

DEGRADATION OF NATURAL RUBBER VIA CROSS-METATHESIS WITH FUNCTIONALIZED OLEFINS USING RUTHENIUM ALKYLIDEN CATALYSTS

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Abstract

Metathesis degradation of natural rubber (NR) in the presence of *cis*-1,2-dicarbomethoxy-ethylene (dimethyl maleate) (DMM), *cis*-1,4-diacetoxy-2-butene (DAB) and *cis*-1,4-dichloro-2-butene (DCB) as chain transfer agents (CTAs) using a tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidene] ruthenium dichloride [(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (PCy₃)Cl₂Ru=CHPh] (**I**) was studied. The perfectly diacetoxy- and diallyl chloride telechelics were synthesized using DAB and DCB as cross-metathesis partners while DMM did not control the molecular weights of NR. This phenomena was explained by the non-productive complex formation between a carbonyl oxygen of the monomer (DMM) and a Ru-active center.

Keywords: Degradation, Natural Rubber, Metathesis, Telechelics

Resumen

La degradación vía metátesis cruzada del hule natural (NR) en presencia de *cis*-1,2-dicarbometoxi-etileno (dimetil maleato) (DMM), *cis*-1,4-diacetoxi-2-buteno (DAB) y *cis*-1,4-dicloro-2-buteno (DCB) como agentes de transferencia de cadena (CTAs) usando dicloruro de triciclohexilfosfina [1,3-bis(2,4,6-trimetilfenil)-4,5-dihidroimidazol-2-ilideno][bencilideno] rutenio [1,3-bis(2,4,6-trimetilfenil)-4,5-dihidroimidazol-2-ilideno] (PCy₃)Cl₂Ru=CHPh (**I**) ha sido estudiada. Telequélidos perfectamente difuncionales diacetoxi- y dicloro alil han sido sintetizados vía metátesis cruzada usando DAB y DCB a diferencia de DMM que no permite el control del peso molecular. Este fenómeno ha sido explicado por la complejación del oxígeno carbonílico del DMM y el centro activo del Ru.

Palabras Claves: Degradación, Hule Natural, Metátesis, Telequélidos

1. INTRODUCTION

The intramolecular metathesis degradation of many polyalkenamers and their cross-metathesis with linear olefins as chain transfer agents (CTAs) to produce cyclic oligomers and end-functionalized polymers (telechelics) have been studied [1]. For example, telechelic polybutadienes with different functional groups, such as dihydroxyl, diamino, dichloro, diepoxy have been synthesized by metathesis degradation of *cis*-polybutadiene (*cis*-PB) or ring-opening metathesis polymerization (ROMP) of *cis*, *cis*-1,5-cyclooctadiene [2-5]. Telechelics serve as key components in the synthesis of block copolymers and polymeric networks and as cross-linking agents to enhance thermal and mechanical properties of other materials [6].

Few reports exist on the metathesis degradation of natural rubber (NR) or *cis*-1,4-polyisoprene (*cis*-PI) [7-15]. This may be explain by the fact that NR is very sensitive to the side reactions [8] and this polymer with trisubstituted unsaturations degraded much more slower than other disubstituted polyalkenamers [12]. The authors [12] reported that metathesis degradation of *cis*-PI using the classical tungsten based catalyst took more than 48 hours to form oligomers. Hence, sterically hindered polymers and olefins require long-time stable and high active and selective metathesis catalysts. The development of a highly active Ru-alkylidene catalysts opens new possibilities in olefin metathesis and their application to controlled polymer synthesis [16]. Thus, ROMP of challenging *cis,cis*-1,5-dimethyl-1,5-cyclooctadiene to polyisoprene, degradation of styrene-isoprene and styrene-butadiene ABA triblock copolymers to oligomers using high active

ruthenium alkylidene catalysts containing a N-heterocyclic carbene ligand have been reported [17].

