Polym. Bull. (2011) 66:1029–1038
DOI 10.1007/s00289-010-0330-x

ORIGINAL PAPER

Metathesis of renewable products: degradation of natural rubber via cross-metathesis with β-pinene using Ru-alkylidene catalysts

Selena Gutiérrez · Mikhail A. Tlenkopatchev

Received: 17 May 2010 / Revised: 18 June 2010 / Accepted: 20 June 2010 /

Abstract Renewable β-pinene and natural rubber (NR) were used in the cross-metathesis reactions for the synthesis of terpene-terminated oligomers. The metathesis was carried out under solvent-free conditions using the second generation Grubbs catalyst (**I**). Isolated yields of oligomers were high and ranged between 80 and 90%. It was shown that the molecular weights of products may be changed in a wide range by controlling the ratio of β-pinene to NR. The formation of β-pinene and NR cross-metathesis products during chain transfer was confirmed using a model reaction of β-pinene with (*Z*)-3-methyl-2-pentene.

Keywords Metathesis degradation · Natural rubber · β-Pinene · Ruthenium alkylidene catalysts

Introduction

In recent years, bio-based products have attracted much attention because these resources are renewable and can be used for energy, chemicals, and other important materials production [1]. In many cases the molecules from bio-based resources already contain olefinic carbon–carbon bonds which can participate in the metathesis reactions. For example, various plant *cis–trans* (*Z,E*)-polyprenols and dolichols, tocotrienols, vitamin K_1, and natural rubber are some of the examples of olefinic carbon–carbon bonds containing compounds [2–4]. It is worth noting that

---

S. Gutiérrez
Facultad de Química, Universidad Nacional Autónoma de México, Apartado Postal 70-360,
CU, Coyoacán, México, DF 04510, México

M. A. Tlenkopatchev (✉)
Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Apartado Postal 70-360, CU, Coyoacán, México, DF 04510, México
e-mail: tma@sevidor.unam.mx

metathesis of these molecules is challenging [5] due to the presence of an alkyl group directly linked to the double bond which can impede the coordination reaction with a metal active center. Thus, relatively few reports exist on the metathesis reactions of natural rubber (NR) or *cis*-1,4-polyisoprene (*cis*-PI) [6–10]. This may be explained by the fact that NR is a very sensitive to the side reactions and this polymer with trisubstituted unsaturations degraded much slower than *cis*-polybutadiene and other polyalkenamers with disubstituted unsaturations [6]. The authors [11] reported that *cis*-PI degradation occurs very slowly using the classical tungsten based catalyst. Hence, sterically hindered substrates require highly stable and selective metathesis catalysts. The development of highly active Ru-alkylidene catalysts opens vast new possibilities in olefin metathesis and their application to controlled synthesis of desired products [12, 13]. Thus, ring-opening metathesis polymerization (ROMP) of trisubstituted *cis,cis*-1,5-dimethyl-1,5-cyclooctadiene to polyisoprene and cross-metathesis degradation of isoprene containing copolymers to oligomers using high active ruthenium alkylidene catalysts containing a *N*-heterocyclic carbene ligand have been reported [14, 15]. Monoterpenes are available in large quantities. Thus, α-pinene and β-pinene are extracted from turpentine oil (350,000 t/year) and widely used for the synthesis of flavours and fragrances [1]. Previously, monoterpenes such as *D*-limonene and β-pinene have been used as chain transfer agents (CTAs) for the ROMP of cycloolefins [16, 17].

The goal of this report is to study the metathesis degradation of NR in the presence of β-pinene as a CTA using a second generation Ru-alkylidene catalyst.

Experimental

Experimental procedures and details

Materials

NR was obtained from fresh field latex of AGROS (Guatemala and México) and used without purification. Guatemala NR ($M_n = 1.7 \times 10^6$, PDI = 1.5), México NR ($M_n = 4.9 \times 10^5$, PDI = 2.1). β-pinene (Aldrich, $\geq$99%), (*Z*)-3-methyl-2-pentene (Fluka, >99%) and [(1,3-dimethyl-4,5-dihydroimidazol-2-ylidene) $(PCy_3)Cl_2Ru = CHPh$] (Grubbs catalyst 2nd generation) (**I**) were used as received. 1,2-dichloroethane (Baker, >97%) was distilled from CaH_2 prior to use.

