

Citrus oils as chain transfer agents in the cross-metathesis degradation of polybutadiene in block copolymers using Ru-alkylidene catalysts

Araceli Martínez^{1*}, Selena Gutiérrez², Mikhail A. Tlenkopatchev^{1*}

¹Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, México City, México;

*Corresponding Author: arampmx@yahoo.com.mx, tma@unam.mx

²Centro de Investigaciones Biológicas del Noroeste, CIBNOR, México City, México

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ABSTRACT

The cross-metathesis degradation of poly(styrene-co-butadiene) (styrene, 30 wt%) (SB-1) and poly(styrene-co-butadiene) (styrene, 21 wt%) (SB-2) in the presence of essential oils and *d*-limonene as chain transfer agents (CTAs) using Ru-alkylidene catalysts (PCy₃)₂(Cl)₂Ru = CHPh (I) and (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) (PCy₃)Cl₂Ru=CHPh (II) was studied. Terpene-terminated butadiene oligomers and polystyrene blocks were obtained as products of the degradation of SB-1 and SB-2. Catalysts I and II showed high activity in the degradation of SB copolymers to produce the low molecular weight products ($M_n = 276 - 335 \text{ g}\cdot\text{mol}^{-1}$) and yields ranging from 91% - 95%. The cross-metathesis degradation of copolymers in organic solvents and in citrus oils (mandarin, orange and lemon oils) proceeded with similar efficiency and resulted in the same molecular weight butadiene oligomers. According to GS/MS (EI) analysis, the main products of the degradation of SB-1 copolymer with *d*-limonene were limonene-terminated oligomers of series A_m ($m = 1 - 4$).

Keywords: Metathesis Degradation; Polybutadiene in Block; Natural Oils; *d*-Limonene; Ru-Alkylidene Catalysts

1. INTRODUCTION

Mandarin, lemon and other citrus oils are very attractive terpene based compounds. Terpenes are a class of natural products that typically contain carbon atom units built from isoprene molecules. A wide variety of bio-

based structures is synthesized by transformations of isoprene monomer units. For example, pinene, β -carotene, natural rubber, carvone and steroids such as testosterone, cholesterol and estrogen are set of terpene based compounds. In plants, terpenes are found as a main component of the essential oils, that are used as medicines, spices and perfumes [1]. Commercial polymers of monoterpenes prepared usually by Lewis acid catalyzed polymerization are used in many industrial applications for example, as pressure-sensitive adhesives, hot-melt coatings, packaging gum and additives [2,3]. The transformations of terpene based molecules using efficient catalysts are of great interest for the development of new applications for these biomass-derived compounds. In this perspective, metathesis transformations are becoming more attractive as the availability and choice of effective catalysts increased [4-6]. The computational modeling of β -pinene ring-opening metathesis using Grubbs, Schrock and Fischer type metal carbene revealed that the successful catalysts for metathesis of terpene based molecules should have small substituent at a metal active center and a carbon carbene atom. Thus, the lowest activation and reaction energies were found for methylene metallocarbenes [7]. Metathesis transformations of several terpenoids such as citronellal, citronellol and citral using the Ru-alkylidene catalysts have been reported [8-10]. Monoterpenes such as *d*-limonene and β -pinene have been used in the cross-metathesis reactions with cycloolefins [11-13] and natural rubber [14,15]. The intramolecular and intermolecular metathesis degradation reactions of alternating, random and block copolymers of butadiene and isoprene have been studied [16-23]. Thus, it was reported that the cyclodegradation of the alternating copolymer of butadiene and propene using classical metathesis catalysts can produce non-polymerizable via ring-opening metathesis polymerization 4-methylcyclo-

hexene [17]. The effect of dichloromethane and hexane solvents on the metathesis degradation of polyalkenamers in block copolymers has been reported [22]. It is worth noting that the cross-metathesis degradation of block copolymers containing polybutadiene and polyisoprene units has been less studied [22].

The goal of this study is the cross-metathesis degradation of polybutadiene in block copolymers in the presence citrus oils as chain transfer agents (CTAs) and green solvents using commercially accessible Ru-alkylidene catalysts $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru} = \text{CHPh}$ (**I**) and (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) $(\text{PCy}_3)\text{Cl}_2\text{Ru} = \text{CHPh}$ (**II**).

