(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 November 2019 (28.11.2019)

WIPO | PCT

(10) International Publication Number
WO 2019/222852 A1

(51) International Patent Classification:
C08F 32/04 (2006.01) *C09J 145/00* (2006.01)
C09D 5/16 (2006.01)

(21) International Application Number:
PCT/CA2019/050704

(22) International Filing Date:
23 May 2019 (23.05.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/675,465 23 May 2018 (23.05.2018) US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

(54) Title: NOVEL AMINE FUNCTIONALIZED POLYMERS AND METHODS OF PREPARATION

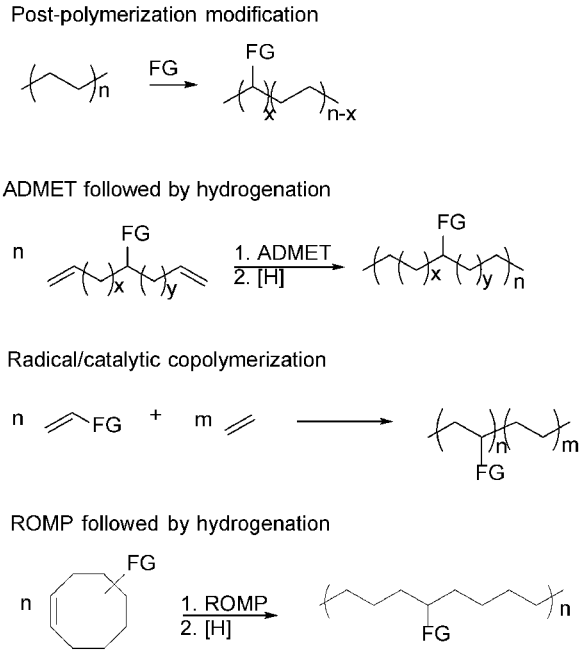


Figure 1

(57) Abstract: This application pertains to amine-functionalized polymers by ring-opening metathesis (ROMP) of amine functionalized cycloalkenes.

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TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

NOVEL AMINE FUNCTIONALIZED POLYMERS AND METHODS OF PREPARATION

RELATED APPLICATIONS

This application claims priority to US patent application no. 62/675,465 filed on May 23, 2018, the contents of which are incorporated herein by reference in their entirety.

FIELD OF THE INVENTION

This disclosure relates to amine functionalized polymers. More particularly, this application relates to novel amine functionalized polymers that can be produced by ring-opening metathesis (ROMP) of amine functionalized cycloalkenes.

BACKGROUND

The catalytic functionalization of alkenes represents a sustainable and efficient method for the synthesis of molecules that are relevant for the chemical, pharmaceutical, and agrochemical industry. Such organic transformations are attractive as valuable building blocks, which are obtained economically from relatively inexpensive starting materials. Notably, the direct C–H functionalization of amines with alkenes, or hydroaminoalkylation, has gained notoriety due to the fact that polysubstituted amines can now be easily obtained in the absence of any protecting/directing groups or photoinitiators.[i]

It is known in the art that group 3 (Sc), 4 (Ti, Zr), and 5 (Nb, Ta) metal complexes may serve as powerful precatalysts in hydroaminoalkylation reactions. For example, *N,O*-chelated pyridonate tantalum based complexes were shown capable of reacting with sterically demanding internal alkenes and facilitate their reaction with secondary anilines. These reactions occurred in a 100% regioselective manner to give the branched products.

Despite the high demand of simple and economical methods for synthesis of amine building blocks in the chemical, pharmaceutical, and agrochemical industry, there are known issues with the catalytic systems presently in use. For instance, hydroaminoalkylation often requires high reaction temperatures (>110 °C) and quite long reaction times (> 20 h), which many catalysts are not robust enough to tolerate. Moreover, substrate compatibility of these catalysts is known to be problematic, especially for internal alkenes such as cyclohexene and cyclooctene. The fact that excess alkene (at least 1.5 equivalents excess) is needed to achieve full substrate conversion remains a challenge as well.

In the case of the catalytic systems, where the active species have a Ta–NMe_2 moiety, the excess alkene is often justified by the deleterious side reactions between the released $HNMe_2$ and the alkene reagents, thereby affecting the stoichiometry of the reaction. The use of $TaMe_3Cl_2$ proved to be successful, as hydroaminoalkylations of amine and alkene substrates was achieved using this catalyst in stoichiometric amounts, but with the caveat that $TaMe_3Cl_2$ is light and temperature sensitive and therewith not suitable for large scale industrial processes. Using a similar approach, the addition of 1-octene to 4-methoxy-*N*-methylaniline at room temperature was achieved with a phosphoramidate supported Ta-Me complex as the catalyst. Although this catalyst demonstrated high reactivity, the phosphoramidate Ta-Me complex actually required excess alkene in order to fully convert the substrates. To improve the stability of early transition metal complexes, steric bulk in the form of e.g. bulky alkyl groups, such as for example CH_2SiMe_3 and CH_2CMe_3, may be complexed to the metal centre. Earlier, Wilkinson and Schrock have described the alkyl tantalum complexes $Ta(CH_2SiMe_3)_3Cl_2$ and $Ta(CH_2CMe_3)_3Cl_2$. However, their activity in hydroaminoalkylation reactions has not been reported in the art.

Martinez et al. (Applied Petrochemical Research, 5: 19-25) have adopted a strategy that utilizes ring-opening metathesis polymerization (ROMP) of amine functionalized, strained cylooctene monomers, followed by hydrogenation, to

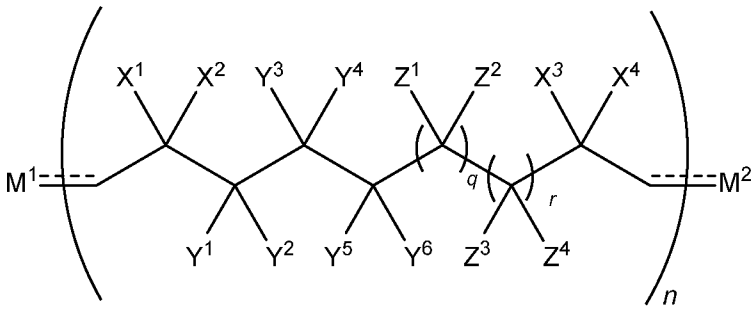
obtain linear polymers analogous to polyethylene with the key introduction of a covalently bound functional group to the backbone. However, the often observed incompatibility of the commercially available Grubbs Catalyst to monomers bearing unprotected amine functional groups limits the usefulness of this approach, as the Grubbs metathesis catalyst is deactivated during ROMP with amine containing cycloalkene monomers.

Thus, the efficient preparation of amine-containing polyolefinic materials remains a synthetic challenge.

SUMMARY OF THE INVENTION

This disclosure is based in part on the discovery that hydroaminoalkylation of a cycloalkene followed by ring-opening polymerization and optionally hydrogenation leads to functionalized polymers comprising at least one amine group. In various embodiments, said amine group introduces useful properties, such as self-healing, adhesive, and/or antimicrobial properties.

Aspects of the disclosure pertain to an amine-functionalized compound of Formula 2:



(Formula 2);

wherein (---) indicates an optional double bond;

wherein each of M^1 and M^2 is independently -OH, a substituted or unsubstituted C_{1-15} alkyl, a substituted or unsubstituted aromatic cycle, a substituted or unsubstituted heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2; and

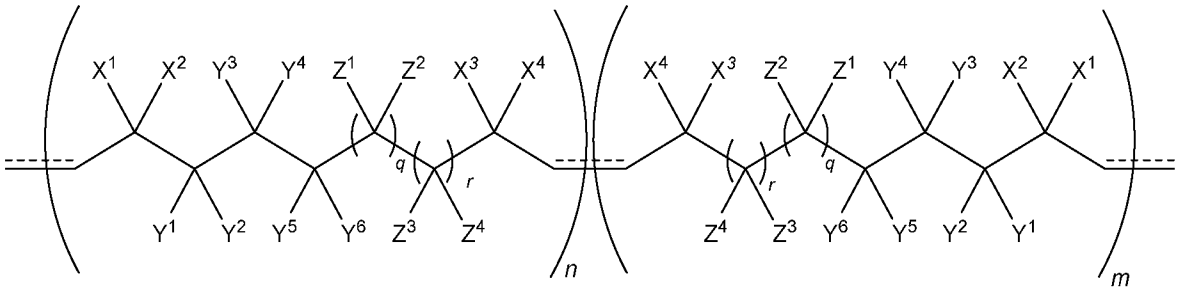
wherein n is a natural number greater than 1.

In various embodiments, the monomers forming the amine-functionalized compound of Formula 2 are connected head to tail, head to head, tail to tail, or any combination thereof.

Aspects of the disclosure pertain to block copolymers comprising: an amine functionalized compound as described above; and a polymer formed by radical or anionic polymerization, for which the functional end-groups M1 and M2 of the amine functionalized compound serves as an initiation point.

A block copolymer prepared comprising: an amine functionalized compound as described above; and at least one additional polymer.

Aspects of the disclosure pertain to a polymer comprising an oligomer of Formula 3:



(Formula 3)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

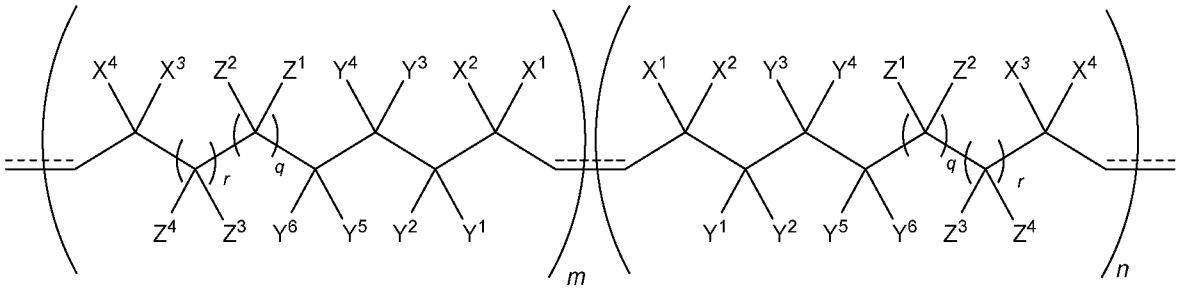
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomers are connected in a head to head fashion.

Aspects of the disclosure pertain to a polymer comprising an oligomer of Formula 4:



(Formula 4)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

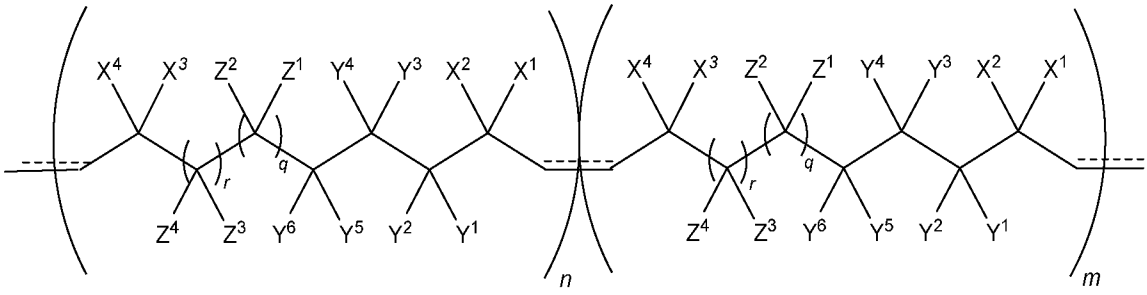
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomers are connected in a tail to tail fashion.

Aspects of the disclosure pertain to a polymer comprising an oligomer of Formula 7:



(Formula 7)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

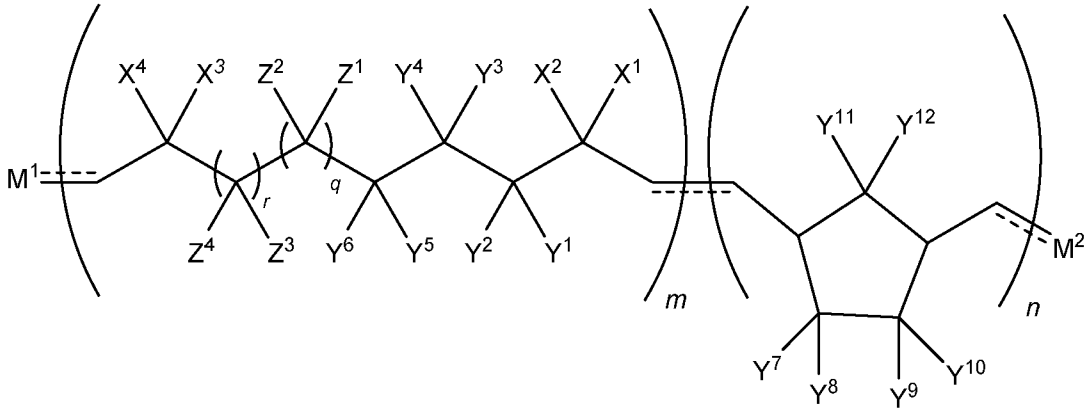
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomers are connected in a head to tail fashion.

Aspects of the disclosure pertain to polymers of Formula X:



(Formula X)

wherein (---) indicates an optional double bond;

wherein each of M^1 and M^2 is independently -OH, a substituted or unsubstituted $C_{1\text{-}15}$ alkyl, a substituted or unsubstituted aromatic cycle, a substituted or unsubstituted heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11}, Y^{12}, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

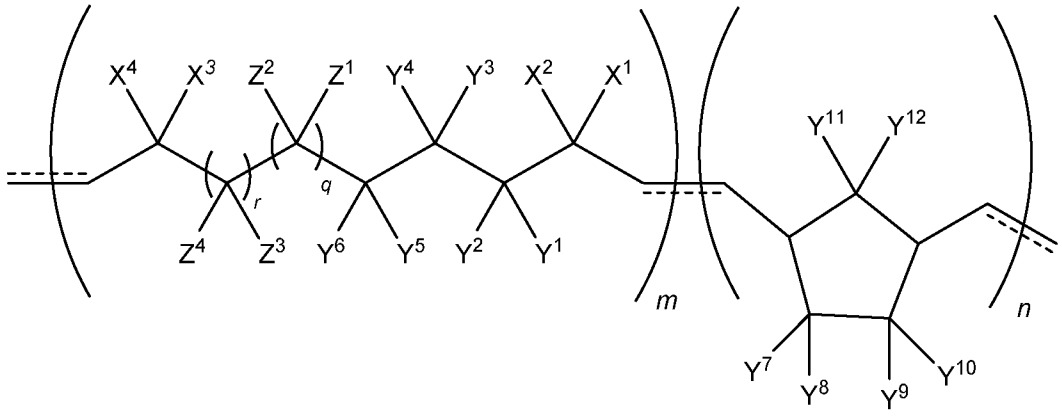
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomers are connected in a head to head fashion.

Aspects of the disclosure pertain to polymers comprising an oligomer of Formula XI:



(Formula XI)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11}, Y^{12}, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

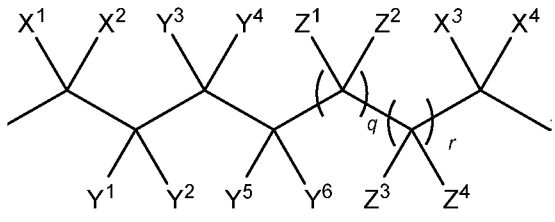
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomers are connected in a head to head fashion.

Aspects of the disclosure pertain to co-polymers comprising a mixture of different amine-functionalized monomer units of Formula 6:



(Formula 6)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Y^7, Y^8 , Y^9, Y^{10}, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

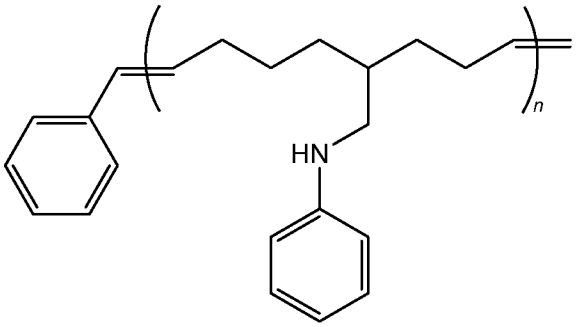
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2; and

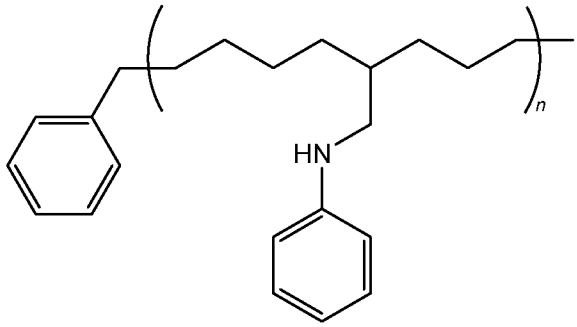
wherein the monomer units are connected in a head to head fashion, head to tail fashion, tail to tail fashion, or any combination thereof.

Aspects of the disclosure pertain to a brush copolymer comprising a polymer as described above and polymeric bristles or brushes, wherein at least one of X^1, X^2, X^3, X^4, Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, Z^4, R', R'', R^1, R^2, R^3, and R^4 serves as an initiation point for subsequent synthesis of polymeric bristles or brushes.

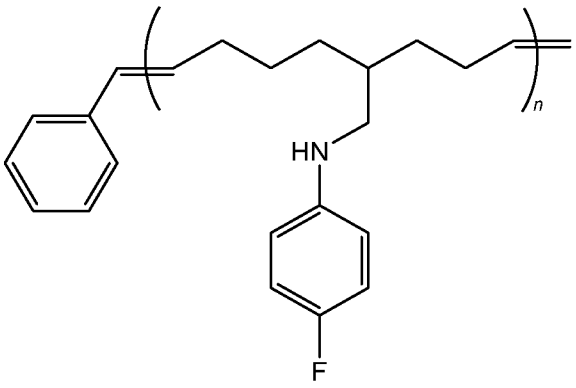
Aspects of the disclosure pertain to an amine functionalized polyalkene or polyalkane, wherein the polyalkene or polyalkane comprises:



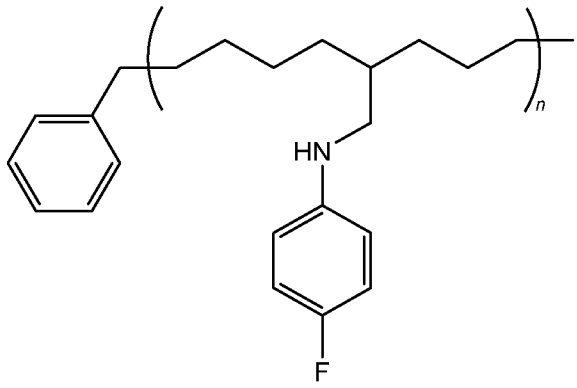
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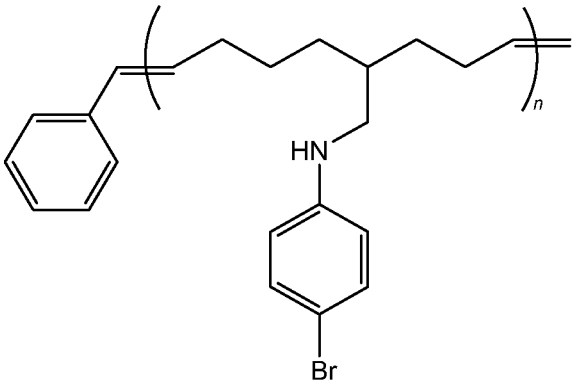
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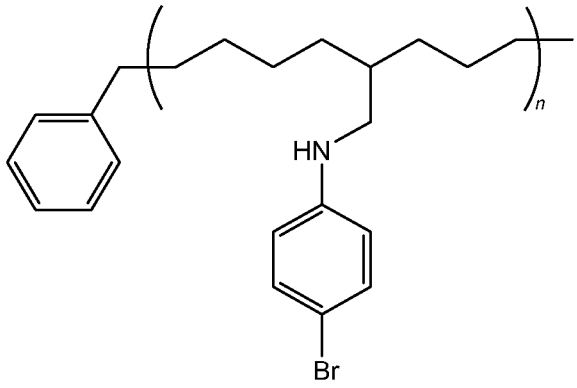


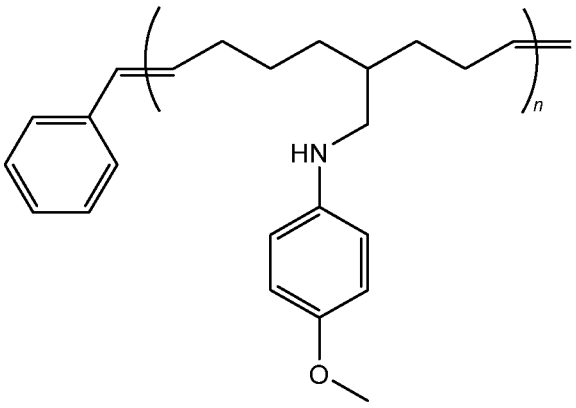
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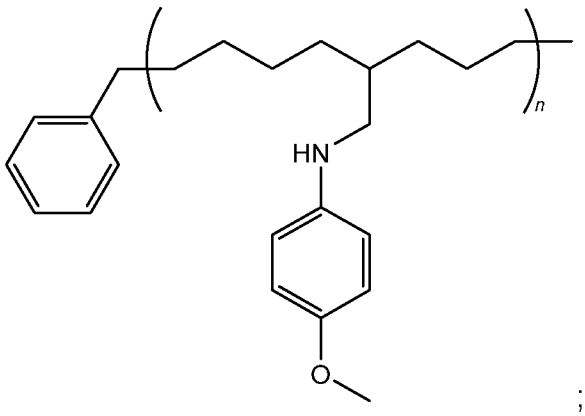


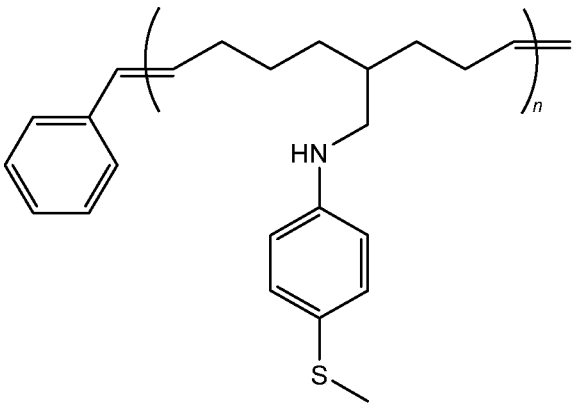
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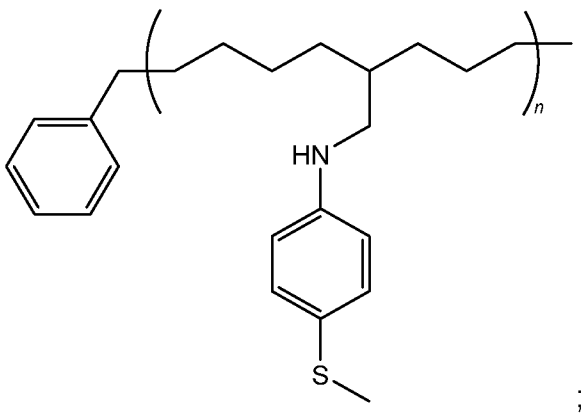

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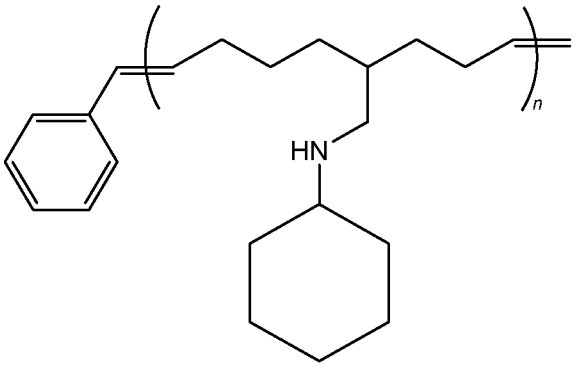

HN
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Br
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HN
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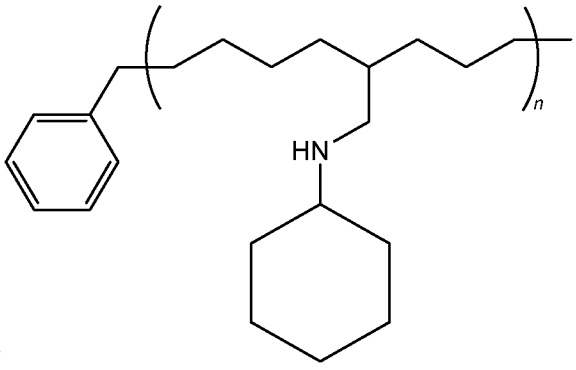

HN
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HN
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HN
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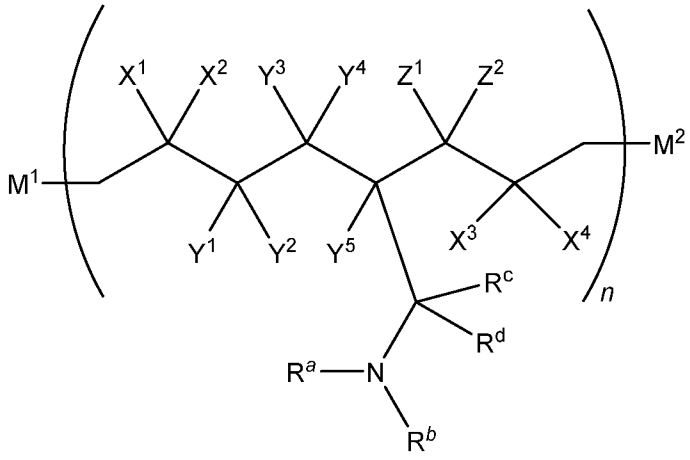
; or



,

wherein *n* is a natural number greater than 1.

Aspects of the disclosure pertain to a polyalkane of Formula 5:



(Formula 5);

wherein each of M^1 and M^2 is independently -OH, a substituted or unsubstituted $C_{1\text{-}15}$ alkyl, a substituted or unsubstituted aromatic cycle, a substituted or unsubstituted heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each of X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each of Y^1, Y^2, Y^3, Y^4, Y^5, Z^1, and Z^2 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'';

wherein each of R' and R'' is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein each of R^a, R^b, R^c, and R^d is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^b and R^a are linked to form a cyclic moiety, or wherein one of R^a and R^b is linked with one of R^c and R^d to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2; and

wherein n is a natural number greater than 1.

In various embodiments, the monomers are connected head to tail, head to head, tail to tail, or any combination thereof.

Polymers, polyalkanes, polyalkenes, and amine-functionalized compounds as described above may be useful as antimicrobial agents. Polymers, polyalkanes, polyalkenes, and amine-functionalized compounds as described above may be useful for reducing fouling. Fouling may include biofouling. Polymers as described above may be useful as adhesive agents. The adhesive agent may for adhering to a substrate. The substrate may be Teflon, glass, or metal.

Polymers, polyalkanes, polyalkenes, and amine-functionalized compounds as described above may be useful as a coating, a compatibilizer, a stabilizer, metal scavenger, a membrane a gasket, an anticoagulant, a drug delivery agent, or a scavenger agent. In various embodiments, the scavenger agent is for binding pollutants during environmental remediation in marine environments. In various embodiments, the pollutants include oil, plastic particles, or a combination thereof. In various embodiments the membrane is an electrolyte membrane or a filtering membrane for water purification.

Aspects of the disclosure pertain to substrates coated with polymers, polyalkanes, polyalkenes, and amine-functionalized compounds as described above.

Other aspects and features of the present invention will become apparent to those ordinarily skilled in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

In drawings which illustrate embodiments of the invention,

Figure 1 is a schematic diagram of general strategy for synthesis of functionalized linear polyethylenes according to embodiments of the disclosure.

Figure 2 is a diagram depicting hydroaminoalkylation of cyclooctadiene to access amine-functionalized cyclooctadiene derivatives according to embodiment of the disclosure. Gravimetric yields reported post-chromatography (%).

Figure 3 is a diagram depicting a ring-opening metathesis polymerization (ROMP) to obtain amine-containing polycyclooctenes according to an embodiment of the disclosure

Figure 4a is a graph of mass loss rate (%/min) as a function of temperature for five polymers of the present disclosure, i.e. “P1”, “P2”, “P3”, “P4”, and “P1H”.

Figure 4b is a graph of weight loss (%) as a function of temperature for five polymers of the present disclosure.

Figure 5 are DSC thermograms of five polymers of the present disclosure.

Figure 6 shows master curves of the storage (G’) and loss (G”) moduli and complex viscosity (|η*|) (symbols) of (a) P1 at 50°C; (b) P2 at 30°; (c) P3 at 50 °C; (d) P4 at 50 °C; (e) P1H at 50 °C.

Figure 7a is a ^{1}H-NMR spectrum (300 MHz) of amine-functionalized cycloalkene “M1” of the present disclosure in $CDCl_3$ at 293 K.

Figure 7b is a ^{13}C-NMR spectrum (75 MHz) of amine-functionalized cycloalkene “M1” of the present disclosure in $CDCl_3$ at 293 K.

Figure 8a is a ^{1}H-NMR spectrum (300 MHz) of amine-functionalized cycloalkene “M2” of the present disclosure in $CDCl_3$ at 293 K.

Figure 8b is a ^{13}C-NMR spectrum (75 MHz) of amine-functionalized cycloalkene "M2" of the present disclosure in $CDCl_3$ at 293 K.

Figure 8c is a ^{19}F-NMR spectrum (282 MHz) of amine-functionalized cycloalkene "M2" of the present disclosure in $CDCl_3$ at 293 K.

Figure 9a is a ^{1}H-NMR spectrum (300 MHz) of amine-functionalized cycloalkene "M3" of the present disclosure in $CDCl_3$ at 293 K.

Figure 9b is a ^{13}C-NMR spectrum (75 MHz) of amine-functionalized cycloalkene "M3" of the present disclosure in $CDCl_3$ at 293 K.

Figure 10a is a ^{1}H-NMR spectrum (300 MHz) of amine-functionalized cycloalkene "M4" of the present disclosure in $CDCl_3$ at 293 K.

Figure 10b is a ^{13}C-NMR spectrum (75 MHz) of amine-functionalized cycloalkene "M4" of the present disclosure in $CDCl_3$ at 293 K.

Figure 11a is a ^{1}H-NMR spectrum (300 MHz) of polymer "P1" of the present disclosure in $CDCl_3$ at 293 K.

Figure 11b is a solid state spectrum of polymer "P1" of the present disclosure in $CDCl_3$ at 293 K.

Figure 12a is a ^{1}H-NMR spectrum (300 MHz) of polymer "P2" of the present disclosure in $CDCl_3$ at 293 K.

Figure 12b is a solid state spectrum of polymer "P2" of the present disclosure in $CDCl_3$ at 293 K.

Figure 13a is a ^{1}H-NMR spectrum (300 MHz) of polymer "P3" of the present disclosure in $CDCl_3$ at 293 K.

Figure 13b is a solid state spectrum of polymer "P3" of the present disclosure in $CDCl_3$ at 293 K.

Figure 14a is a ^{1}H-NMR spectrum (300 MHz) of polymer "P4" of the present disclosure in $CDCl_3$ at 293 K.

Figure 14b is a solid state spectrum of polymer "P4" of the present disclosure in $CDCl_3$ at 293 K.

Figure 15a is a ^{1}H-NMR spectrum (300 MHz) of polymer "P1H" of the present disclosure in $CDCl_3$ at 293 K.

Figure 15b is a solid state spectrum of polymer "P1H" of the present disclosure in $CDCl_3$ at 293 K.

Figure 16 is photographic images of macroscopic self-healing of polymer P1 spheres: (A) dried spheres on PTFE; (B) spheres brought just into contact; (C) and (D) after 24 hrs under ambient conditions (C), spheres no longer show discrete boundary when pulled apart (D).

Figure 17 is a photographic image depicting the adhesive properties of the polymer.

Figure 18 is a graph showing the effect of the ratio of CAN-1 and P2 monomer ratio in copolymer on observed glass transition temperature.

Figure 19 shows master curves of the storage (G') and loss (G") moduli and complex viscosity (|η*|) (symbols) of polymer P2 at 50 °C, co-polymer P(ACN-1-*co*-P2) at 50 °C, and homopolymer of ACN-1 at 50 °C.

DETAILED DESCRIPTION

Definitions

"Catalyst", as used herein, refers to a chemical compound that accelerates a chemical reaction without itself being affected. "Catalyst" may be used interchangeably with terms such as "pre-catalyst", "catalyst system", or "catalytic system". "Catalyst", as used herein, includes catalytic intermediates or species formed *in situ*.

"Group 5 metal" as used herein, refers to the d-electron comprising transition metals listed in the periodic table of the elements as group 5, including transition metals vanadium (V), niobium (Nb), tantalum (Ta), and dubnium (Db).

"Hydroaminoalkylation", as used herein, refers to a reaction between a secondary amine containing moiety and an olefin. A catalyst may often be used to promote such reaction.

"Secondary amine", as used herein, refers to an amine in which the amino group is directly bonded to two C-atoms of any hybridization. The two C-atoms in α-position to the N-atom may be sp^3 hybridized.

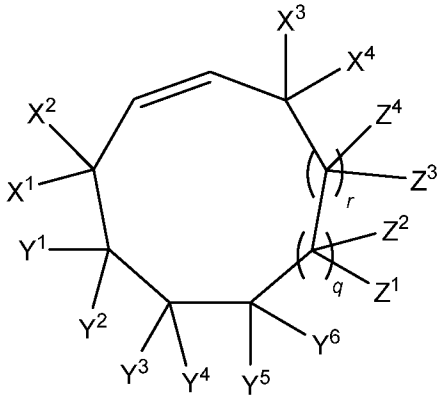
"Olefin" or "alkene", as used herein, refers to an unsaturated hydrocarbon containing one or more pairs of C-atoms linked by a double bond.

"TOF", as used herein, refers to "turnover frequency".

Numeric ranges are inclusive of the numbers defining the range. The word "comprising" is used herein as an open-ended term, substantially equivalent to the phrase "including, but not limited to", and the word "comprises" has a corresponding meaning. As used herein, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a thing" includes more than one such thing. Citation of references herein is not an admission that such references are prior art to an embodiment of the present invention. The invention includes all embodiments and variations substantially as hereinbefore described and with reference to the examples and drawings. Titles, headings, or the like are provided to enhance the reader's comprehension of this document, and should not be read as limiting the scope of the present invention.

Amine-functionalized Cycloalkenes

This disclosure pertains to amine-functionalized cycloalkenes of Formula 1:



(Formula 1);

wherein:

X^1, X^2, X^3, and X^4 independently are H or CH_3;

Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 are each independently: H; a substituted or unsubstituted linear or cyclic alkyl or alkenyl; a substituted or unsubstituted aryl; a substituted or unsubstituted heterocycle; an amine-compatible protection group; -C(=O)R'; or -C(OR')R''; wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group; and

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2.

Each of R^1, R^2, R^3, and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Alternatively, R^3 and R^4 are linked to form a cyclic moiety, wherein each of R^1 and R^2 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Yet alternatively, one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety in which case each of remaining groups of R^1, R^2, R^3, and R^4, as the case may be, is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group.

In various embodiments of the amine-functionalized cycloalkenes, each of X^1, X^2, X^3, and X^4 is H. In various embodiments of the amine-functionalized cycloalkenes, only one of X^1, X^2, X^3, and X^4 is CH_3. In various embodiments of the amine-functionalized cycloalkenes, each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3. In various embodiments of the amine-functionalized cycloalkenes, at least one of R^1 and R^2 is H. In various embodiments of the amine-functionalized cycloalkenes, at least one of R^3 and R^4 is H.

In various embodiments of the amine-functionalized cycloalkenes, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR3R4$, at least one ring-carbon atom adjacent to the ring-carbon atomsubstituted with $-CR^1R^2–NR^3R^4$ is substituted with two H atoms. In various embodiments, Y^3 is $-CR^1R^2–NR^3R^4$, and : eachY^1 and Y^2 is H; each of Y^5 and Y^6 is H; or each of each Y^1, Y^2, Y^5, and Y^6 is H.

In various embodiments of the amine-functionalized cycloalkenes, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is further substituted with a hydrogen atom. In various embodiments, Y^3 is $-CR^1R^2–NR^3R^4$ and Y^4 is H.

This disclosure further pertains to polymers prepared by the ring opening metathesis polymerization (ROMP) of an amine-functionalized cycloalkene as described above.

This disclosure further pertains to polymers prepared by the ring opening metathesis polymerization (ROMP) of a mixture of different amine-functionalized cycloalkenes as described above. In various embodiments, the mixture comprises amine-functionalized cycloalkenes that are regioisomers. In various embodimetns, the position of $-CR^1R^2–NR^3R^4$ groups on adjacent carbons is swapped between regioisomers.

In various embodiments, the monomer units are polymerized head-to-head, head-to-tail, tail-to-tail, or any combination thereof.

In various embodiments, the polymer is hydrogenated to remove double bonds in the polymer.