Analytical equipment and methods

^{1}H-NMR (^{13}C NMR) spectra were recorded in $CDCl_3$, on a VARIAN spectrometer operating at 300 (75.5) MHz frequencies. Chemicals shifts (δ) are reported in parts per million relative to the internal standard tetramethylsilane (TMS, $\delta = 0.00$ ppm).

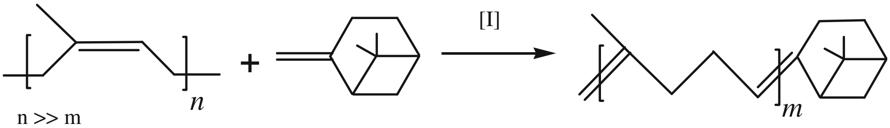
Infrared (IR) spectra were obtained using a Thermo Scientific NICOLET 6700 FT-IR spectrometer fitted with an ATR cell (diamond 30,000–200 cm^{-1}). Data are presented as the frequency of absorption (cm^{-1}).

Molecular weights and molecular weights distributions (M_n, PDI) were determined with a VARIAN 9012 GPC instruments, with reference to polystyrene standards at 30 °C in chloroform (universal column and flow rate of 1 mL min^{-1}).

GC/MS chromatograms were recorded using a GC-2010/MS-QP2010 s system equipped with an AOC-20i autosampler, with the injector temperature of 335 °C, at 1:5 split ratio and injection volume of 1 μL. Capillary column separation was using a 0.25 μL thick film [30 m × 0.32 mmID Rtx-5MS (RESTEK) with a 5 m integra-guard column] a flow rate of 1.22 mL/min and 68 kPa helium press, using helium as carrier gas. The column initial temperature is the 45 °C, isothermal for 3 min then heated at a rate 10 °C/min to 150 °C, ramp at 15 °C/min to 340 °C, and isothermal for 14 min. The interface and ion source were set at 340 and 220 °C, respectively. The chromatograms were acquired in the electron impact (EI) scan mode at 70 eV with a mass range of 40–300 (m/z) at rate of 0.1 scan s^{-1}. The dates were acquire and processed using Shimadzu GCMS solutions software.

Degradation procedure

Metathesis degradation of NR (3 g) using β-pinene as a CTA (Scheme 1), was carried out under nitrogen atmosphere, in a reactor stirred magnetically, with a temperature 45 °C. The catalyst [(1,3-dimethyl-4,5-dihydroimidazol-2-ylidene) $(PCy_3)Cl_2Ru = CHPh$] (**I**) was added in solution (1,2-dichloroethane) in molar ratio NR/catalyst = 1,000. Thus, reactions were carried out in bulk, the solvent was added only with the catalysts. β-Pinene (CTA) was used in several molar ratios of NR to CTA Rub/CTA = 1:1, 5:1, and 10:1. Adding ethyl vinyl ether (0.3 mL, 3 mmol) under a nitrogen atmosphere terminated the reactions. The products were dried under vacuum and characterized by ^1H NMR (^{13}C NRM), GPC, FT-IR and GC/MS (EI). Isolated yields of oligomers were high and ranged between 80 and 90%. ^1H NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 0.9$ (s, CH_3 aliphatic terpene), 1.2 (s, CH_3 aliphatic terpene), 1.44, 2.32 (d, m, CH_2 terpene), 1.68 (s, CH_3 isoprene), 1.79–1.84 (m, CH_2 terpene), 1.97 (m, CH terpene), 2.24, 2.53 (m, m, CH_2 terpene), 2.46 (t, CH terpene), 4.82 (s, CH_2=C vinylic), 5.18 (s, CH=C isoprene), 5.34 (s, CH=CH) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 152.1$ (s, C=C terpene), 142.8 (s, C=C isoprene), 115.2 (s, CH isoprene), 105.9 (s, CH_2=C vinylic), 51.7 (s, CH terpene), 40.4 (s, CH terpene), 32.2 (s, CH_2 isoprene) 26.9 (s, CH_2 terpene), 26.0 (s, CH_3 aliphatic terpene), 23.6 (s, CH_2 isoprene), 21.9 (s, CH_3C=C), 23.5 (s, CH_2 terpene), 21.7 (s, CH_3 aliphatic terpene). IR: ν_{max}(liquid)/cm^{-1} 3035 (C=CH–H), 2959 (ν_{as} CH_3 st), 2913(ν_{as} CH_2 st), 2851 (ν_{as} CH_3 st), 1670 (C=C trisubstituted), 1650 (C=C vinylidene), 1446 (δas CH_3 bending), 1375 (δs CH_3 bending), 886 (C=C vinylidene), 804 (C=C trisubstituted). GC/MS (EI) min