2. EXPERIMENTAL

2.1. Reagents

Mandarin, lemon and orange oils were obtained from Natural Oils & Chemical and used without purification. Poly(styrene-co-butadiene) (styrene, 30 wt%) ($M_n = 1.70 \times 10^5$, MWD = 1.5, **SB-1**) and poly(styrene-co-butadiene) (styrene, 21 wt%) ($M_n = 1.92 \times 10^5$, MWD = 1.4, **SB-2**); *d*-limonene (Aldrich, $\geq 97\%$); $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru} = \text{CHPh}$ (first generation Grubbs catalyst) (**I**) and (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) $(\text{PCy}_3)\text{Cl}_2\text{Ru} = \text{CHPh}$ (second generation Grubbs catalyst) (**II**); methanol, hexane and chlorobenzene anhydrous solvents were purchased from Aldrich Chemical Co. and used as received. 1,2-dichloroethane was dried over calcium hydride (CaH_2) and distilled.

2.2. Techniques

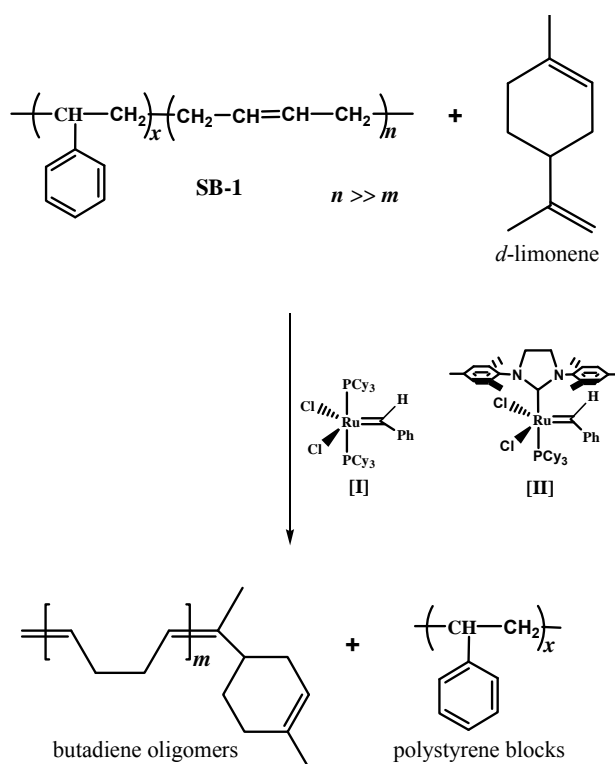
$^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded on a Varian spectrometer Inova Unit 300 model at 300 and 75 MHz, respectively in CDCl_3 . Tetramethylsilane (TMS) was used as internal standards. FT-IR spectra were obtained on a Nicolet 5700 using a diamond tip as dispersing agent. Number-average molecular weight (M_n) and molecular weight distributions (MWD) were determined with reference to monodisperse polystyrene standards on a waters 2695 ALLIANCE Separation Module GPC at 30°C in tetrahydrofuran (THF) using a universal column and a flow rate of 0.3 ml/min.

GC-MS (EI) chromatograms were recorded using a GC-2010/MS-QP2010s system equipped with an AOC-20i autosampler, with the injector temperature of 335°C , at 1:5 split ratio and injection volume of 1 mL. Capillary column separation was used a 0.25 mL thick film [30 m \times 0.32 mmID Rtx-5MS (RESTEK) with a 5 m integraguard 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 $10^\circ\text{C}/\text{min}$ to 150°C , ramp at $15^\circ\text{C}/\text{min}$ to 340°C , and isothermal for 14 min. The interface and ion source were set at 340°C and 220°C , respectively. The

chromatograms were acquired in the electron impact (EI) scan mode at 70 eV with a mass range of 40 - 600 (m/z) at rate of $0.1 \text{ scan}\cdot\text{s}^{-1}$. The data were acquire and processed using Shimadzu GCMS solutions software.