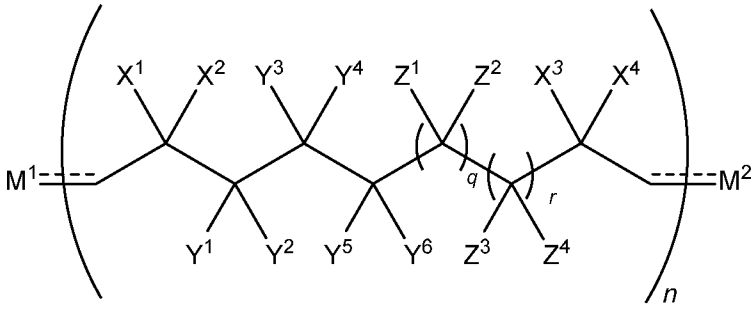
In various embodiments, the polymer has self-healing properties. In various embodiments, the polymer has adhesive properties. In various embodiments, the polymer has antimicrobial activity.

Polymers as described above may be useful as antimicrobial agents. Polymers as described above may be useful for reducing fouling. Fouling may include biofouling. Polymers as described above may be useful as adhesive agents. The adhesive agent may for adhering to a substrate. The substrate may be Teflon, glass, or metal.

Polymers as described above may be useful as a coating, a compatibilizer, a stabilizer, metal scavenger, a membrane a gasket, an anticoagulant, a drug delivery agent, or a scavenger agent. In various embodiments, the scavenger agent is for binding pollutants during environmental remediation in marine environments. In various embodiments, the pollutants include oil, plastic particles, or a combination thereof. In various embodiments the membrane is an electrolyte membrane or a filtering membrane for water purification.

Amine-functionalized compounds

This disclosure further pertains to amine-functionalized compounds of Formula 2:



(Formula 2);

wherein (---) indicates an optional double bond;

wherein each of M^1 and M^2 is independently -OH, a substituted or unsubstituted C_{1-15} alkyl, a substituted or unsubstituted aromatic cycle, a substituted or unsubstituted heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2; and

wherein n is a natural number.

Each of R^1, R^2, R^3, and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Alternatively, R^3 and R^4 are linked to form a cyclic moiety, wherein each of R^1 and R^2 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Yet alternatively, one of R^3 and R^4 is linked with one of R^1 and R^2 to

form a cyclic moiety in which case each of remaining groups of R^1, R^2, R^3, and R^4, as the case may be, is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group.

In various embodiments, the monomer units forming the amine-functionalized compound of Formula 2 are connected head to tail, head to head, tail to tail, or any combination thereof.

In various embodiments, n is in the range of 3 to 1000. In various embodiments, n is in the range of 3 to 1000. In various embodiments, n is in the range of 3 to 600. In various embodiments, n is in the range of 5 to 400.

In various embodiments, each of X^1, X^2, X^3, and X^4 is H. In various embodiments, only one of X^1, X^2, X^3, and X^4 is CH_3. In various embodiments, each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3. In various embodiments, at least one of R^1 and R^2 is H. In various embodiments, at least one of R^3 and R^4 is H.

In various embodiments, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR3R4$, at least one ring-carbon atom adjacent to the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is substituted with two H atoms. For example, where Y^3 is $-CR^1R^2–NR^3R^4$: eachY^1 and Y^2 is H; each of Y^5 and Y^6 is H; or each of each Y^1, Y^2, Y^5, and Y^6 is H.

In various embodiments, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is further substituted with a hydrogen atom. For example, where Y^3 is $-CR^1R^2–NR^3R^4$, Y^4 is H.

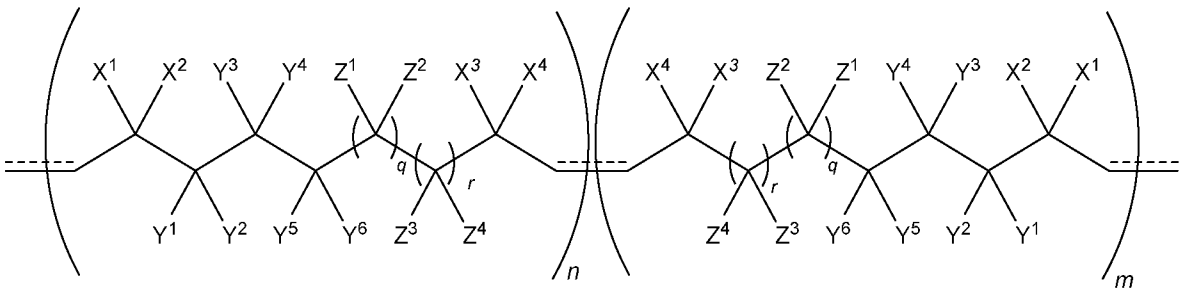
Amine-functionalized compounds as described above may be useful as antimicrobial agents. Amine-functionalized compounds as described above may be useful for reducing fouling. Fouling may include biofouling. Amine-functionalized compounds as

described above may be useful as adhesive agents. The adhesive agent may for adhering to a substrate. The substrate may be Teflon, glass, or metal.

Amine-functionalized compounds as described above may be useful as a coating, a compatibilizer, a stabilizer, metal scavenger, a membrane a gasket, an anticoagulant, a drug delivery agent, or a scavenger agent. In various embodiments, the scavenger agent is for binding pollutants during environmental remediation in marine environments. In various embodiments, the pollutants include oil, plastic particles, or a combination thereof. In various embodiments the membrane is an electrolyte membrane or a filtering membrane for water purification. .

Polymers of formulae 3, 4, and 7

This disclosure further pertains to polymers comprising an oligomer of Formula 3:



(Formula 3)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

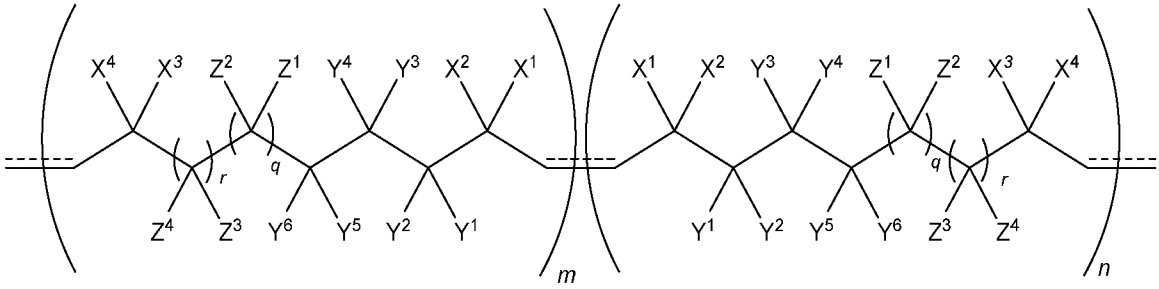
wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein r = 0 or 1 and q = 0 or 1, wherein $r + q$ = 0, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomers are connected in a head to head fashion.

This disclosure further pertains to polymers comprising an oligomer of Formula 4:



(Formula 4)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

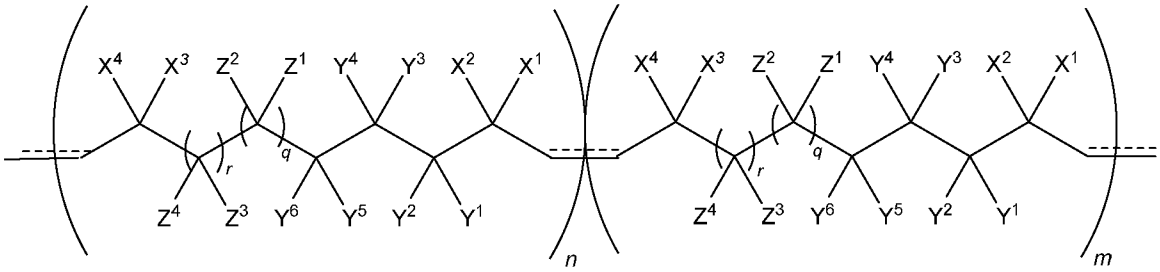
wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein r = 0 or 1 and q = 0 or 1, wherein $r + q$ = 0, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomers are connected in a tail to tail fashion.

This disclosure further pertains to polymers comprising an oligomer of Formula 7:



(Formula 7)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomers are connected in a head to tail fashion.

For oligomers of Formulae 3, 4, and 7, each of R^1, R^2, R^3, and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Alternatively, R^3 and R^4 are linked to form a cyclic moiety, wherein each of R^1 and R^2 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Yet alternatively, one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety in which case each of remaining groups of R^1, R^2, R^3, and R^4, as the case may be, is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or

unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group.

While Formulae 3, 4, and 7 currently specify that the monomers are connected in a head to tail fashion, head to head fashion, or a tail to tail fashion, as the case may be, the skilled person will understand that the monomers could be connected in any combination thereof.

In various embodiments of polymers comprising an oligomer of Formulae 3, 4, and 7, n+m is in the range of 3 to 1000. In various embodiments, n is in the range of 3 to 1000. In various embodiments, n+m is in the range of 3 to 600. In various embodiments, n+m is in the range of 5 to 400.

In various embodiments of polymers comprising an oligomer of Formulae 3, 4, and 7, the polymer is capped with -OH, a substituted or unsubstituted C_{1-15} alkyl, a substituted or unsubstituted aromatic cycle, a substituted or unsubstituted heterocycle, a functional end-group suitable for ring opening metathesis polymerization, or any combination thereof.

In various embodiments of polymers comprising an oligomer of Formulae 3, 4, and 7, each of X^1, X^2, X^3, and X^4 is H. In various embodiments of polymers of Formulae 3 and 4, only one of X^1, X^2, X^3, and X^4 is CH_3. In various embodiments of polymers of Formulae 3 and 4, each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3. In various embodiments of polymers of Formulae 3 and 4, at least one of R^1 and R^2 is H. In various embodiments of polymers of Formulae 3 and 4, at least one of R^3 and R^4 is H.

In various embodiments of polymers comprising an oligomer of Formulae 3, 4, and 7, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR3R4$, at least one ring-carbon atom adjacent to the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is substituted

with two H atoms. For example, when Y^3 is $-CR^1R^2–NR^3R^4$: eachY^1 and Y^2 is H; each of Y^5 and Y^6 is H; or each of each Y^1, Y^2, Y^5, and Y^6 is H.

In various embodiments of polymers comprising an oligomer of Formulae 3, 4, and 7, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is further substituted with a hydrogen atom. For example, where Y^3 is $-CR^1R^2–NR^3R^4$, Y^4 is H.

In various embodiments, the polymer has self-healing properties. In various embodiments, the polymer has adhesive properties. In various embodiments, the polymer has antimicrobial activity.

Aspects of the disclosure also pertain to block copolymers prepared by ring opening metathesis polymerization of: an amine-functionalized cycloalkene as described above; and at least one additional cycloalkene. The at least one additional cycloalkene includes norbornene or an arylamine substituted norbornene.

Aspects of the disclosure also pertain to block copolymers comprising: an amine functionalized compound as described above; and a polymer formed by radical or anionic polymerization, for which the functional end-group M of the amine functionalized compound serves as an initiation point.

Aspects of the disclosure also pertain to brush copolymers comprising a polymer as described above and polymeric bristles or brushes, wherein at least one of X^1, X^2, X^3, X^4, Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, Z^4, R', R'', R^1, R^2, R^3, and R^4 serves as an initiation point for subsequent synthesis of polymeric bristles or brushes.

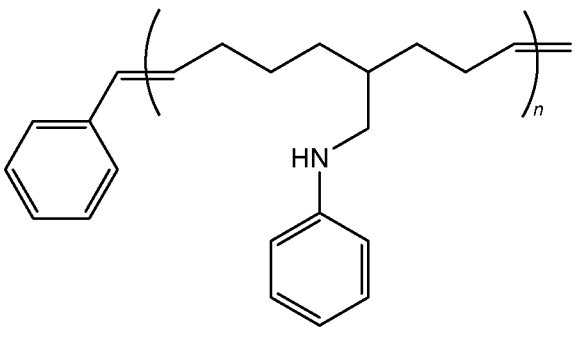
Aspects of the disclosure also pertain to random copolymers prepared by ring opening metathesis polymerization of: an amine-functionalized cycloalkene as described above; and at least one additional cycloalkene. The at least one additional cycloalkene includes includes norbornene or an arylamine substituted norbornene.

Polymers as described above may be useful as antimicrobial agents. Polymers as described above may be useful for reducing fouling. Fouling may include biofouling. Polymers as described above may be useful as adhesive agents. The adhesive agent may for adhering to a substrate. The substrate may be Teflon, glass, or metal.

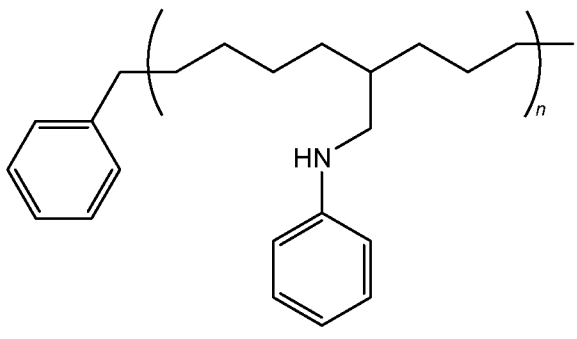
Polymers as described above as described above may be useful as a coating, a compatibilizer, a stabilizer, metal scavenger, a membrane a gasket, an anticoagulant, a drug delivery agent, or a scavenger agent. In various embodiments, the scavenger agent is for binding pollutants during environmental remediation in marine environments. In various embodiments, the pollutants include oil, plastic particles, or a combination thereof. In various embodiments the membrane is an electrolyte membrane or a filtering membrane for water purification.

Amine Functionalized Polyalkenes and Polyalkanes

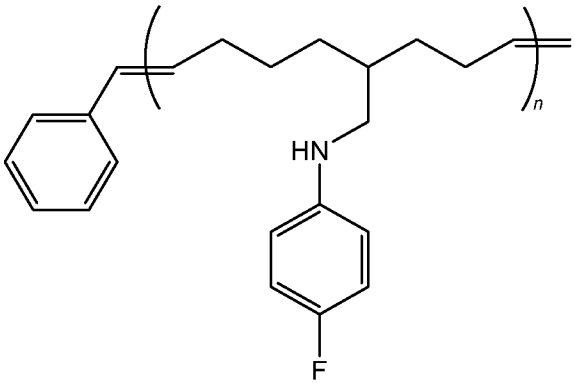
Aspects of the disclosure also pertain to an amine functionalized polyalkene or polyalkane, wherein the polyalkene or polyalkane comprises:

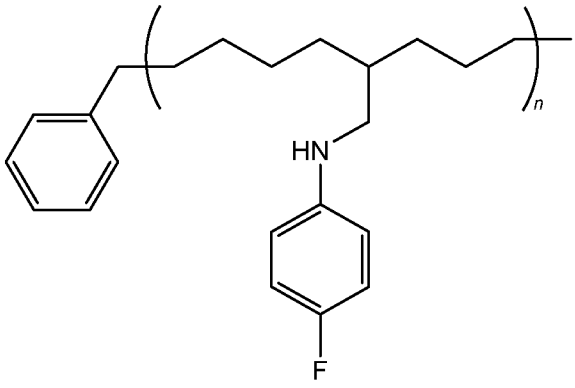


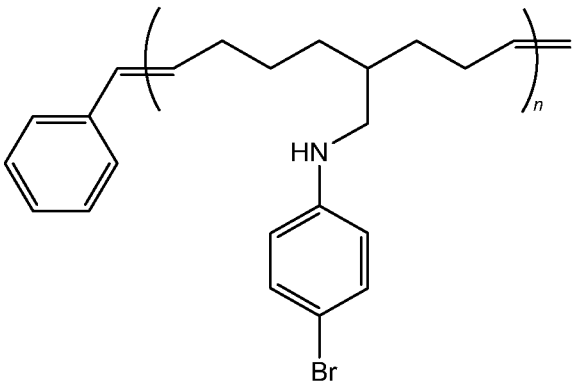
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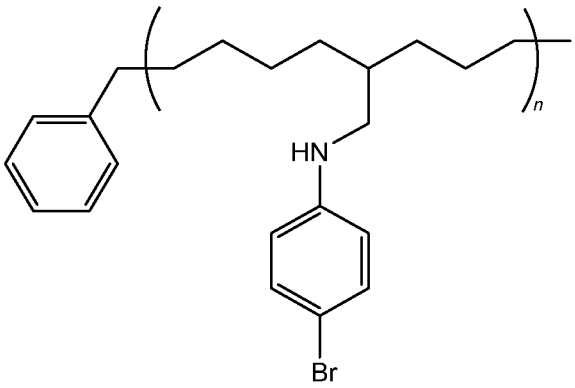


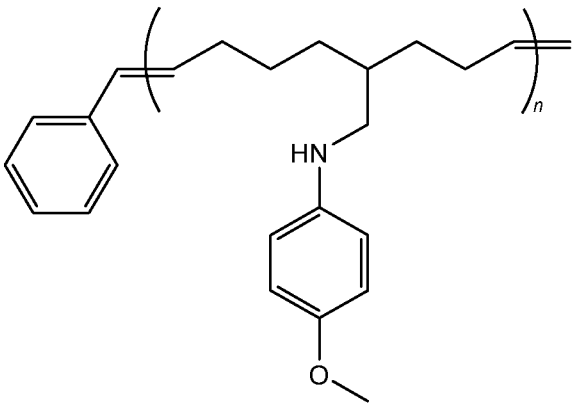
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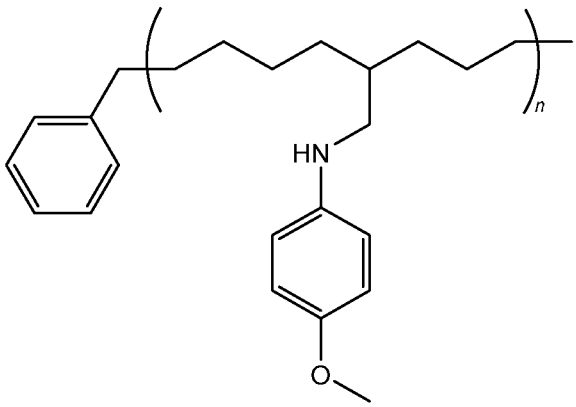

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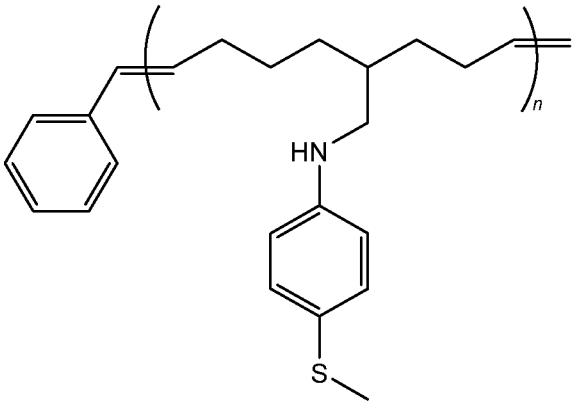

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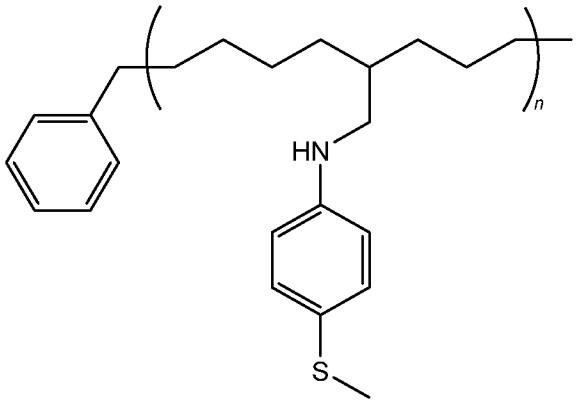

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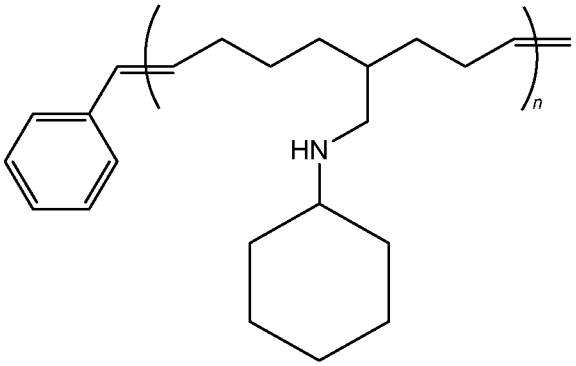

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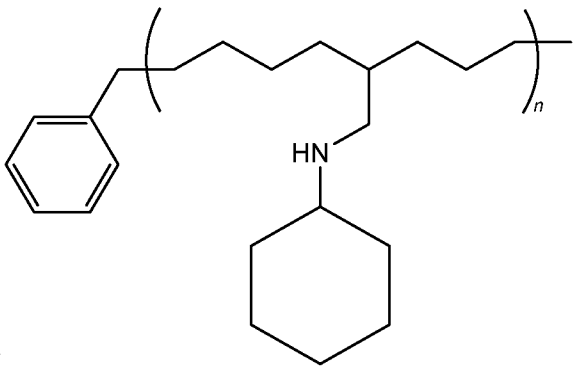
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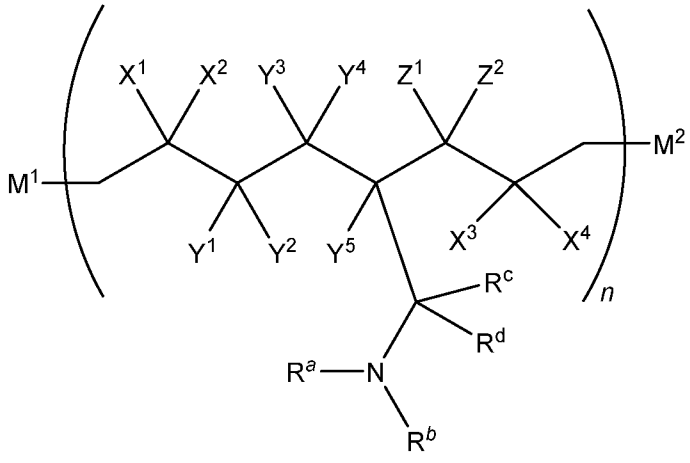


,

wherein *n* is a natural number greater than 1.

In various embodiments, n is in the range of 3 to 1000. In various embodiments, n is in the range of 3 to 600. In various embodiments, n is in the range of 5 to 400.

Aspects of the disclosure also pertain to polyalkanes of Formula 5:



(Formula 5);

wherein each of M^1 and M^2 independently is -OH, a substituted or unsubstituted C_{1-15} alkyl, a substituted or unsubstituted aromatic cycle, a substituted or unsubstituted heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each of X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each of Y^1, Y^2, Y^3, Y^4, Y^5 , Z^1, and Z^2 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'';

wherein each of R' and R'' is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein r = 0 or 1 and q = 0 or 1, wherein $r + q$ = 0, 1, or 2; and

wherein n is a natural greater than 1.

Each of R^a, R^b, R^c, and R^d is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Alternatively, R^b and R^a are linked to form a cyclic moiety, wherein each of R^c, and R^d is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Yet alternatively, one of R^a and R^b is linked with one of R^c and R^d to form a cyclic moiety in which case each of remaining groups of R^a, R^b, R^c, and R^d, as the case may be, is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group.

In various embodiments, at least one of R^b and R^a is H. In various embodiments, one of R^b and R^a is H. In various embodiments, R^b is $-CR^1R^2–NR^3R^4$, wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or

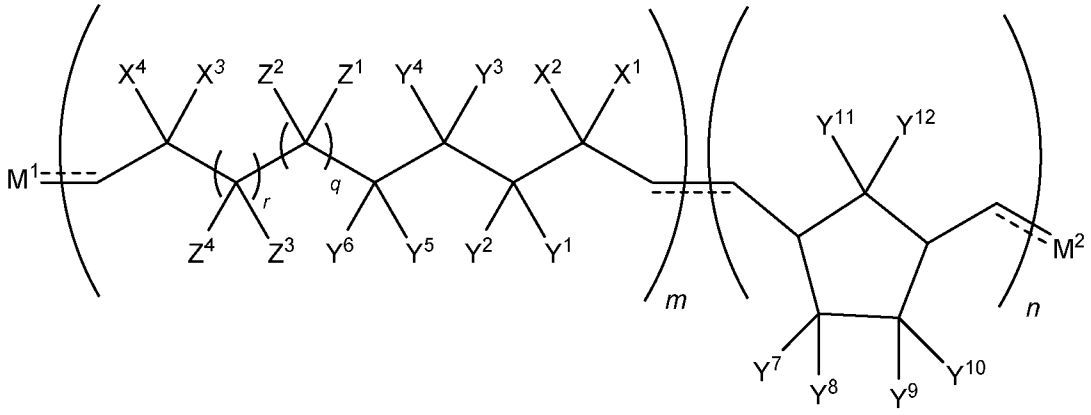
alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group.

In various embodiments, the monomer units forming the polyalkanes of Formula 5 are connected head to tail, head to head, tail to tail, or any combination thereof.

In various embodiments, n is in the range of 3 to 1000. In various embodiments, n is in the range of 3 to 600. In various embodiments, n is in the range of 5 to 400.

In various embodiments, each of X^1, X^2, X^3, and X^4 is H. In various embodiments, only one of X^1, X^2, X^3, and X^4 is CH_3. In various embodiments, only one of X^1, X^2, X^3, and X^4 is CH_3. In various embodiments, each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3. In various embodiments, at least one of R^1 and R^2 is H. In various embodiments, at least one of R^3 and R^4 is H.

Aspects of the disclosure pertain to co-polymers of Formula X:



(Formula X)

wherein (---) indicates an optional double bond;

wherein each of M^1 and M^2 is independently -OH, a substituted or unsubstituted $C_{1\text{-}15}$ alkyl, a substituted or unsubstituted aromatic cycle, a substituted or

unsubstituted heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11}, Y^{12}, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2; and

wherein n and m are natural numbers; and

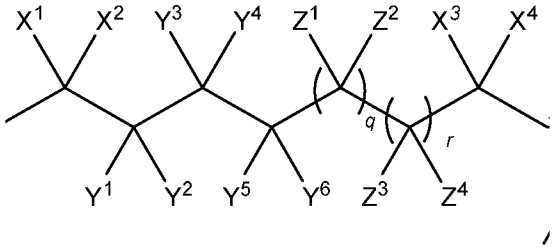
Each of R^1, R^2, R^3, and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Alternatively, R^3 and R^4 are linked to form a cyclic moiety, wherein each of R^1 and R^2 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Yet alternatively, one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety in which case each of remaining groups of R^1, R^2, R^3, and R^4, as the case may be, is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group.

In various embodiments, the monomer units forming the co-polymers of Formula X are connected head to tail, head to head, tail to tail, or any combination thereof. In various embodiments, the monomer units are connected in a head to head fashion.

In various embodiments of polymers of Formulae X, n+m is in the range of 3 to 1000. In various embodiments, n+m is in the range of 3 to 600. In various embodiments, n+m is in the range of 5 to 400.

In various embodiments, each of X^1, X^2, X^3, and X^4 is H. In various embodiments, only one of X^1, X^2, X^3, and X^4 is CH_3. In various embodiments, each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3. In various embodiments, at least one of R^1 and R^2 is H. In various embodiments, at least one of R^3 and R^4 is H. In various embodiments, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, at least one ring-carbon atom adjacent to the ring-carbon atomsubstituted with $-CR^1R^2–NR^3R^4$ is substituted with two H atoms. In various embodiments, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is further substituted with a hydrogen atom.

Aspects of the disclosure pertain to co-polymers comprising a mixture of different amine-functionalized monomer units of Formula 6:



(Formula 6)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible

protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group; and

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2.

Each of R^1, R^2, R^3, and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Alternatively, R^3 and R^4 are linked to form a cyclic moiety, wherein each of R^1 and R^2 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group. Yet alternatively, one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety in which case each of remaining groups of R^1, R^2, R^3, and R^4, as the case may be, is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group.

In various embodiments, the monomer units of formula 6 forming the co-polymer are connected head to tail, head to head, tail to tail, or any combination thereof.

In various embodiments the number of monomer units of formula 6 forming the polymer is in the range of 3 to 1000. In various embodiments the number of monomer units of formula 6 forming the polymer is in the range of 3 to 600. In various embodiments, n+m is in the range of 5 to 400.

In various embodiments, each of X^1, X^2, X^3, and X^4 is H. In various embodiments, only one of X^1, X^2, X^3, and X^4 is CH_3. In various embodiments, each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3. In various embodiments, at least one of R^1 and R^2 is H. In various embodiments, at least one of R^3 and R^4 is H. In various embodiments, when

Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, at least one ring-carbon atom adjacent to the ring-carbon atomsubstituted with $-CR^1R^2–NR^3R^4$ is substituted with two H atoms. In various embodiments, when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is further substituted with a hydrogen atom.

Various polyalkene or polyalkanes as described above may be useful as an antimicrobial agent. Various polyalkene or polyalkanes as described above may be useful for reducing fouling. Fouling may include biofouling. Various polyalkene or polyalkanes as described above may be useful as an adhesive agent. The adhesive agent may for adhering to a substrate. The substrate may be Teflon, glass, or metal.

Various polyalkene or polyalkanes as described above may be useful as a coating, a compatibilizer, a stabilizer, metal scavenger, a membrane a gasket, an anticoagulant, a drug delivery agent, or a scavenger agent. In various embodiments, the scavenger agent is for binding pollutants during environmental remediation in marine environments. In various embodiments, the pollutants include oil, plastic particles, or a combination thereof. In various embodiments the membrane is an electrolyte membrane or a filtering membrane for water purification.

Substrates

Aspects of the disclosure pertain to a substrate coated with a polyalkene or polyalkane, amine-functionalized compound, or polymer as described above.
In various embodiments, the substrate reduces biofouling.

Methods of Preparing Polymers

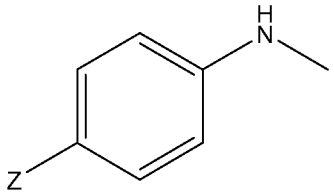
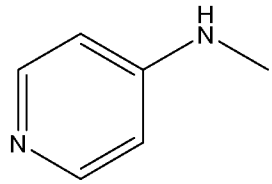
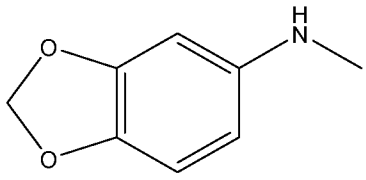
The novel amine-containing polymers disclosed herein are enabled by the presently developed and disclosed catalytic synthesis using a combination of hydroaminoalkylation and ring-opening metathesis polymerization (ROMP) using

Grubbs second generation catalyst ("G2"). This preparation transforms commercially available starting materials to a rich and diverse class of novel polymers without the use of additives or directing/protecting groups, thereby minimizing waste generation. The development of this atom-economic, gram-scale preparation was conducted for a series of secondary aryl-amine containing cyclooctene derivatives. The preparation of such amine-functionalized polyethylene analogs comprises two, and optionally three, steps. First, monomers are synthesized by the catalytic hydroaminoalkylation of a cycloalkene, e.g. cyclooctadiene, an alkene aminoalkylation reaction that proceeds in an atom-economic fashion. This methodology avoids amine directing or protecting groups (see Figure 2). Secondly, these amine-containing monomers are then polymerized using ROMP to provide linear poly(cyclooctene) with pendant secondary amines (see Figure 3). Thirdly and optionally, subsequent alkene hydrogenative reduction then furnished amine functionalized polyethylene in which every eighth carbon contains a secondary amine functional group.

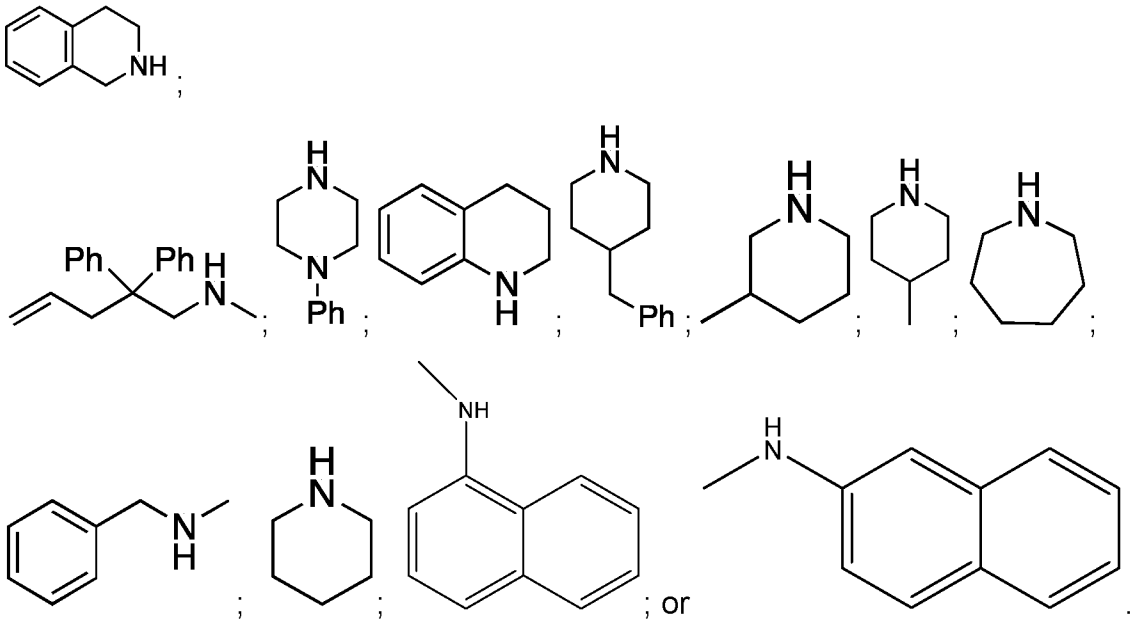
Aspects of the disclosure pertain to methods of preparing polyalkanes of Formula 5 as defined above, methods of preparing amine-functionalized compounds as defined above, methods of preparing a polyalkene or polyalkane of as defined above, or methods of preparing a polymer comprising an oligomer of Formula 3, Formula 4, or Formula 7 as defined above. These methods comprise: (i) contacting a cycloalkene with a secondary amine containing moiety in the presence of a group 5 metal based catalytic complex to obtain a hydroaminoalkyl-substituted cycloalkene; (ii) performing ring-opening metastasis polymerization of said hydroaminoalkyl-substituted cycloalkene to obtain an amine-functionalized polyalkene; and, optionally, (iii) hydrogenating said amine-functionalized polyalkene from step (ii) to obtain the amine-functionalized polyalkane of Formula 5, the polyalkene, polyalkane, or polymer as the case may be.

Aspects of the disclosure further pertain to a method of preparing an amine-functionalized cycloalkene of Formula 1, said method comprising: (i) contacting a

cycloalkene with a secondary amine containing moiety in the presence of a group 5 metal based catalytic complex to obtain a hydroaminoalkyl-substituted cycloalkene.

In various embodiments of the methods described above, the secondary amine-containing moiety comprises at least two α-sp^3 hybridized C-H bonds. In various embodiments, the secondary amine-containing moiety is a C_4-C_{100} linear, branched, or cyclic alkyl, optionally substituted and/or comprising heterotaoms. In various embodiments, the secondary amine-containing moiety is substituted with a halogen, an ether, another amine, an alkyl, an alkene, an acetal, a phosphine, an amide, an alkyne, an imine, a nitrile, an isocyanide, an epoxide, a boronic acid ester; a phenyl that optionally may be substituted and/or part of a condensed ring system, or any combination thereof. In various embodiments, the secondary amine-containing moiety is: pyrrolidine; piperidine; ; ; or ;

wherein Z is H, OCF_3,F, Cl, Br, I, or OCH_3. In various embodiments, the secondary amine-containing moiety is:

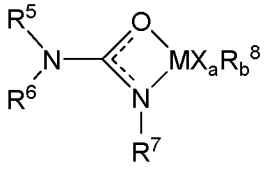


Cycloalkenes

In various embodiments of the methods disclosed above, the cycloalkene contacted with the secondary amine containing moiety is cyclooctadiene. However, the skilled person would understand other cycloalkenes could be used in the context of this disclosure.

Catalyst complexes

In various embodiments of the methods disclosed above, the group 5 metal based catalytic complex has the structure of Formula I:



(Formula I)

wherein:

R^5 and R^6 are:

each independently: H; a C_1–C_{40} substituted or unsubstituted linear, branched or cyclic alkyl or alkenyl or alkynyl; a substituted or unsubstituted aryl; or a substituted or unsubstituted heterocyclic group; or

bonded together thereby forming, together with the nitrogen atom they are both bound to, a heterocycle;

R^7:

is H; a C_1–C_{40} substituted or unsubstituted linear, branched or cyclic alkyl or alkenyl or alkynyl; or a substituted or unsubstituted aryl; or a substituted or unsubstituted heterocyclic group; or

bonded together with R^5 and/or R^6 to form a heterocycle.