In this paper we describe the metathesis degradation of natural rubber (NR) in the presence of high functionalized olefins *cis*-1,2-dicarbomethoxy-ethylene (dimethyl maleate) (DMM), *cis*-1,4-diacetoxy-2-butene (DAB) and *cis*-1,4-dichloro-2-butene (DCB) as chain transfer agents (CTAs) using a tricyclohexylphosphine [1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene] [benzylidene] ruthenium dichloride [(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene)

(PCy₃)Cl₂Ru=CHPh] (**I**) (Figure 1).

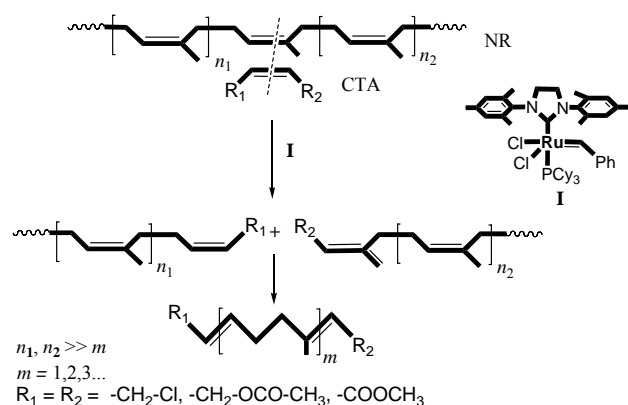


Figure 1. Degradation of natural rubber using olefins as CTAs.

2. EXPERIMENTAL SECTION

2.1 Materials

NR was obtained from fresh field latex of AGROS (Guatemala) and used without purification. NR ($M_n = 1.7 \times 10^6$, PDI=1.5). The olefins *cis*-1,2-dicarbomethoxy-ethylene (dimethyl maleate), *cis*-1,4-diacetoxy-2-butene and *cis*-1,4-dichloro-2-butene were purchased from Aldrich. 1,2-Dichloroethane was purchased from Baker and distilled from CaH₂ prior to use.

2.2 Measurements

¹H NMR and ¹³C NMR spectra were recorded on a Varian spectrometer at 300 and 75.5 MHz frequencies, respectively, in CDCl₃ with tetramethylsilane (TMS) as internal standard. FTIR spectra were obtained on a Nicolet 510 p spectrometer. Molecular weights and molecular weight distributions with reference to polystyrene standards were determined with a Varian 9012 GPC instrument at 30 °C in chloroform (universal column and a flow rate of 1 mL min⁻¹).

2.1 Degradation procedure

The NR was dissolved in 1,2-dichloroethane at concentration 10 mol%. The olefins used as CTA were added to the stirred solution of NR. The olefins used as CTAs were *cis*-1,2-dicarbomethoxy-ethylene (dimethyl maleate) (96%), *cis*-1,4-diacetoxy-2-butene (95%) and *cis*-1,4-dichloro-2-butene (95%) and these were used in several molar ratio of NR to CTA Rub/CTA= 1:1, 2:1, 4:1, 8:1 and 10:1. The catalyst [(1,3-dimesityl-4,5-dihydroimidazol-2-ylidene) (PCy₃)Cl₂Ru=CHPh] (**I**) was added in different molar ratio NR /catalyst = 1000 and 2000. Metathesis degradation of NR was carried out under a nitrogen atmosphere and with a temperature 45 °C. Adding ethyl vinyl ether under a nitrogen atmosphere terminated the reactions. After cooling, the solutions were poured into an excess of methanol.

3. RESULTS AND DISCUSSION

Table 1 presents the results of NR degradation in the presence of DMM, DAB and DCB as CTAs by catalyst (**I**) using a variety of NR/CTA ratios. The initial molecular weight of NR was $M_n = 1.7 \times 10^6$ ($M_w/M_n = 1.5$). From these results, it can be concluded that DMM is a poor cross-metathesis partner and this high functionalized olefin did not control the molecular weight of NR. On the other hand, it appears that NR degraded in the presence of DAB and DCB by (**I**) to yield well-defined products. The experimental molecular weights of telechelics determined by gel permeation chromatography (GPC) and end-group analysis using ¹H NMR spectroscopy were in good agreement with theoretical ones based on the initial NR/CTA ratio (Table 1, entries 1-7). The molecular weight of products may be controlled in a wide range by changing the ratio CTAs to NR (entries 1-5). As seen from Table 1 (entry 5), degradation of NR was also performed in bulk and the solvent was added only with the catalyst. Within 2 hours the surface of NR began to visually liquefy to form after 5-6 h the homogeneous viscous liquid. After 24 h, the end-functionalized isoprene oligomers were isolated and a residual catalyst was removed using silica gel chromatography. Isolated yields of oligomers were high and ranged between 83 and 90 %. It is worth noting that the use of high NR/catalyst ratio (Table 1) permitted the synthesis of well-defined telechelics with end-group functionality ratio near 2.0.

