was calculated by GPC relative to polystyrene standards.
[c] Data obtained using a Perkin-Elmer DSC 7 at 10 °C/min.
[d] No T_g observed over the scanned range of −80 to 180 °C.
[e] No T_m observed over the scanned range of −80 to 180 °C.
[f] The T_m reported is that of the solvent crystallized sample; no T_m was observed from the melt crystallized sample.

Table 2
Molecular weight and thermal data for the leucine branched bio-olefins

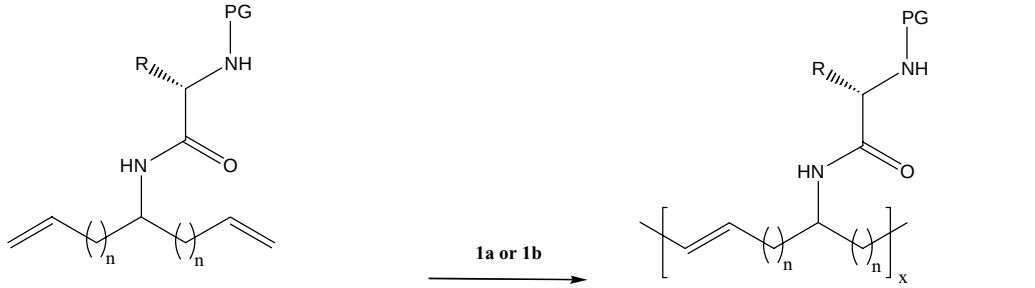
Polymer	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	PDI	T_m (°C)[c]	T_g (°C)[c]
10a	36,000[a]	25,000[a]	1.45	N/A[e]	18
10b	73,000[a]	47,000[a]	1.55	132	N/A[d]
10c	25,000[a]	13,000[a]	1.91	N/A[e]	5
10d	42,000[a]	23,000[a]	1.85	N/A[e]	−10
10e	29,000[a]	18,000[a]	1.59	N/A[e]	3
10f	17,000[b]	13,000[b]	1.34	59[f]	N/A[d]
10g	39,000[b]	20,000[b]	1.96	N/A[e]	34

[a] $\bar{M}_w$ values were calculated by GPC using LALLS.
[b] $\bar{M}_n$ values were calculated by GPC relative to polystyrene standards.
[c] Data obtained using a Perkin-Elmer DSC 7 at 10 °C/min.
[d] No T_g observed over the scanned range of −80 to 180 °C.
[e] No T_m observed over the scanned range of −80 to 180 °C.
[f] The T_m reported is that of the solvent crystallized sample; no T_m was observed from the melt crystallized sample.



4a) n = 3, R = CH_3, PG = Bz
4b) n = 9, R = CH_3, PG = Bz
5a) n = 3, R = $CH_2CH(CH_3)_2$, PG = Bz
5b) n = 3, R = $CH_2CH(CH_3)_2$, PG = CH_3
5c) n = 9, R = $CH_2CH(CH_3)_2$, PG = OtBu
5d) n = 9, R = $CH_2CH(CH_3)_2$, PG = Bz
5e) n = 9, R = $CH_2CH(CH_3)_2$, PG = CH_3
6a) n = 3, R = $(CH_2)_4NHCBz$, PG = CH_3
6b) n = 9, R = $(CH_2)_4NHCBz$, PG = CH_3
7) n = 9, R = $(CH_2)_3NHC(NH)NH(PBf)$, PG = CH_3

9a) n = 3, R = CH_3, PG = Bz
9b) n = 9, R = CH_3, PG = Bz
10a) n = 3, R = $CH_2CH(CH_3)_2$, PG = Bz
10b) n = 3, R = $CH_2CH(CH_3)_2$, PG = CH_3
10c) n = 9, R = $CH_2CH(CH_3)_2$, PG = OtBu
10d) n = 9, R = $CH_2CH(CH_3)_2$, PG = Bz
10e) n = 9, R = $CH_2CH(CH_3)_2$, PG = CH_3
11a) n = 3, R = $(CH_2)_4NHCBz$, PG = CH_3
11b) n = 9, R = $(CH_2)_4NHCBz$, PG = CH_3
12) n = 9, R = $(CH_2)_3NHC(NH)NH(PBf)$, PG = CH_3