M is a group 5 metal;

a = 0 to 4 and *b* = 0 to 4, wherein the sum of *a* and *b* is 4;

each X is a halogen substituent;

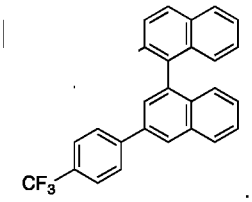
each R^8 is independently: H; or a C_1-C_{20} substituted or unsubstituted, linear, branched or cyclic alkyl, optionally comprising heteroatoms. In various embodiments, each X is independently Cl or Br. In various embodiments, a= 1 or a=2.

In various embodiments, R^5 and R^6 are each independently: methyl; ethyl; isopropyl; cyclohexyl; phenyl; 2,6-dimethyl phenyl; 2,4,6-trimethyl phenyl; 4-methyl phenyl; optionally substituted piperidine; optionally substituted pyrrolidine; or substituted morpholine.

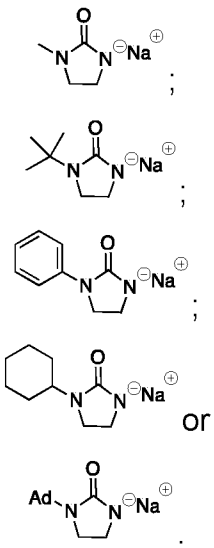
In various embodiments, R^5 and R^6 are bonded together to form, together with the nitrogen atom they are both bound to, a 6-membered ring, which optionally may be substituted.

In various embodiments: R^5 and R^6 are each phenyl; R^5 is phenyl and R^6 is isopropyl; R^5 and R^6 are bonded together to form, together with the nitrogen atom they are both bound to, piperidinyl; R^5 is phenyl and R^6 is methyl; R^5 is methyl and R^6 is 1-phenylethyl; R^5 is methyl and R^6 is isopropyl; or R^5 is phenyl and R^6 is diphenylmethyl.

In various embodiments, R^7 is: phenyl; 2,6-dimethyl phenyl; 2,6-di(isopropyl) phenyl; or



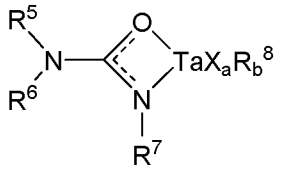
In various embodiments, R^7 is bonded together with R^5 and/or R^6 to form, together with each of the nitrogen atoms they are bound to, a 5-membered ring, which optionally may be substituted.R^7 is bonded together with R^5 and/or R^6, and each of the nitrogen atoms they are bound to, to form:



In various embodiments, R^8 is $-CH_3$, $-NMe_2$, $-CH_2C(CH_3)_3$, or $-CH_2Si(CH_3)_3$.

In various embodiments, M is tantalum (Ta), niobium (Nb), or vanadium (V).

In various embodiments of the methods disclosed above, the group 5 metal based catalytic complex has the structure of Formula II



(Formula II);

wherein:

R^5 and R^6 are:

each independently: methyl; ethyl; isopropyl; cyclohexyl; phenyl; 2,6-dimethyl phenyl; 2,4,6-trimethyl phenyl; 4-methyl phenyl; optionally substituted piperidine; optionally substituted pyrrolidine; or substituted morpholine; or

bonded together to form, together with the nitrogen atom they are both bound to, a 6-membered ring, which optionally may be substituted;

R^7 is:

phenyl; 2,6-dimethyl phenyl; or 2,6-di(isopropyl) phenyl; or

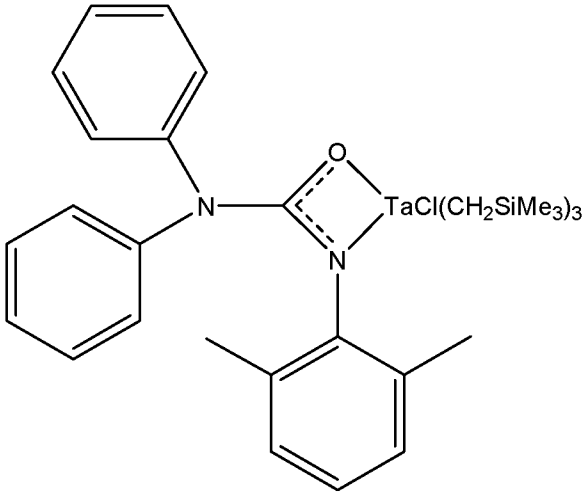
bonded together with R^5 and/or R^6 to form, together with each of the nitrogen atoms they are bound to, a 5-membered ring, which optionally may be substituted;

each X is independently Cl or Br;

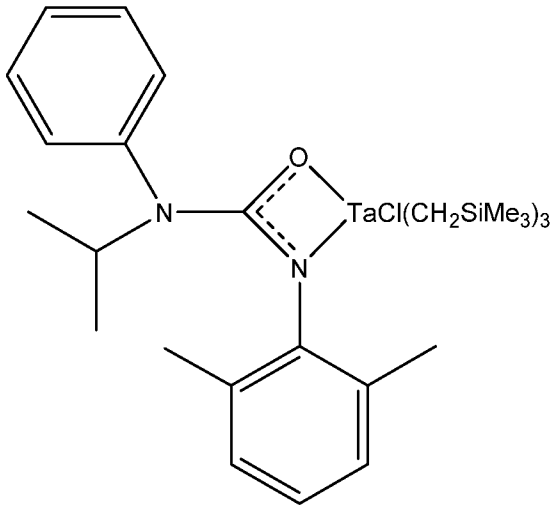
a =1 or 2 and *b* =(4 - *a*); and

R^8 is $-CH_3$, $-NMe_2$, $-CH_2C(CH_3)_3$, or $-CH_2Si(CH_3)_3$.

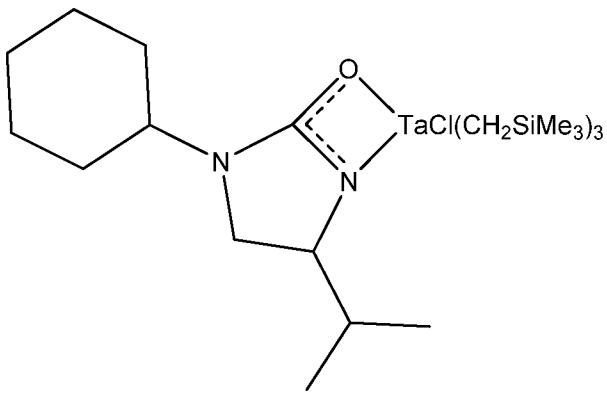
In various embodiments, the group 5 metal based catalytic complex is:



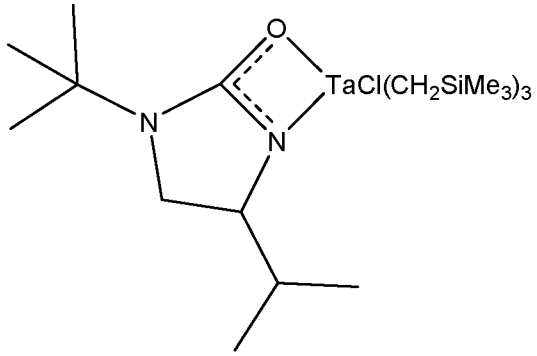
(Formula III);



(Formula IV);



(Formula V);



(Formula VI); or

Chlorotris(dimethylamido)(κ^2-*N,O*-3-methyl-2-pyridonato)tantalum(V).

The reaction conditions may include a reaction temperature in the range from 50°C to 200°C, a reaction temperature in the range from 75°C to 165°C, a reaction temperature in the range from 90°C to 150°C, a reaction temperature in the range from range from 110°C to 130°C, a reaction temperature of about 110°C, or a reaction temperature of about 130°C.

The reaction conditions may include a solvent. The solvent may be non-protic. The solvent may be toluene, benzene, or a mixture thereof.

The secondary amine-containing moiety and said cycloalkene may be provided in a stoichiometric ratio from 0.1 to 1.5. The secondary amine-containing moiety and said cycloalkene may be provided in a stoichiometric ratio of about 1:1.

EXAMPLES

Various alternative embodiments and examples are described herein. These embodiments and examples are illustrative and should not be construed as limiting the scope of the invention. In particular, while tantalum was used as the representative group 5 metal for these studies, the skilled person will expect other group 5 metals, and especially niobium, to perform similarly.

Materials and Methods

The procedures described herein are given for the purposes of example and illustration only and should not be considered to limit the spirit or scope of the invention.

1. General

All reactions were performed under an inert atmosphere using a Schlenk double manifold equipped with N_2 and high vacuum (10^{-3} mbar) or a glovebox filled with N_2. All glassware used was heated above 160 °C in an oven prior to use. Reactions were performed in threaded 20 mL scintillation vials equipped with a Teflon-coated magnetic stir bar and a Teflon-lined polypropylene screw-cap. Toluene and hexane were purified by passing over activated alumina columns prior to collection and storage in the glovebox. Thin layer chromatography (TLC) was performed on EMD Silica gel 60 F254 plates and visualized under a 254 nm UV light. Flash chromatography was performed using an automated Biotage purification system using SilicaFlash F60 silica gel (230-400 mesh) (Silicycle) as a stationary phase and ACS grade Hexanes/Ethyl Acetate as a mobile phase.

2. Reagents

All reagents were purchased from commercial sources. 3-methyl 2-pyridone (Combi-blocks) was purified by sublimation. Cyclooctadiene (Aldrich), N-methyl aniline (Aldrich), 4-fluoro *N*-methyl aniline (Aldrich), and 4-bromo *N*-methyl aniline (Oakwood) were stirred over CaH_2 for a minimum of 2 h, separated by distillation, then manipulated using standard Schlenk techniques. 4-methoxy *N*-methyl aniline was prepared as according to literature and purified *via* sublimation. $[TaCl_2(NMe_2)_3]$ and Chlorotris(dimethylamido)(κ^2-*N,O*-3-methyl-2-pyridonato)tantalum(V) were prepared as per literature precedent. Grubbs Catalyst™ 2nd Generation (Sigma-Aldrich) was purchased and used without further purification.

3. Instrumentation

NMR Spectroscopy. ^{1}H NMR spectra were recorded on Bruker 300 MHz, or 400 MHz, Avance spectrometers at ambient temperature at 293 K. ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance 300 instrument at 293 K. Chemical shifts (δ) are reported in parts per million (ppm). Coupling constants *J* are given in Hertz (Hz). The following abbreviations are used to indicate signal multiplicity: s = singlet; d = doublet; dd = doublet of doublets; t = triplet; q = quartet; m = multiplet; br = broad; appt = apparent. Assignment of the signals was carried out using 1D (^{1}H, $^{13}C\{^{1}H\}$) and 2D (COSY, HSQC and HMBC) NMR experiments.

Infrared (IR) Spectroscopy. Spectra were recorded at room temperature on a Perkin Elmer FTIR equipped with an ATR accessory for direct measurement on oils and polymeric materials. Bands are reported in wavenumbers (cm^{-1}) and assigned with the abbreviations s=strong, m=medium, w=weak, sh=shoulder, br=broad.

Gel Permeation Chromatography. Polymer M_n, M_w and dispersity (Đ) were obtained using triple detection gel permeation chromatography (GPC) using a Waters liquid chromatograph equipped with an Agilent 1200 series isocratic pump and autosampler, Phenomenex Phenogel 5µm narrow bore columns, Wyatt OptilabEx differential refractometer, Wyatt tristar miniDAWN (laser light scattering detector) and a Wyatt ViscoStar viscometer. A flow rate of 0.5 ml·min-1 was used and samples were dissolved in THF (~ 2 $mg \cdot ml^{-1}$). The measurements were carried out at a laser wavelength of 690 nm, at 25 °C. The data was analyzed using the Astra® processing program provided by Wyatt Technology Corp.

Differential Scanning Calorimetry (DSC). DSC was done on a TA Instruments DSC Q2000 equipped with a TA Instruments Refrigerated Cooling System 90. A

heating/cooling rate of 5 °C/min was used for each run in the range of -90 °C to 120 °C. Duplicate runs were measured after the completion of one heating/cooling cycle to remove thermal history.

Thermogravimetric Analysis (TGA). A thermogravimetric analyzer, model Shimadzu TGA-60, was used for TG measurements of the samples. A small amount (3-5 mg) was analyzed using the alumina crucible. The samples were pre-heated at 105 °C for 15 min in the TGA furnace to remove moisture. Then, the samples were tested from 30 °C to 600 °C at a rate of 10 °C/min under the nitrogen atmosphere.

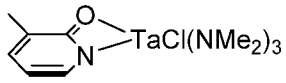
Rheological Measurements. Rheological characterization was conducted using the Anton Paar MCR 702 rotational rheometer, equipped with a cone-partitioned-plate geometry. The main advantage of this geometry is the elimination of the edge fracture[29]. The top part of this type of geometry contains an 8 mm in diameter plate attached to the transducer (center plate), and a coaxial stationary ring (partitioned plate, 25 mm in diameter), which acts as a shield and prevents edge fracture of the sample. The bottom plate is 25 mm in diameter with an angle of 0.07 rad. The experiments were performed at distance gap of 51μm.

The thermal stability of the samples was monitored isothermally for 2 hrs by applying the frequency of 0.1 Hz and shear strain of 0.01. An initial strain sweep test at the frequency of 0.1 Hz was used to determine the threshold of the linear viscoelastic region. Frequency sweep experiments (0.01-100 Hz) at a fixed shear strain of 0.01 were performed at different temperatures, which allows using the time-temperature superposition principle (tTS) and generating the master curve for each sample at the reference temperatures. Experiments were conducted in triplicate, and representative data is presented.

4. Synthesis and Results

General methods of synthesizing Group V metal catalyst complexes useful in the context of the present disclosure, including Chlorotris(dimethylamido)(κ2-N,O-3-methyl-2-pyridonato)tantalum(V), are described in international patent application no. PCT/CA2018/050619, which published as WO 2018/213938, the contents of which are incorporated herein by reference.

4.1 Chlorotris(dimethylamido)(κ^2-N,O-3-methyl-2-pyridonato) tantalum(V).



To a suspension of $[TaCl_2(NMe_2)_3]_2$ (0.23 g, 0.3 mmol) in toluene (~2 mL) was added a suspension of sodium 3-methyl-2-pyridonate (0.075 g, 0.6 mmol) in toluene (~2 mL) at room temperature. Upon stirring overnight, the initially yellow, cloudy mixture became an orange, clear solution. Volatiles were removed *in vacuo* to give 0.250 g orange-brown oil (90 %). The crude residue was dissolved in 1.0 g toluene solvent (0.25 w/w%) and used for hydroaminoalkylation (HAA). **^{1}H NMR** (400 MHz, d_8-tol): δ 8.23 (d of d, 1H, ArH), δ 6.83 (d, 1H, ArH), δ 6.20 (t, 1H, ArH), δ 3.75-3.53 (br s, 18H, $(NCH_3)_2)_3$) δ 2.10 (s, 3H, CH_3). Characterization was consistent with previously reported values.

4.2 Hydroaminoalkylation reaction:

Figure 2 depicts the general scheme for hydroaminoalkylation of cycloalkenes according to the present disclosure. Hydroaminoalkylated monomers derived from cyclooctadiene were prepared by hydroaminoalkylation using catalyst Chlorotris(dimethylamido)(κ^2-*N,O*-3-methyl-2-pyridonato)tantalum(V). While Chlorotris(dimethylamido)(κ^2-*N,O*-3-methyl-2-pyridonato)tantalum(V) was used exclusively in the embodiments exemplified herein for simplicity, the skilled person will understand that other group 5 metal based catalytic complexes as described herein may be useful in the production of the amine-functionalized cycloalkenes and

polymers disclosed herein. Similarly, the skilled person will understand that although cyclooctadience was used exclusively in the embodiments exemplified herein, additional cycloalkenes may be useful in the production oof the amine-functionalized cycloalkenes and polymers disclosed herein. All reported yields are calculated post-column chromatography.

Referring to Figure 2, the catalyst complex demonstrated yielding and multigram scale reactivity (see **Figure 2**). Using this catalytic system, a variety of *para*-substituted *N*-methyl anilines were used to access 4 different amine functionalized monomers (M1 – M4), including halides and methoxy functionalized aniline substituents. By using a slight excess of cyclooctadiene (1.5 equivalent), only small amounts of *bis*-alkylated product were formed as a minor by-product (<15%), and then removed by column chromatography to give high yields of the desired aminated cyclooctene monomers in high yield (>81%).

(Z)-N-(cyclooct-4-en-1-ylmethyl)aniline (amine-functionalized cycloalkene "M1")**.** To a solution of Chlorotris(dimethylamido)(κ^2-*N,O*-3-methyl-2-pyridonato)tantalum(V) (200 mg, 5 mol %) in toluene (~3 mL) was added N-methyl aniline (1 g, 9.34 mmol) followed by cyclooctadiene (1.54 g, 14 mmol). The initially orange, cloudy solution was equipped with a stirring bar, capped, removed from the glovebox, and heated to 145 ^{o}C in an oil-bath. Upon reaching temperature the reaction mixture goes dark red and was then heated with stirring for 20 h. After this time, the reaction was quenched with exposure to ambient atmosphere and the addition of ~1 mL methanol. Purification was completed *via* automated column chromatography (0 to 20% gradient of ethyl acetate/hexanes) to afford 1.68g of pale-yellow oil (84.0%). **^{1}H NMR** (300 MHz, $CDCl_3$, **Figure 7a**): δ 7.20 (d of d, $^{3}J_{AB}$ = 7.35 Hz, $^{3}J_{AC}$ = 8.53 Hz, 2H, 2 × Ar**H**), δ 6.72 (t, $^{3}J_{AB}$ = 7.39 Hz, 1H, Ar**H**), δ 6.64 (d, $^{3}J_{AC}$ = 8.79 Hz, 2H, 2 x Ar**H**), δ 5.68 (m, 2H, 2 x R**H**C=C**H**R), δ 4.09 (br s, 1H, **NH**), δ 2.96 (m, 2H, C**H**$_2$), δ 2.38 (m, 1H, C**H**), δ 2.16 (m, 3H, CH_2), δ 1.81-1.19 (m, 7H, CH_2) **^{13}C{1H} NMR** (75 MHz, $CDCl_3$, **Figure 7b**): δ 148.7 (C), δ 130.2 (CH), δ 130.1 (CH), δ 129.3 (CH), δ 117.0 (CH), δ 112.7 (CH), δ 51.7 (CH_2), δ 37.8 (CH_2), δ 33.5 (CH_2), δ 31.2 (CH_2), δ 28.3 (CH), δ 26.0 (CH), δ 24.9

(CH) **IR** (neat oil, cm^{-1}, int): 3428br, 3019w, 2924s, 2856sh, 1600s, 1506s, 1314m, 1252w, 1125br, 994br, 749s, 689s **HRMS-ESI** (m/z) Calcd: 216.1752; found: ***216.748.***

(Z)-N-(cyclooct-4-en-1-ylmethyl)-4-fluoroaniline (amine-functionalized cycloalkene "M2"). Prepared as per **M1** using 4-fluoro-*N*-methylaniline as the amine substrate to afford 1.53 g of pale-yellow oil (81.7%). **^{1}H NMR** (300 MHz, $CDCl_3$, **Figure 8a**): δ 6.90 (t, 2H, 2 × Ar**H**), δ 6.72 (m, 2H, 2 x Ar**H**), δ 5.69 (m, 2H, 2 x R**H**C=C**H**R), δ 3.50 (br s, 1H, N**H**), δ 2.91 (m, 2H, C**H**$_2$), δ 2.38 (m, 1H, C**H**), δ 2.17 (m, 3H, CH_2), δ 1.79-1.19 (m, 7H, CH_2) **^{13}C{1H} NMR** (75 MHz, $CDCl_3$, **Figure 8b**): δ 157.2 (C), δ 154.1 (CH), δ 145.0 (CH), δ 130.1 (CH), δ 115.4 (CH), δ 113.5 (CH), δ 52.4 (CH_2), δ 37.7 (CH_2), δ 33.4 (CH_2), δ 31.2 (CH_2), δ 28.2 (CH), δ 25.9 (CH), δ 24.8 (CH) **^{19}F{1H} NMR** (282 MHz, $CDCl_3$, Figure 8c): δ −128.6 **IR** (neat oil, cm^{-1}, int): 3428br, 3010w, 2909m, 2856sh, 1615w, 1513s, 1470sh, 1320w, 1221s, 814s, 720m **HRMS-EI** (m/z) Calcd: 233.15798; found: 233.15817.

(Z)-N-(cyclooct-4-en-1-ylmethyl)-4-bromoaniline (amine-functionalized cycloalkene "M3"). Prepared as per **M1** using 4-bromo-*N*-methyl aniline as the amine substrate to afford 1.29 g of pale-yellow oil (81.3%). **^{1}H NMR** (300 MHz, $CDCl_3$, **Figure 9a**): δ 7.25 (d, $^3J_{AB}$ = 8.77 Hz, 2H, 2 × Ar**H**), δ 6.48 (d, $^3J_{AB}$ = 8.77 Hz, 2H, 2 x Ar**H**), δ 5.68 (m, 2H, 2 x R**H**C=C**H**R), δ 3.78 (br s, 1H, N**H**), δ 2.91 (m, 2H, C**H**$_2$), δ 2.36 (m, 1H, C**H**), δ 2.17 (m, 3H, CH_2), δ 1.78-1.18 (m, 7H, CH_2) **^{13}C{1H} NMR** (75 MHz, $CDCl_3$, **Figure 9b**): δ 147.5 (C), δ 131.9 (CH), δ 130.1 (CH), δ 114.3 (CH), δ 108.5 (CH), δ 51.7 (CH_2), δ 37.6 (CH_2), δ 33.4 (CH_2), δ 31.1 (CH_2), δ 28.2 (CH), δ 26.0 (CH), δ 24.8 (CH)) **IR** (neat oil, cm^{-1}, int): 3422br, 3015w, 2922s, 2854sh, 1593s, 1497s, 1313m, 1249m, 1175w, 1073w, 999w, 808s, 723m **HRMS-ESI** (m/z) Calcd: 293.07791; found: 293.07770.

(Z)-N-(cyclooct-4-en-1-ylmethyl)-4-methoxyaniline (amine-functionalized cycloalkene "M4"). Prepared as per **M1** using 4-methoxy *N*-methyl aniline as the amine substrate to afford 1.52 g of yellow oil (85.0%). **^{1}H NMR** (300 MHz, $CDCl_3$, **Figure 10a**): δ 6.81 (d, $^3J_{AB}$ = 9.24 Hz, 2H, 2 × Ar**H**), δ 6.60 (d, $^3J_{AB}$ = 8.79 Hz, 2H, 2 x Ar**H**), δ

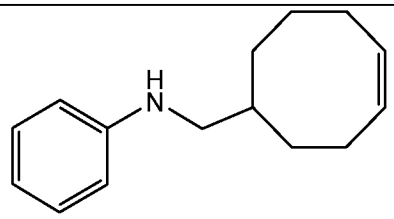
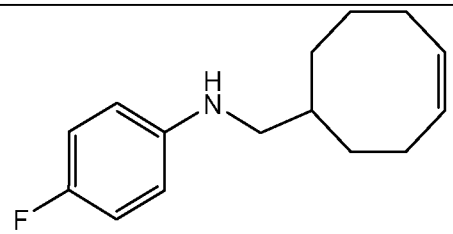
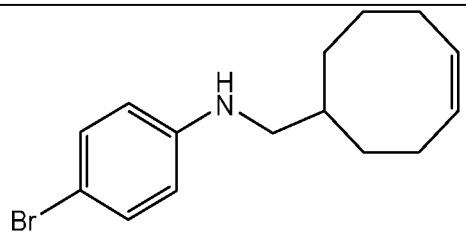
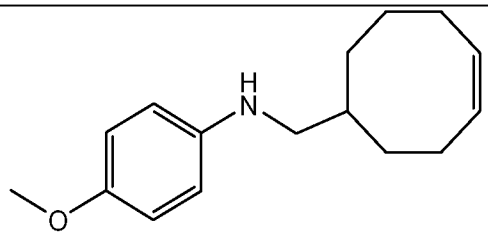
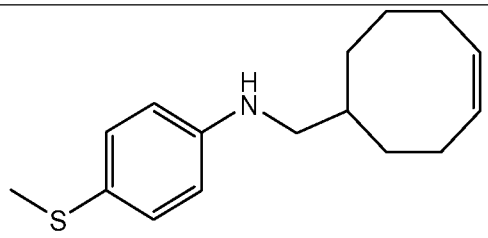
5.68 (m, 2H, 2 x R**H**C=C**H**R), δ 3.77 (s, 3H, OC**H**$_3$), δ 3.38 (br s, 1H, N**H**), δ 2.91 (m, 2H, C**H**$_2$), δ 2.38 (m, 1H, C**H**), δ 2.18 (m, 3H, CH$_2$), δ 1.81-1.19 (m, 7H, CH$_2$) **^{13}C{1H} NMR** (75 MHz, $CDCl_3$, **Figure 10b**): δ 152.0 (C), δ 142.7 (CH), δ 130.2 (CH), δ 115.0 (CH), δ 114.1 (CH), δ 55.9 (CH_3), 52.9 (CH_2) δ 37.7 (CH_2), δ 33.5 (CH_2), δ 31.2 (CH_2), δ 28.2 (CH), δ 26.0 (CH), δ 24.9 (CH). **IR** (neat oil, cm^{-1}): 3415br, 3014w, 2919s, 2854sh, 1620w, 1506s, 1463m, 1228s, 1125w, 1035m, 818s, 724w **HRMS-EI** (m/z) Calcd: 245.17796; found: 245.17794.

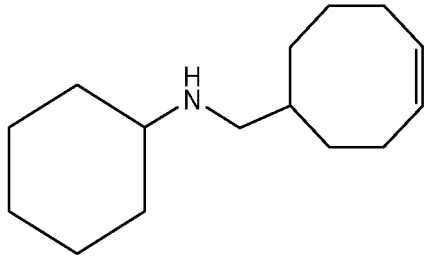
(Z)-N-(cyclooct-4-en-1-ylmethyl)-4-(methylthio)aniline **(**amine-functionalized cycloalkene "**M5")**. Prepared as per **M1** using N-methyl-4-(methylthio)aniline (2.5 g) as the amine substrate to afford 1.52 g of yellow oil (71%) **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.22 (d of d, ^{3}J = 8.7 Hz, ^{3}J = 2.5 Hz, 2H, 2 × Ar**H**), δ 6.54 (t, ^{3}J = 8.7 Hz, 1H, Ar**H**), δ 5.67 (m, 2H, 2 x R**H**C=C**H**R), δ 3.88 (br s, 1H, N**H**), δ 2.93 (m, 2H, C**H**$_2$), δ 2.42 (s, 3H, C**H**$_3$), δ 2.38 (m, 1H, C**H**), δ 2.16 (m, 3H), δ 1.77-1.19 (m, 7H) **^{13}C{1H} NMR** (75 MHz, $CDCl_3$): δ 146.9 (C), δ 131.5 (CH), δ 130.1 (CH), δ 124.2 (C), δ 113.6 (CH), δ 51.9 (CH_2), δ 37.5 (CH_2), δ 33.3 (CH_2), δ 31.1 (CH_2), δ 28.1 (CH), δ 25.9 (CH), δ 24.7 (CH), δ 19.2 (CH_3)**IR** (neat oil, cm^{-1}, int): 3417br, 3013w, 2915vs, 2850s, 1598vs, 1500vs, 1466m, 1437w, 1400w, 1367w, 1312m, 1289m, 1248m, 1201w, 1181w, 1128w, 1103w, 966w, 884w, 812m, 756w, 722m **HRMS-ESI** (m/z) Calcd: 262.1629; found: 262.1637.

(Z)-N-(cyclooct-4-en-1-ylmethyl)-cyclohexanamine **(**amine-functionalized cycloalkene "**M6")**. Prepared as per **M1** using N-methylcyclohexylamine (0.45 g) as the amine substrate to afford 0.6 g of yellow oil (53%) **^{1}H NMR** (300 MHz, $CDCl_3$): δ 5.64 (m, 2H, 2 x R**H**C=C**H**R), δ 2.44 (m, 3H, N-C**H**$_2$,N-C**H**), δ 2.34 (m, 1H, C**H**), δ 2.12 (m, 3H), δ 1.88-1.00 (m, 18H) **^{13}C{1H} NMR** (75 MHz, $CDCl_3$): δ 130.2 (CH), δ 129.9 (CH), δ 56.9 (CH), δ 54.9 (CH_2), δ 38.1 (CH), δ 33.7 (CH_2), δ 33.6 (CH_2), δ 31.6 (CH_2), δ 28.2 (CH), δ 26.2 (CH_2), δ 25.9 (CH_2), δ 25.1 (CH_2), δ 24.9 (CH_2) **IR** (neat oil, cm^{-1}, int): 3014w, 2923vs, 2851s, 1651m, 1612w, 1570w, 1463s, 1449s, 1374w, 1348w, 1258w, 1228w, 1131m, 1028w, 989w, 972w, 941w, 886m, 844w, 775m, 754m, 721vs **HRMS-ESI** (m/z) Calcd: 222.2222; found: 222.2228.

Table 1 provides a summary of the exemplary amine-functionalized cycloalkenes synthesized.

Table 1 Overview of synthesized amine-functionalized cycloalkenes .

Compound ID	**IUPAC Name**	**Chemical Structure**
M1	(Z)-N-(cyclooct-4-en-1-ylmethyl)aniline	
M2	(Z)-N-(cyclooct-4-en-1-ylmethyl)-4-fluoroaniline	
M3	(Z)-N-(cyclooct-4-en-1-ylmethyl)-4-bromoaniline	
M4	(Z)-N-(cyclooct-4-en-1-ylmethyl)-4-methoxyaniline	
M5	(Z)-N-(cyclooct-4-en-1-ylmethyl)-4-(methylthio)aniline	

M6	(Z)-N-(cyclooct-4-en-1-ylmethyl)-cyclohexanamine	

These monomers bearing pendant, secondary aryl amines were amenable to ROMP using Grubbs Catalyst 2nd Generation to obtain linear polymers.

4.3 Polymerization

Figure 3 depicts the general scheme for polymerization of hydroaminoalkylated cycloalkene monomers according to the present disclosure. Polymerization of amine-functionalized cycloalkene monomers M1, M2, M3, and M4 was completed using ring-opening metathesis polymerization (ROMP) using Grubbs Catalyst™ 2nd Generation. Generally, a solution of catalyst in CH_2Cl_2 was added to a solution of the monomer in CH_2Cl_2 with stirring. Reactions were performed on gram-scale quantities at room temperature to access high conversion of monomer. Reactions were allowed to proceed for a minimum 1 hr to ensure full conversion. Upon completion of the reaction the solution slowly goes light amber-yellow/green from the originally dark amber solution. Reactions were quenched *via* exposure to ambient atmosphere and drop-wise addition of an excess of ethyl vinyl ether (min. of 2 drops per mg of [Ru] catalyst), and left to stir for a minimum of thirty minutes, after which the solution slowly changes color to dark amber/black. The polymer was precipitated as a gum-like off-white solid *via* drop-wise addition to a stirring vortex of methanol (-35°C, and a minimum of 1 mL per mg polymer), which was notably different in physical appearance to that of non-functionalized poly(cyclooctene), which precipitated as a white, flocculent solid. Isolation was completed by decanting the supernatant and overnight drying of the collected material under high vacuum. All characterization was thereafter completed with the exception of GPC analysis, for which further purification was completed *via*

two additional precipitations (using addition of a CH_2Cl_2 solution of the polymer into a large excess of methanol) followed by drying in a vacuum oven.

Poly(N-(cyclooct-4-en-1-ylmethyl)aniline) (polymer "P1"). Prepared as above to afford 0.602 g of an off-white gun-like solid (81%). **^{1}H NMR** (300 MHz, $CDCl_3$, **Figure 11a**): δ 7.17 (m, 2H, 2 × Ar**H**), δ 6.73 (br s, 3H, 3 x Ar**H**), δ 5.40 (m, 2H, 2 x R**H**C=C**H**R), δ 3.03 (d, 2H, C**H**$_2$), δ 2.00 (m, 4H, C**H$_2$**), δ 1.68 (br s, 1H, CH), δ 1.49-1.26 (m, 6H, CH_2) **IR** (neat oil, cm^{-1},int, **Figure 11b**): 3425br, 2924s, 2847sh, 1602 s, 1505s, 1430sh, 1320m, 1258m, 1180w, 1023w, 964m, 862w, 743s, 691s.

Poly(N-(cyclooct-4-en-1-ylmethyl)-4-fluoroaniline) (polymer "P2"). Prepared as above to afford 0.690 g of gummy, off-white solid (88%). %). **^{1}H NMR** (300 MHz, $CDCl_3$, **Figure 12a**): δ 6.87 (m, 2H, 2 × Ar**H**), δ 6.55 (br s, 2H, 2 x Ar**H**), δ 5.39 (m, 2H, 2 x R**H**C=C**H**R), δ 2.97 (d, 2H, C**H**$_2$), δ 2.00 (m, 4H, C**H$_2$**), δ 1.63 (br s, 1H, CH), δ 1.36 (br s, 6H, CH_2) **^{19}F{1H} NMR** (282 MHz, $CDCl_3$): δ −127.7 **IR** (neat oil, cm^{-1}, int, **Figure 12b**): 3419br, 2919m, 2850sh, 1614w, 1510s, 1473sh, 1316w, 1214s, 1101w, 816s

Poly(N-(cyclooct-4-en-1-ylmethyl)-4-bromoaniline) (polymer "P3"). Prepared as above to afford 0.592 g of gummy, off-white solid (94%). **^{1}H NMR** (400 MHz, $CDCl_3$, **Figure 13a**): δ 7.27 (m, 2H, 2 × Ar**H**), δ 6.52 (br s, 2H, 2 x Ar**H**), δ 5.42 (m, 2H, 2 x R**H**C=C**H**R), δ 3.00 (d, 2H, C**H**$_2$), δ 2.01 (br s, 4H, C**H$_2$**), δ 1.66 (br s, 1H, CH_2), δ 1.38 (br s, 6H, CH_2) **IR** (neat oil, cm^{-1}, int, **Figure 13b**): 3422br, 2922s, 2854sh, 1593s, 1497s, 1313m, 1249m, 1175m, 1073m, 964m, 808s.

Poly(N-(cyclooct-4-en-1-ylmethyl)-4-methoxyaniline (polymer "P4"). Prepared as above to afford 0.541 g of gummy, off-white solid (88%). **^{1}H NMR** (400 MHz, $CDCl_3$, **Figure 14a**): δ 6.78 (d, 2H, 2 × Ar**H**), δ 6.59 (br s, 2H, 2 x Ar**H**), δ 5.39 (m, 2H, 2 x R**H**C=C**H**R), δ 3.74 (s, 3H, OC**H**$_3$), δ 2.98 (d, 2H, C**H**$_2$), δ 2.01 (br s, 4H, C**H$_2$**), δ 1.63

(br s, 1H, CH_2), δ 1.37 (br s, 6H, CH_2) **IR** (neat oil, cm^{-1}, int, **Figure 14b**): 3394br, 2923s, 2848sh, 1655br, 1510s, 1464sh, 1233s, 1017s, 816s, 668m.

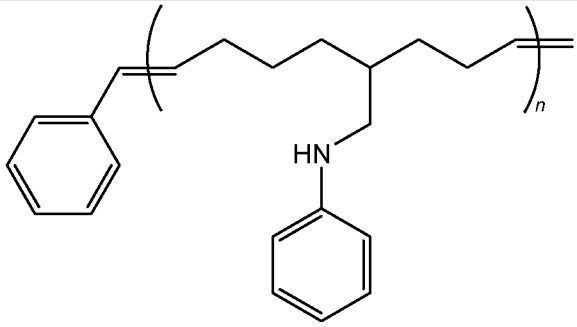
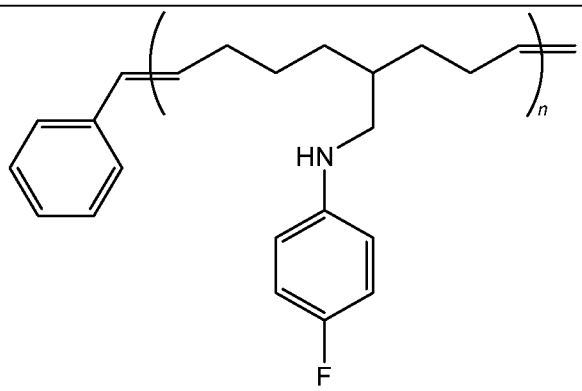
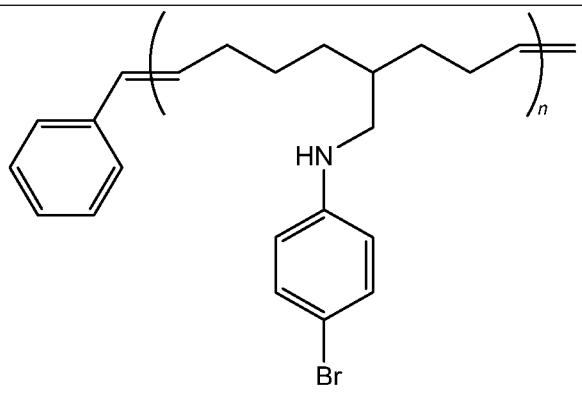
Poly(N-(oct-4-en-1-ylmethyl)-4-(methylthio)aniline (polymer "P5"). Prepared as above to afford a dark purple solid (70%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.22 (m, 2H, 2 × Ar**H**), δ 6.54 (m, 2H, 2 × Ar**H**), δ 5.40 (br s, 2H, 2 x R**H**C=C**H**R), δ 3.69 (br s, 1H, **NH**), δ 2.99 (m, 2H, C**H**$_2$), δ 2.42 (m, 3H, C**H**$_3$), δ 1.99 (m, 4H), δ 1.77-1.19 (m, 7H) **IR** (neat oil, cm^{-1}, int): 3414br, 2917s, 2852m, 1597vs, 1500vs, 1474m, 1455m, 1435w, 1401w, 1312m, 1289m, 1250m, 1181m, 1101w, 966s, 812s, 735w.