Scheme 1 Metathesis degradation of NR using β-pinene as CTA

(Component, *m/z,* abundance): 3.3 (A$m = 2$, 164, 9%), 4.2 (Trimer, 204, 11%), 4.8 (B$m = 1$, 204, 31%), 5.6 (A$m = 3$, 232, 2%), 6.5 (B$m = 2$, 272, 11%), 11.6 (C$m = 1$, 312, 10%), 14.9 (C$m = 2$, 380, 7%).

Cross-metathesis of (Z)-3-methyl-2-pentene with β-pinene

The cross-metathesis reactions of (*Z*)-3-methyl-2-pentene (1.5 mL, 12 mmol) with *β*-pinene (1.93 mL, 12 mmol) were carried out under identical conditions to those described for the NR degradation reactions. The products (80% yields) were examined by ^{1}H NMR (^{13}C NMR), FT-IR and GC/MS (EI).

^{1}H NMR (300 MHz, $CDCl_3$, Me_4Si): $\delta = 0.9$ (s, CH_3 aliphatic terpene), 1.2 (s, CH_3 aliphatic terpene), 1.44, 2.32 (d, m, CH_2 terpene), 1.67 (m, CH_3), 1.79–1.84 (m, CH_2 terpene), 1.97 (m, CH terpene), 2.24, 2.53 (m, m CH_2 terpene), 2.46 (t, CH terpene), 2.53 (1H, m, terpene), 4.82 (s, CH_2=C vinylic), 5.18 (s, CH=C) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 152.1$ (s, C=C terpene), 142.8 (s, C=CCH_3), 105.9 (s, CH_2=C vinylic), 51.7 (s, CH terpene), 40.4 (s, CH terpene), 26.9 (s, CH_2 terpene), 26.0 (s, CH_3 aliphatic terpene), 23.6 (s, CH_2), 21.9 (s, CH_3C=C), 23.5 (s, CH_2 terpene), 21.7 (s, CH_3 aliphatic terpene), 12.4 (s, CH_3). IR: ν_{max}(liquid)/cm^{-1} 3068 (C=CH–H), 2977 (ν_{as} CH_3 st), 2918 (ν_{as} CH_2 st), 2867 (ν_{as} CH_3 st), 1660 (C=C trisubstituted), 1634 (C=C vinylidene), 1456 (δas CH_3 bending), 1382 (δs CH_3 bending), 882 (C=C vinylidene, 809 (C=C trisubstituted). GC/MS (EI) min (Component, *m/z,* abundance): 8.7 (D, 150, 58%), 3.5 (E, 70, 8%), 10.6 (F, 178, 16%).

Results and discussion

Scheme 1 depicts the cross-metathesis degradation of NR with *β*-pinene. Table 1 summarizes the results of NR degradation in the presence of *β*-pinene as a CTA under solvent-free conditions by catalyst (**I**) using a variety of NR/CTA ratios. From these results, it is concluded that NR degraded to form oligomers with the molecular weight distributions close to 2. Table 1 (entries 1–4) also presents the effect of time on the cross-metathesis degradation of NR with *β*-pinene. It is seen that the molecular weight of NR decreased as a function of time.

The molecular weights of products may be changed in a wide range by controlling the ratio of *β*-pinene to NR (entries 4–6, 9–11). The experimental molecular weights of oligomers were determined by gel permeation chromatography (GPC) and end-group analysis using ^{1}H NMR spectroscopy. Figure 1 shows GPC chromatogram of oligomers after the degradation of NR in the presence of *β*-pinene (Table 1, entry 11). The M_n values of oligomers were calculated from ^{1}H NMR assuming that each oligomer chain had one vinyl group and one monoterpene unit. Isolated yields of oligomers were high and ranged between 80 and 90%. It is worth noting that the use of high NR/catalyst ratios (Table 1) permitted the synthesis of the desired oligomers.