4c) n = 3, R = CH_3, PG = BOC
4d) n = 8, R = CH_3, PG = BOC
4e) n = 8, R = CH_3, PG = CBz
4f) n = 9, R = CH_3, PG = BOC
5f) n = 3, R = $CH_2CH(CH_3)_2$, PG = BOC
5g) n = 9, R = $CH_2CH(CH_3)_2$, PG = BOC
6c) n = 3, R = $(CH_2)_4NHBOC$, PG = BOC
6d) n = 8, R = $(CH_2)_4NHBOC$, PG = BOC
6e) n = 9, R = $(CH_2)_4NHCBz$, PG = CBz
6f) n = 9, R = $(CH_2)_4NHBOC$, PG = BOC
8) n = 9, R = CH_2SCBz, PG = CBz

9c) n = 3, R = CH_3, PG = BOC
9d) n = 8, R = CH_3, PG = BOC
9e) n = 8, R = CH_3, PG = CBz
9f) n = 9, R = CH_3, PG = BOC
10f) n = 3, R = $CH_2CH(CH_3)_2$, PG = BOC
10g) n = 9, R = $CH_2CH(CH_3)_2$, PG = BOC
11c) n = 3, R = $(CH_2)_4NHBOC$, PG = BOC
11d) n = 8, R = $(CH_2)_4NHBOC$, PG = BOC
11e) n = 9, R = $(CH_2)_4NHCBz$, PG = CBz
11f) n = 9, R = $(CH_2)_4NHBOC$, PG = BOC
13) n = 9, R = CH_2SCBz, PG = CBz

Fig. 4. Illustration of the amino acid branched polymers prepared to date [33–39]. Explanation of numbering system: (**4**/**9**) alanine branched monomers/polymers, (**5**/**10**) leucine branched monomers/polymers, (**6**/**11**) lysine branched monomers/polymers, (**7**/**12**) arginine branched monomer/polymer, and (**8**/**13**) cysteine branched monomer/polymer (note stereocenter for **8**/**13** is *R* not *S*).

protected alanine branched polymers **9b** and **9e** are semicrystalline when the functionality is located on every 19th or 21st carbon [37,38]. In addition, both only demonstrated semicrystallinity when crystallized via solvent evaporation, and not after cooling at 10 °C per minute in the DSC. All of the other alanine branched dienes prepared to date are amorphous.

A variety of leucine branched bio-olefins (**10a**–**10g**) have been prepared as well, and the molecular weights and thermal data are reported in Table 2. Similar to that mentioned above for polymer **9a**, monomer **5f** yielded only oligomeric product when catalyzed with **1a** [37], but yielded high polymer when polymerized with **1b** (Table 2). All other leucine branched monomers, even **5a** with the same branch frequency as **5f**, yielded high molecular weight polymer using catalyst **1a**. Again, there appears to be a relationship between polymerizability and the point of amino acid attachment.

An analysis of the DSC data collected for the leucine branched polymers in Table 2 demonstrates that branch frequency determines the semicrystalline nature of the resulting polymers. Polymers **10a** and **10f**, both have leucine branches located on each and every 9th carbon of the

Table 3
Molecular weight and thermal data for the lysine, arginine, and cysteine branched bio-olefins

Polymer	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	PDI	T_m (°C)[c]	T_g (°C)[c]
11a	63,000[a]	38,000[a]	1.67	N/A[e]	7
11b	44,000[a]	24,000[a]	1.80	79	N/A[d]
11c	37,000[b]	60,000[b]	1.63	N/A[e]	N/A[d]
11d	35,000[b]	20,000[b]	1.76	64	N/A[d]
11d	48,000[b]	25,000[b]	1.92	96	N/A[d]
11e	21,000[b]	11,000[b]	1.92	60	N/A[d]
12	36,000[a]	26,000[a]	1.40	N/A[e]	69
13	25,000[b]	14,000[b]	1.76	110	N/A[d]