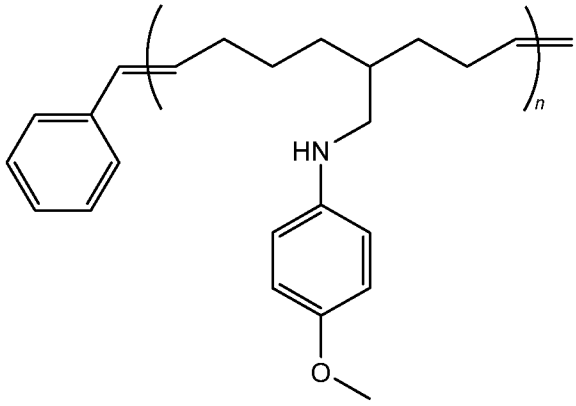
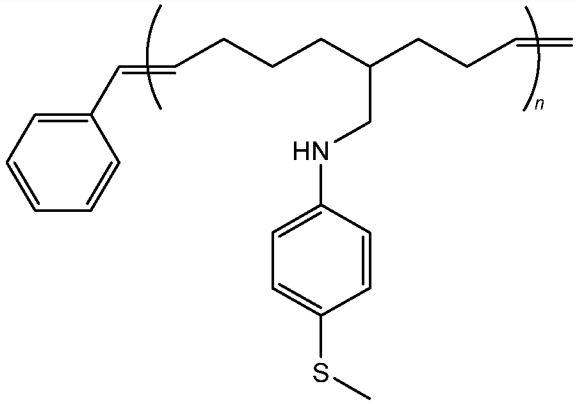
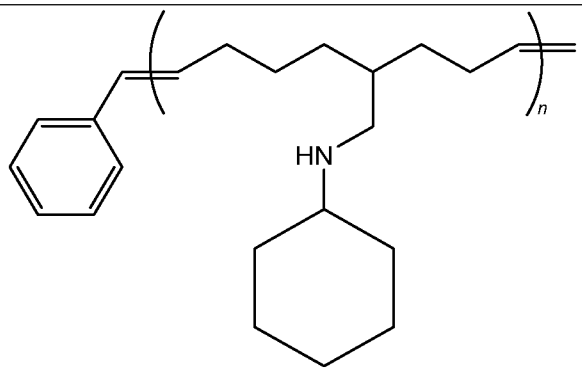
Poly(N-(oct-4-en-1-ylmethyl)-cyclohexanamine (polymer "P6"). Prepared as above to afford a dark orange solid (42%).**^{1}H NMR** (300 MHz, C_7D_8): δ 5.53 (br s, 2H, 2 x R**H**C=C**H**R), δ 2.55 (br s, 2H, C**H**$_2$), δ 2.37 (m, 1H, C**H**), δ 2.11 (br s, 4H, C**H$_2$**), δ 1.86-1.07 (m, 17H, C**H**, C**H$_2$**), δ 0.52 (br s, 1H, N**H**) **IR** (neat oil, cm^{-1},int): 2921vs, 2851s, 1670w, 1449s, 1365w, 1347w, 1259w, 1241w, 1130m, 966vs, 922w, 888m, 845m, 845w, 786w, 723s.

Polymers P1 to P6 were obtained in high yield (>80%) regardless of the pendant secondary amine substituent. Analysis of chemical shifts in ^{1}H NMR spectra showed broadened signals consistent with polymer formation. For example, for polymer **P2** one major peak was observed in the ^{19}F NMR spectrum; a broad singlet at δ -127.7 ppm, while for polymer **P4** the methoxy substituent provided a diagnostic NMR signal, which was observed as a broad singlet (δ 3.74 ppm) in the ^{1}H NMR spectrum; furthermore this peak integrated in a 3:2 ratio, when compared with the olefinic resonances at δ 5.41 ppm. In the case of M1, a crude reaction mixture from hydroaminoalkylation was found to be amenable to ROMP without purification by column chromatography, however the resulting material could, like P2 and P4, only be characterized by NMR and IR spectroscopy.

Table 2 provides a summary of the exemplary polymers synthesized.

Table 2 Overview of polymers synthesized.

Compound ID	IUPAC Name	Chemical Structure
P1	Poly(N-(oct-4-en-1-ylmethyl)aniline)	
P2	Poly(N-(oct-4-en-1-ylmethyl)-4-fluoroaniline)	
P3	Poly(N-(oct-4-en-1-ylmethyl)-4-bromoaniline)	

P4	Poly(N-(oct-4-en-1-ylmethyl)-4-methoxyaniline	
P5	Poly(N-(oct-4-en-1-ylmethyl)-4-(methylthio)aniline	
P6	Poly(N-(oct-4-en-1-ylmethyl)-cyclohexanamine	

4.4 Hydrogenation

Hydrogenative reduction of the polymer backbone of polymer P1 was targeted in order to obtain a saturated polymer analogous to polyethylene. The reduction could be realized using tosyl hydrazine as a hydrogen source that selectively reduced the C=C

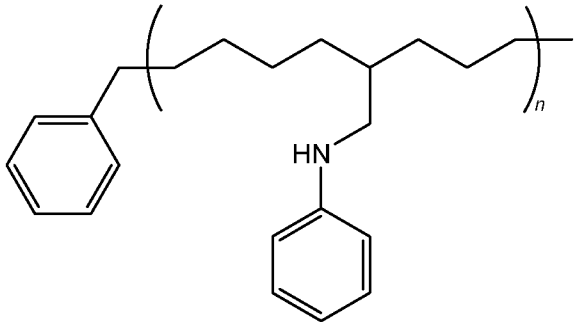
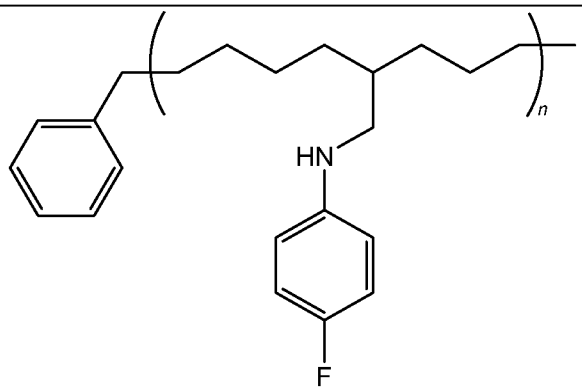
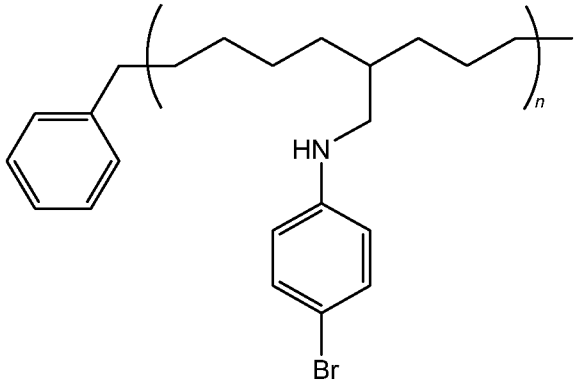
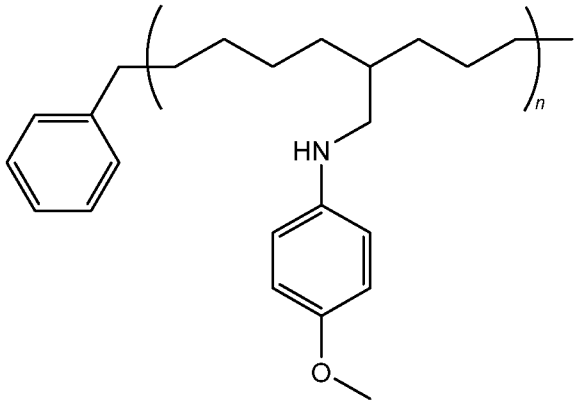
double bond of polymer **P1**. Due to the pendant secondary amine, a basic work-up of the polymer was required.

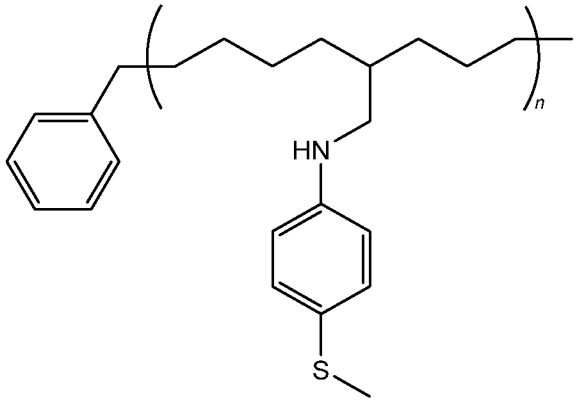
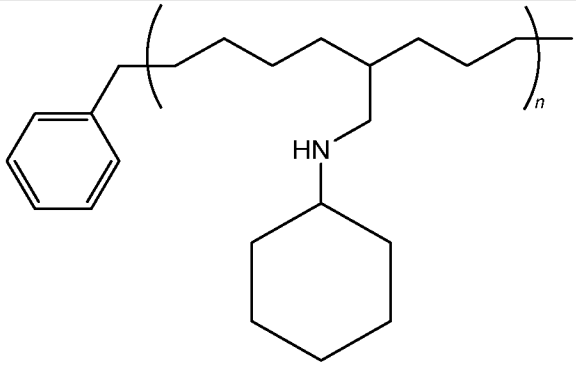
Poly(N-(cyclooct-4-an-1-ylmethyl)aniline) (polymer "P1H"). **P1** (480 mg, 2 mmol alkene) and *p*-toluenesulfonyl hydrazide (1.5 g, 8 mmol) in xylene (15 mL), along with a few mgs of 2,4,6-tri-*tert*-butyl phenol added as a radical sponge, were added to a 100 mL reaction vessel equipped with a Teflon capped-valve and side-arm and a Teflon-coated stir bar. The resulting heterogeneous mixture was filled with N_2, freeze-pump-thawed three times, then back-filled with N_2. The vessel was sealed and heated to 130 ^{o}C in an oil-bath for a minimum of 8 hours. After the duration of the reaction, a pale-yellow, clear solution was obtained. The vessel was opened and the mixture transferred to a separatory funnel, using ethyl acetate (50 mL) to quantitatively transfer. The organic layer was washed three times with 3 M NaOH, then once with brine, then reduced to ~ 3 mL *via* rotary evaporation under reduced pressure. This residue was then added drop-wise to a large excess of vortexing methanol (-35 ^{o}C, 250 mL) to afford the product as an off-white, gummy solid. After three excessive precipitations, 0.350 g of material was obtained (73.0 %). **^{1}H NMR** (300 MHz, $CDCl_3$, **Figure 15a**): δ 7.17 (m, 2H, 2 × Ar**H**), δ 6.69 (t, 1H, Ar**H**), δ 6.63 (d, 2H, Ar**H**), δ 3.01 (d, 2H, C**H**$_2$), δ 1.61 (br s, 1H, CH), δ 1.28 (m, 14H, CH_2) **IR** (neat oil, cm^{-1}, int, **Figure 15b**): 3420br, 3045w, 2922s, 2849sh, 1601s, 1504s, 1466sh, 1316m, 1261m, 1095br, 1030br, 804s, 746s, 689s.

Table 3 provides a summary of the exemplary hydrogenated polymers that were synthesized.

Table 3 Overview of example compounds.

Compound ID	**IUPAC Name**	**Chemical Structure**

P1H	Poly(N-(oct-4-an-1-ylmethyl)aniline)	
P2H	Poly(N-(oct-4-an-1-ylmethyl)-4-fluoroaniline)	
P3H	Poly(N-(oct-4-an-1-ylmethyl)-4-bromoaniline)	
P4H	Poly(N-(oct-4-an-1-ylmethyl)-4-methoxyaniline	

P5H	Poly(N-(oct-4-an-1-ylmethyl)-4-(methylthio)aniline	
P6H	Poly(N-(oct-4-an-1-ylmethyl)-cyclohexanamine	

The secondary aryl amine and its substituents may be varied to tune hydrogen bonding interactions which may result in polymers displaying various physical properties, e.g. a liquid, gel-like, soft, or solid structure

Example 2: NMR Polymerization Study. The polymerization of M1 was monitored by NMR spectroscopy. To a sealed NMR tube was added the Grubbs initiator, 100 equivalents of M1 and *ca.* 1 mL deuterated chloroform. After 10 min, approximately 35% of the monomer had been consumed; after 30 minutes the reaction had exceeded 95% completion. In contrast to other amine-functionalized monomers which are incompatible with Grubbs initiators, the rapid conversion of M1 shows that aryl substituted secondary amines are amenable to ROMP. Notably, throughout the polymerization, the signal assigned to the benzylidene Ru=C***H***Ph proton at 19.2 ppm remained present in the spectrum (**Figure X**), wherein this observation may suggest incomplete initiation of the catalyst and rates of propagation that are greater than rates of catalyst initiation.

To probe whether the chain termination took place upon reaction completion, an aliquot of *ca.* 25 equivalents of **M2** was added long after monomer **M1** had been fully consumed (12 hours). Upon addition of M2, rapid polymerization took place and no signals consistent with the internal alkene of M2 was observed after 30 minutes, while the overlapping alkene peaks of P1 and P2 suggest that polymerization is not self-terminating and the addition of a quenching reagent is required to complete the reaction. Furthermore, the ^{19}F NMR spectrum showed a single broad singlet consistent with ring-opened M2 polymeric material, corroborating the evidence present in the ^{1}H NMR spectrum.

4.4 Molecular Weight and Dispersity.

Polymers that possessed solubility in tetrahydrafuran (THF) were subjected to analysis using gel-permeation chromatography (GPC) to probe polymer molecular weight and dispersity (**Table 2**). Experimental molecular weights did not correlate exactly to the predicted by monomer-to-initiator ratios ($M_{n,theo}$ = [M]/[I]), while dispersity (Đ) values from 1.1 to 1.6 suggested that polymerization proceeded with only moderate control. As discussed previously, reaction monitoring suggested that rates of propagation were fast relative to initiation, resulting in larger than expected molecular weight and increased polymer dispersity. Notably, not all isolated polymers possessed solubility in THF for GPC analysis; for example, P4, with its hydrogen bonding methoxy subsituent, could be characterized in chloroform by NMR spectroscopy but was not completely soluble in THF or chloroform. This observation may indicate that the formation of extensive hydrogen-bonding networks may result in lower solubility of the polymer, due to increased *inter-* and *intra*-molecular forces. P2 also showed this lack of solubility, presumably due to the strong H-bond accepting potential of the fluorine substituent.

Table 2. Experimental and theoretical molecular weight (M_n).

Entry	Polymer	[Ru] / mol%	*Theo.* M_n / g•mol^{-1}	*Exp.* M_n[a] / g•mol^{-1}	Đ[a]

2	P1	0.5	43,000	82,970	1.32
3	P1	1	21,500	18,100	1.40
5	P2	1	23,400	-	-
6	P3	1	29,600	35,080	1.65
7	P4	1	24,700	-	-

[a]Determined by Gel-permeation chromatography (GPC)

4.5 Thermal Stability.

Thermal stabilities (weight losses) of the polymers were determined by employing dynamic TGA experiments. Each sample was pre-heated at 105 °C for 5 min then heated from 30 °C to 600 °C at a heating rate of 10 °C/min under nitrogen and oxygen.

An average of three independent measurements was made. There was no difference in TGA curves for samples tested under nitrogen or oxygen atmosphere, indicating good thermo-oxidative stability. **Figures 4a and 4b** show selected weight loss curves and **Table 4** summarizes 5% weight loss temperatures for tested polymers. Results demonstrate that P(Cyclooctene) is a thermally stable polymer with only one weight loss step at 415 °C, which was assigned to the degradation of the polymer chain. Functionalized P1 shows a two-step weight loss. An initial weight loss at around 300°C was assigned to the loss of the *N*-methyl aniline side group. The second thermal degradation around 420°C refers to the degradation of the main polymer chain. In general, polymers follow free radical degradation mechanisms which are initiated by bond dissociation at the temperature of pyrolysis. By observing the polymer structure and bond strengths, a probable initial degradation mechanism for the poly(pendantamine) (PPA) polymers may be via side-group elimination.

The derivative TGA, or DTG curves were useful for determination of the overlapping mass loss events, identification of minor mass loss steps, and finding the maxima of weight loss processes, wherein every peak in the TG curves may be an isolated event that may indicate the maximum rate of mass loss. Referring to Figure 5, the thermograms obtained from differential scanning calorimetry (DSC) show behavior typical of amorphous polymers. The glass transition temperatures were attributed to chain transformation from glassy to rubbery regions and their values are summarized in **Table 4** for each polymer.

Table 4. Thermal characterization by differential scanning calorimetry and thermogravimetric analysis.

Polymers	**T_g (°C)**	**$T_{5\%}$ (°C)**
P(cyclooctene)	-	415
P1	-13.7	275
P2	-10.4	280
P3	-2.0	255
P4	-4.7	287
P1H	-16.8	400

4.6 Rheology

Representative master curves of shifted storage and loss moduli and complex viscosity of various amine derivatives of poly(cyclooctene) as a function of shifted angular frequency are depicted in **Figure 6a to 6e**. A plethora of distinctively different rheological behaviors was obtained, which may be attributed to the various hydrogen bonding environments promoted by the different aryl amines. Information obtained for P1, P1H pre-hydrogenation, P1H, and P3 is eported in Tables 5A to 5D below.

P1 showed liquid-like behavior (G" > G'), whereas, P3, and P4 exhibited the transition from liquid-like to solid-like behavior through gel-like behavior. P2 exhibited soft solid-like behavior (G' ≥ G"), which became more evident by introducing the polar F functional group that may also engage in hydrogen bonding interactions. Furthermore, the presence of strong F-H bonds may be responsible for formation of 3D network resulting in a material that behaves as an viscoelastic solid with a higher melting temperature than the reference material. In comparing storage moduli for P1 and P2, the transition from liquid-like to solid-like behavior is evident. Strong physical crosslinking of P2 was observed during the fabrication/formation of film using solution casting. This may be explained by the alignment of polymer chains in solution allowing for easier formation of hydrogen bonds. P3 and P4 exhibited clear zero-shear viscosities which were higher than for P3. Bromine functionalized poly(cyclooctene) may form stronger hydrogen bonded structure due to possibly higher molecular weight.

Table 5A. Rheological behaviors of polymer P1.

Configuration	**Notes:** **Concentration** **Source:** RI **Flow Rate:** 0.500 mL/min **Light Scattering Instrument:** miniDAWN TREOS **Cell** **Type:** Fused Silica **Wavelength:** 659.4 nm **Calibration Constant:** 4.8798×10^{-5} 1/(V cm) **RI Instrument:** Optilab rEX **Viscometer:** ViscoStar **Dilution Factor:** 0.4972 **Solvent:** thf **Temperature** **Correction** **Enabled:** no

	Refractive Index: 1.402
Processing	**Collection Time:** Tuesday June 20, 2017 12:35:00 PM Pacific Daylight Time **Processing Time:** Wednesday June 21, 2017 11:02:17 AM Pacific Daylight Time **Peak settings:** **Peak Name** Peak 1 **Peak Limits (min)** 10.360 - 18.692 **Light Scattering Model** Zimm **Fit Degree** 1 **dn/dc (mL/g)** 0.1068 **A2 (mol mL/g²)** 0.000 **UV Ext. Coef. (mL/(mg cm))** 0.000 **Viscometry Model** Huggins **Huggins Equation Parameter** 0 **Kraemers Equation Parameter** 0 **Molar Mass & Radius from LS:** **Enabled Detectors:** 1 2 3 **Results Fitting Procedure:** **Data** **Fit Model** **Degree** **R^2** **Extrapolation**

	Molar Mass	None	n/a	n/a	none
	Rms Radius	None	n/a	n/a	none
	Mean Square Radius	None	n/a	n/a	none
	Hydrodynamic Radius (Q)	None	n/a	n/a	none

Results

Peak Results

	Peak 1
Hydrodynamic radius (v) moments (nm)	
Rh(v)n	2.604 (±2.059%)
Rh(v)w	3.097 (±1.947%)
Rh(v)z	3.709 (±2.067%)
Masses	
Calculated Mass (µg)	243.98
Mass Recovery (%)	100.0
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	1.810×10^4 (±4.998%)
Mp	2.505×10^4 (±4.301%)
Mv	2.355×10^4 (±0.234%)
Mw	2.527×10^4 (±4.388%)
Mz	3.526×10^4 (±9.764%)
Polydispersity	
Mw/Mn	1.397 (±6.651%)
Mz/Mn	1.949 (±10.969%)
rms radius moments (nm)	
Rn	2.7 (±2275.8%)
Rw	7.6 (±273.0%)
Rz	10.1 (±148.5%)
Intrinsic viscosity moments (mL/g)	
[η]n	6.663 (±3.679%)
[η]w	8.11 (±3.49%)
[η]z	9.881 (±4.059%)

Mark-Houwink-Sakurada **a:** 0.595 (±0.459%)

Mark-Houwink-Sakurada K: 2.041×10^{-2} (±2.803%) mL/g

Table 5B. Rheological behaviors of polymer P1H prior to hydrogentation.

Configuration	**Notes:** **Concentration** **Source:** RI **Flow Rate:** 0.500 mL/min **Light Scattering Instrument:** miniDAWN TREOS **Cell** **Type:** Fused Silica **Wavelength:** 659.4 nm **Calibration Constant:** 4.8798×10^{-5} 1/(V cm) **RI Instrument:** Optilab rEX **Viscometer:** ViscoStar **Dilution Factor:** 0.4972 **Solvent:** thf **Temperature** **Correction** **Enabled:** no **Refractive Index:** 1.402
Processing	**Collection Time:** Thursday July 27, 2017 09:21:33 AM Pacific Daylight Time **Processing Time:** Thursday August 10, 2017 11:29:41 AM Pacific Daylight Time **Peak settings:** **Peak Name** Peak 1

	Peak Limits (min) 10.273 - 15.431 **Light Scattering Model** Zimm **Fit Degree** 1 **dn/dc (mL/g)** 0.1217 **A2 (mol mL/g²)** 0.000 **UV Ext. Coef. (mL/(mg cm))** 0.000 **Viscometry Model** Huggins **Huggins Equation Parameter** 0 **Kraemers Equation Parameter** 0 **Molar Mass & Radius from LS:** **Enabled Detectors:** 1 2 3 **Results Fitting Procedure:**

Data	Fit Model	Degree	R^2	Extrapolation
Molar Mass	None	n/a	n/a	none
Rms Radius	None	n/a	n/a	none
Mean Square Radius	None	n/a	n/a	none
Hydrodynamic Radius (Q)	None	n/a	n/a	none

Results	**Peak Results**	
		Peak 1
	Hydrodynamic radius (v) moments (nm)	
	Rh(v)n	6.465 (±0.962%)
	Rh(v)w	7.437 (±0.918%)
	Rh(v)z	9.278 (±1.010%)
	Masses	
	Calculated Mass (µg)	147.97

	Mass Recovery (%) 100.0 **Mass Fraction (%)** 100.0 **Molar mass moments (g/mol)** **Mn** 7.357×10^4 (±2.562%) **Mp** 9.930×10^4 (±2.425%) **Mv** 9.110×10^4 (±0.177%) **Mw** 9.831×10^4 (±2.461%) **Mz** 1.587×10^5 (±5.461%) **Polydispersity** **Mw/Mn** 1.336 (±3.553%) **Mz/Mn** 2.156 (±6.032%) **rms radius moments (nm)** **Rn** 21.4 (±21.5%) **Rw** 21.7 (±20.7%) **Rz** 22.3 (±19.2%) **Intrinsic viscosity moments (mL/g)** **[η]n** 24.537 (±1.116%) **[η]w** 28.97 (±0.94%) **[η]z** 37.624 (±1.610%) **Mark-Houwink-Sakurada** **a:** 0.587 (±0.163%) **Mark-Houwink-Sakurada K:** 3.619×10^{-2} (±1.111%) mL/g

Table 5C. Rheological behaviors of polymer P1H.

Configuration	**Notes:** **Concentration** **Source:** RI **Flow Rate:** 0.500 mL/min **Light Scattering Instrument:** miniDAWN TREOS **Cell** **Type:** Fused Silica **Wavelength:** 659.4 nm **Calibration Constant:** 4.8798×10^{-5} 1/(V cm) **RI Instrument:** Optilab rEX

	Viscometer: ViscoStar **Dilution Factor:** 0.4972 **Solvent:** thf **Temperature Correction Enabled:** no **Refractive Index:** 1.402
Processing	**Collection Time:** Wednesday August 16, 2017 01:48:03 PM Pacific Daylight Time **Processing Time:** Thursday August 17, 2017 12:32:27 PM Pacific Daylight Time **Peak settings:** **Peak Name** Peak 1 **Peak Limits (min)** 9.078 - 17.166 **Light Scattering Model** Zimm **Fit Degree** 1 **dn/dc (mL/g)** 0.1182 **A2 (mol mL/g²)** 0.000 **UV Ext. Coef. (mL/(mg cm))** 0.000 **Viscometry Model** Huggins **Huggins Equation Parameter** 0 **Kraemers Equation Parameter** 0 **Molar Mass & Radius from LS:** **Enabled Detectors:** 1 2 3 **Results Fitting Procedure:**

	Data	**Fit Model**	**Degree**	**R^2**	**Extrapolation**
	Molar Mass	None	n/a	n/a	none
	Rms Radius	None	n/a	n/a	none
	Mean Square Radius	None	n/a	n/a	none
	Hydrodynamic Radius (Q)	None	n/a	n/a	none

Results

Peak Results

	Peak 1
Hydrodynamic radius (v) moments (nm)	
Rh(v)n	6.165 (±1.466%)
Rh(v)w	6.804 (±1.444%)
Rh(v)z	7.984 (±1.516%)
Masses	
Calculated Mass (µg)	159.99
Mass Recovery (%)	100.0
Mass Fraction (%)	100.0
Molar mass moments (g/mol)	
Mn	7.123×10^4 (±3.741%)
Mp	8.224×10^4 (±3.418%)
Mv	8.257×10^4 (±0.218%)
Mw	8.710×10^4 (±3.581%)
Mz	1.201×10^5 (±8.008%)
Polydispersity	
Mw/Mn	1.223 (±5.179%)
Mz/Mn	1.686 (±8.839%)
rms radius moments (nm)	
Rn	23.5 (±23.9%)
Rw	23.2 (±23.9%)
Rz	23.1 (±23.6%)
Intrinsic viscosity moments (mL/g)	
[η]n	21.831 (±1.685%)
[η]w	24.71 (±1.68%)
[η]z	29.566 (±2.407%)

Mark-Houwink-Sakurada **a:** 0.601 (±0.222%)

Mark-Houwink-Sakurada K: 2.989×10^{-2} (±1.536%) mL/g

Table 5D. Rheological behaviors of polymer P3.

Configuration	**Notes:** **Concentration** **Source:** RI **Flow Rate:** 0.500 mL/min **Light Scattering Instrument:** miniDAWN TREOS **Cell** **Type:** Fused Silica **Wavelength:** 659.4 nm **Calibration Constant:** 4.8798×10^{-5} 1/(V cm) **RI Instrument:** Optilab rEX **Viscometer:** ViscoStar **Dilution Factor:** 0.4972 **Solvent:** thf **Temperature** **Correction** **Enabled:** no **Refractive Index:** 1.402
Processing	**Collection Time:** Thursday July 27, 2017 12:04:40 PM Pacific Daylight Time **Processing Time:** Thursday August 10, 2017 11:22:31 AM Pacific Daylight Time **Peak settings:** **Peak Name** Peak 1

	Peak Limits (min) 8.699 - 17.441 **Light Scattering Model** Zimm **Fit Degree** 1 **dn/dc (mL/g)** 0.1179 **A2 (mol mL/g²)** 0.000 **UV Ext. Coef. (mL/(mg cm))** 0.000 **Viscometry Model** Huggins **Huggins Equation Parameter** 0 **Kraemers Equation Parameter** 0 **Molar Mass & Radius from LS:** **Enabled Detectors:** 1 2 3 **Results Fitting Procedure:**

Data	Fit Model	Degree	R^2	Extrapolation
Molar Mass	None	n/a	n/a	none
Rms Radius	None	n/a	n/a	none
Mean Square Radius	None	n/a	n/a	none
Hydrodynamic Radius (Q)	None	n/a	n/a	none

Results	**Peak Results**	
		Peak 1
	Hydrodynamic radius (v) moments (nm)	
	Rh(v)n	3.615 (±2.518%)
	Rh(v)w	4.737 (±1.844%)
	Rh(v)z	6.387 (±1.847%)
	Masses	
	Calculated Mass (µg)	133.00
	Mass Recovery (%)	100.0

	Mass Fraction (%) 100.0 **Molar mass moments (g/mol)** **Mn** 3.508×10^4 (±2.050%) **Mp** 5.788×10^4 (±2.766%) **Mv** 5.136×10^4 (±0.167%) **Mw** 5.802×10^4 (±2.577%) **Mz** 1.007×10^5 (±6.010%) **Polydispersity** **Mw/Mn** 1.654 (±3.293%) **Mz/Mn** 2.870 (±6.350%) **rms radius moments (nm)** **Rn** n/a **Rw** 10.5 (±71.9%) **Rz** 15.7 (±35.9%) **Intrinsic viscosity moments (mL/g)** **[η]n** 9.733 (±5.087%) **[η]w** 13.61 (±3.65%) **[η]z** 18.507 (±4.394%) **Mark-Houwink-Sakurada** **a:** 0.580 (±0.380%) **Mark-Houwink-Sakurada K:** 2.753×10^{-2} (±2.463%) mL/g

4.7 Self-Healing Properties

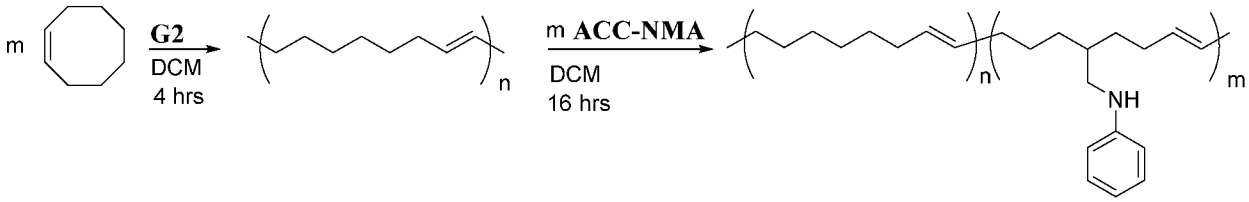
Referring to Figure 17, polymers as disclosed herein exhibit self-healing properties. The self-healing properties of these polymers appears to be related to their ability to possess chain mobility as amorphous materials.

4.8 Copolymers

4.8.1 Copolymers with Cyclooctene

In an attempt to explore the extent to which the advantageous properties of these novel polymers could be retained with lower incorporations of amine in the polymer, the amine incorporation in the final polymer was reduced by adding excess equivalents of cyclooctene to the ROMP reaction. The ultimate goal is to maintain the desirable properties imparted by the amine functional group while lowering its incorporation in less expensive, less functionalized polyolefins.

Synthesis of polymer with reduced amine incorporation was conducted according to the following scheme.



P(P1-*co*-cyclooctene) General preparation for a 1:1 by mol copolymer was prepared as follows: To a 20 mL scintillation vial was added the first monomer, *eg.* cyclooctene (51 mg, 0.4 mmol) and a solution of G2 (3.7 mg, 0.004 mmol) in THF (1 mL) with a stir bar. After reacting the first monomer at room temperature for the time required (*eg.* 4 hrs for cyclooctene), the second monomer, *eg.* M1 (100 mg, 0.4 mmol. 1:1 mol ratio with cyclooctene). After time required to react second monomer, the entire reaction was quenched and polymer isolated using standard practice with addition of ethyl vinyl ether and precipitation into methanol. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.19 (m, 2H, 2 × ArH), δ 6.71 (br s, 3H, 3 x ArH), δ 5.40 (m, 4H, RHC=CHR), δ 3.03 (d, 2H, CH_2), δ 2.00 (m, 8H, CH_2), δ 1.68 (br s, 1H, CH), δ 1.49-1.26 (m, 14H, CH_2). The results of the synthesis are further reported in Table 6 below.

Table 6

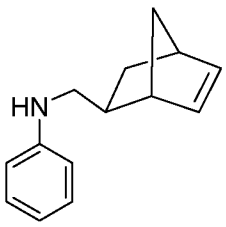
First monomer	Second monomer	Characterization
cyclooctene	M1	$M_{n,\ calc}$ = 19,019 ; Đ = 1.48*. ^{1}H NMR: 59/41 M1:M2

cyclooctene	M1	$M_{n,\ calc}$ = 36,951 ; Đ = 1.07*. ^{1}H NMR: 57/43 M1:M2

$M_{n,\ calc}$ determined using molecular weight of quenched aliquot of P1 then relating MW of P2 by using integrations in ^{1}H NMR spectrum.

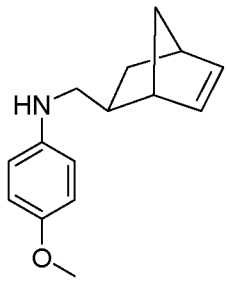
4.8.2 Copolymers with arylamine substituted norbornene monomer units

In contrast to the polymers disclosed and prepared herein, polymers formed from arylamine substituted norbornene monomers do not show self-healing behaviour. It was of interest to combine these monomers to explore whether this behavior could be tuned and allow for the preparation of materials with variable physical properties
Co-polymers of the amine-functionalized cycloalkene monomers disclosed above and several arylamine substituted norbornene monomers including:



("ACN-1")

and

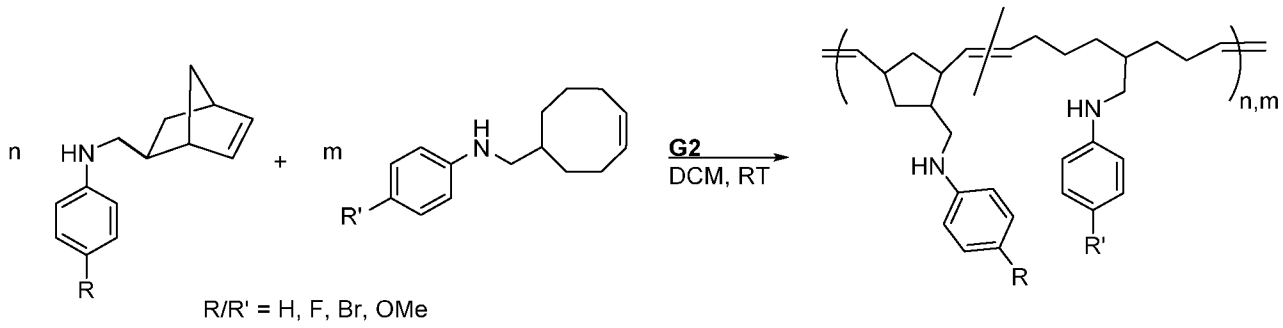


("ACN-4")

.

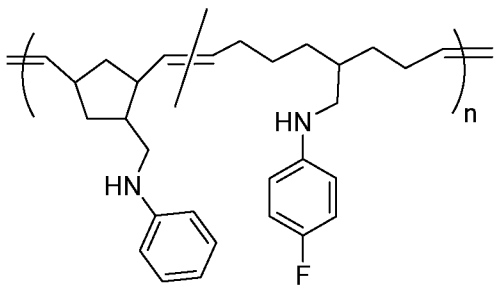
Monomers ACN-1 and ACN-4 can be prepared as disclosed by Perry et al. (Macromolecules, 49: 4423 to 4430).