Table 1. Degradation of NR in presence of DAB, DCB and DMM as CTAs by catalyst (I) (Reaction conditions: 1,2-dichloroethane as solvent, temperature 45 °C, concentration of NR in 1,2-dichloroethane 10 mol%).

Entry	CTA	Rub/ CTA ^b	NR/ Catal. ^c	Time (h)	Yield (%) ^d	MW (theor) ^e	Mn (NMR) ^f	Mn (GPC) ^g	PDI ^g
1	DAB	1	2000	24	87	240	274	-	-
2	DAB	4	2000	36	93	440	539	594	1.9
3	DAB	8	2000	36	95	716	716	860	1.9
4	DAB	10	2000	36	95	852	852	989	1.8
5	DAB ^h	10	1000	36	92	852	852	808	2.1
6	DCB	2	2000	24	85	261	533	-	-
7	DCB	10	1000	8	83	805	971	1052	1.9
8	DMM	4	1000	24	76	416	2320	1655	2.4
9	DMM	10	1000	8	75	824	9256	8552	2.3

a: Natural Rubber (Mn = 1.7x10⁶; Mw/Mn = 1.5).

b: Molar ratio of NR to CTA.

c: Molar ratio NR /catalyst

d: Isolated yield of polymer. After the solvent evaporation.

e: Theoretical MW based on complete NR and CTA conversion.

f: Mn determined by ¹H NMR end group analysis.

An average of two CH₂Cl (CH₂COOCH₃) groups per polymer chain was assumed.

g: Determined using GPC with chloroform as the eluent.

Values reported relative to polystyrene standards.

h: degradation of NR in bulk. The solvent was added only with the catalyst.

The ¹H and ¹³C NMR spectroscopy as well as IR study of degraded NR were carried out to find evidence for functionalization and preparation of well-defined oligomers. Figure 2 and Figure 3 present ¹H-NMR spectra of oligomers prepared using DAB and DCB as CTAs by I. The new peaks observed in the 5.75-5.90 ppm are attributed to an olefin proton in =CH-CH₂OCOCH₃ and in =CH-CH₂Cl bonds confirming the formation of diester- (diallyl-) terminated isoprene oligomers.

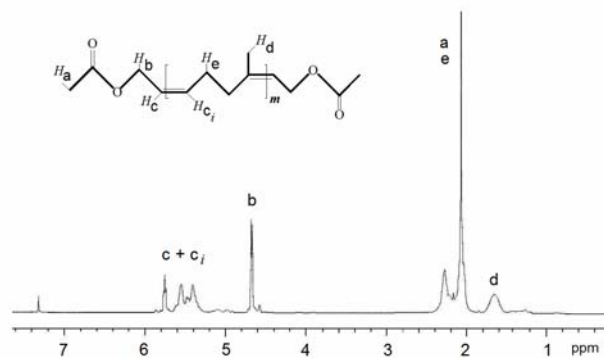
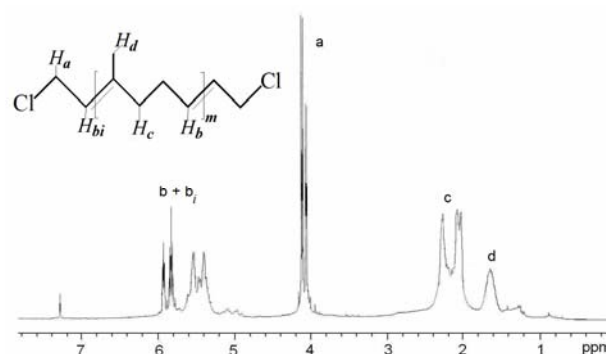
**Figure 2.** ¹H NMR spectra of the products of degradation via cross-metathesis of NR with DAB (Table 1, entry 3).**Figure 3.** ¹H NMR spectra of the products of degradation via cross-metathesis of NR with DCB (Table 1, entry 6).