[a] $\bar{M}_w$ values were calculated by GPC using LALLS.
[b] $\bar{M}_n$ values were calculated by GPC relative to polystyrene standards.
[c] Data obtained using a Perkin-Elmer DSC 7 at 10 °C/min.
[d] No T_g observed over the scanned range of −80 to 180 °C.
[e] No T_m observed over the scanned range of −80 to 180 °C.

polymer backbone, and both are semicrystalline with T_ms of 132 and 59 °C, respectively. Interestingly, the leucine branched polymers **10e** and **10g**, possessing the same protecting groups as **10a** and **10f**, with branches located every 21st carbon are amorphous [37,38]. At this point we do not have an explanation for the semicrystalline nature of these polymers, but current research is underway to try to explain this interesting phenomena.

In addition to the alkyl branched amino acids, alanine and leucine, many polar bio-olefins were prepared to investigate the effect of the high degree of polarity on polymerizability and thermal characteristics (Fig. 4) [37,38]. All of the lysine branched monomers were converted to high molecular weight polymer using catalyst **1a**. Contrary to the findings for alanine and leucine "C-terminus" monomers (**4c** and **4f**), monomer **6c** was converted to a higher molecular weight using **1a** (Table 3) than **1b** ($\bar{M}_n$=14,000 g/mol), and future work in our group will investigate this finding. Also, the "N-terminus" arginine branched monomer (**12**) was polymerized to high molecular weight, whereas a "C-terminus" arginine branched monomer (not shown) with the same amount of methylenes between branch point and olefins as monomer **12** was not polymerizable using catalyst **1a**—no other catalysts have been tried to date. This finding again illustrates the impact of amino acid attachment on monomer reactivity, even when the functionality is located on every 21st carbon. In addition to the highly functional arginine moiety, a cysteine branched monomer (**13**) was polymerized to high molecular weight,