Table 2 shows the composition and yields of products obtained during the cross-metathesis of NR with *β*-pinene (Table 1, entry 3) According to GC/MS (EI)

Table 1 Degradation of NR in the presence of β-pinene using catalyst **I** (degradation in bulk, molar ratio NR/Catalyst = 1,000, $T = 45$ °C)

Entry	NR	NR/CTA[c]	Time (h)	Yield (%)[d]	MW (Theor)[e]	M_n (NMR)[f]	M_n (GPC)[g]	PDI[g]
1	Rubber[a]	1	3	87	204	1576	1841	1.6
2	Rubber[a]	1	6	93	204	972	1774	1.7
3	Rubber[a]	1	24	95	204	899	1331	1.9
4	Rubber[a]	1	48	95	204	695	1145	1.8
5	Rubber[a]	5	24	97	476	1102	1889	1.8
6	Rubber[a]	10	24	94	816	2960	3221	2.2
7	Rubber[b]	1	6	96	204	3060	2709	2.2
8	Rubber[b]	1	24	95	204	1445	1523	2.1
9	Rubber[b]	1	48	98	204	1292	1418	2.1
10	Rubber[b]	5	24	97	476	1673	1811	2.2
11	Rubber[b]	10	24	96	816	2536	2406	2.5

[a] México NR; $M_n = 4.9 \times 10^5$, PDI = 2.1, relative to PS standards

[b] Guatemala NR; $M_n = 1.7 \times 10^6$, PDI = 1.5, relative to PS standards

[c] Molar ratio of NR to CTA

[d] Isolated yield of oligomers

[e] Theoretical MW based on complete NR and CTA conversion

[f] M_n determined by ^{1}H NMR end group analysis

[g] Determined using GPC with THF as the eluent, values reported relative to PS standards

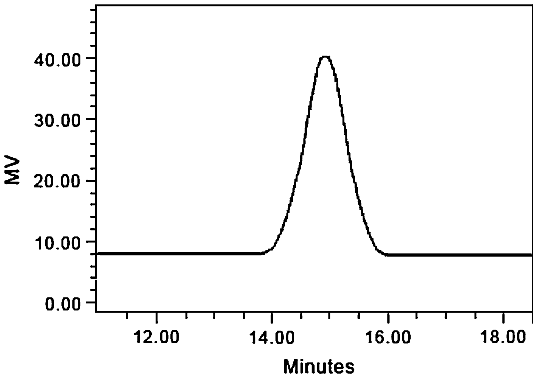


Fig. 1 GPC chromatogram of oligomers after the degradation of Guatemala NR in the presence of β-pinene. Degradation conditions: Degradation in bulk, molar ratio NR/catalyst = 1,000, $T = 45$ °C, molar ratio NR/CTA = 10:1 and reaction time 24 h

analysis the isolated yields of series of products A*m*, B*m*, and C*m* were about 70% (Scheme 2). Table 2 also shows that the primarily product formed was B*m* (42%), while A*m* was recovered only in 11% yield. It is important to note that the product A*m* with methylene terminal groups is able to participate in acyclic diene metathesis oligomerization (ADMET) to form products such as ethylene and oligomers (Table 2, A*m*, where $m = 2,3$).

The experimental data and computational modeling show that these kinds of reactions easily proceeded for α-ω dienes [18, 19]. Cross-metathesis of NR and β-pinene is accompanied by the cyclodegradation reaction of NR to form the cyclic