A simultaneous addition of monomers was employed in the attempted formation of copolymers



A series of different combinations of monomers with varying *para* R/R' substituents were co-polymerized *via* ROMP (50 equivalents of each monomer). Copolymers were prepared as in homopolymers using various stoichiometric amounts of the differnet monomers to give theoretical ratio in polymer product. A typical procedure is as follows:

P(ACN-1-*co*-P2)



To a 20 mL scintillation vial was added ACN-1 (50 mg, 0.25 mmol) and polymer P2 (58 mg, 0.25 mmol) with *ca.* 1 mL CH_2Cl_2. To this solution was added a solution of Grubbs Catalyst™ 2nd Generation ("G2"; 4.2 mg, 0.005 mmol) in *ca.* 1 mL CH_2Cl_2. The reaction was stirred for 20 h at room temperature, during which the solution slowly goes brown-green from the initial amber color. The polymer was isolated using standard practice with addition of ethyl vinyl ether and precipitation into methanol; yields are quantitative with losses due to collection from precipitation. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.16 (s, 2H, 2 × ArH), δ 6.87 (m, 2H, 2 × ArH), δ 6.75 (m, 3H, 3 ArH), δ 6.55 (br s, 2H, 2 x ArH), δ 5.39-5.27 (m, 4H, 2 x RHC=CHR), δ 3.05-2.97 (d, 4H, CH_2),

δ 2.90 (s, 1H, CH), δ 2.53 (s, 1H, CH), δ 2.00-1.95 (m, 6H, CH_2), δ 1.65-1.63 (br s, 3H), δ 1.36 (br s, 6H, CH_2), δ 1.19 (s, 1H, CH).

Isolation of quenched reaction solutions by precipitation gave a material with physical properties that are intermediate to the respective homopolymers. Where homopolymers made from arylamine substituted norbornene monomers are stiff threads, and homopolymers as disclosed herein are sticky and tough gums, the copolymers aggregate and are tacky as in the latter, however with more pronounced stiffness. By ^{1}H NMR spectroscopy, it was found that the resultant polymers had higher incorporations of the given ACN (52-74 %). ACN-1 (R = H) and ACC-2 (R' = F) was chosen as a model system as both monomers were evenly incorporated (52:48 ACN:ACC). To ensure that a copolymer was formed, rather than two homopolymers, GPC analysis was performed on this sample; one peak was observed with reasonable agreement to the theoretical value ($M_{n,\ exp}$ = 18,130 g•mol^{-1}, Đ = 1.61, $M_{n,\ theo.}$ = 21,630 g•mol^{-1}).

To explore whether the thermal properties can be tuned based on the relative incorporation of monomers, three different ratios of the polymer **P(ACN-1-*co*-P2)** model system were prepared. The experimental ratios determined by ^{1}H NMR spectroscopy are indicated in Table 7. The glass transition temperatures as determined by DSC are shown in Table 7 and Figure 18. As indicated in Figure 18, the glass transition could be tuned by adjusting the feed ratio of both monomers. The observation of a single glass transition in each sample is also indicative of copolymer synthesis in which both blocks possess miscibility.

Table 7. Ratios of monomer in co-polymer.

% ACN theo.	% ACN exp.[a]	T_g[b] / °C
0.00	0.00	-10.4
0.25	0.28	8.55
0.50	0.52	17.3
0.75	0.81	37.6
1.00	1.00	58.4

[a]Calculated by ^{1}H NMR spectroscopy [b]Determined by DSC

The effects of these varied ratios on viscoelasticity was examined. Referring to Figure 19, melt rheology was conducted on the model copolymer with equal incorporation of ACN-1 and M2 segments. The P(ACN-1-*co*-P2) copolymer demonstrates rheological characteristics that are intermediate to the two pure homopolymers. Polymer P2 shows that loss modulus is dominant over the entire frequency range, suggesting liquid-like behavior. Storage modulus predominates in P(ACN-1) as a soft-solid material. In the copolymer, storage and loss moduli are roughly equivalent at low frequency; at higher frequencies storage modulus is dominant, with a cross-over point at the terminal zone. This observed rheological behavior also suggests a copolymer with miscible domains.

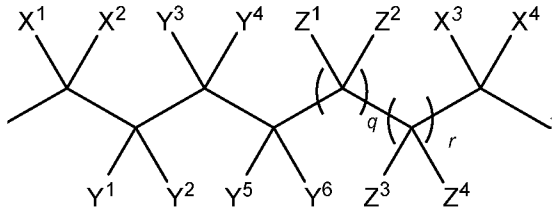
Qualitative healing tests were performed to explore the effect of varying the glass transition temperature (T_g). It was hypothesized that all samples that had a glass transition below room temperature would demonstrate self-healing. Of the three copolymers, only the sample with 3:1 M2:ACN-1 ratio (T_g = 8.6 ^{0}C) demonstrated healing within 24 hours. The sample with 1:1 M2:ACN-1 (T_g = 17.3 ^{0}C) did not demonstrate healing at the ambient conditions. These results suggest that tuning the thermal behavior may allow tuning of healing time depending on the needs of the material.

While specific embodiments of the invention have been described and illustrated, such embodiments should be considered illustrative of the invention only and not as limiting

the invention as construed in accordance with the accompanying claims. Many adaptations and modifications may be made within the scope of the invention in accordance with the common general knowledge of those skilled in this art. Such modifications include the substitution of known equivalents for any aspect of the invention in order to achieve the same result in substantially the same way.

What is claimed is:

1. A polymer comprising a mixture of different amine-functionalized monomer units of Formula 6:



(Formula 6)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein the monomer units are connected in a head to head fashion, head to tail fashion, tail to tail fashion, or any combination thereof.

2. The polymer of claim 1, wherein each of X^1, X^2, X^3, and X^4 is H.

3. The polymer of claim 1, wherein only one of X^1, X^2, X^3, and X^4 is CH_3.

4. The polymer of claim 1, wherein each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3.

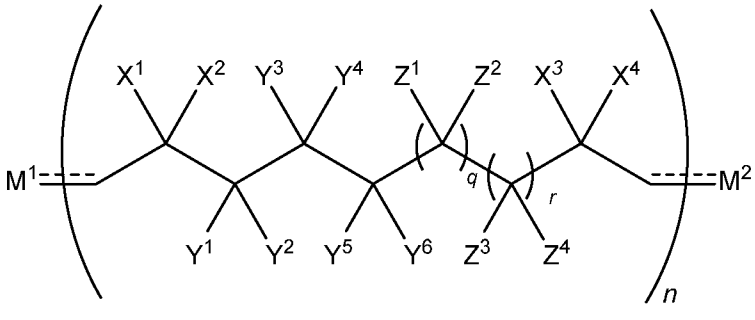
5. The polymer of any one of claims 1 to 4, wherein at least one of R^1 and R^2 is H.

6. The polymer any one of claims 1 to 5, wherein at least one of R^3 and R^4 is H.

7. The polymer of any one of claims 1 to 6, wherein when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, at least one ring-carbon atom adjacent to the ring-carbon atomsubstituted with $-CR^1R^2–NR^3R^4$ is substituted with two H atoms.

8. The polymer of any one of claims 1 to 7, wherein when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is further substituted with a hydrogen atom.

9. An amine-functionalized compound of Formula 2:



(Formula 2);

wherein (---) indicates an optional double bond;

wherein each of M^1 and M^2 independently is -OH, a substituted or unsubstituted $C_{1\text{-}15}$ alkyl, a substituted or unsubstituted aromatic cycle, a substituted or unsubstituted

heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2; and

wherein n is a natural number greater than 1.

10. The amine-functionalized compound of claim 9, wherein each of X^1, X^2, X^3, and X^4 is H.

11. The amine-functionalized compound of claim 9, wherein only one of X^1, X^2, X^3, and X^4 is CH_3.

12. The amine-functionalized compound of claim 9, wherein each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3.

13. The amine-functionalized compound of any one of claims 9 to 12, wherein at least one of R^1 and R^2 is H.

14. The amine-functionalized compound of any one of claims 9 to 13, wherein at least one of R^3 and R^4 is H.

15. The amine-functionalized compound of any one of claims 9 to 14, wherein when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, at least one ring-carbon atom adjacent to the ring-carbon atomsubstituted with $-CR^1R^2–NR^3R^4$ is substituted with two H atoms.

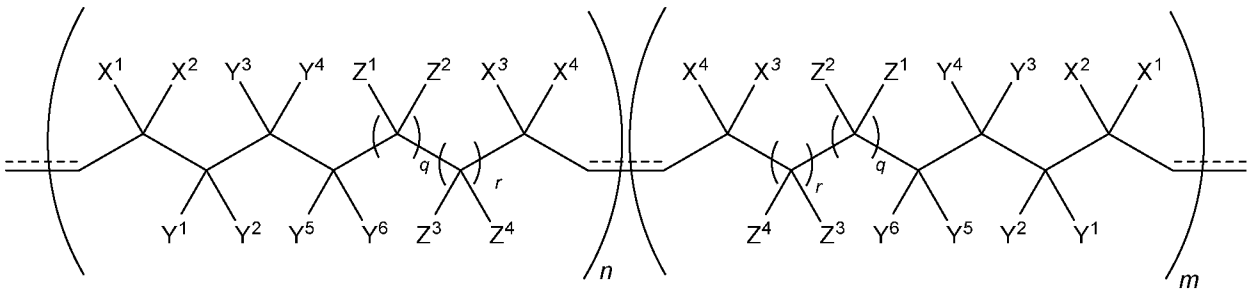
16. The amine-functionalized compound of any one of claims 9 to 15, wherein when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is further substituted with a hydrogen atom.

17. The amine-functionalized compound of any one of claims 9 to 16, wherein the polymer has self-healing properties.

18. The amine-functionalized compound of any one of claims 9 to 17, wherein the polymer has adhesive properties.

19. The amine-functionalized compound of any one of claims 9 to 18, wherein the polymer has antimicrobial activity.

20. A polymer comprising an oligomer of Formula 3:



(Formula 3)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

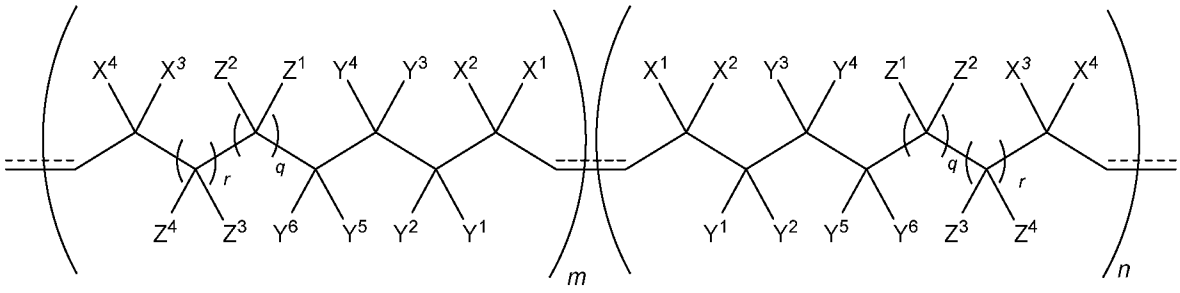
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomer units are connected in a head to head fashion.

21. A polymer comprising an oligomer of Formula 4:



(Formula 4)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or

unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

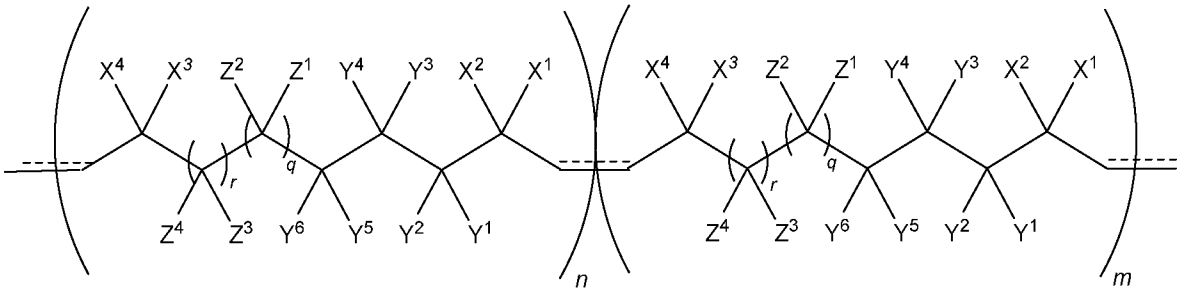
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomer units are connected in a tail to tail fashion.

22. A polymer comprising an oligomer of Formula 7:



(Formula 7)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

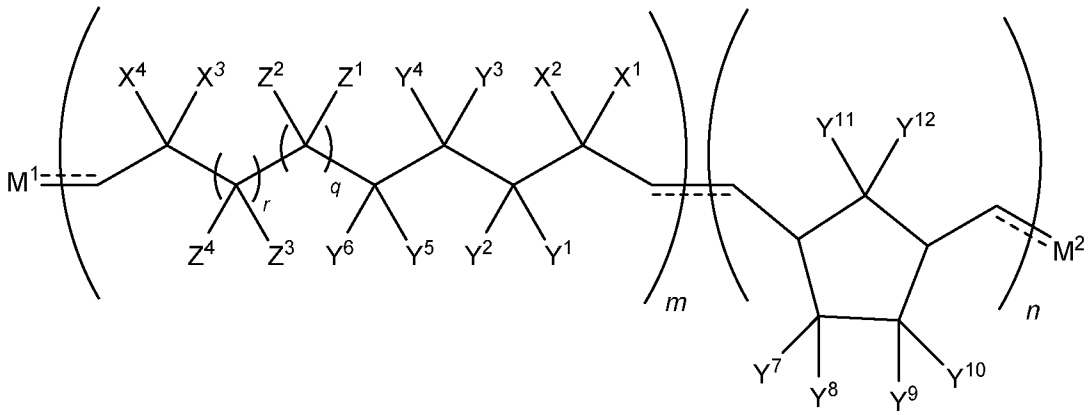
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomer units are connected in a head to tail fashion.

23. A polymer of Formula X:



(Formula X)

wherein (---) indicates an optional double bond;

wherein each of M^1 and M^2 is independently -OH, a substituted or unsubstituted $C_{1\text{-}15}$ alkyl, a substituted or unsubstituted aromatic cycle, a substituted or unsubstituted heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11}, Y^{12}, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

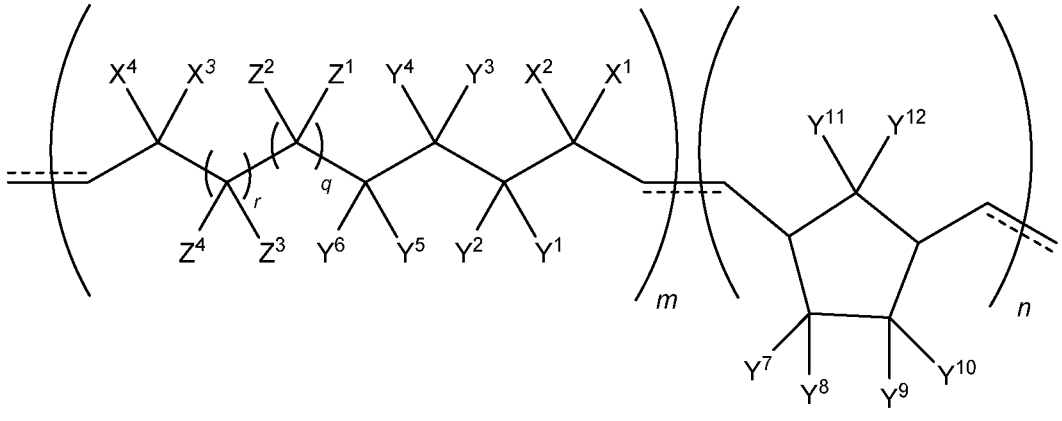
wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomer units are connected in a head to head fashion, a head to tail fashion, a tail to tail fashion, or any combination thereof.

24. A polymer comprising an oligomer of Formula XI:



(Formula XI)

wherein (---) indicates an optional double bond;

wherein each X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Y^7, Y^8, Y^9, Y^{10}, Y^{11}, Y^{12}, Z^1, Z^2, Z^3, and Z^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'', and wherein at least one of Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, and Z^4 is $-CR^1R^2–NR^3R^4$;

wherein each of R' and R'' is independently H , a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein each of R^1, R^2, R^3 and R^4 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^3 and R^4 are linked to form a cyclic moiety, or wherein one of R^3 and R^4 is linked with one of R^1 and R^2 to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n and m are natural numbers; and

wherein the monomer units are connected in a head to head fashion, a head to tail fashion, a tail to tail fashion, or any combination thereof.

25. The polymer of claim 23 or 24, wherein the monomer units are connected in a head to head fashion.

26. The polymer of any one of claims 20 to 25, wherein each of X^1, X^2, X^3, and X^4 is H.

27. The polymer of any one of claims 20 to 25, wherein only one of X^1, X^2, X^3, and X^4 is CH_3.

28. The polymer of any one of claims 20 to 25, wherein each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3.

29. The polymer of any one of claims 20 to 28, wherein at least one of R^1 and R^2 is H.

30. The polymer any one of claims 20 to 29, wherein at least one of R^3 and R^4 is H.

31. The polymer of any one of claims 20 to 30, wherein when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, at least one ring-carbon atom adjacent to the ring-carbon atomsubstituted with $-CR^1R^2–NR^3R^4$ is substituted with two H atoms.

32. The polymer of any one of claims 20 to 31, wherein when Y^1, Y^2, Y^3, Y^4, Y^5, Y^6, Z^1, Z^2, Z^3, or Z^4 is $-CR^1R^2–NR^3R^4$, the ring-carbon atom substituted with $-CR^1R^2–NR^3R^4$ is further substituted with a hydrogen atom.

33. A block copolymer prepared comprising: an amine functionalized compound as defined in any one of claims 9 to 19; and a polymer formed by radical or anionic polymerization, for which the functional end-groups M1 and M2 of the amine functionalized compound serves as an initiation point.

34. A block copolymer prepared comprising: an amine functionalized compound as defined in any one of claims 9 to 19; and at least one additional polymer.

35. A block copolymer prepared from an amine functionalized compound as defined in any one of claims 9 to 19; and at least one additional hydroaminoalkylated cycloalkene.

36. The block polymer of claim 35, wherein the at least one additional polymer includes an arylamine substituted norbornene

37. A brush copolymer comprising a polymer as defined in any one of claims 1 to 8 and 20 to 33 and polymeric bristles or brushes, wherein at least one of X^1, X^2, X^3, X^4,

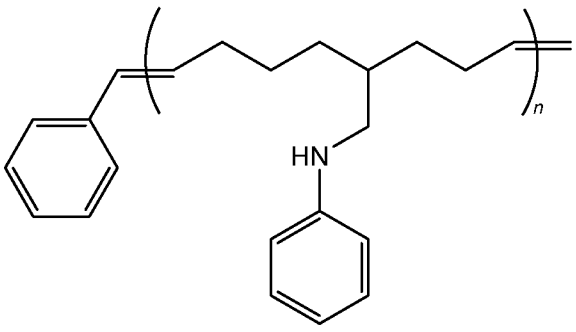
Y^1, Y^2, Y^3, Y^4, Y^5 , Y^6, Z^1, Z^2, Z^3, Z^4, R', R'', R^1, R^2, R^3, and R^4 serves as an initiation point for subsequent synthesis of polymeric bristles or brushes.

38. The polymer of any one of claims 1 to 8 and 20 to 37, wherein the polymer has self-healing properties.

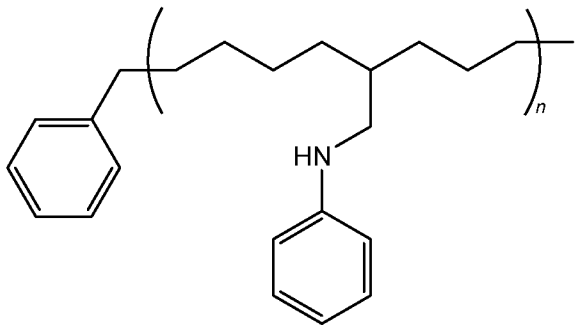
39. The polymer of any one of claims 1 to 8 and 20 to 37, wherein the polymer has adhesive properties.

40. The polymer of any one of claims 1 to 8 and 20 to 37, wherein the polymer has antimicrobial activity.

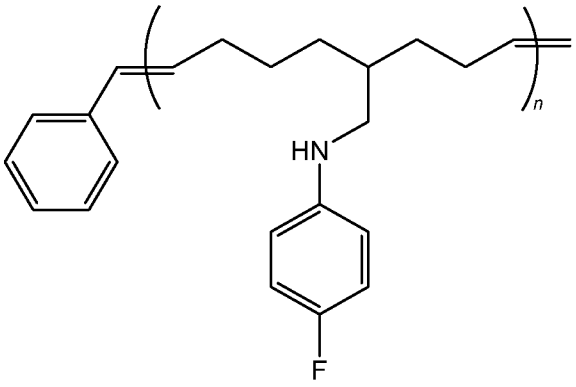
41. An amine functionalized polyalkene or polyalkane, wherein the polyalkene or polyalkane comprises:



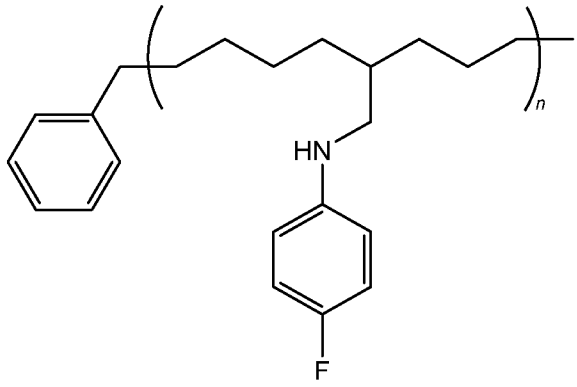
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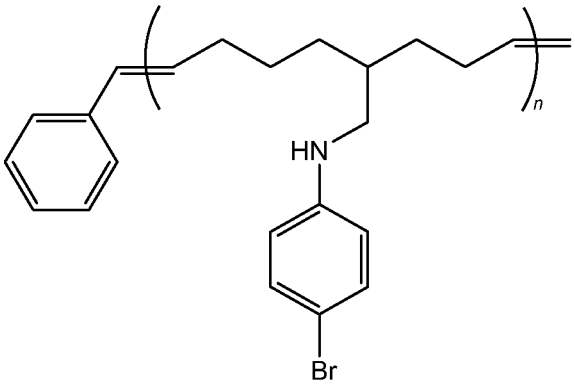
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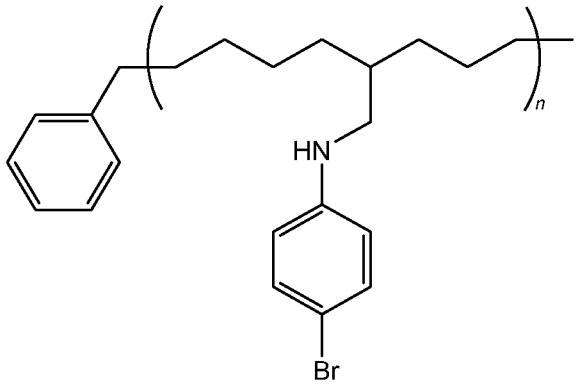


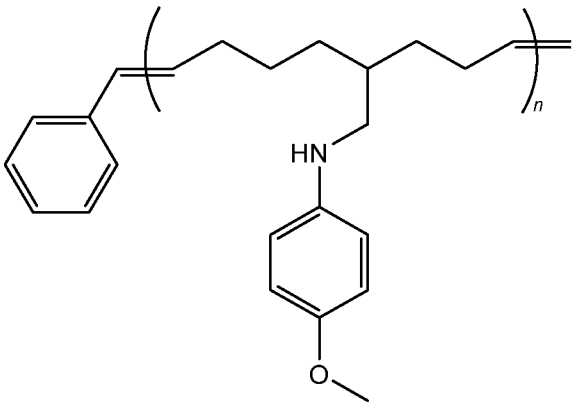
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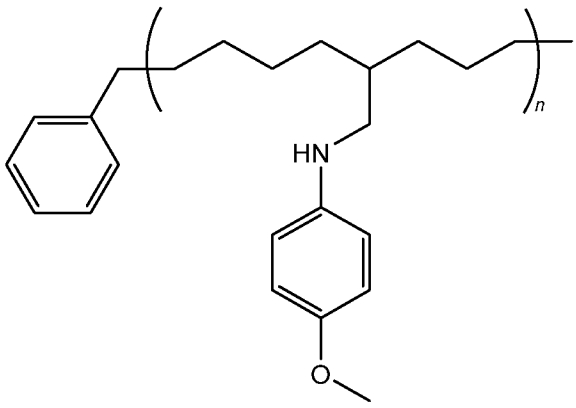


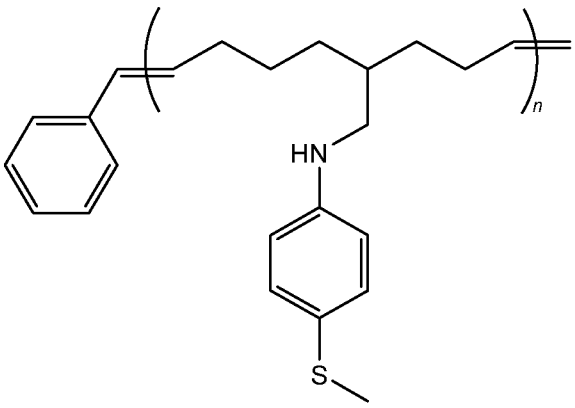
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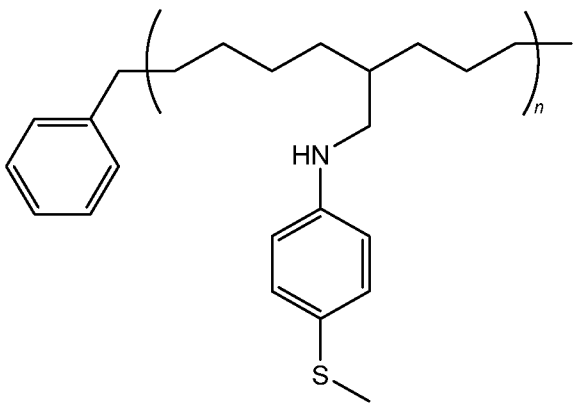

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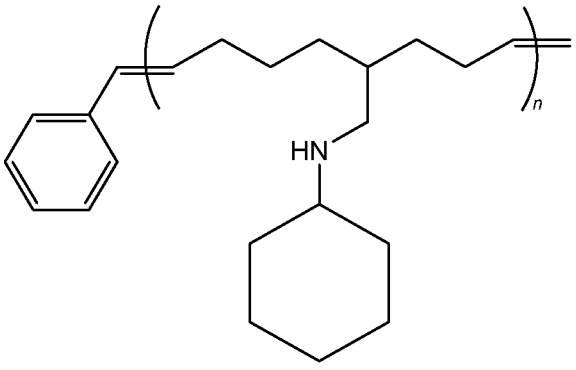

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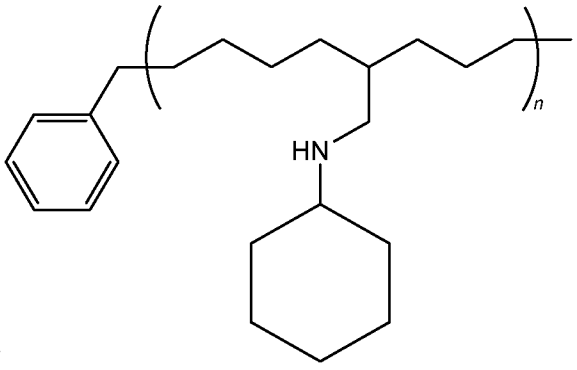

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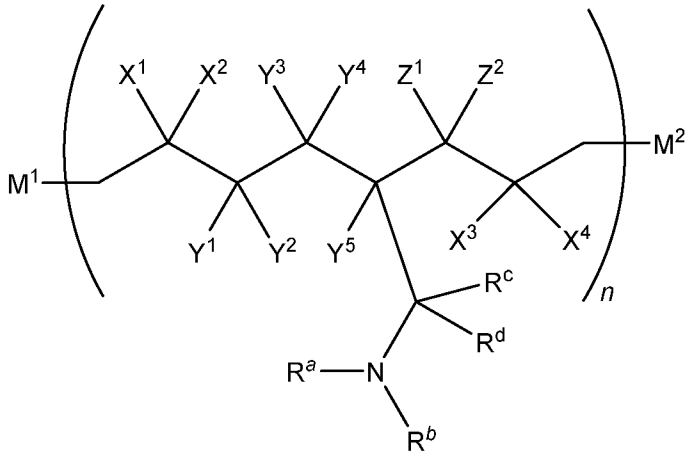
wherein *n* is a natural number greater than 1.

42. The amine functionalized polyalkene or polyalkane of claim 41, wherein the polymer has self-healing properties.

43. The amine functionalized polyalkene or polyalkane of claim 41 or 42, wherein the polymer has adhesive properties.

44. The amine functionalized polyalkene or polyalkane of claim 41, 42, or 43, wherein the polymer has antimicrobial activity.

45. A polyalkane of Formula 5:



(Formula 5);

wherein each of M^1 and M^2 is independently -OH, a substituted or unsubstituted $C_{1\text{-}15}$ alkyl, a substituted or unsubstituted aromatic cycle, a substituted or

unsubstituted heterocycle, or a functional end-group suitable for ring opening metathesis polymerization;

wherein each of X^1, X^2, X^3, and X^4 is independently H or CH_3;

wherein each of Y^1, Y^2, Y^3, Y^4, Y^5 , Z^1, and Z^2 is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, an amine-compatible protection group, -C(=O)R', or -C(OR')R'';

wherein each of R' and R'' is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group;

wherein each of R^a, R^b, R^c, and R^d is independently H, a substituted or unsubstituted linear or cyclic alkyl or alkenyl, a substituted or unsubstituted aryl, a substituted or unsubstituted heterocycle, or an amine-compatible protection group, or wherein R^b and R^a are linked to form a cyclic moiety, or wherein one of R^a and R^b is linked with one of R^c and R^d to form a cyclic moiety;

wherein $r = 0$ or 1 and $q = 0$ or 1, wherein $r + q = 0$, 1, or 2;

wherein n is a natural number greater than 1; and

wherein the monomer units are connected in a head to head fashion, a head to tail fashion, a tail to tail fashion, or any combination thereof.

46. The polyalkane of claim 45, wherein each of X^1, X^2, X^3, and X^4 is H.

47. The polyalkane of claim 45, wherein only one of X^1, X^2, X^3, and X^4 is CH_3.

48. The polyalkane of claim 45, wherein each of X^1 and X^3 is H and each of X^2 and X^4 is CH_3.

49. The polyalkane of any one of claims 45 to 48, wherein at least one of R^1 and R^2 is H.

50. The polyalkane of any one of claims 45 to 49, wherein at least one of R^3 and R^4 is H.

51. The polymer of any one of claims 45 to 50, wherein one of R^b and R^a is H.

52. The polymer of any one of claims 45 to 51, wherein the polymer has self-healing properties.

53. The polymer of any one of claims 45 to 52, wherein the polymer has adhesive properties.

54. The polymer of any one of claims 45 to 53, wherein the polymer has antimicrobial activity.

55. Use of an amine functionalized polyalkene or polyalkane as defined in claim 41 as an antimicrobial agent.

56. Use of a polymer as defined in any one of claims 1 to 8 and 20 to 37 as an antimicrobial agent.

57. Use of an amine-functionalized compound as defined in any one of claims 9 to 19 as an antimicrobial agent.

58. Use of an amine functionalized polyalkene or polyalkane as defined in claim 41 for reducing fouling.

59. Use of a polymer as defined in any one of claims 1 to 8 and 20 to 37 for reducing fouling.

60. Use of an amine-functionalized compound as defined in any one of claims 9 to 19 for reducing fouling.

61. The use of claim 58, 59, or 60, wherein fouling includes biofouling.

62. Use of an amine functionalized polyalkene or polyalkane as defined in claim 41 as an adhesive agent.

63. Use of a polymer as defined in any one of claims 1 to 8 and 20 to 37 as an adhesive agent.

64. Use of an amine-functionalized compound as defined in any one of claims 9 to 19 as an adhesive agent.

65. The use of claim 62, 63, or 64, wherein the adhesive agent is for adhering to a substrate.

66. The use of claim 65, wherein the substrate is Teflon, glass, or metal.

67. Use of an amine functionalized polyalkene or polyalkane as defined in claim 41 as a coating, a compatibilizer, a stabilizer, metal scavenger, a membrane a gasket, an anticoagulant, a drug delivery agent, or a scavenger agent.

68. Use of a polymer as defined in any one of claims 1 to 8 and 20 to 37 as a coating, a compatibilizer, a stabilizer, metal scavenger, a membrane a gasket, an anticoagulant, a drug delivery agent, or a scavenger agent.

69. Use of an amine-functionalized compound as defined in any one of claims 9 to 19 as a coating, a compatibilizer, a stabilizer, metal scavenger, a membrane a gasket, an anticoagulant, a drug delivery agent, or a scavenger agent.

70. The use of claim 67, 68, or 69, wherein the scavenger agent is for binding pollutants during environmental remediation in marine environments.

71. The use of claim 70, wherein the pollutants include oil, plastic particles, or a combination thereof.

72. The use of claim 67, 68, or 69, wherein the membrane is an electrolyte membrane or a filtering membrane for water purification.

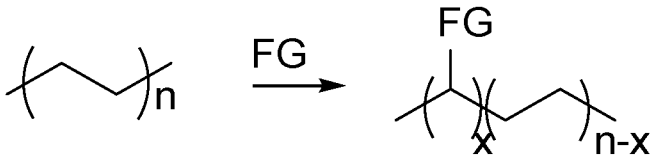
73. A substrate a substrate coated with amine functionalized polyalkene or polyalkane as defined in claim 41.

74. A substrate a substrate coated with an amine-functionalized compound as defined in any one of claims 9 to 19.

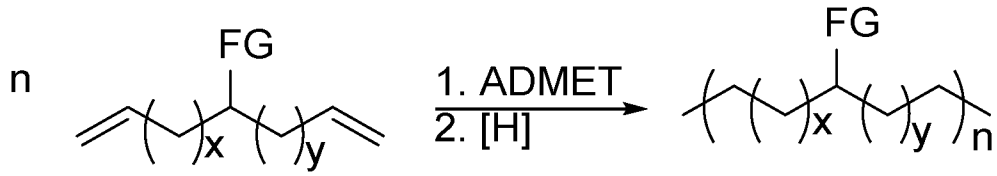
75. A substrate coated with a polymer as defined in any one of claims 1 to 8 and 20 to 37.