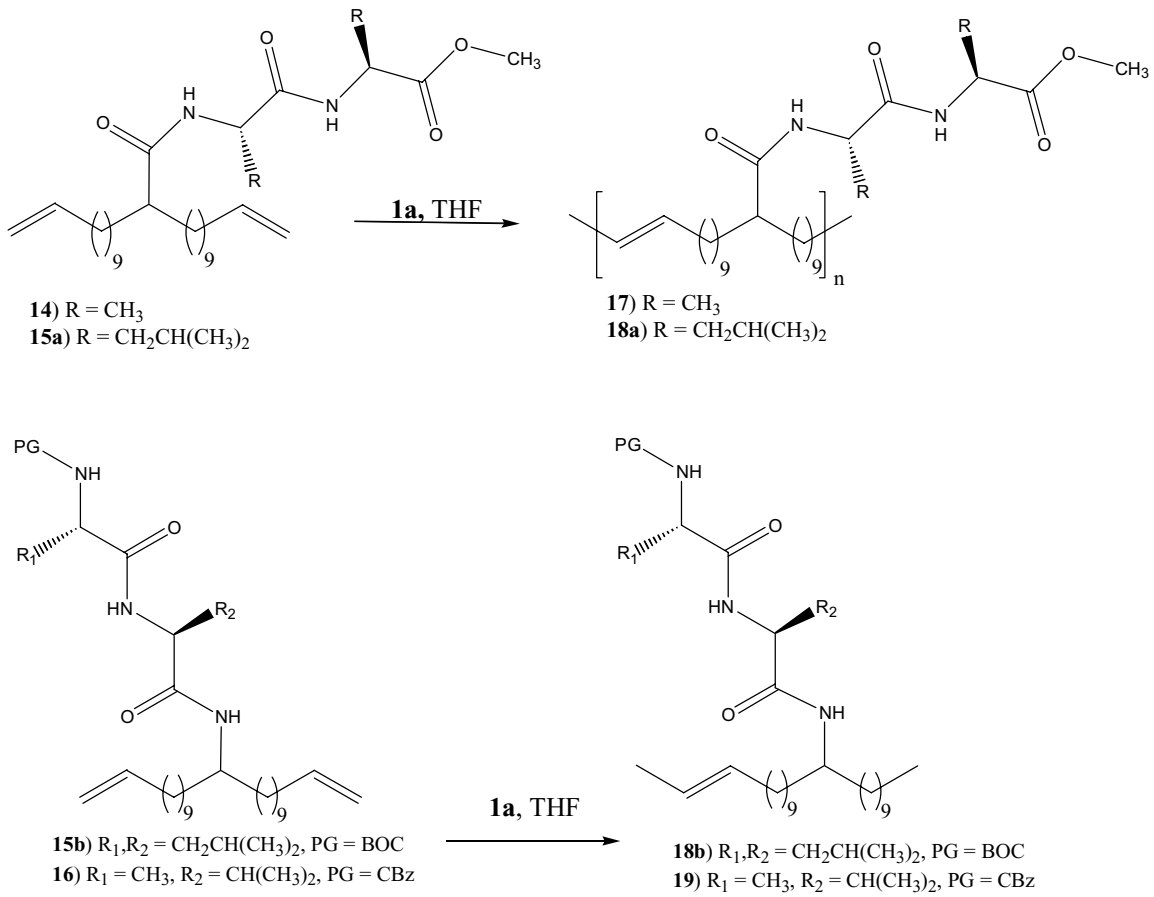


Fig. 5. Illustration of the dipeptide branched polymers prepared to date. Explanation of numbering system: (**14**/**17**) alanine–valine branched monomers/polymers (**15**/**18**) leucine–leucine branched monomers/polymers (**16**/**19**) alanine–alanine branched monomers/polymers.

which is an interesting finding since sulfur is known to kill Ru catalysts, once again demonstrating the high functional group tolerance of the second generation Grubbs' catalyst **1a**.

The highly polar amino acid branched dienes (Fig. 4, Table 3) were primarily semicrystalline with melting points (T_m) of up to 110 °C [37,38]. Only the lysine branched polymer **11a** having a branch on every 9th carbon and the arginine branched polymer **13** were amorphous. The results for the lysine branched polymers are opposite of that seen for leucine; the polymers with a branch on every 9th carbon are amorphous, whereas bio-olefins with a lysine branch on every 21st carbon are semicrystalline. The fact that these highly polar and bulky amino acid branched polymers show high semicrystalline tendencies (up to 60% by initial WAXD data) suggests that the amino acids and not the polyolefin backbone could be responsible for the semicrystalline nature of these bio-olefins.

Further work, to demonstrate the potential for this methodology was accomplished through the preparation of dipeptide branched monomers (Fig. 5). Since the goal of this work is to prepare biologically active surfaces, the methodology for polymerizing longer amino acid sequences had to be determined. The sequences were chosen according to their availability, and were successfully polymerized to high molecular weight using the methodology described above (Table 4). Also, it is worth noting the differences in molecular weights obtained for the "N-terminus" versus "C-terminus" polymers, which further demonstrates a higher reactivity for monomers with amino acids attached through the N-terminus.

DSC data on the dipeptide branched bio-olefins further supported the concept that the amino acids and not the polyolefin backbone are responsible for the semicrystalline nature of the bio-olefins. Three of the four dipeptide branched bio-olefins prepared to date are semicrystalline; only the "C-terminus" BOC protected leucine–leucine dipeptide branched polymer was amorphous (**18b**)—a sample much more "greasy" than the other dipeptide branched moieties.

Table 4
Molecular weight and thermal data for the peptide branched bio-olefins

Polymer	$\bar{M}_w$ (g/mol)	$\bar{M}_n$ (g/mol)	PDI	T_m (°C)[c]	T_g (°C)[c]
17	31,000[b]	12,000[b]	2.61	150	N/A[d]
18a	11,000[b]	6,500[b]	1.66	N/A[e]	40
18b	38,000[a]	23,000[a]	1.64	74	N/A[d]
19	21,000[a]	15,000[a]	1.40	71[f]	N/A[d]

[a] Calculated by GPC using LALLS.
[b] Calculated by GPC relative to polystyrene standards.
[c] Data obtained using a Perkin-Elmer DSC 7 at 10 °C/min.
[d] No T_g observed over the scanned range of −80 to 180 °C.
[e] No T_m observed over the scanned range of −80 to 180 °C.
[f] The T_m reported is that of the solvent crystallized sample; no T_m was observed from the melt crystallized sample.