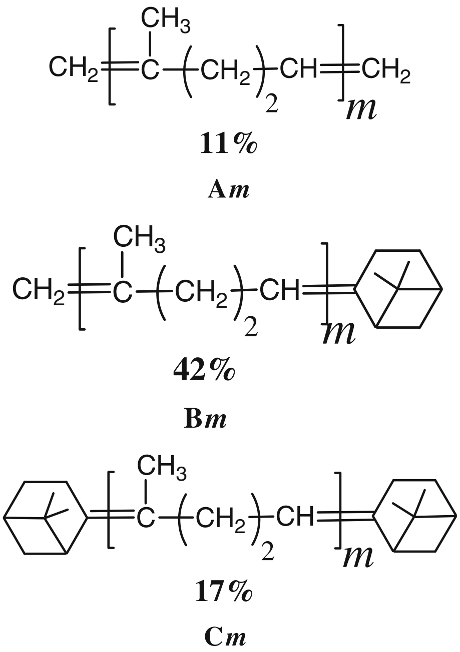
Table 2 Products of the NR degradation via cross-metathesis with *β*-pinene

Product	Monomer units, *m*	Composition (%)[a]
A*m*	1	–
	2	9
	3	2
		Subtotal = 11
B*m*	1	31
	2	11
	3	–
		Subtotal = 42
C*m*	1	10
	2	7
	3	–
		Subtotal = 17
Trimer	–	11
		Subtotal = 11

[a] Composition determined using GC/MS (EI)

trimer. Thus, the formation of *trans–trans–trans*-1,5,9-trimethyl-1,5,9-cyclododecatriene was detected by GC/MS (EI) min (Component, *m/z,* abundance): 11.9 (trimer, 204, 11%) (Table 2). The experimental and computational studies also demonstrated that NR and *cis*-polybutadiene metathesis degradation reactions are accompanied by the intramolecular cyclizations leading to the formation of the all *trans* cyclic trimers as the most thermodynamically favored among the all cyclic molecules [20, 21]. The experimental molecular weights of the oligomers obtained were higher than the theoretical molecular weights (Table 1). This could be explained not only by the intramolecular cyclization reactions of the NR but also by the ADMET of methylene terminated cross-metathesis products (Table 2). The ^{1}H and ^{13}C NMR spectroscopy as well as the IR study of degraded NR were performed to find the evidence for the preparation of terpene-terminated oligomers. In Fig. 2 it is shown the ^{1}H NMR spectra of NR before (a) and after (b) the degradation via cross-metathesis with *β*-pinene (Table 1, entry 11). The new signal observed at 4.82 ppm was assigned to the protons of the vinyl group in the oligomers obtained, while the signals arising in the 0.9–1.2 ppm region were attributed to aliphatic protons of terpene-terminated oligomers.

The small signal at 5.34 ppm could be attributed to the protons of the internal olefin of methylene terminated cross-metathesis products (A*m*) that have further participated in ADMET as a side reaction. It is well known that *β*-pinene undergoes isomerization reactions to produce *β*-myrcene, α-pinene, and limonene [22] besides participating in the self-metathesis reactions. In this regard, control experiments with *β*-pinene were carried out using catalyst (**I**) at 45 °C. The products of these experiments were examined by GC/MS, ^{1}H NMR and ^{13}C NMR, respectively. In all the cases, the chromatograms as well as the ^{1}H and ^{13}C NMR spectra did not show evidence on the formation of new productive metathesis compounds (cyclic dimer or ethylene) neither on the isomerization reactions products such as *β*-myrcene, α-pinene or limonene. These results indicate that *β*-pinene in these conditions did



Scheme 2 Composition and yields of products obtained during the cross-metathesis of NR with *β*-pinene

not participate in the self-metathesis reactions or the isomerization reactions. It has been reported that terminal olefin metathesis is accompanied by the exchange of methylene groups and this reaction occurs significantly faster than the metathesis of olefins with internal double bonds [6].

The experimental and computational investigations demonstrated that self-metathesis of α-olefins proceeded via a secondary metallacarbene complex as the most energetically favorable route [23, 24]. Since NR is a challenging polymer, its metathesis and degradation reactions using monoterpenes as CTAs have not been reported, therefore the cross-metathesis of *β*-pinene with a model compound of NR such as (Z)-3-methyl-2-pentene was investigated (Scheme 3). The cross-metathesis products D (2-ethylidene-6,6-dimethyl-bicyclo[3.1.1] heptane), E (2-methyl-but-1-ene) and F (2-sec-butylidene-6,6-dimethyl-bicyclo[3.1.1] heptane) were obtained in yields around 80% and detected by GC/MS.