76. The substrate of claim 73, 74, or 75, wherein the substrate reduces biofouling.

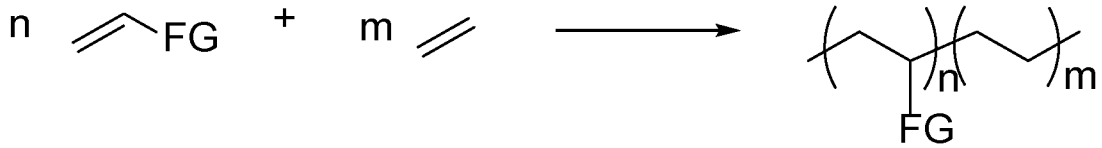
Post-polymerization modification



ADMET followed by hydrogenation



Radical/catalytic copolymerization



ROMP followed by hydrogenation

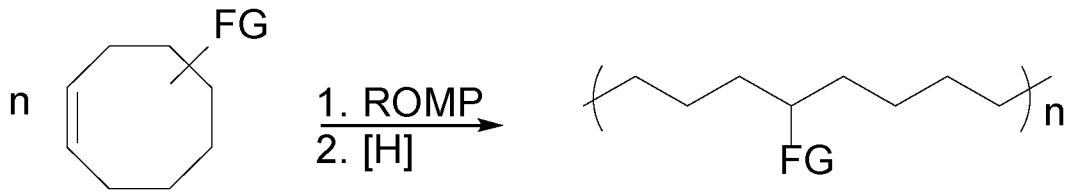


Figure 1

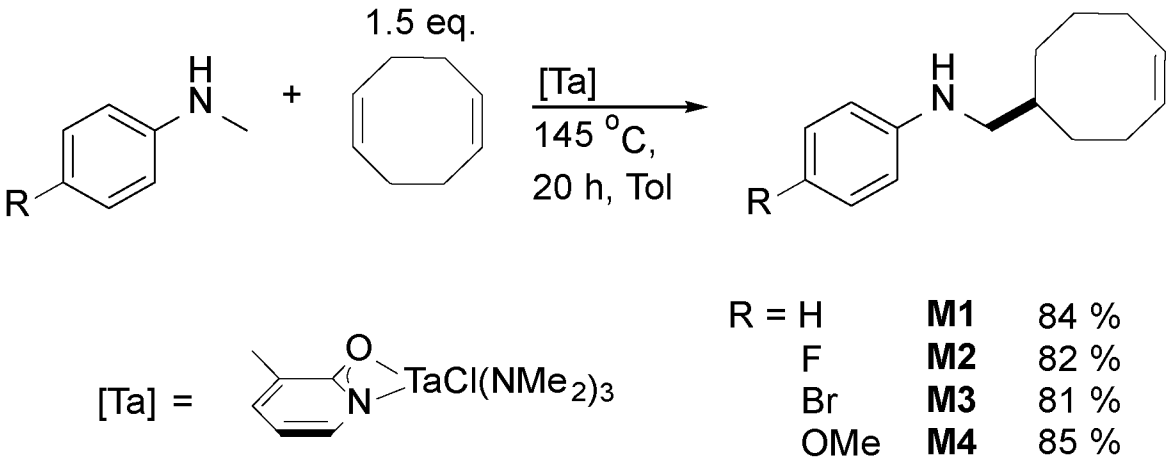


Figure 2

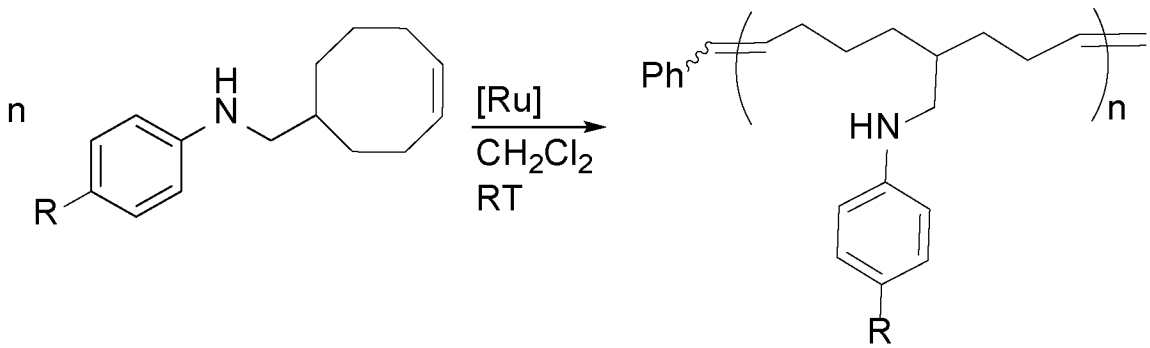


Figure 3

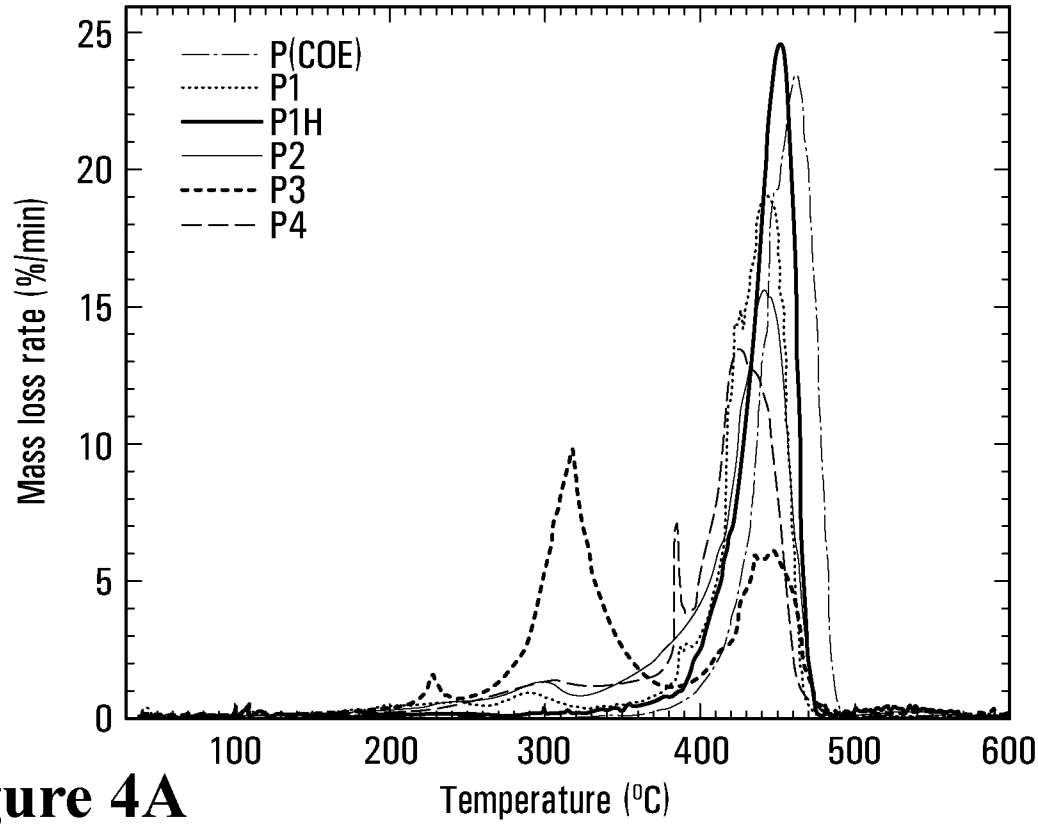


Figure 4A

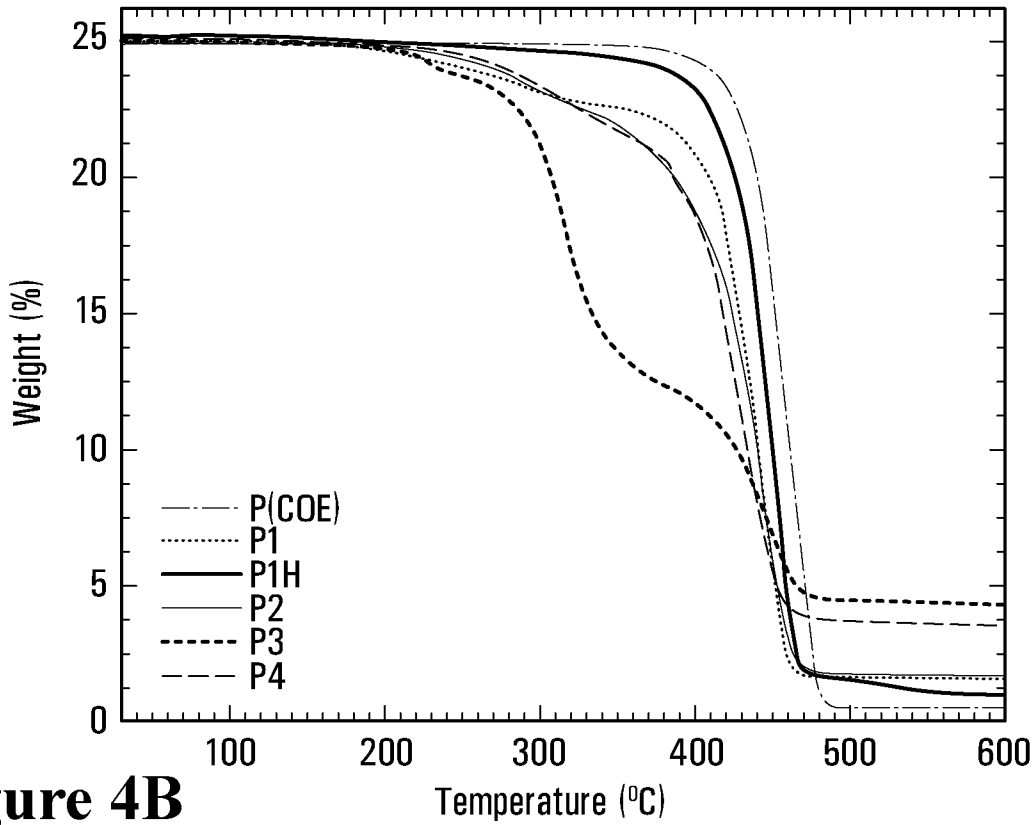


Figure 4B

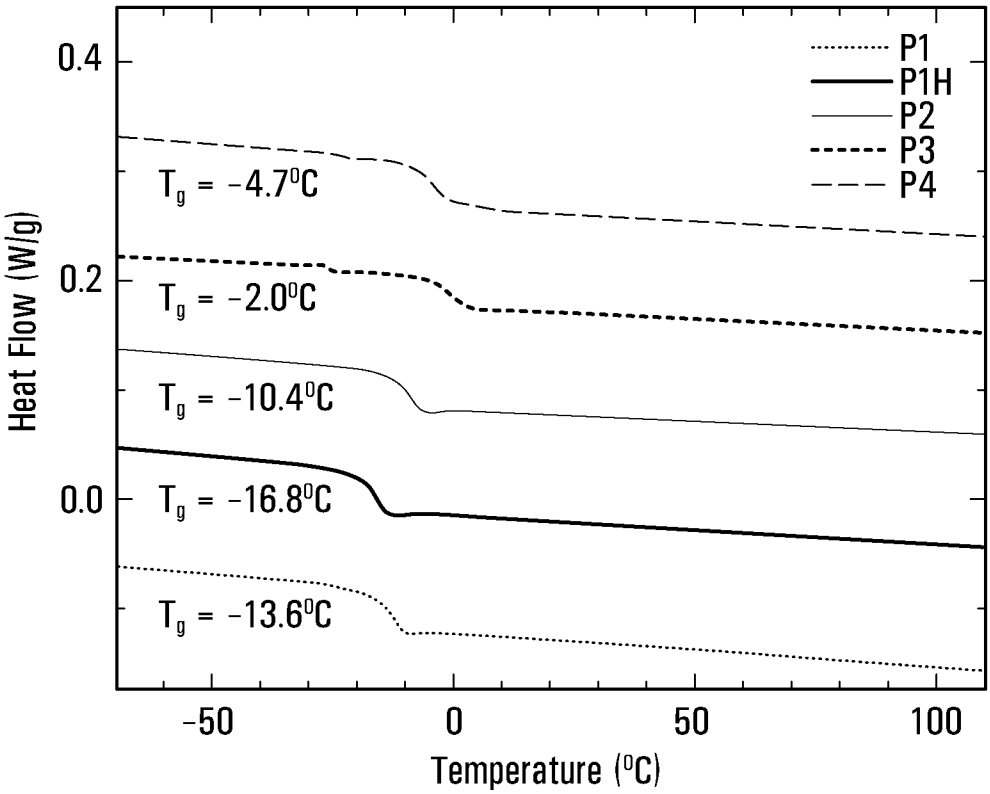

0.4
0.2
0.0
Heat Flow (W/g)
P1
P1H
P2
P3
P4
T_g = -4.7°C
T_g = -2.0°C
T_g = -10.4°C
T_g = -16.8°C
T_g = -13.6°C
-50
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100
Temperature (°C)

Figure 5

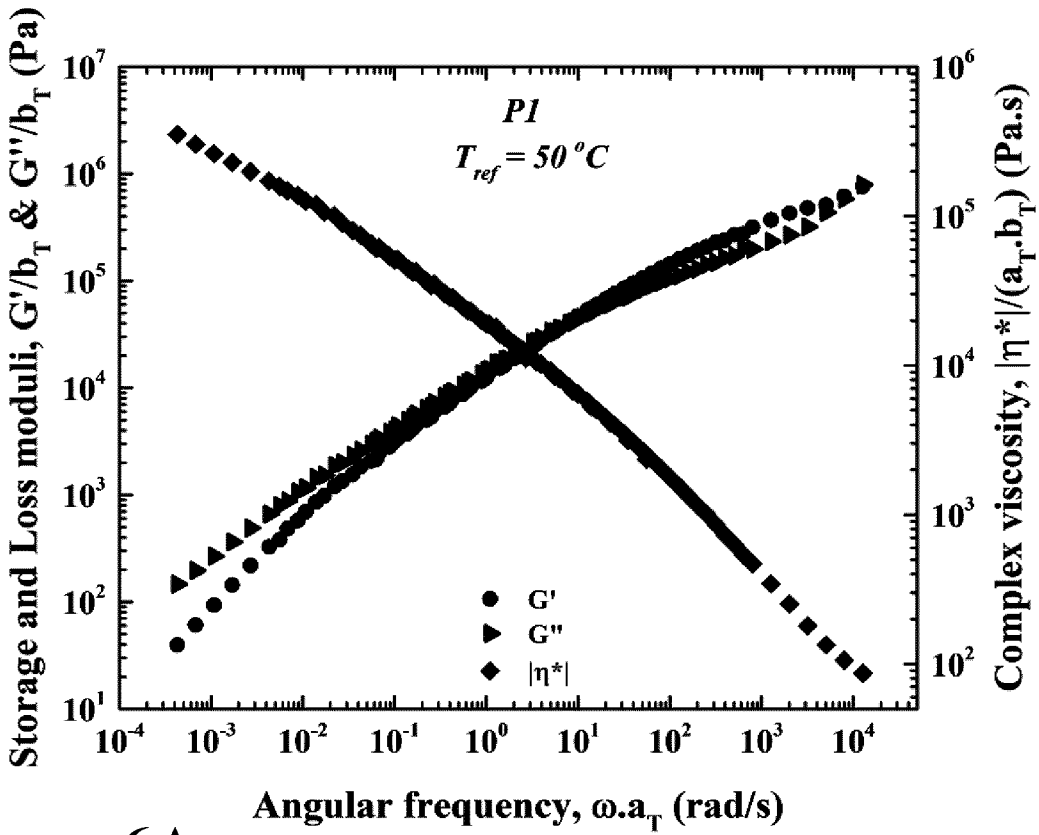


Figure 6A

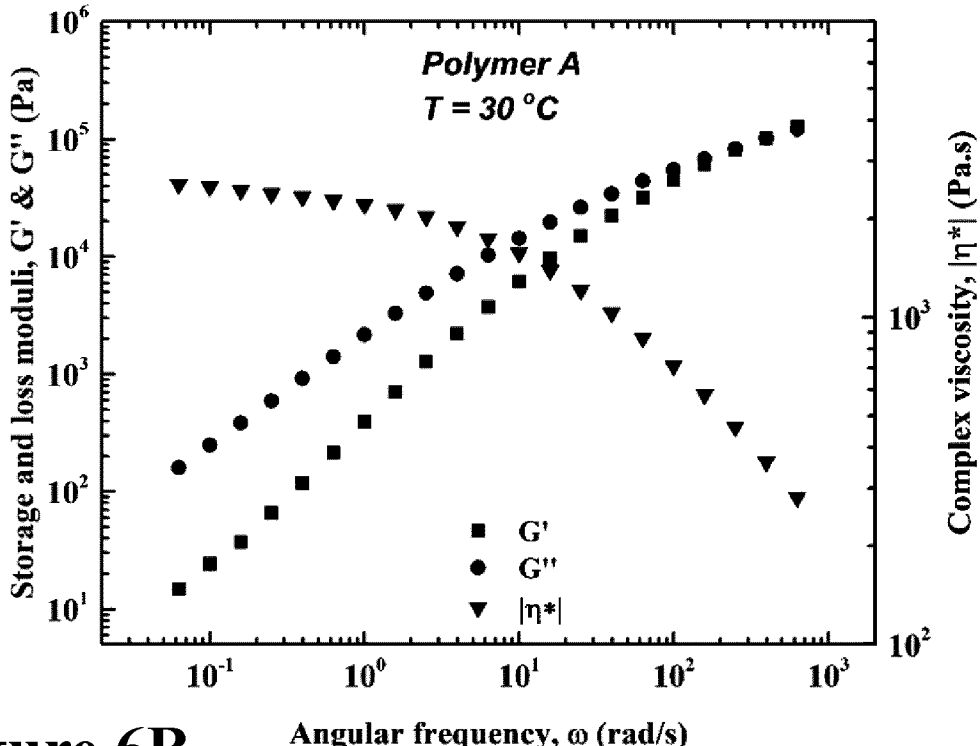


Figure 6B

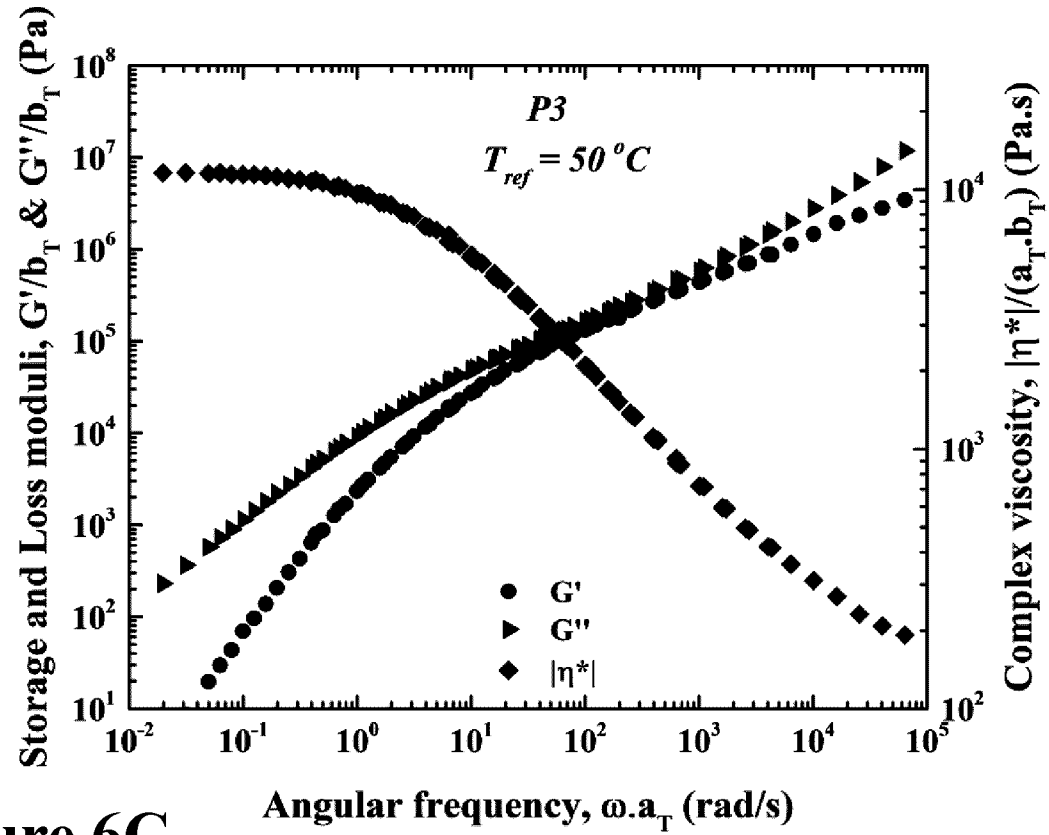


Figure 6C

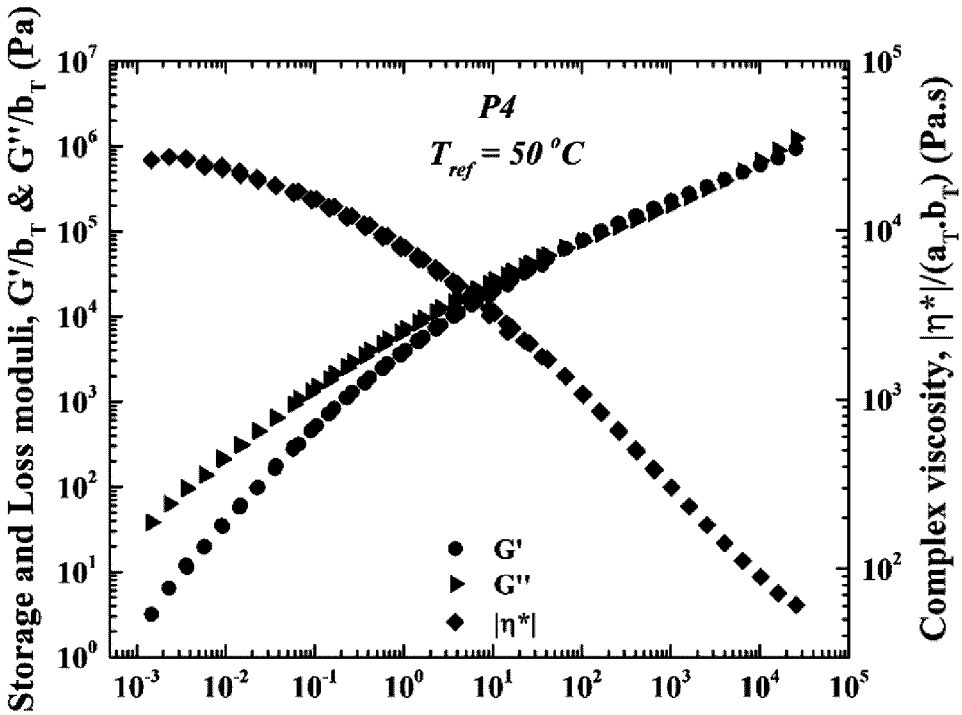


Figure 6D

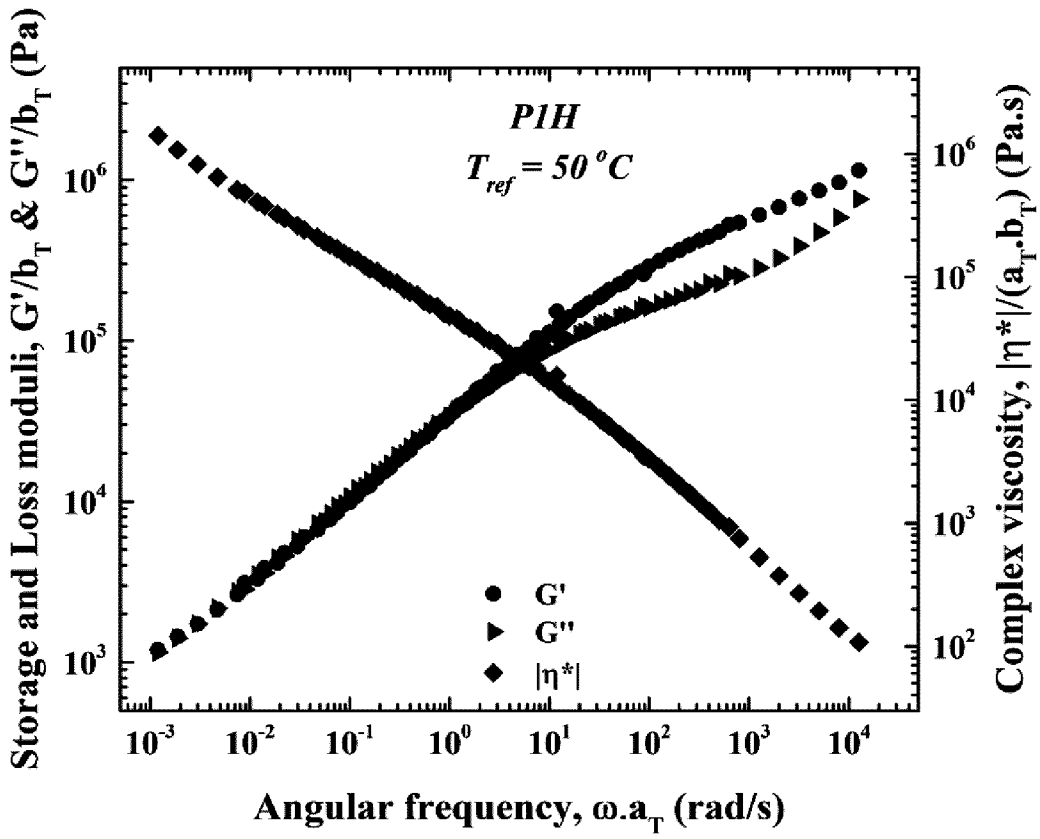

P1H
T_{ref} = 50 °C
G'
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Storage and Loss moduli, G'/b_T & G''/b_T (Pa)
Complex viscosity, |η*|/(a_T.b_T) (Pa.s)
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Figure 6E

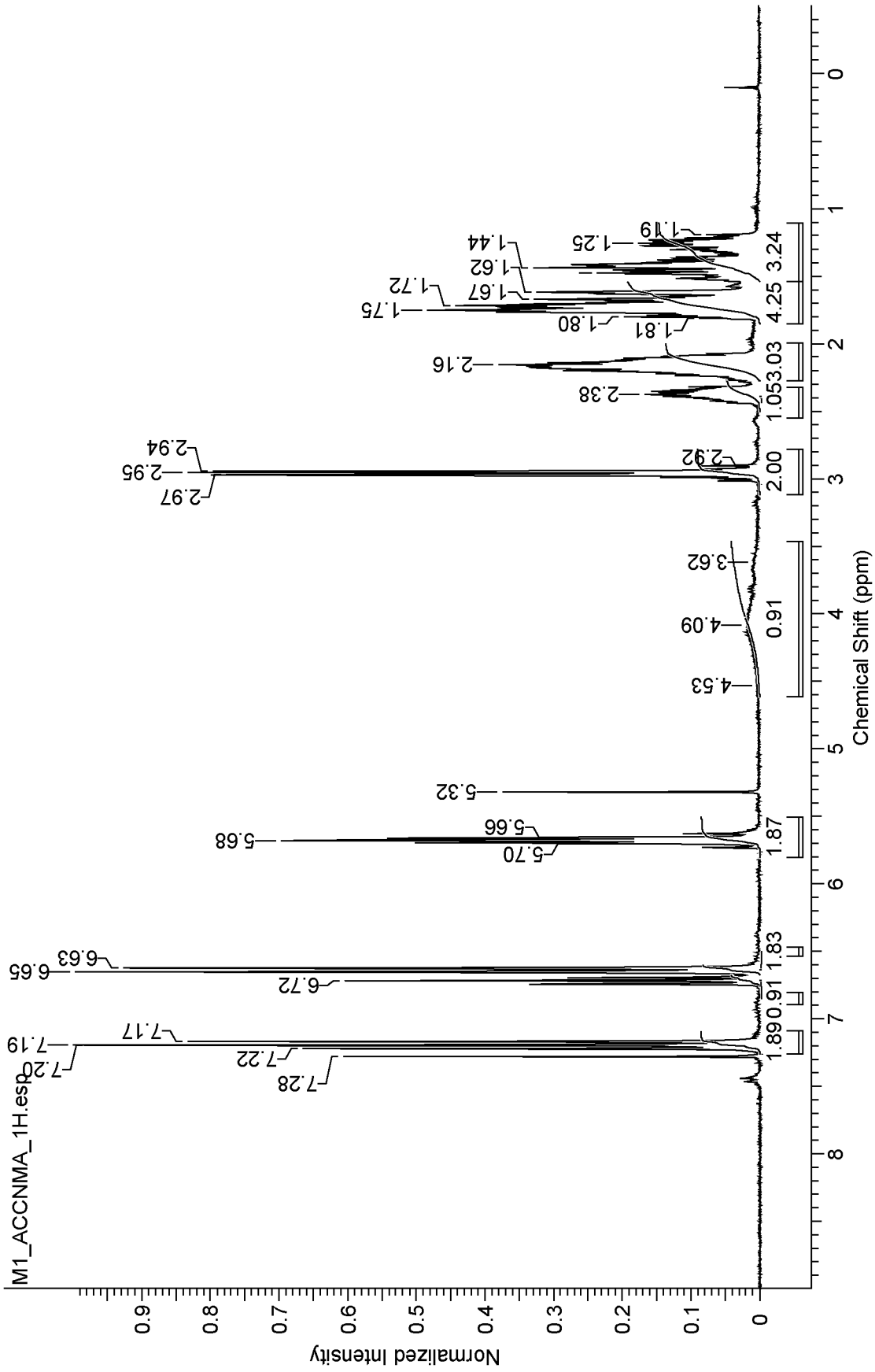

M1_ACCNMA_1H.esp
Normalized Intensity
Chemical Shift (ppm)
7.28
7.22
7.20
7.19
7.17
6.65
6.63
6.72
5.68
5.70
5.66
5.32
4.53
4.09
3.62
2.97
2.95
2.94
2.92
2.38
2.16
1.81
1.80
1.75
1.72
1.67
1.62
1.44
1.25
1.19
1.89
0.91
1.83
1.87
0.91
2.00
1.05
3.03
4.25
3.24

Figure 7A

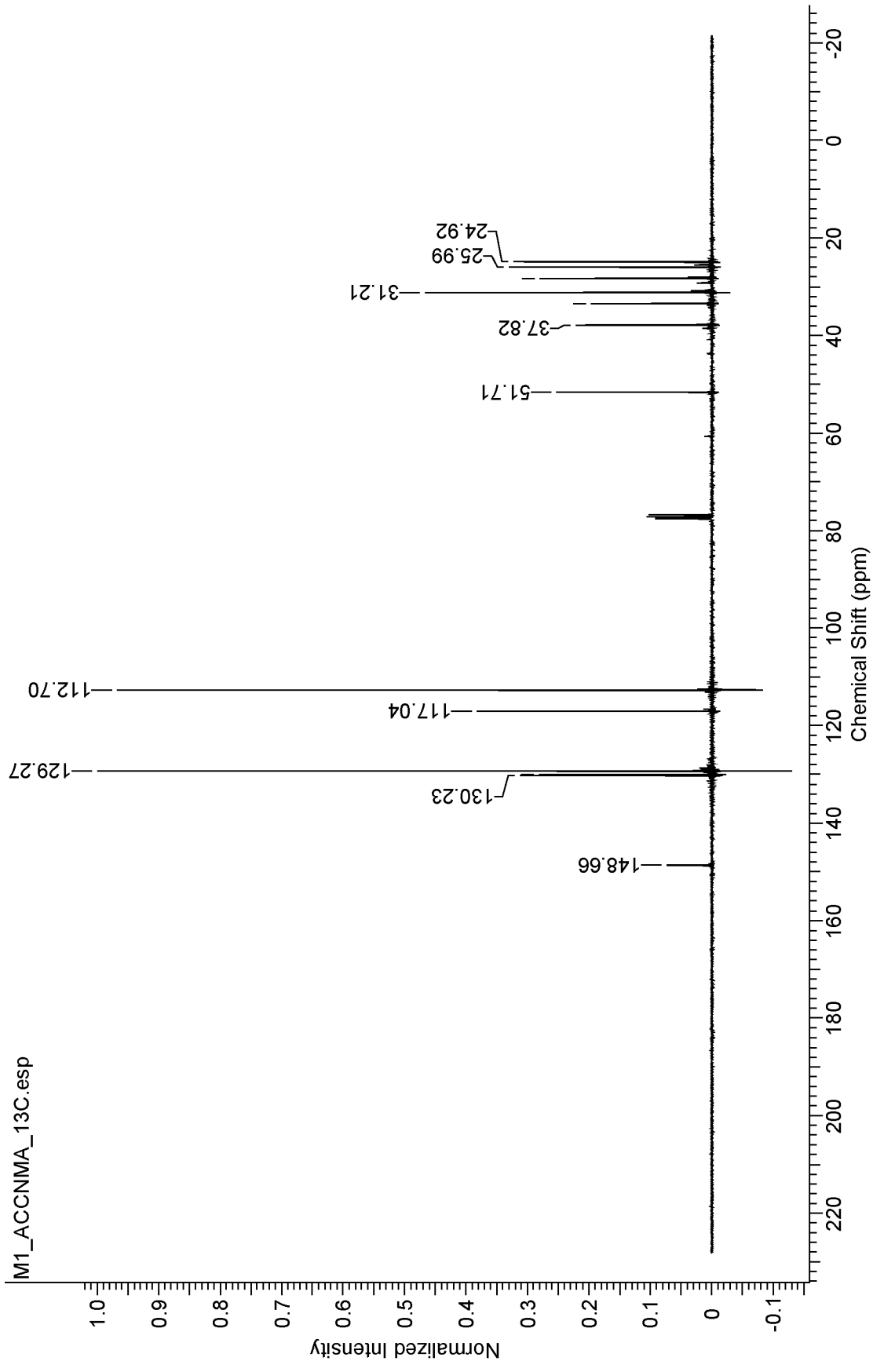

M1_ACCNMA_13C.esp
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
Chemical Shift (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
-20
148.66
130.23
129.27
117.04
112.70
51.71
37.82
31.21
25.99
24.92

Figure 7B

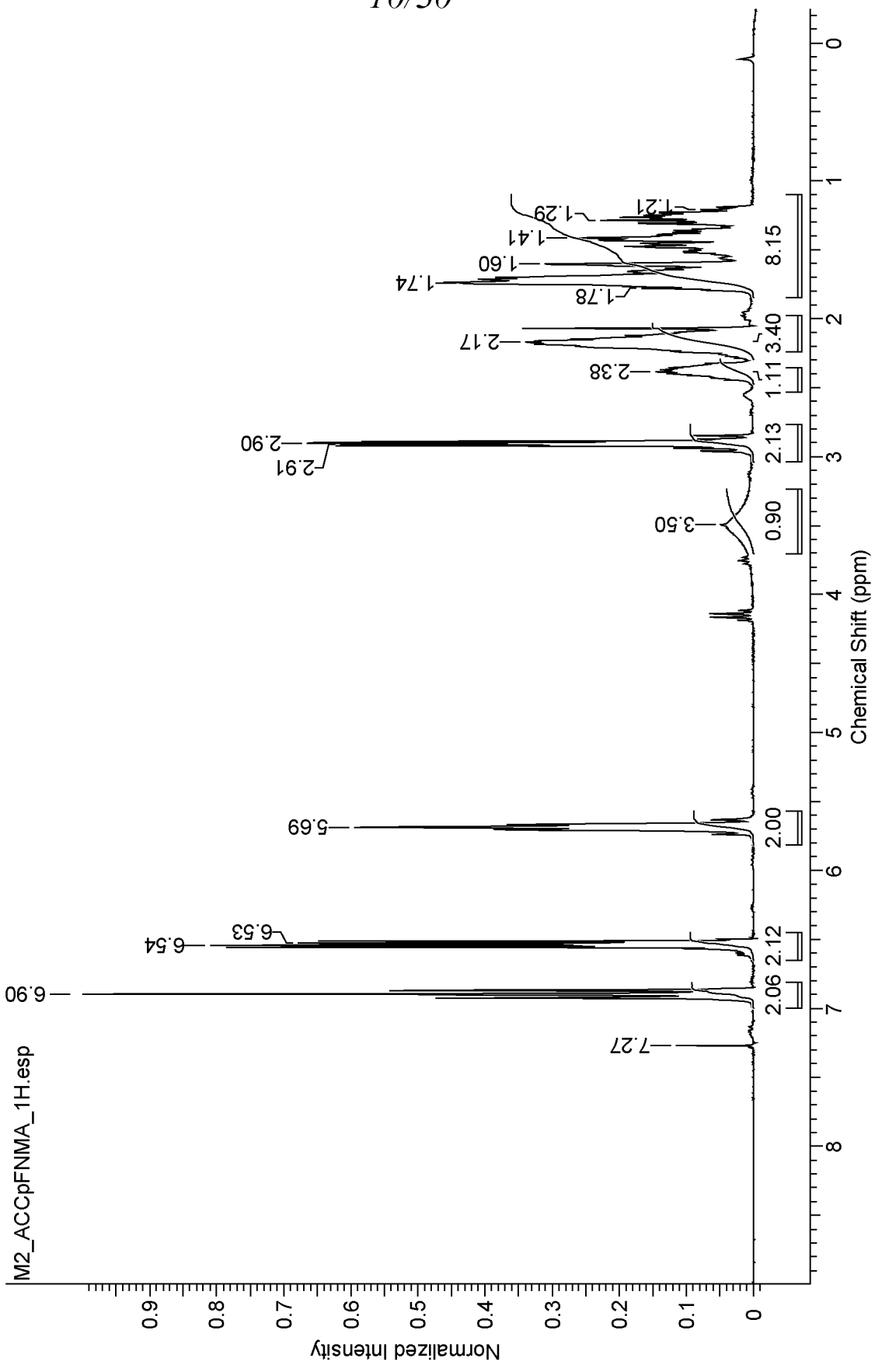

M2_ACCpFNMA_1H.esp
Normalized Intensity
Chemical Shift (ppm)
7.27
6.90
6.54
6.53
5.69
3.50
2.91
2.90
2.38
2.17
1.78
1.74
1.60
1.41
1.29
1.21
2.06
2.12
2.00
0.90
2.13
1.11
3.40
8.15