2.3. Procedure for the Metathesis Degradation of SB-1 and SB-2

Metathesis degradation of SB-1 and SB-2 copolymers (2 g, 37 mmol) using *d*-limonene (**Scheme 1**) and mandarin, lemon and orange oils as CTAs was carried out under nitrogen atmosphere, in a glass vial, with a temperature of 50°C . The catalyst $(\text{PCy}_3)_2(\text{Cl})_2\text{Ru} = \text{CHPh}$ (**I**) or (1,3-diphenyl-4,5-dihydroimidazol-2-ylidene) $(\text{PCy}_3)\text{Cl}_2\text{Ru} = \text{CHPh}$ (**II**) was added in molar ratio $[\text{C} = \text{C}]/\text{catalyst} = 1000$. The reactions were carried out in bulk (solvent was added only with the catalysts) or using essential oils, 1,2-dichloroethane and dichlorobenzene as solvents (initial copolymer concentration $[\text{M}_0] = 1 \text{ mol/L}$). Essential oils and *d*-limonene (CTAs) were used in several molar ratios of NR to CTA $[\text{C} = \text{C}]/[\text{CTA}] = 1:1$, 5:1 and 10:1. After terminating the reaction by addition of a small amount of ethyl vinyl ether, the solution was poured into an excess of methanol. The polystyrene blocks could be isolated in hexane. The products were dried under vacuum and characterized by ^1H , $^{13}\text{C-NMR}$, FT-IR, GPC, SEC and GC/MS (EI). Isolated yields of butadiene oligomers were high and ranged between 91% - 95%.



Scheme 1. Cross-metathesis of poly(styrene-co-butadiene) (styrene, 30 wt%) (SB-1) with *d*-limonene.

¹H-NMR (300 MHz, CDCl₃, ppm). δ 5.65 (br, CH = C cyclic terpene); δ 5.41 (s, CH = C butadiene); δ 5.09 - 4.92 (m, CH₂ = C terpene); δ 2.03, 0.88 - 0.82 (m, CH₂ butadiene); δ 1.26 (s, CH₃); δ 7.09 - 6.37 (m, CH styrene aromatic); δ 1.87 - 1.84 (m, CH₂); δ 1.54 - 1.24 (m, CH styrene).

¹³C-NMR (75 MHz, CDCl₃, ppm). δ 133.5 (s, C = C butadiene); δ 132.6, 130.7 (s, C = C terpene); δ 130.0, 129.3 and 128.8 (s, CH = CH butadiene); δ 118.5 (s, CH = C cyclic terpene); δ 114.6 (s, CH₂ = C vinylic); δ 39.2 (s, CH terpene); δ 34.5 and 32.8 (s, CH₂ terpene); 29.1 (s, CH₂ butadiene); δ 22.8, 14.2 (s, CH₃ aliphatic terpene); δ 145.3, 130.0 - 129.4, 128.0, 125.6 (m, =C-H styrene aromatic); δ 40.5 (s, CH styrene); δ 32.7 (s, CH₂ styrene).

FT-IR (ν , cm⁻¹). Butadiene oligomers: 2921 (ν_{as} C-H, CH₂, str); 2851 (ν_s C-H, CH₂, str); 1658 (C = CH₂, str).

Polystyrene blocks: 3024 (CH aromatics, str); 2922 (ν_{as} C-H, CH₂, str); 2825 (ν_s C-H, CH₂, str); 1600 (C = C, str).

GC/MS (EI) min (Component, m/z, abundance): 14.98

(**A**_m = 1, 190, 43%), 28.64 (**A**_m = 2, 244, 2%), 11.48 (**A**_m = 3, 298, 6%), 13.81 (**A**_m = 4, 352, 1%), 7.58 (**B**_m = 2, 136, 13%), 18.06 (**B**_m = 3, 190, 10%), 18.24 (**C**_m = 1, 298, 15%), 12.72 (**trimer**, 162, 10%).

3. RESULTS AND DISCUSSION

The major constituent of citrus oils is *d*-limonene with 74% for mandarin, 87% for lemon and 97% for orange oils. **Table 1** presents the composition of used citrus oils according to GS/MS (EI) analysis. The citrus oils were used as chain transfer agents (CTAs) and green solvents in the cross-metathesis degradation of poly(styrene-co-butadiene) (styrene, 30 wt%) (SB-1) and poly(styrene-co-butadiene) (styrene, 21 wt%) (SB-2). The copolymers contain more than 96% of *trans*-1,4-butadiene units. The **Scheme 1** depicts the cross-metathesis of SB-1 with *d*-limonene.

Table 2 summarizes the results of SB-1 and SB-2 degradation via cross-metathesis with citrus oils and *d*-limonene by catalysts **I** and **II**.

Table 1. Composition of mandarin, lemon and orange oils determined by GC/MS (EI).

No.	Compounds	Composition %		
		Mandarin oil	lemon oil	Orange oil
1	<i>d</i> -limonene	74.0	87.0	97.0
2	β -myrcene	1.3	1.3	1.5
3	β -pinene	3.0	3.1	1.5
4	α -pinene	4.2	3.7	
5	γ -terpinene	15.6		
6	<i>p</i> -cymene	0.6		
7	Dimethyl anthranilate	0.5		
8	Geraniol acetate, citronellol	0.8		
9	Terpinolene		1.1	
10	1,3,7-octatriene		1.7	
11	Citral		2.1	

Table 2. Degradation of SB-1 and SB-2 with essential oils and *d*-limonene using catalyst **I** and **II** (degradation was in bulk using molar ratio: [C = C]/[Catalyst] = 1000 and T = 50°C).