Thus, the yields of products D, E, and F were 58% ($m/z = 150$), 8% ($m/z = 70$), and 16% ($m/z = 178$), respectively. Figure 3 presents the mass-spectrum of D obtained during the cross-metathesis reaction. This model reaction confirmed the formation of desired monoterpene-terminated oligomers (series B*m*) during the cross-metathesis degradation of NR with *β*-pinene. The computational study of (*Z*)-3-methyl-2-pentene metathesis mediated by Ru-alkylidene catalysts shows that the relative stability of the secondary and tertiary metallacarbenes formed depends on the interplay between steric and electronic factors [25]. The secondary metallacarbene was found to be more active in the metathesis reactions due to less sterically hindered transition states [25]. The formation of D (2-ethylidene-6,6-dimethyl-bicyclo[3.1.1] heptane) as the main product in the cross-metathesis

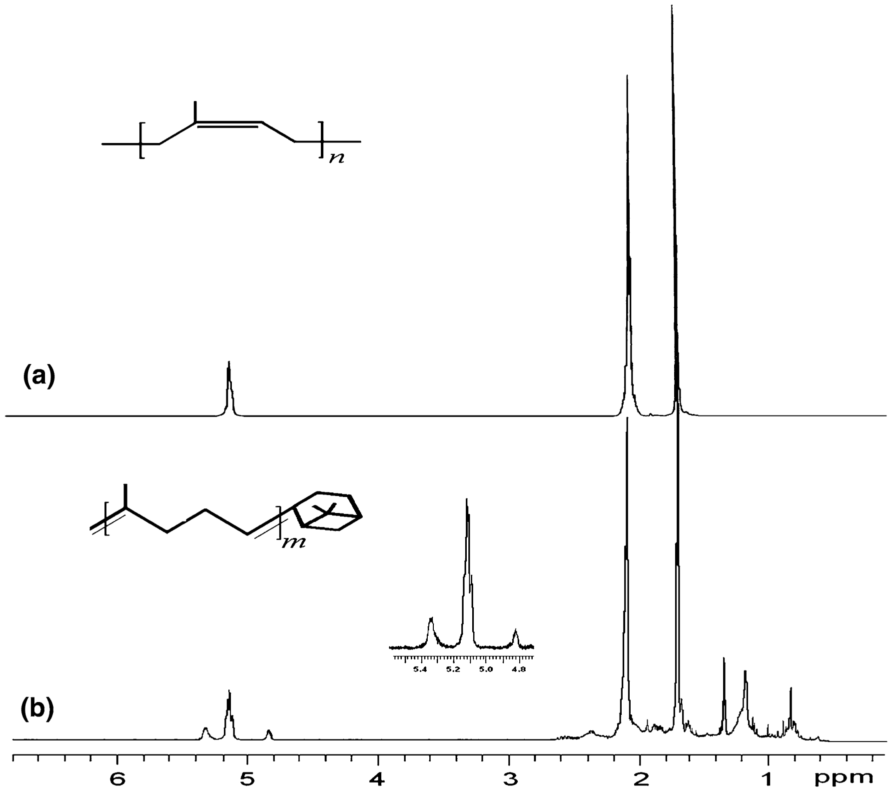
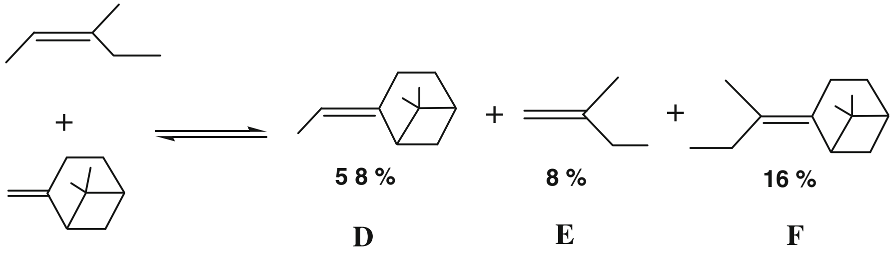


Fig. 2 ^{1}H NMR spectra of Guatemala NR before (**a**) and after (**b**) the cross-metathesis degradation with *β*-pinene (products: A*m*, B*m*, C*m*)