Figure 4 presents GPC data of NR degradation via cross-metathesis with DMM (entries 8-9 Table 1). After 8 hours (Figure 4b), GPC analysis revealed a molecular weight decrease of 3 orders of magnitude (Mn = 8.5 x10³ g/mol). Degradation is completed after 24 h to give oligomers with molecular weight Mn = 1.6 x10³ g/mol (Mw/Mn=2.4, vs polystyrene) (Figure 4c).

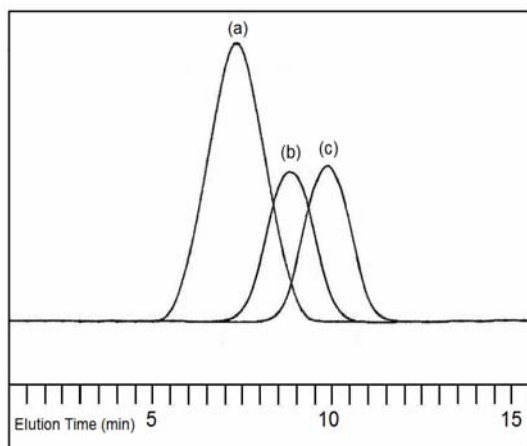


Figure 4. GPC data of (a) NR degradation via cross-metathesis with DMM; (b) degradation of NR with DMM Rub/CTA = 8:1 (Table 1, entry 9) (c) degradation of NR with DMM Rub/CTA = 4:1 (Table 1, entry 8).

The computational modeling shows that the carbonyl oxygen of DMM can coordinate with the 14-electron Ru-alkylidene active center to form the stable complex that impedes metathesis [18]. On the other hand, the carbonyl containing olefin DAB easily participated in cross-metathesis to control the molecular weight of oligomers. According to our calculations at B3LYP/LACVP* level of theory, in the case of DMM the non productive complex between a carbonyl oxygen and a 14-electron Ru active center is 3.1 kcal/mol more stable compared to the productive complex of the double bond of DMM and d-orbitals of a Ru catalyst. The situation changes for DAB where the non productive complex of a carbonyl group with a Ru center is 6.0 kcal/mol less stable compared to productive one.

It is worth noting, that degradation of NR in the presence of DCB as a CTA is completed with 6-8 h (Table 1 entry 7), while the same reaction with DAB proceeded more slower (Table 1 entry 4). This can be explained by the fact that the metathesis degradation of NR in the presence of DAB proceeded via the formation of a Ru-acetoxyethylidene ($\text{Ru}=\text{CHCH}_2\text{OCOCH}_3$) complex which is more stable than an usually Ru-benzylidene ($\text{Ru}=\text{CHPh}$) active center due to the complex formation between a carbonyl oxygen and a Ru active center. The transformation of a Ru-alkylidene (benzylidene) active center to the Ru-acetoxyethylidene species during the reaction may slow down the metathesis degradation.

4. CONCLUSIONS

Degradation of NR via cross-metathesis with high functionalized olefins cis-1,4-diacetoxy-2-butene (DAB) and cis-1,4-dichloro-2-butene (DCB) using de second generation Grubbs-alkylidene catalyst proceeded to give diacetoxy- and diallyl chloride telechelics with controlled molecular weights. It was shown that cross-metathesis of NR with olefins can be performed in solvent free conditions adding the solvent only with catalyst. This method permitted the synthesis of well-defined products with end-group functionality ratio near 2.0. On the other hand, α -carbonyl containing olefin dimethyl maleate (DMM) was poor substrate for the metathesis degradation and did not control the molecular weights of NR.

5. ACKNOWLEDGEMENTS

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