Entry	Rubber	Catalyst	CTA	[C = C]/[CTA]	Time h	Yield ^b (%)	M_n^c (¹ H-NMR)	M_n^d (SEC)
			poly(styrene-co-butadiene) (styrene, 30 wt%) (SB-1)					1.70×10^5
			poly(styrene-co-butadiene) (styrene, 21 wt%) (SB-2)					1.92×10^5
1	SB-1	I	<i>d</i> -limonene	1:1	1	76	-	71,629
2	SB-1	I	<i>d</i> -limonene	1:1	10	80	-	9400
3	SB-1	I	<i>d</i> -limonene	1:1	14	87	1603	1532
4	SB-1	I	<i>d</i> -limonene	1:1	24	91	270	305
5	SB-1	I	Mandarin oil	1:1	24	91	251	276
6	SB-1	I	Mandarin oil	5:1	24	94	496	512
7	SB-1	I	Mandarin oil	10:1	24	95	687	706
8	SB-1	I	Lemon oil	1:1	24	92	290	313
9	SB-1	I	Orange oil	1:1	24	93	285	325
10	SB-1	II	Mandarin oil	1:1	12	92	276	299
11	SB-1	II	Mandarin oil	5:1	12	93	452	468
12	SB-1	II	Mandarin oil	10:1	12	93	681	697
13	SB-2	I	Mandarin oil	1:1	24	95	297	335
14	SB-2	II	Mandarin oil	1:1	12	94	263	287

^aMolar ratio of [C = C] to CTA; ^bYields of the isolated products; ^c M_n determined by ¹H-NMR, end groups analysis where one unit of terpene is attached to the end-group of the butadiene oligomeric chain; ^dNumber-average molecular weights (M_n) of the butadiene oligomers were determined by size exclusion chromatography (SEC) in THF with polystyrene calibration standards. M_n of the oligomers butadiene (entries 6, 7, 11, 12) and polystyrene blocks were calculated by gel permeation chromatography (GPC) (THF as eluent with polystyrene calibration standards) and SEC.

It is important to note that the control experiments showed that the monoterpenes of citrus oils in the presence of Ru-alkylidene catalysts did not participate in the isomerization and *self*-metathesis reactions to produce non-desired products [15].

The evaluation of SB-1 molecular weights with increasing reaction time using *d*-limonene and catalyst **I** is represented in **Table 2**. The rapid decrease of the polymer molecular weight, corresponding to a M_n drop from 71,629 to about 9,400 $\text{g}\cdot\text{mol}^{-1}$ is observed.

Kinetics of the cross-metathesis degradation indicates that the butadiene oligomers are mainly formed during the first 10 h. Then, in the second stage, from about 14 to 24 h, copolymer molecular weights slowly decreased to finally reach the butadiene products with a molecular weight of about 305 $\text{g}\cdot\text{mol}^{-1}$.

As observed, both catalysts **I** and **II** showed high efficiency to produce the similar low molecular weight products (**Table 2**).

It is worth noting, that the first generation Ru-alkylidene catalyst **I** exhibited poor efficiency in the cross-metathesis degradation of natural rubber with *d*-limonene, when the second generation catalyst **II** in the same conditions allowed the formation of isoprene oligomers with controlled molecular weights [15]. These results are a real confirmation of the fact that the activation energy of metathesis of challenging olefins, especially trisubsti-

tuted internal olefins by the first generation Grubbs catalyst is higher than that of the second generation one [24]. Thus, the experimental and computational studies revealed that the *N*-heterocyclic carbene containing Ru-alkylidenes are the best catalysts for challenging substrates. [20,24,25]. After the cross-metathesis degradation butadiene oligomers with yields ranging from 91% - 95% and values around $M_n = 276 - 335 \text{ g}\cdot\text{mol}^{-1}$ (entries 4, 5, 8 - 10, 13 and 14), and polystyrene blocks with values around $M_n = 13 - 15 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ were isolated.