Scheme 3 Cross-metathesis of (*Z*)-3-methyl-2-pentene with *β*-pinene. Products: D: 2-ethylidene-6,6-dimethyl-bicyclo[3.1.1] heptane, E: 2-methyl-but-1-ene and F: 2-*sec*-butylidene-6,6-dimethyl-bicyclo [3.1.1] heptane

reaction of *β*-pinene with (*Z*)-3-methyl-2-pentene support the calculation data provided that the secondary Ru-carbene complex is principal reactive intermediate in this reaction. Computational modeling reveals that the metathesis reactions of trisubstituted olefins or olefins with bulky side groups will always have higher activation energies compared to those of disubstituted olefins. The metallacarbene

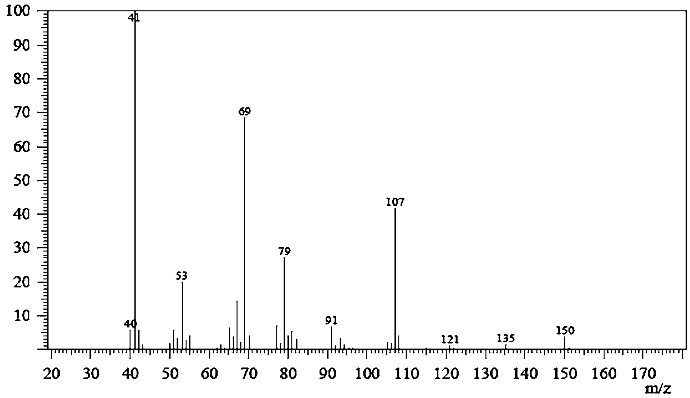


Fig. 3 MS chromatogram of product D (2-ethylidene-6,6-dimethyl-bicyclo[3.1.1] heptane). GC/MS (EI) min (Component, *m/z,* abundance): 8.7 (D, 150, 58%)

active center having a highly substituted carbene will show the elevated activation energy compared to the less substituted metallacarbene [24].

Conclusion

The metathesis degradation of natural rubber in the presence of β-pinene as a chain transfer agent was described. The cross-metathesis reactions were carried out under solvent free conditions using the second generation Grubbs catalyst. The main products of the cross-metathesis degradation were monoterpene-terminated oligomers of series B*m*. β-Pinene is a suitable chain transfer agent for the metathesis degradation of rubber. The NR degradation with β-pinene was confirmed using cross-metathesis of β-pinene with a model compound of NR, (*Z*)-3-methyl-2-pentene.

Acknowledgments Financial support from the National Council for Science and Technology of Mexico (CONACYT) (PhD Scholarship to S.G.) is gratefully acknowledged. We thank CONACyT-SEMARNAT (contract 23432) and ICyTDF (contract 4312) for generous support to this research. We are grateful to Alejandrina Acosta, Gerardo Cedillo, Salvador López Morales and Miguel Ángel Canseco Martínez for their assistance in NMR, GPC, and IR.

References

1. Gallezot P (2007) Catalytic routes from renewable to fine chemicals. Catal Today 121:76–91
2. Tanaka Y, Hirasawa H (1989) Sequence analysis of polyprenols by 500 MHz ^{1}H-NMR spectroscopy. Chem Phys Lipids 51:183–189
3. Baldenius KU, von dem Bussche-Hünnefeld L, Hilgemann E, Hoppe P, Stürmer R (1966) Ullmanns encyclopedia of industrial chemistry, vol 7. VCH Verlagsgesellschaft, Veinheim, pp 478–488, 594–597
4. Stevens MP (1999) Molecular weight and polymer solutions, free radical polymerization, vinyl polymerization with complex coordination catalysts. In: Polymer chemistry. Oxford University Press, New York, pp 35–37, 169–170, 252–254