3. Conclusions

ADMET chemistry has been used to prepare high molecular weight materials, termed bio-olefins, having melting points of up to 132 and 150 °C for amino acid/dipeptide branched polymers, respectively [37,38]. Also, a difference in reactivity between monomers with amino acids/peptides attached through the N-terminus of the amino acid and monomers with amino acids/peptides attached through the C-terminus was observed; "N-terminus" monomers polymerize much more readily than "C-terminus" monomers.

In addition, roughly half of the bio-olefins prepared to date are semicrystalline, which has spawned collaborative efforts to investigate X-ray scattering in order to determine the true cause of crystallization. However, an analysis of the thermal data suggests that the more polar amino acid branched polymers (lysine, cysteine) tend to form semicrystalline materials, and the non-polar amino acid branched monomers (leucine) tend to be amorphous.

The polymerizability of highly polar monomers bearing groups such as cysteine and arginine, as well as the dipeptide branched monomers, support the concept of applying this methodology to highly polar and potentially biologically active peptides such as RGD (arginine–glycine–aspartic acid). Current research is underway to prepare this type of bio-olefin, which if successful will be tested for biological activity.

We have prepared a new class of polyolefins termed bio-olefins that possess material and thermal properties unheard of for typical highly branched polyolefins, e.g. tensile strength similar to low density polyethylene and melting points up to 150 °C. This is possible due to the ADMET mechanism, which allows for specific branch placement along a polyolefin backbone, resulting in a perfect copolymer structure, i.e. a branch on every 9th, 21st, etc. carbon of a polyolefin. These properties have stimulated collaborative efforts in the areas of X-ray scattering, mechanical properties, and surface properties, results of which will be the subject of future articles.

Acknowledgements

We would like to thank the National Science Foundation, Division of Materials Research, and the Army Research Office for financial support of the research. We would like to thank Mr. Travis Baughman, Dr. Stephen Lehman, and Mr. John Sworen for help in the preparation of the acid premonomers, and Mrs. Florence Courchay and Mr. Piotr Matloka for synthesizing the catalysts used in this work. In addition, we acknowledge Mr. Fred Tep, Mr. Shahab Akvon, Mr. Wendell Bob, and Mr. Xavier Guerrero for their contributions during the course of this work. We also thank Mr. John Sworen, Dr. Ravi Orugunty, Dr. Claud Robotham, Dr. Shane Waybright, Professor Jean M.J. Fréchet, Professor

Dave Tirrell, Professor Eric Enholm, and Professor Dennis Wright for helpful discussions. We acknowledge Mr. Clay Bohn and Professor Anthony Brennan for their help in obtaining initial material property data on these polymers. We thank Mr. John Sworen and Mr. Travis Baughman for their help in the preparation of this manuscript. Finally, we are grateful to Dr. Richard Pederson of Materia, Inc. for providing the THP solution required for removal of the catalyst from the polymers.