Figure 8A

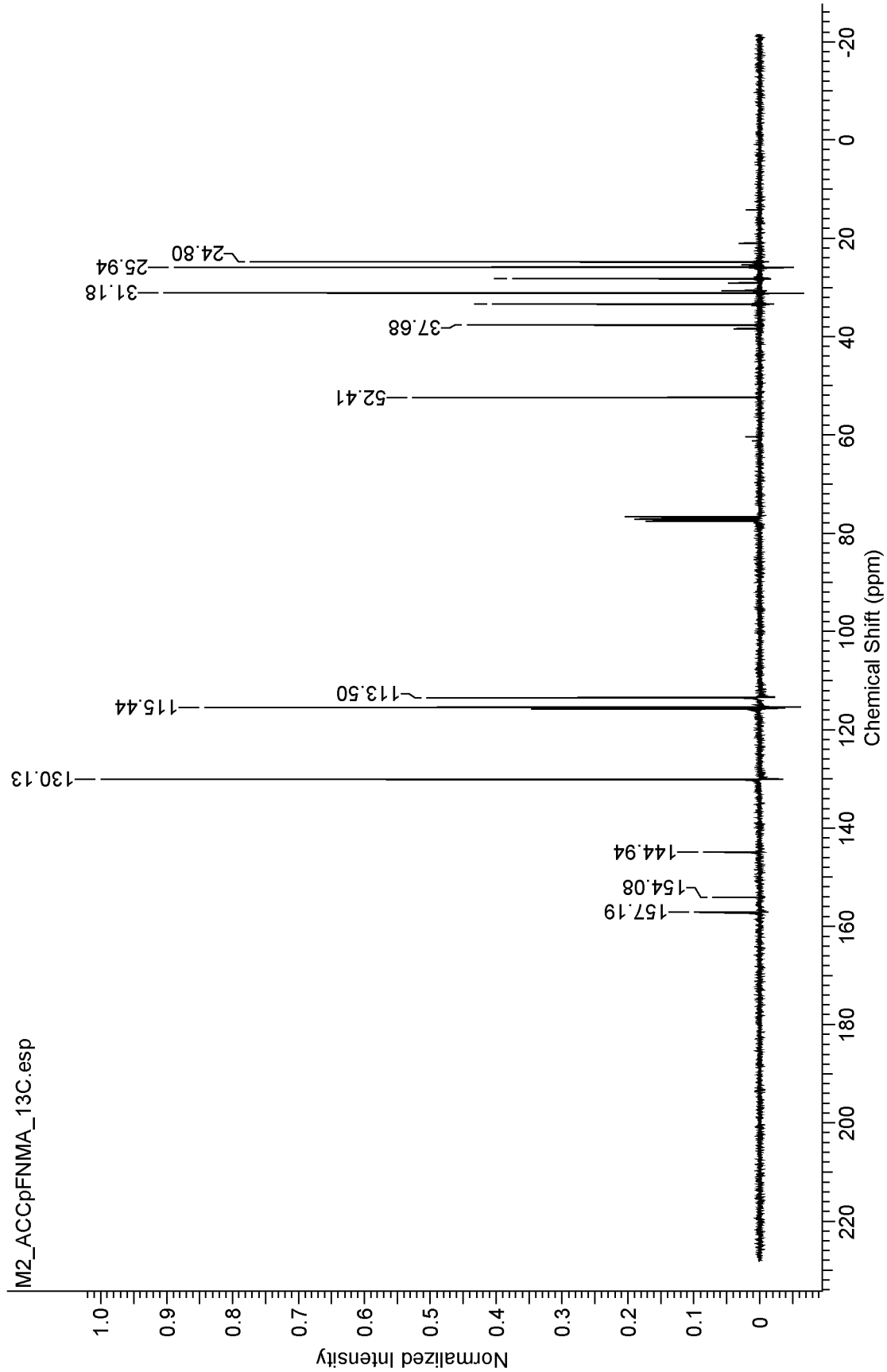

M2_ACCpFNMA_13C.esp
Normalized Intensity
Chemical Shift (ppm)
157.19
154.08
144.94
130.13
115.44
113.50
52.41
37.68
31.18
25.94
24.80

Figure 8B

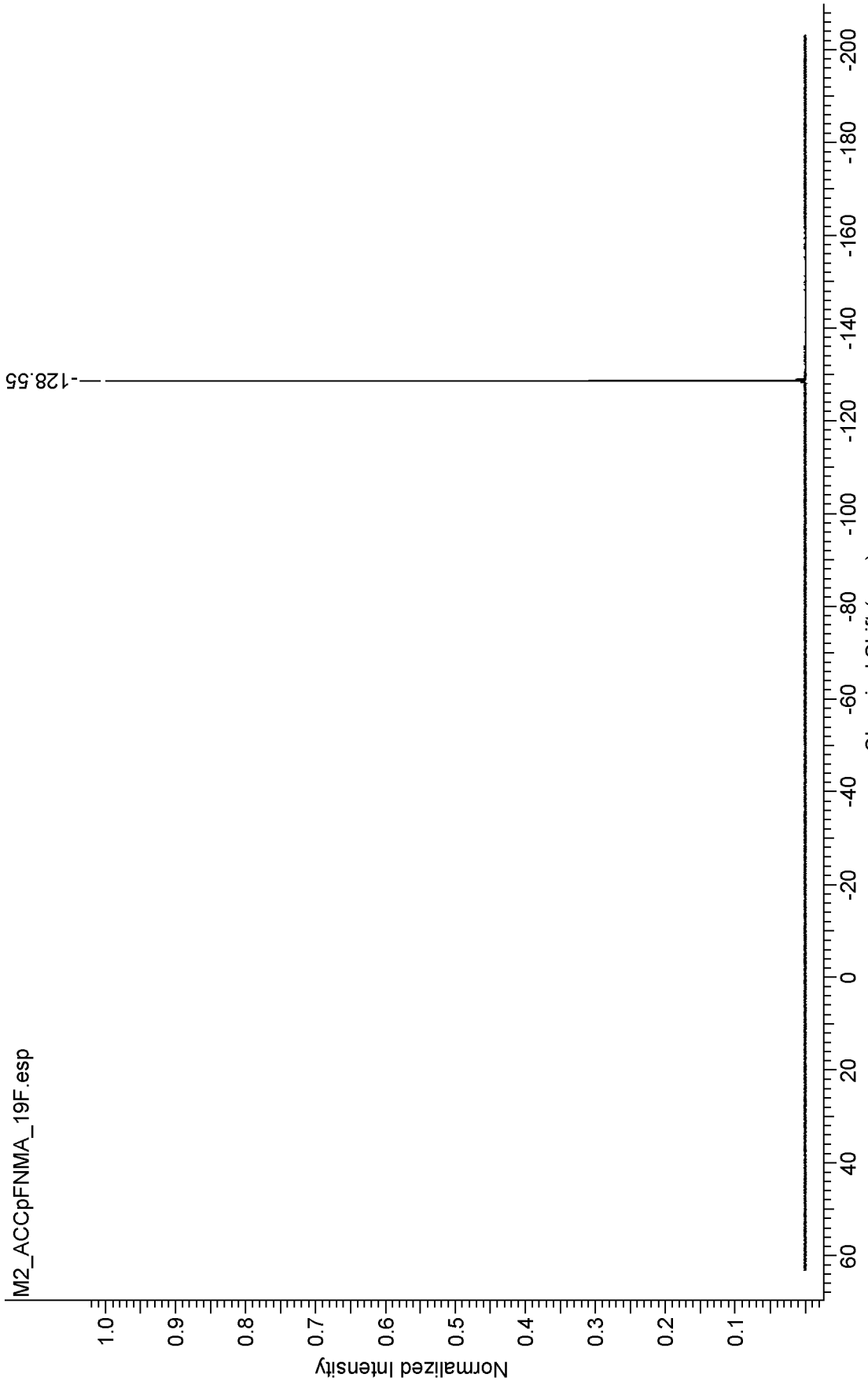

M2_ACCpFNMA_19F.esp
-128.55
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
Chemical Shift (ppm)

Figure 8C

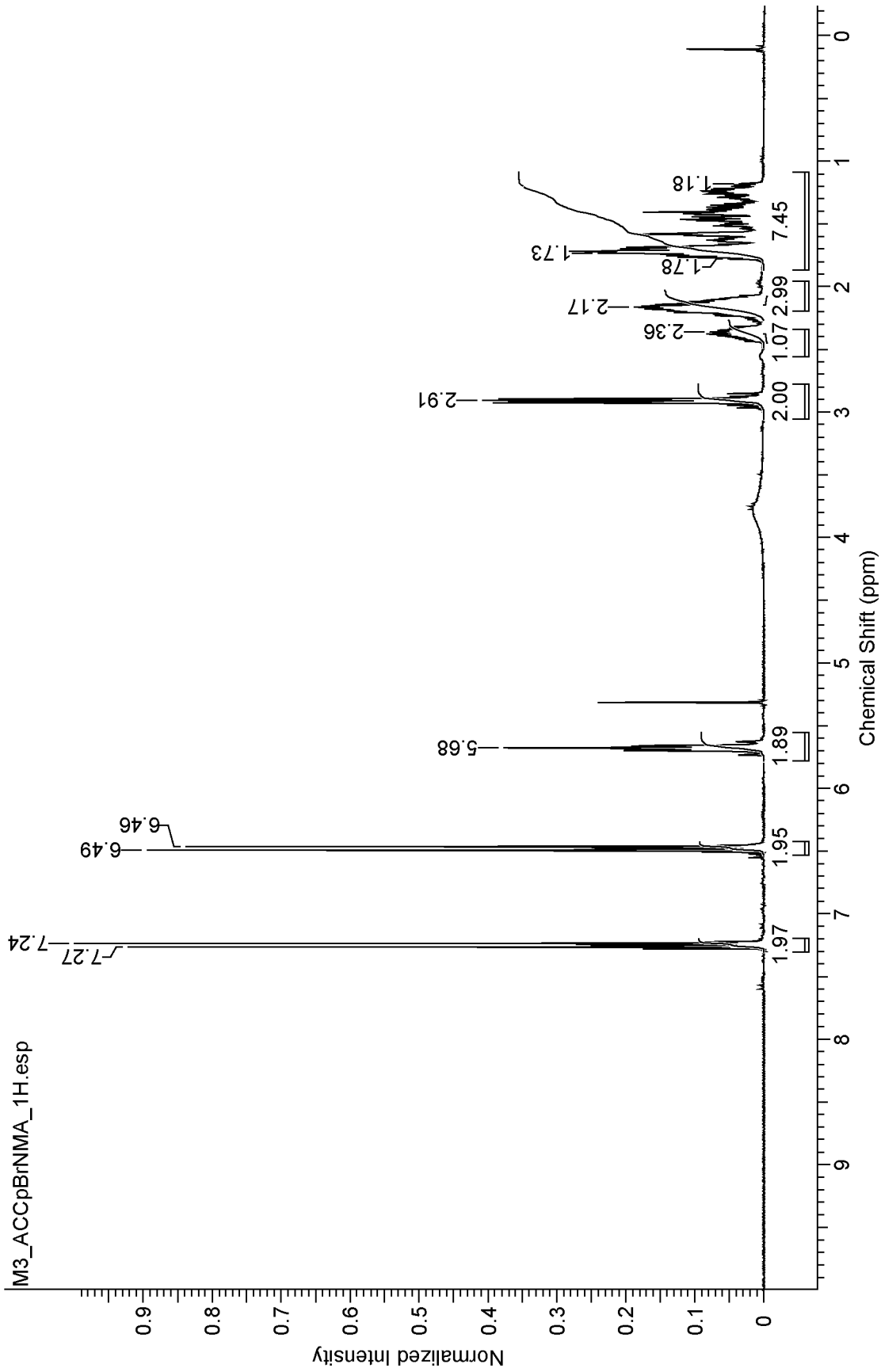

M3_ACCpBrNMA_1H.esp
Normalized Intensity
Chemical Shift (ppm)
7.24
7.27
6.49
6.46
5.68
2.91
2.36
2.17
1.78
1.73
1.18
1.97
1.95
1.89
2.00
1.07
2.99
7.45

Figure 9A

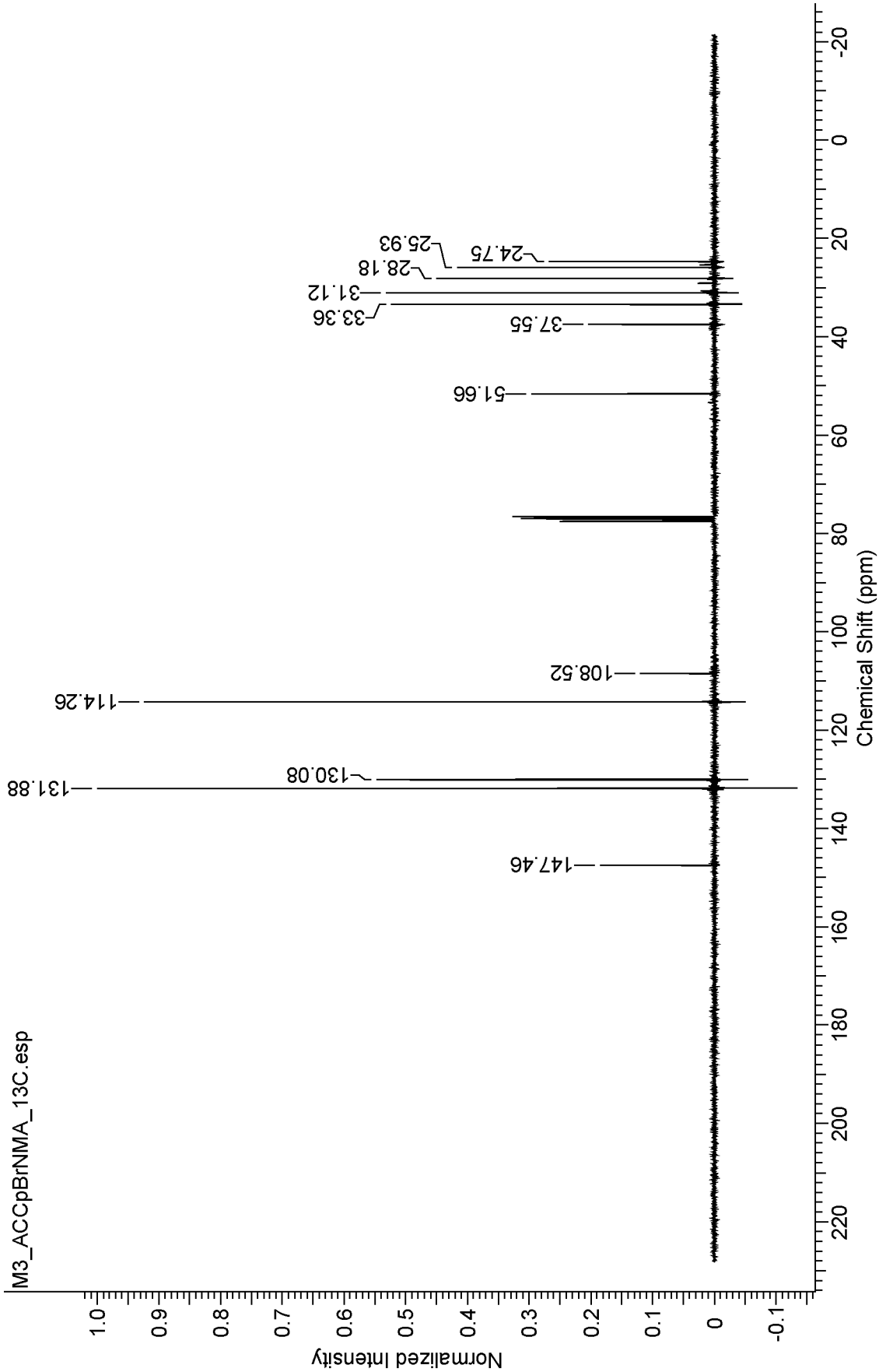

M3_ACCpBrNMA_13C.esp
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
Chemical Shift (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
-20
147.46
131.88
130.08
114.26
108.52
51.66
37.55
33.36
31.12
28.18
25.93
24.75

Figure 9B

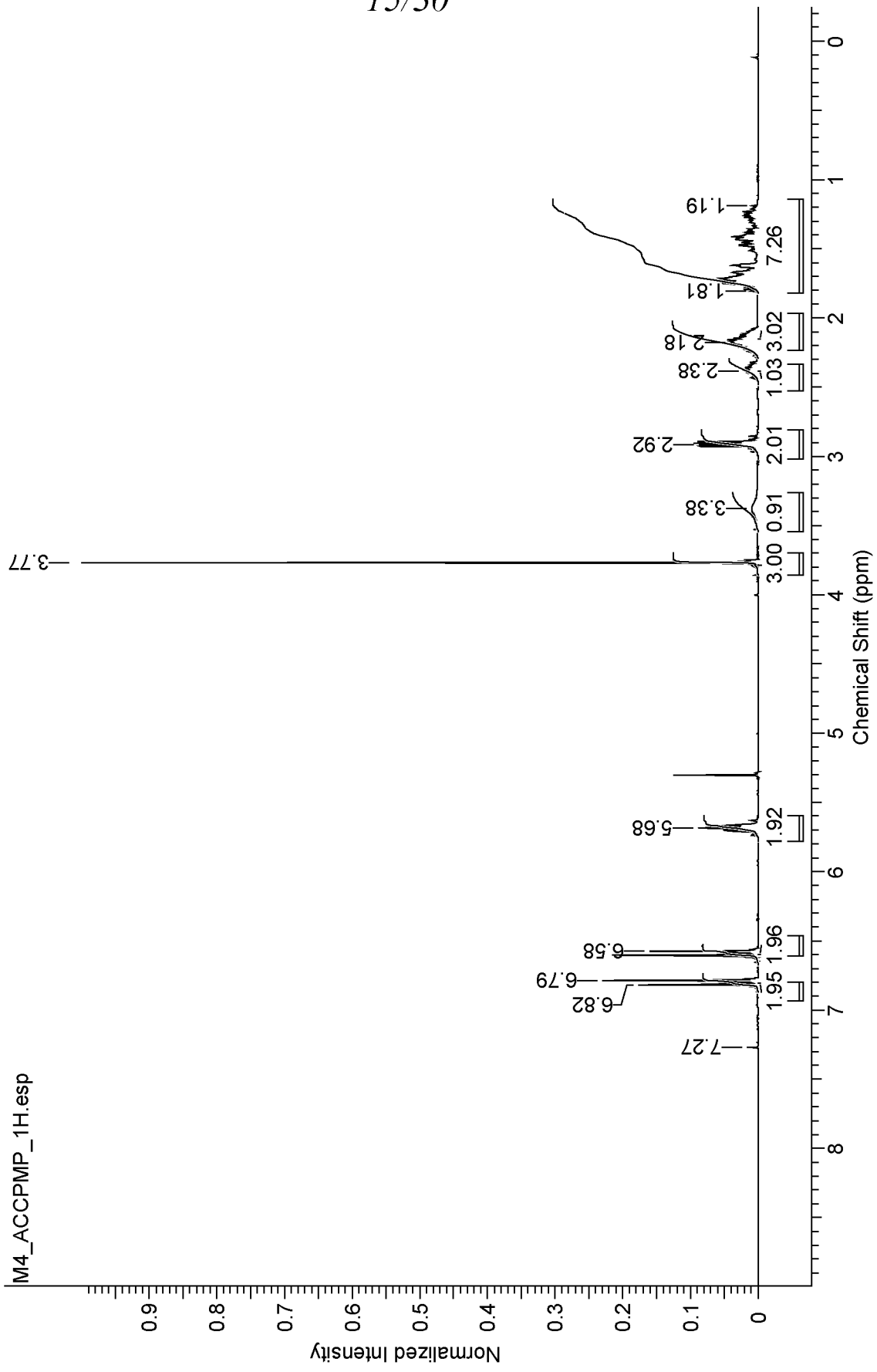

M4_ACCPMP_1H.esp
Normalized Intensity
Chemical Shift (ppm)
7.27
6.82
6.79
6.58
5.68
3.77
3.38
2.92
2.38
2.18
1.81
1.19
1.95
1.96
1.92
3.00
0.91
2.01
1.03
3.02
7.26

Figure 10A

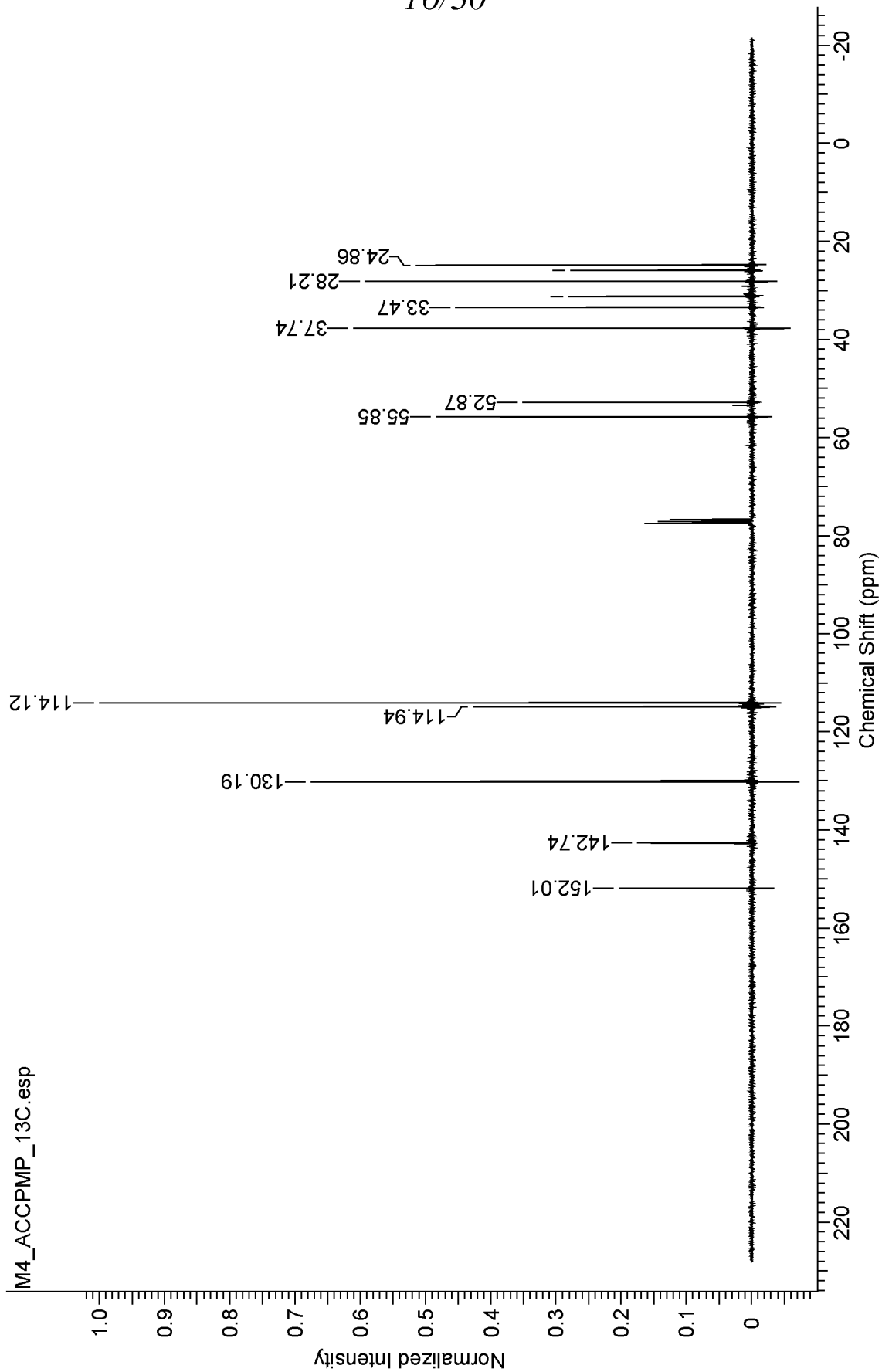

M4_ACCPMP_13C.esp
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)
114.12
114.94
130.19
142.74
152.01
24.86
28.21
33.47
37.74
52.87
55.85

Figure 10B

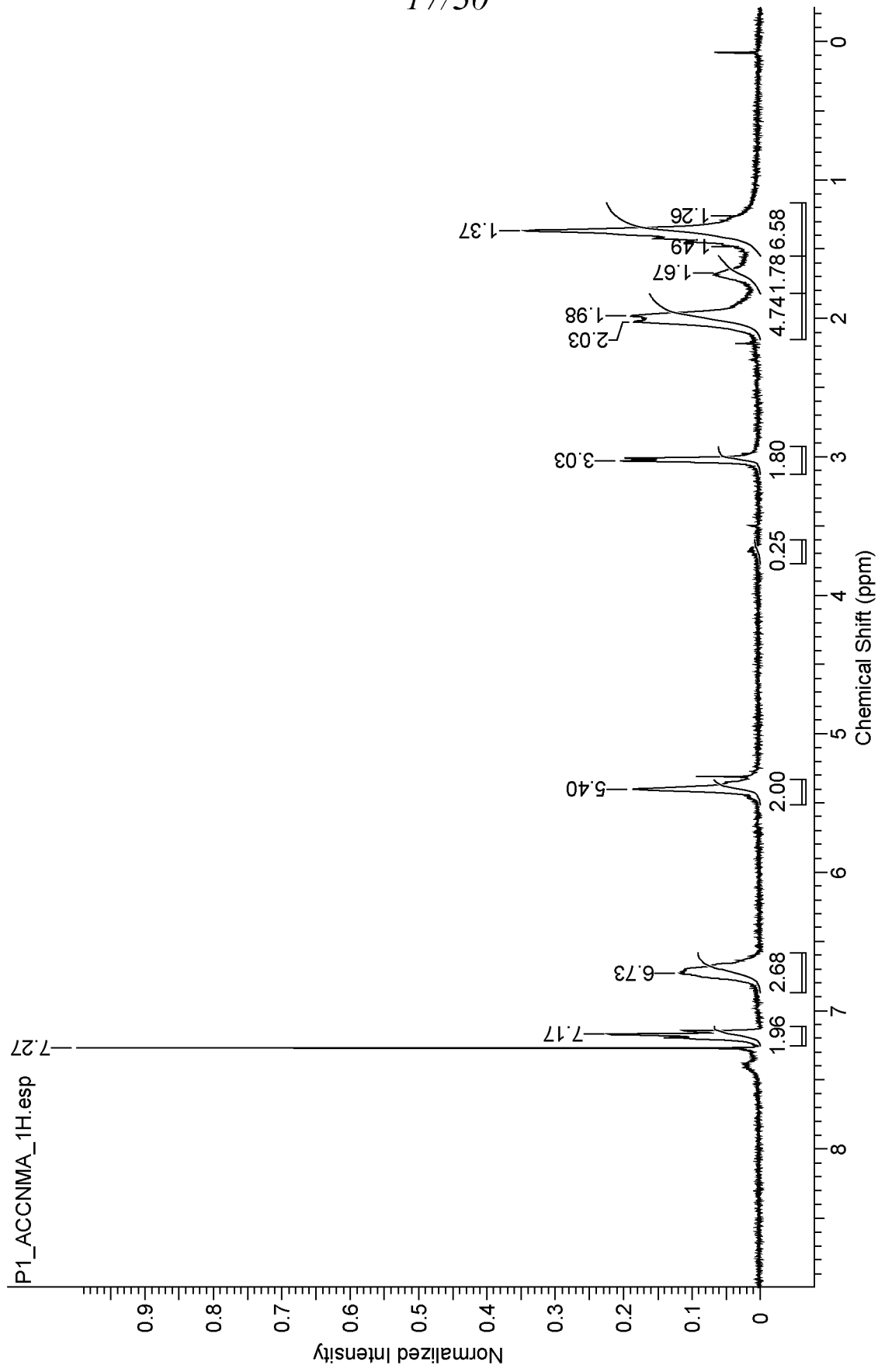

P1_ACCNMA_1H.esp
Normalized Intensity
Chemical Shift (ppm)
7.27
7.17
6.73
5.40
3.03
2.03
1.98
1.67
1.49
1.37
1.26
1.96
2.68
2.00
0.25
1.80
4.74
1.78
6.58

Figure 11A

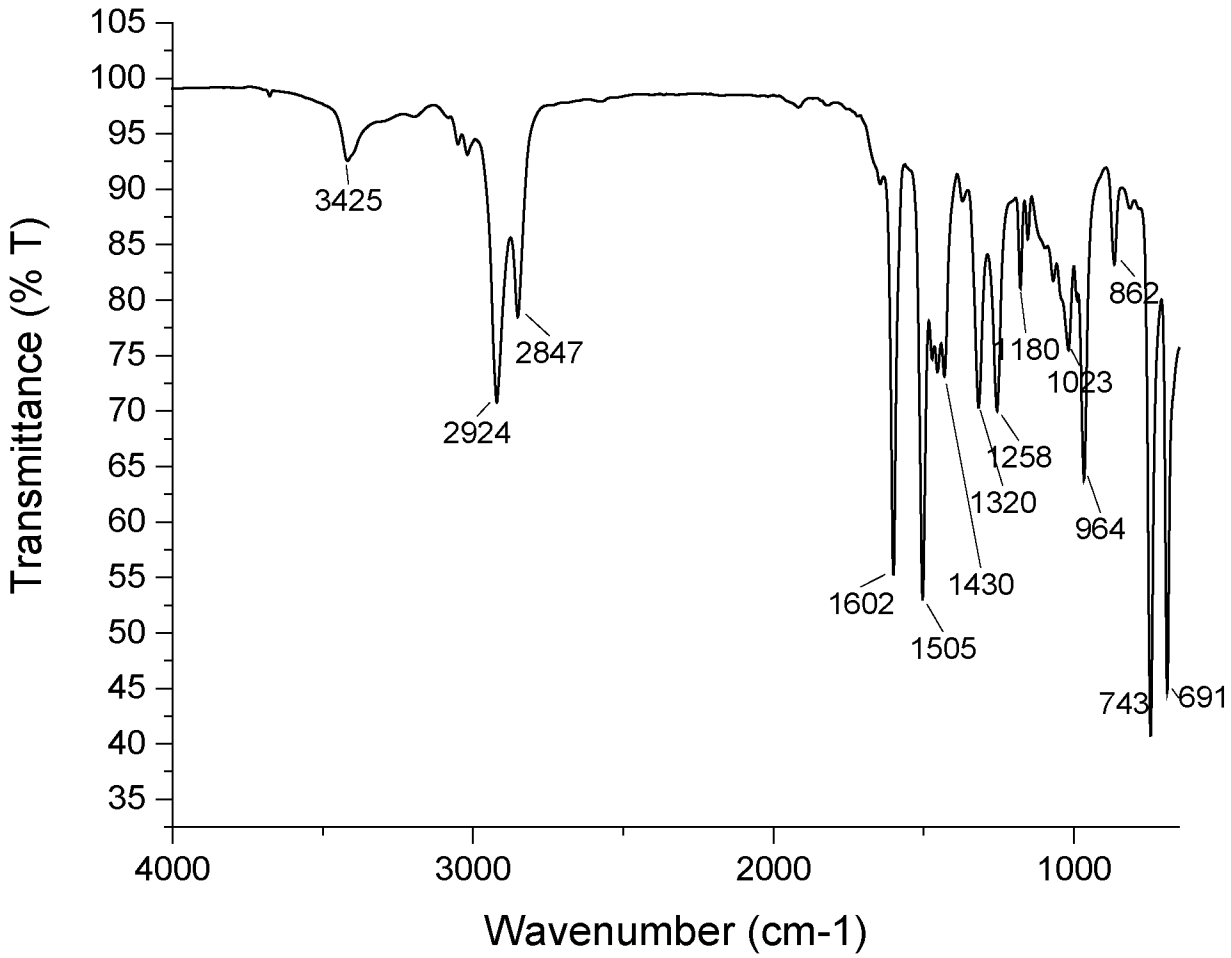

Transmittance (% T)
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3000
2000
1000
Wavenumber (cm-1)
3425
2924
2847
1602
1505
1430
1320
1258
1180
1023
964
862
743
691

Figure 11B

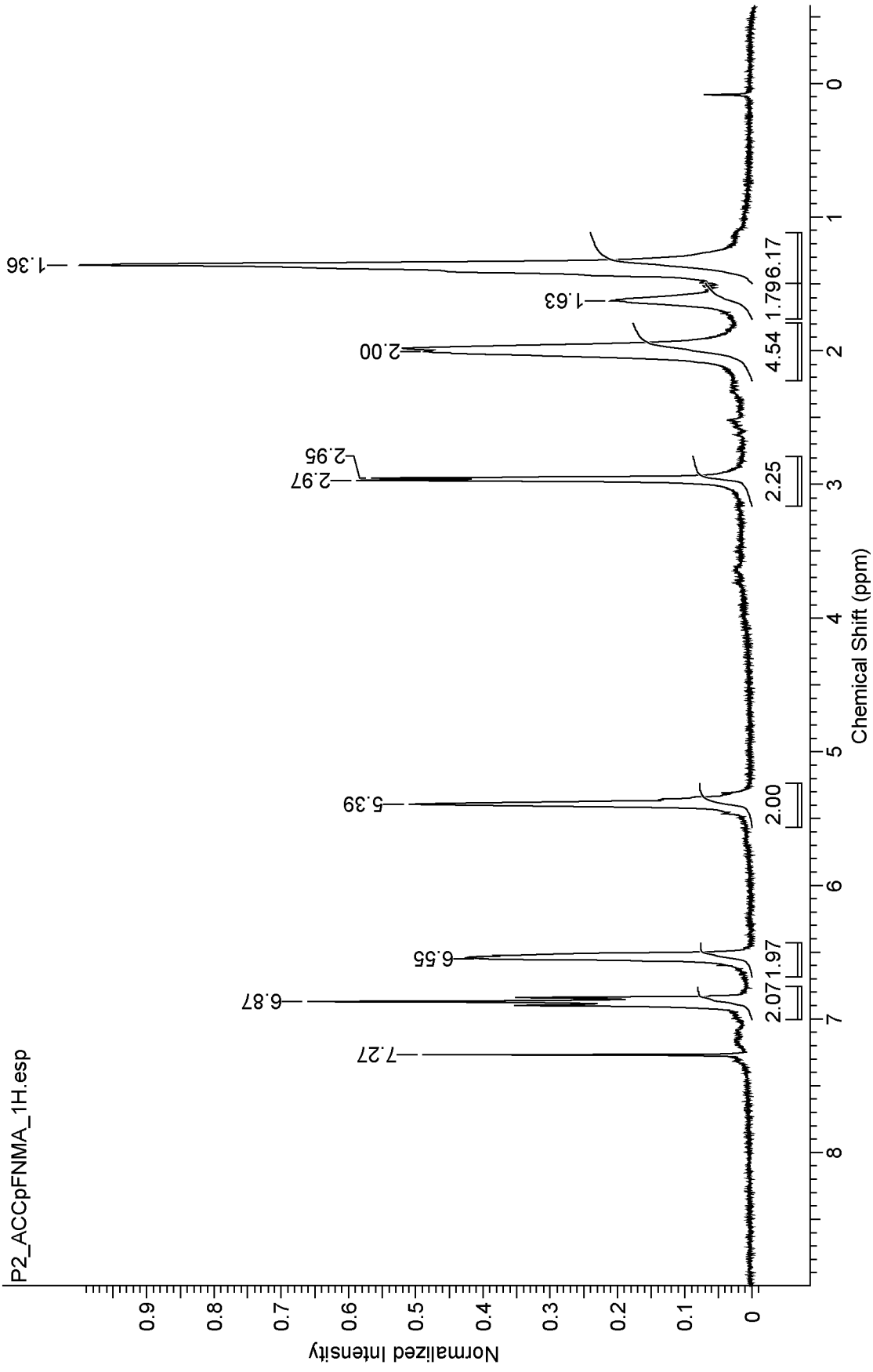

P2_ACCpFNMA_1H.esp
Normalized Intensity
Chemical Shift (ppm)
7.27
6.87
6.55
5.39
2.97
2.95
2.00
1.63
1.36
2.07
1.97
2.00
2.25
4.54
1.79
6.17

Figure 12A

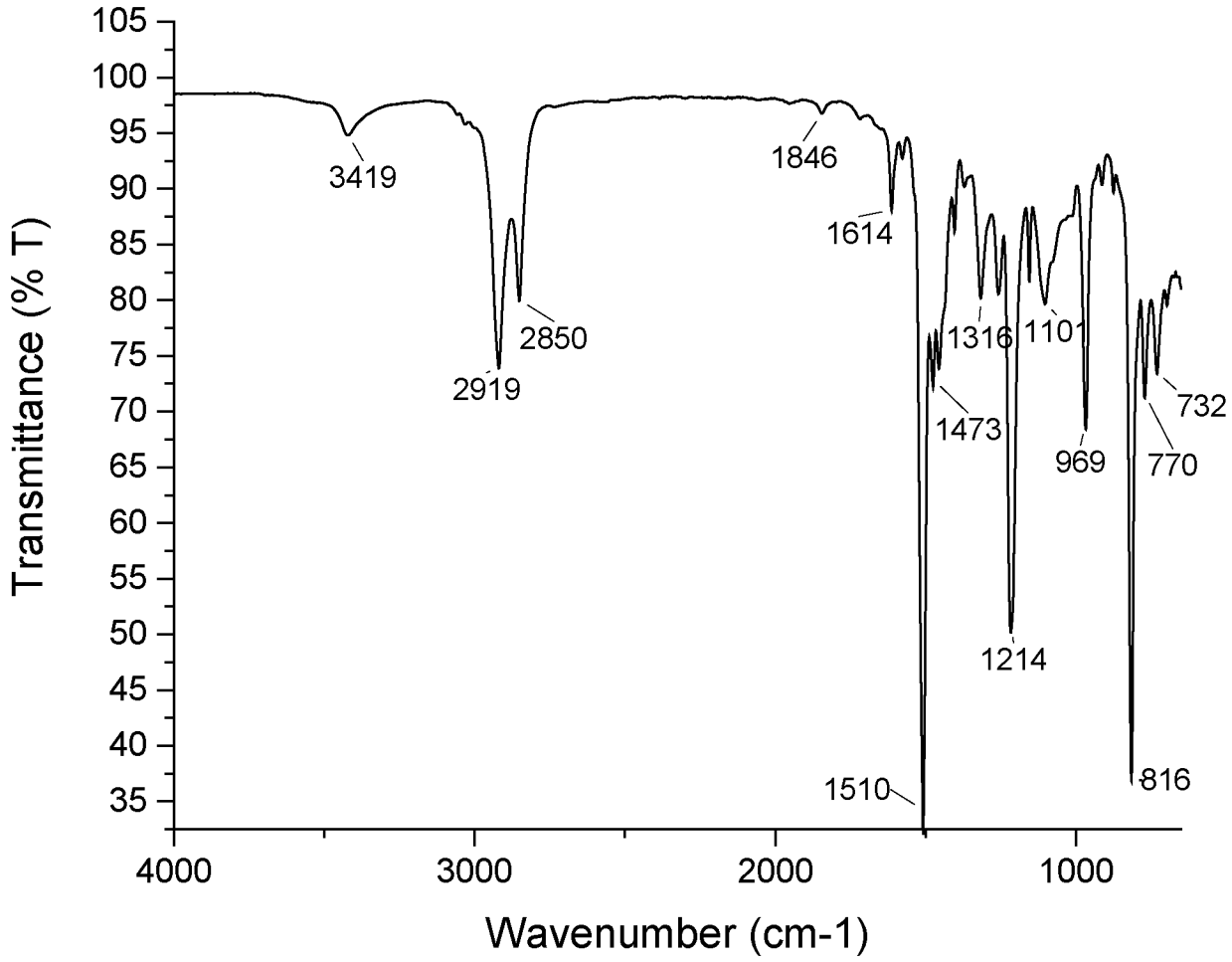

Transmittance (% T)
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3000
2000
1000
Wavenumber (cm-1)
3419
2919
2850
1846
1614
1316
1101
1473
969
770
732
1214
1510
816