5. Chatterjee AK, Grubbs RH (2003) Olefin cross-metathesis. In: Handbook of metathesis–applications in organic synthesis, vol 2. Wiley-VCH, Weinheim, pp 246–295
6. Ivin KJ, Mol JC (1997) Degradation of unsatured polymers by metathesis. In: Olefin metathesis and metathesis polymerization. Academic Press, San Diego, CA, p 375
7. Thorn-Csanyi E, Zilles JU (2002) Structure/property relationships of Schrock-type alkylidene complexes based on tungsten and molybdenum. J Mol Catal A 190:85–100
8. Lapinte V, Fontaine L, Montembault V, Campistron I, Reyx D (2002) Ring-opening metathesis polymerization (ROMP) of isomerically pure functional monomers and acyclic diene metathesis depolymerization (retro-ADMET) of functionalized polyalkenamers. J Mol Catal A 190:117–129
9. Gutiérrez S, Vargas SM, Tlenkopatchev MA (2004) Computational study of metathesis degradation of rubber. Distributions of products for the ethenolysis of 1,4-polyisorene. Polym Degrad Stab 83:149–156
10. Solanky SS, Campistron I, Laguerre A, Pilard J-F (2005) Metathetic selective degradation of polyisoprene: low-molecular-weight telechelic oligomer obtained from both synthetic and natural rubber. Macromol Chem Phys 206:1057–1063
11. Korshak YV, Tlenkopatchev MA, Dolgoplosk BA, Avdeikina EG, Kutepov D (1982) Intra- and intermolecular metathesis reactions in the formation and degradation of unsaturated polymers. J Mol Catal 15:207–218
12. Grubbs RH (2003) The discovery and development of well-defined ruthenium-based olefin metathesis catalysts. In: Handbook of metathesis. Wiley-VCH, Weinheim, Germany, p 61
13. Bielawski CW, Grubbs RH (2007) Living ring-opening metathesis polymerization. Prog Polym Sci 32:1–29
14. Bielawski CW, Grubbs RH (2000) Highly efficient ring-opening metathesis polymerization (ROMP) using new ruthenium catalysts containing N-heterocyclic carbene ligands. Angew Chem Int Ed 39:2903–2906
15. Craig SW, Manzer JA, Coughlin EB (2001) Highly efficient acyclic diene metathesis depolymerization using a ruthenium catalyst containing a N-heterocyclic carbene ligand. Macromolecules 34:7929–7931
16. Mathers RT, McMahon KC, Damodaran K, Retarides CJ, Kelly DJ (2006) Ring-opening metathesis polymerization in *D*-limonene: a renewable polymerization solvent and chain transfer agent for the synthesis of alkene macromonomers. Macromolecules 39:8982–8986
17. Mathers RT, Damodaran K, Rendos MG, Lavrich MS (2009) Functional hyperbranched polymers using ring-opening metathesis polymerization of dicyclopentadiene with monoterpenes. Macromolecules 42:1512–1518
18. Wagener KB, Boncella JM, Nell JG, Konzelman J (1990) Acyclic diene metathesis copolymerisation of 1,5-hexadiene and 1,9-decadiene. Macromolecules 23:5155–5157
19. Vargas JO, Fomine S, Tlenkopatchev MA (2004) Molecular modelling of metathesis degradation of polyalkenamers: 1. Degradation of polynorbornene via cross-metathesis with linear olefins. Polym Degrad Stab 86:85–93
20. Thorn-Csanyi E, Ruhland K (1999) Quantitative description of the metathesis polymerization/depolymerization equilibrium in the 1,4-polybutadiene system, 1. Influence of feed concentration and temperature. Macromol Chem Phys 200:1662–1671
21. Tlenkopatchev MA, Barcenas A, Fomine S (2001) Computational study of metathesis degradation of rubber, 2. Distribution of cyclic oligomers via intramolecular metathesis degradation of natural rubber. Macromol Theory Simul 10:441–446
22. Breitmaier E (2006) Terpenes: flavors, fragrances, pharmaca, pheromones. Wiley-VCH, New-York
23. McGinnis J, Katz TJ, Hurwitz S (1976) Selectivity in the olefin metathesis of unsymmetrically substituted ethylenes. J Am Chem Soc 98:605–606
24. Tlenkopatchev MA, Fomine S (2001) Molecular modeling of the olefin metathesis by tungsten (0) carbene complexes. J Organomet Chem 630:157–160
25. Fomine S, Tlenkopatchev MA (2010) Computational modeling of renewable molecules. Ruthenium alkylidene-mediated metathesis of trialkyl-substituted olefins. Organometallics 29:1580–1587