References

[1] F. Sanda, T. Endo, Macromol. Chem. Phys. 200 (1999) 2651.
[2] J. Morcellet-Sauvage, M. Morcellet, C. Loucheux, Makromol. Chem. 182 (1981) 949.
[3] J. Morcellet-Sauvage, M. Morcellet, C. Loucheux, Makromol. Chem. 183 (1982) 821.
[4] J. Morcellet-Sauvage, M. Morcellet, C. Loucheux, Makromol. Chem. 183 (1982) 831.
[5] C. Methenitis, J. Morcellet, M. Morcellet, Polym. Bull. 12 (1984) 133.
[6] C. Methenitis, J. Morcellet, M. Morcellet, Polym. Bull. 12 (1984) 141.
[7] C. Methenitis, J. Morcellet, G. Pneumatikakis, M. Morcellet, Macromolecules 27 (1994) 1455.
[8] H. Murata, F. Sanda, T. Endo, Macromolecules 29 (1996) 5535.
[9] R. Katakai, Y. Nakayama, J. Chem. Soc., Chem. Commun. 22 (1977) 805.
[10] H. Murata, F. Sanda, T. Endo, Macromolecules 30 (1997) 2902.
[11] F. Sanda, F. Ogawa, T. Endo, Polymer 39 (1998) 5543.
[12] F. Sanda, J. Kamatani, H. Handa, T. Endo, Macromolecules 32 (1999) 2490.
[13] H. Kudo, F. Sanda, T. Endo, Macromol. Chem. Phys. 200 (1999) 1232.
[14] S.M. Bush, M. North, Polymer 37 (1996) 4649.
[15] S.M. Bush, M. North, Polymer 39 (1998) 933.
[16] S.M. Bush, M. North, S. Sellarajah, Polymer 39 (1998) 2991.
[17] L. Ayres, M.R.J. Vos, P.J.H.M. Adams, I.O. Shklyarevskiy, J.C.M. van Hest, Macromolecules 36 (2003) 5967.
[18] H. Murata, F. Sanda, T. Endo, J. Polymer. Sci., Part A: Polym. Chem. 36 (1998) 1679.
[19] A.C. Birchall, S.M. Bush, M. North, Polymer 42 (2001) 375.
[20] S.B. Garber, J.S. Kingsbury, B.L. Gray, A.H. Hoveyda, J. Am. Chem. Soc. 122 (2000) 8168.
[21] H.D. Maynard, S.Y. Okada, R.H. Grubbs, Macromolecules 33 (2000) 6239.
[22] H.D. Maynard, R.H. Grubbs, Macromolecules 32 (1999) 6917.
[23] S.C.G. Biagini, R.G. Davies, V.C. Gibson, M.R. Giles, E.L. Marshall, M. North, Polymer 42 (2001) 6669.
[24] H.D. Maynard, S.Y. Okada, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 1275.
[25] K.R. Brzezinska, T.J. Deming, Macromolecules 34 (2001) 4348.
[26] K.R. Brzezinska, S.A. Curtin, Macromolecules 35 (2002) 2970.
[27] M. Lindmark-Hamburg, K.B. Wagener, Macromolecules 20 (1987) 2949.
[28] K.B. Wagener, J.G. Nel, J. Konzelman, J.M. Boncella, Macromolecules 23 (1990) 5155.
[29] J.A. Smith, K.R. Brzezinska, D.J. Valenti, K.B. Wagener, Macromolecules 33 (2000) 3781–3794.
[30] J.C. Sworen, J.A. Smith, K.B. Wagener, L.S. Baugh, S.P. Rucker, J. Am. Chem. Soc. 125 (2003) 2228.
[31] A.C. Church, J.H. Pawlow, K.B. Wagener, Macro. Chem. Phys. 204 (2003) 32.
[32] A.C. Church, J.A. Smith, J.H. Pawlow, K.B. Wagener, in: M.E. Rogers, T. Long (Eds.), Synthetic Methods and Step-Growth Polymers, Wiley, New York, 2003, Chapter 8, p. 431.
[33] T.E. Hopkins, J.H. Pawlow, K.S. Deters, S.M. Solivan, J.A. Davis, D.L. Koren, F.J. Gómez, K.B. Wagener, Macromolecules 34 (2001) 7920.
[34] T.E. Hopkins, J.H. Pawlow, F. Tep, K.B. Wagener, Polym. Prep. 43 (2002) 281.
[35] T.E. Hopkins, J.H. Pawlow, K.S. Deters, S.M. Solivan, J.A. Davis, D.L. Koren, F.J. Gómez, K.B. Wagener, Polym. Prep. 41 (2000) 1533.
[36] T.E. Hopkins, K.B. Wagener, Adv. Mat. 14 (2002) 1703.
[37] T.E. Hopkins, K.B. Wagener, Macromolecules 36 (2003) 2206.
[38] T.E. Hopkins, K.B. Wagener, Macromolecules, 2003, in press.
[39] F. Courchay, J.C. Sworen, K.B. Wagener, Macromolecules 36 (2003) 8231.