Figure 12B

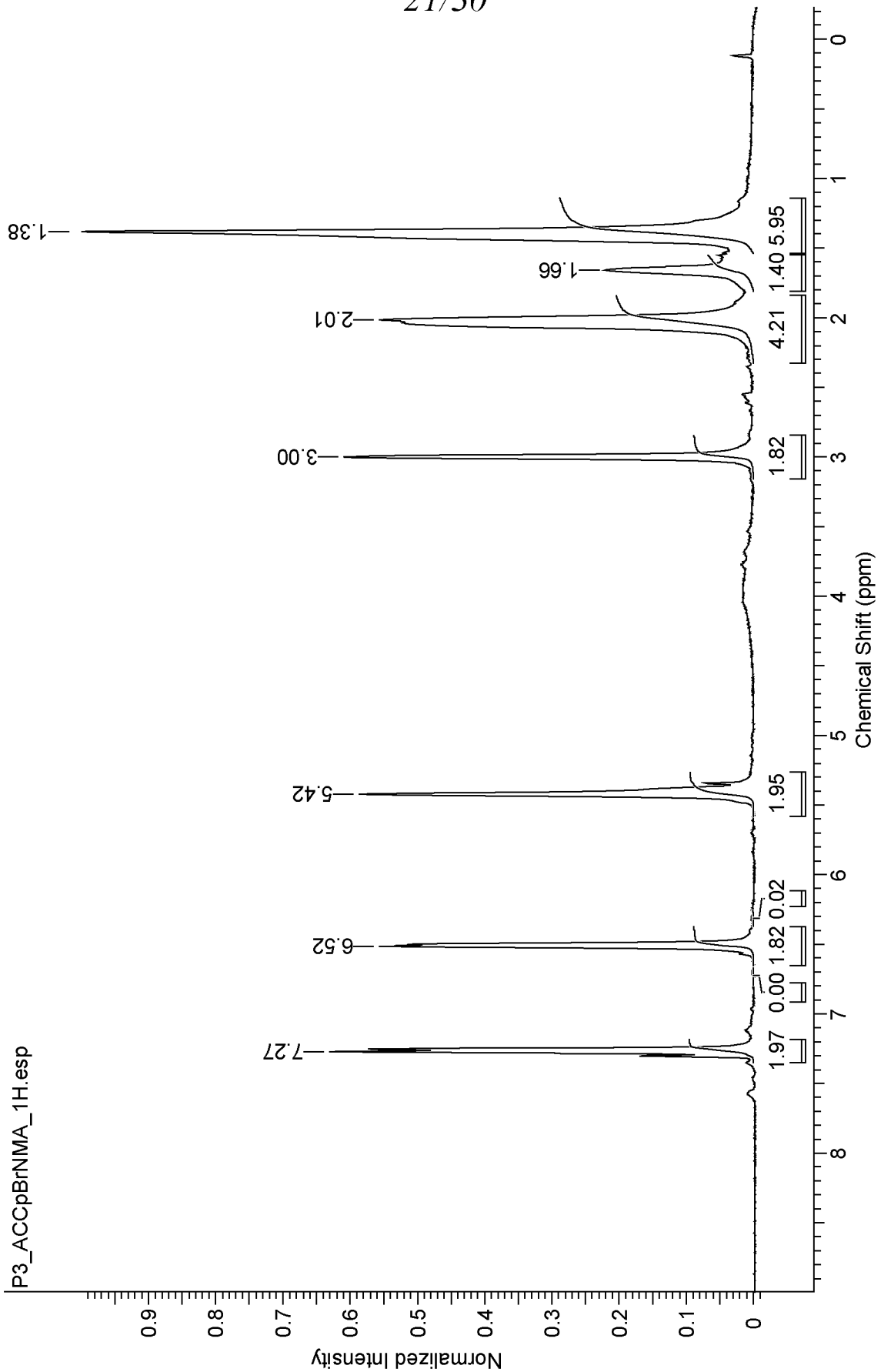

P3_ACCpBrNMA_1H.esp
Normalized Intensity
Chemical Shift (ppm)
7.27
6.52
5.42
3.00
2.01
1.66
1.38
1.97
0.00
1.82
0.02
1.95
1.82
4.21
1.40
5.95

Figure 13A

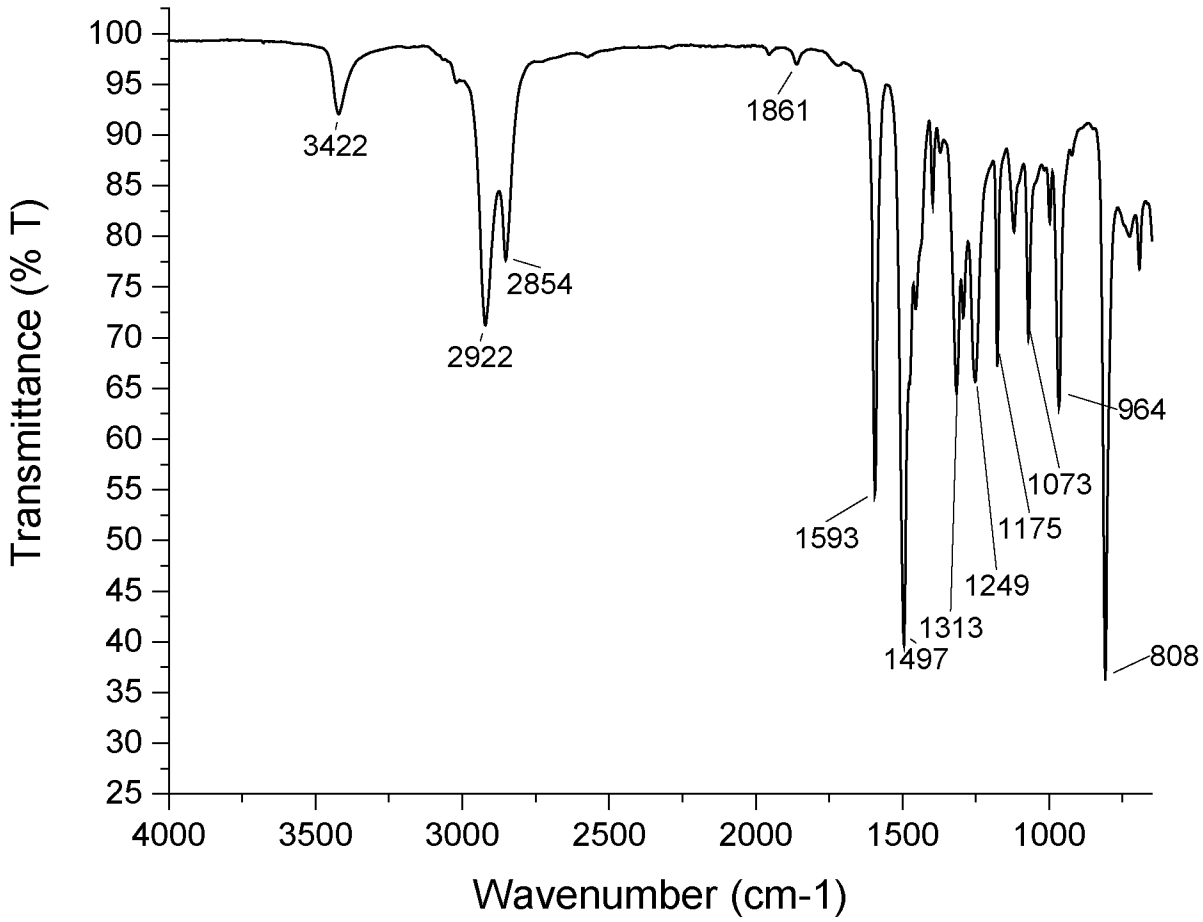

Transmittance (% T)
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
3422
2922
2854
1861
1593
1497
1313
1249
1175
1073
964
808

Figure 13B

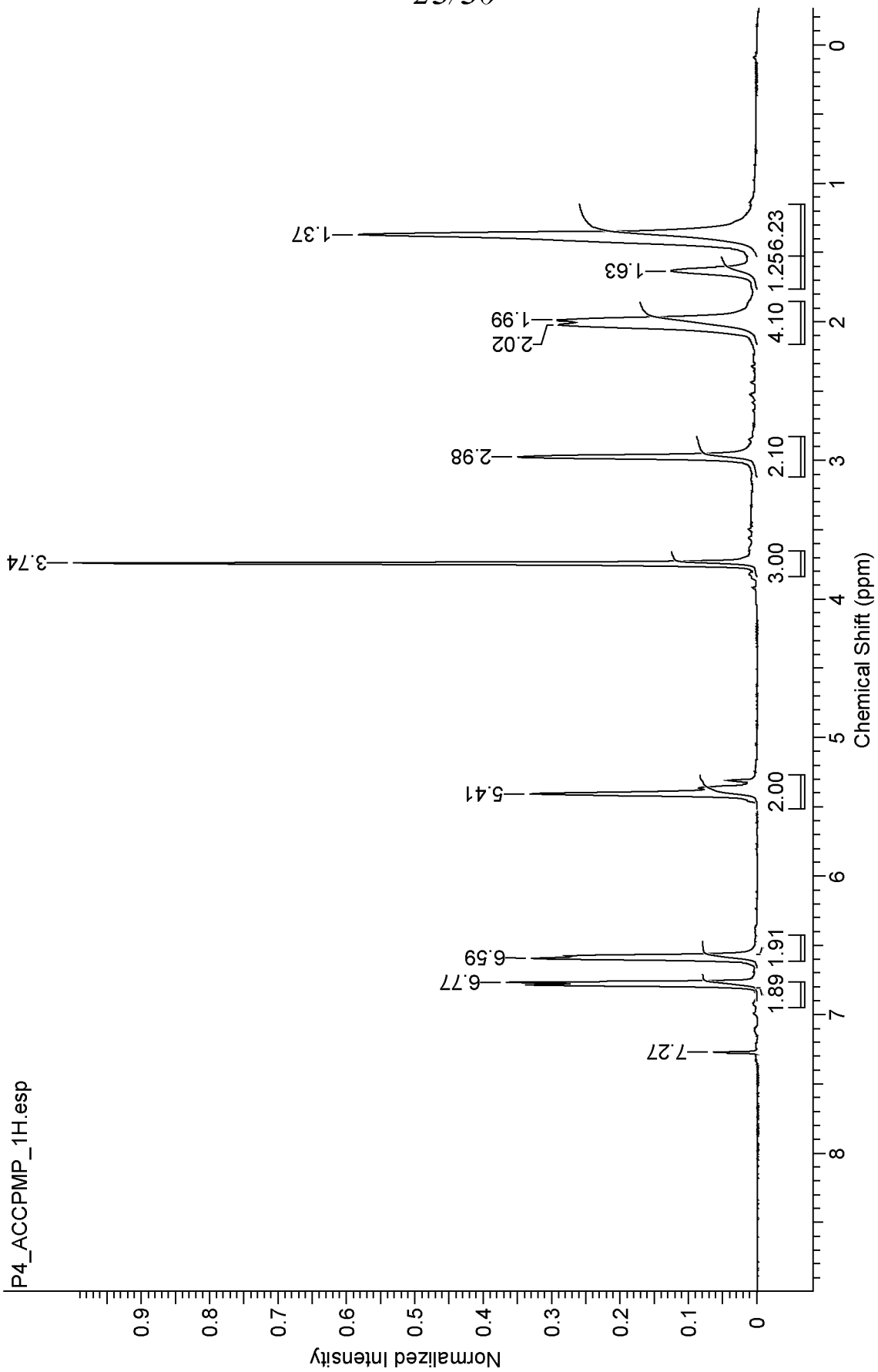

P4_ACCPMP_1H.esp
Normalized Intensity
Chemical Shift (ppm)
7.27
6.77
6.59
5.41
3.74
2.98
2.02
1.99
1.63
1.37
1.89
1.91
2.00
3.00
2.10
4.10
1.25
6.23

Figure 14A

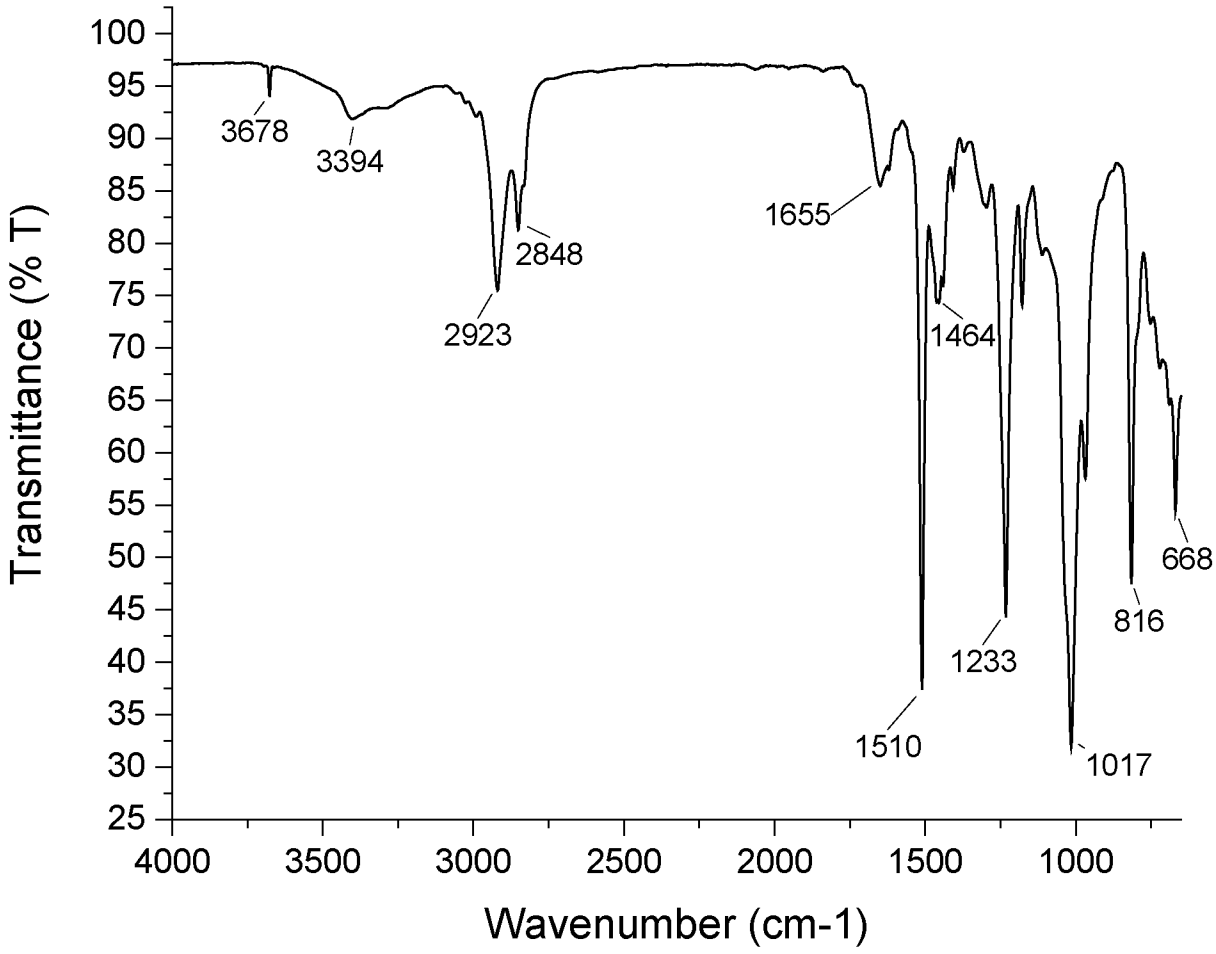

Transmittance (% T)
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
4000
3500
3000
2500
2000
1500
1000
Wavenumber (cm-1)
3678
3394
2923
2848
1655
1464
1510
1233
1017
816
668

Figure 14B

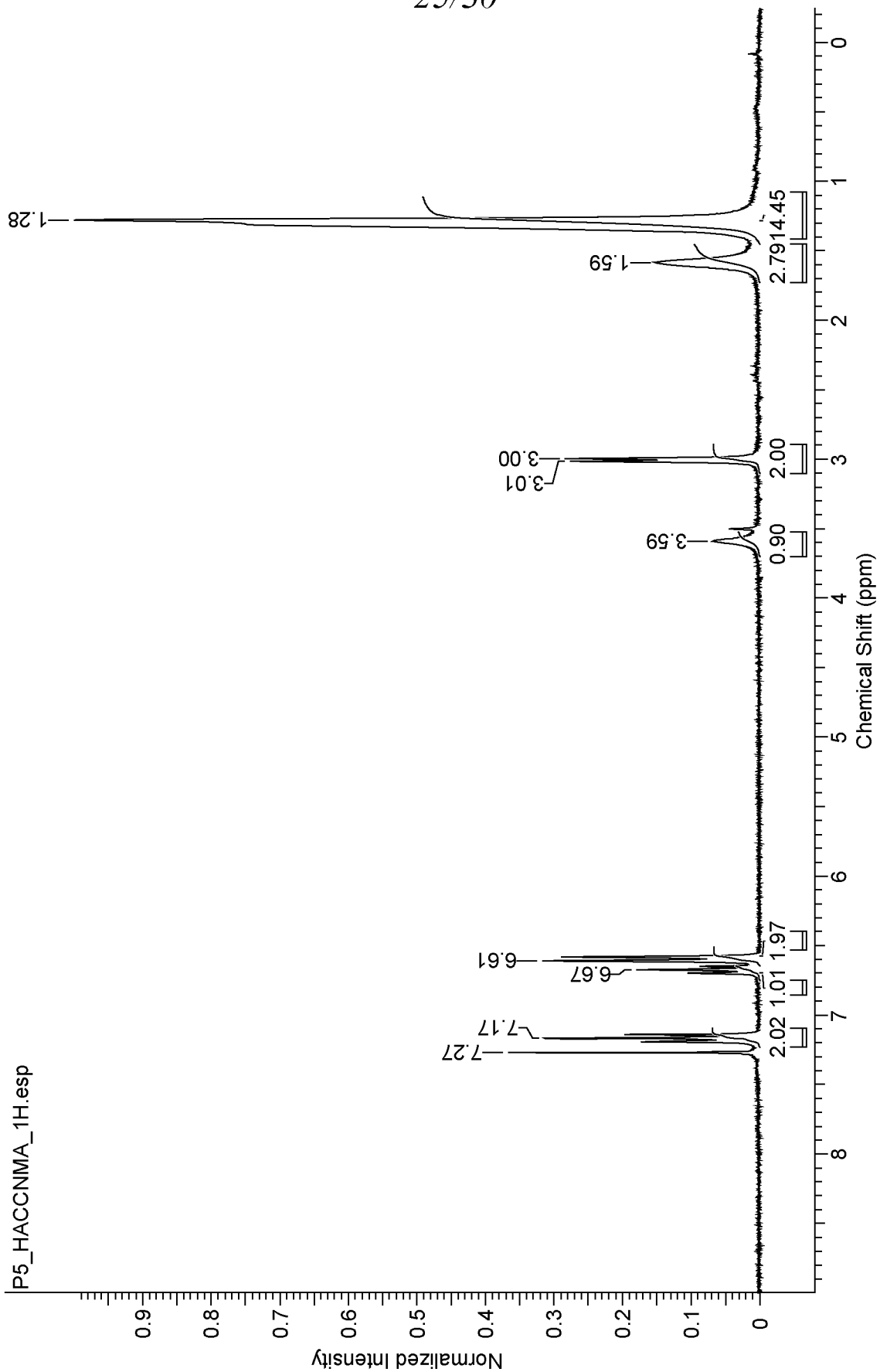

P5_HACCNMA_1H.esp
Normalized Intensity
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Chemical Shift (ppm)
0
1
2
3
4
5
6
7
8
1.28
1.59
3.01
3.00
3.59
6.61
6.67
7.17
7.27
2.02
1.01
1.97
0.90
2.00
2.79
14.45

Figure 15A

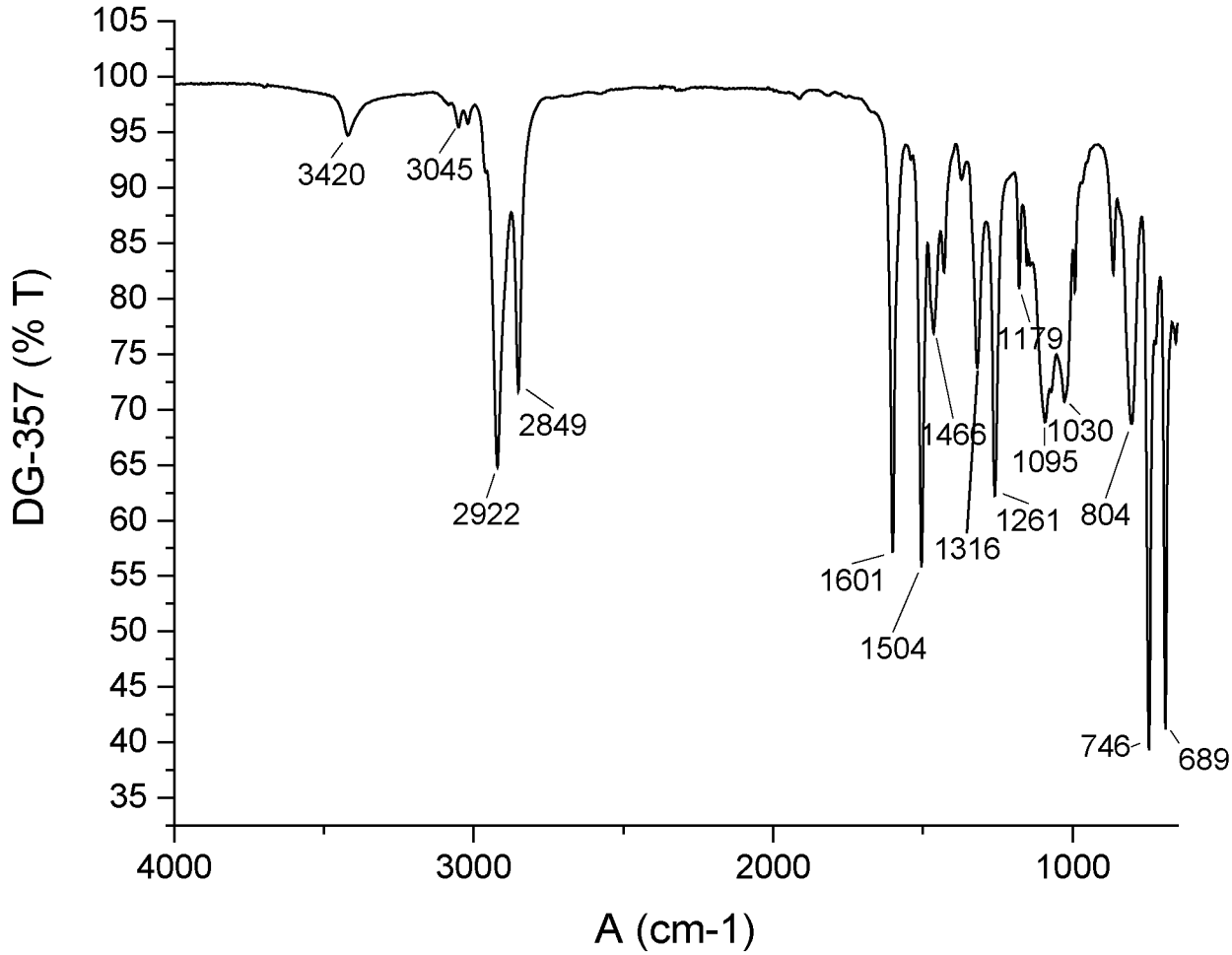

DG-357 (% T)
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
4000
3000
2000
1000
A (cm-1)
3420
3045
2922
2849
1601
1504
1466
1316
1261
1179
1095
1030
804
746
689

Figure 15B

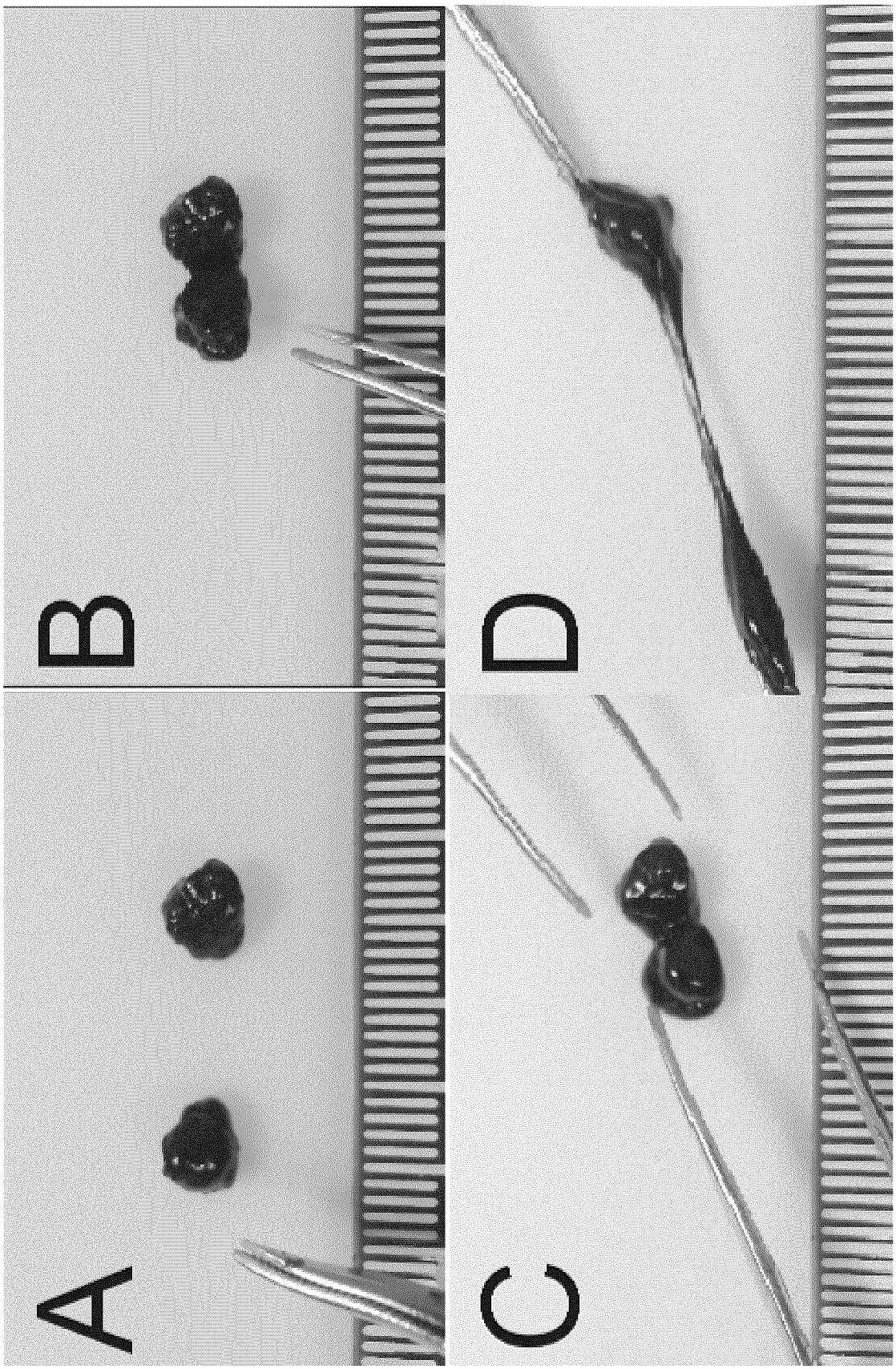


Figure 16

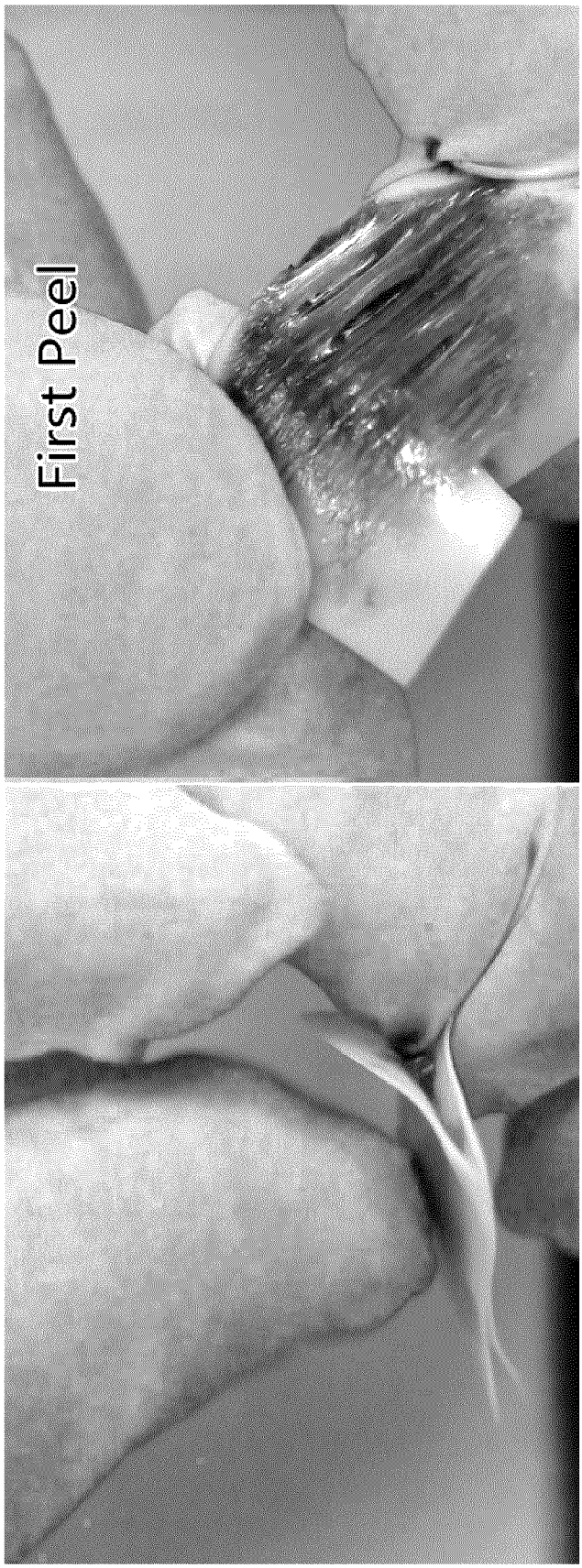
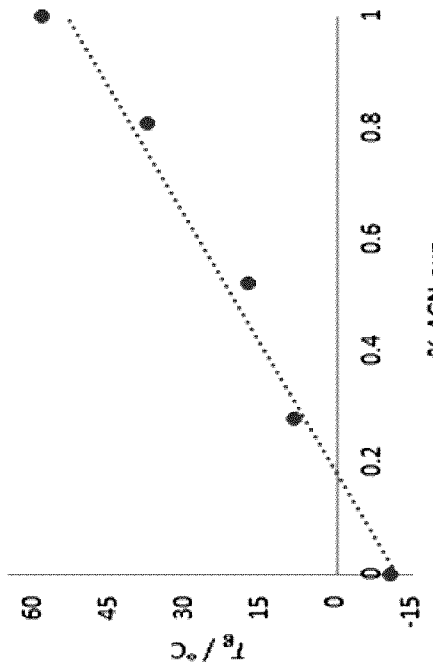


Figure 17



% ACN theo.	% ACN exp.[a]	T_g[b] / °C
0.00	0.00	-10.4
0.25	0.28	8.55
0.50	0.52	17.3
0.75	0.81	37.6
1.00	1.00	58.4

[a]Calculated by ^{1}H NMR spectroscopy [b]Determined by DSC

Figure 18

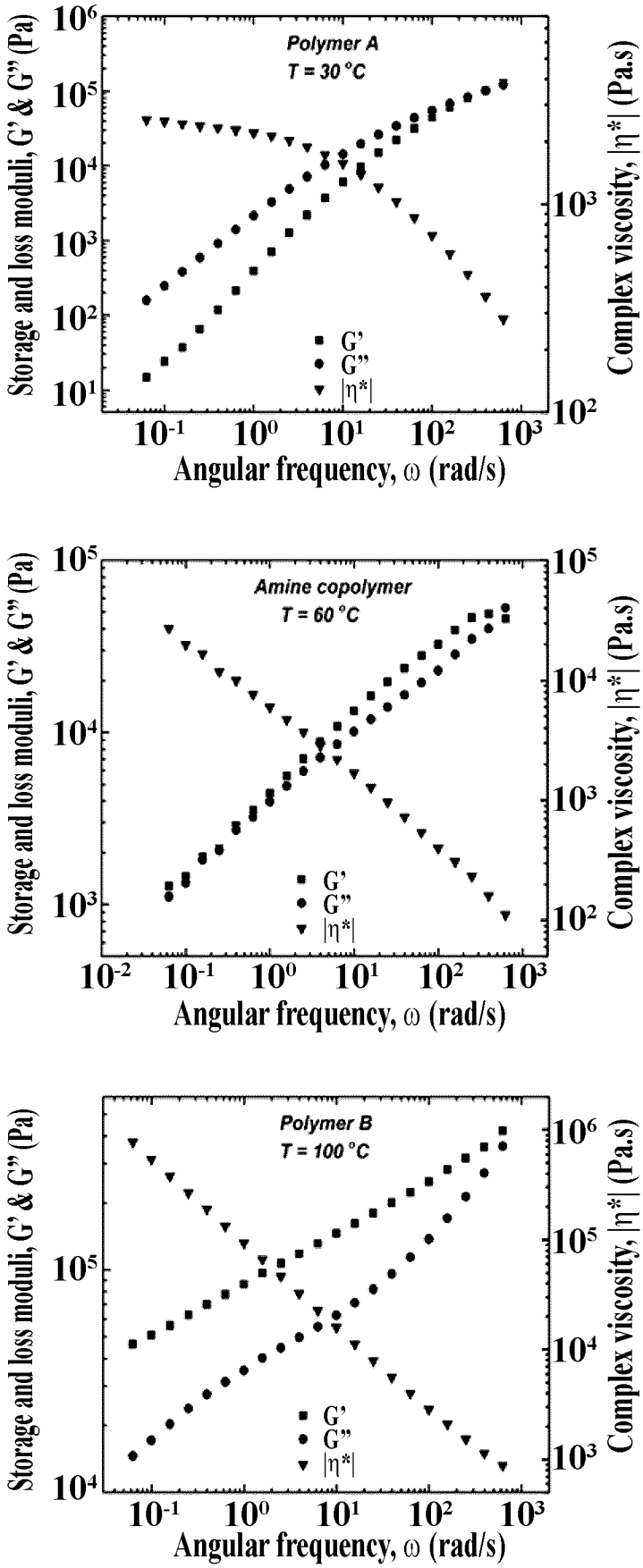

Polymer A
T = 30 °C
Storage and loss moduli, G' & G" (Pa)
Complex viscosity, |η*| (Pa.s)
G'
G"
|η*|
Angular frequency, ω (rad/s)
Amine copolymer
T = 60 °C
Storage and loss moduli, G' & G" (Pa)
Complex viscosity, |η*| (Pa.s)
G'
G"
|η*|
Angular frequency, ω (rad/s)
Polymer B
T = 100 °C
Storage and loss moduli, G' & G" (Pa)
Complex viscosity, |η*| (Pa.s)
G'
G"
|η*|
Angular frequency, ω (rad/s)

Figure 19