Figure 1 showed $^1\text{H-NMR}$ spectra of SB-1 before (**a**) and after (**b**), (**c**) the degradation via cross-metathesis with mandarin oil (**Table 2**, entry 5). The spectrum (**b**) corresponded to the liquid fraction of butadiene oligomers. The signals arising in the 5.09 - 4.92 ppm region were assigned to the protons of a vinyl group, while the signal observed at 5.65 ppm was attributed to the protons of the double bond in the terpene cycle. The signals of the aliphatic protons of *d*-limonene are observed at 0.88 - 0.82 ppm. The signals in the spectrum (**c**) at 7.09 - 6.37 ppm corresponded to the aromatic protons, while the signals arising in the 1.84 - 1.87 and 1.54 - 1.24 ppm regions were attributed to protons of CH_2 and CH groups in the polystyrene units [26].

The experimental molecular weights of butadiene oligomers determined by GPC, SEC and end-group analysis using $^1\text{H-NMR}$ spectroscopy (**Table 2**) were slightly

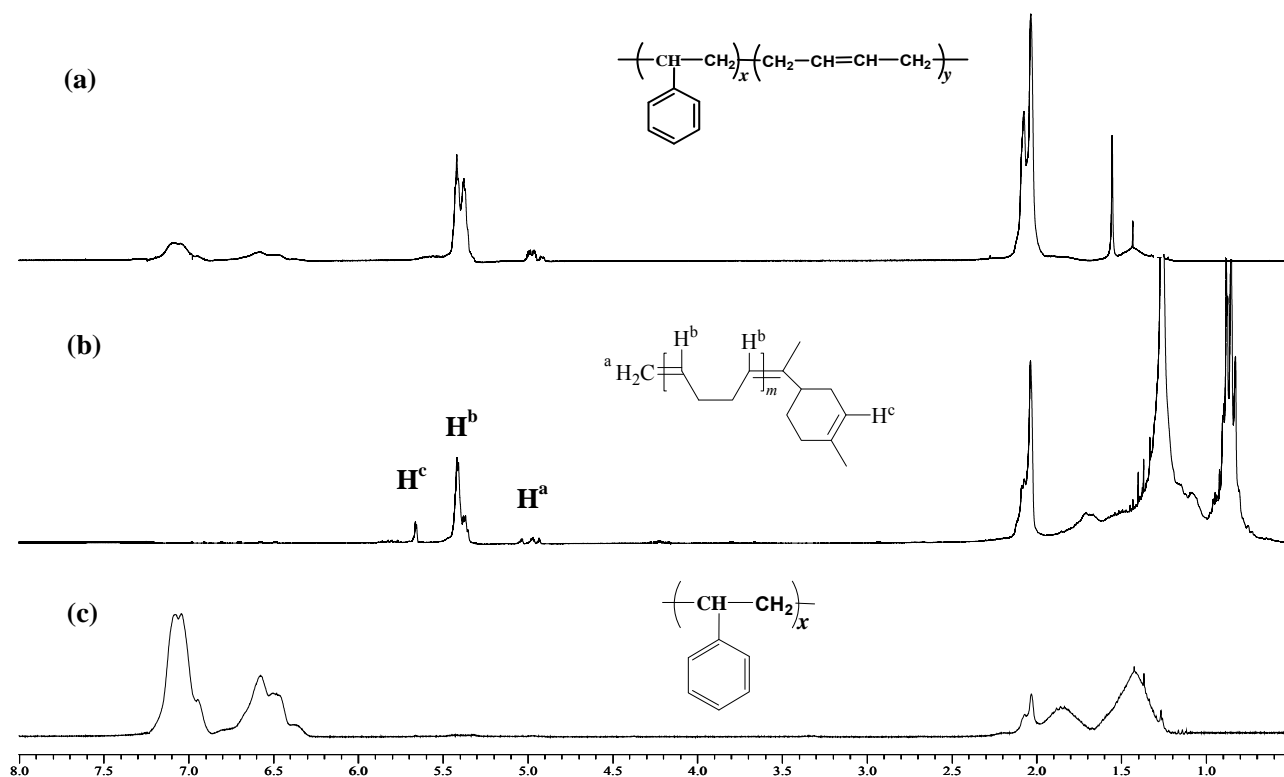


Figure 1. $^1\text{H-NMR}$ (300 MHz, CDCl_3) spectra of SB-1 before (a) and after (butadiene oligomers (b) and polystyrene blocks (c)) the cross-metathesis degradation with mandarin oil.

higher than the theoretical molecular weights. This phenomenon could be explained by the intramolecular cyclizations reactions of polymer chains and acyclic diene metathesis polymerization obtained during the cross-metathesis of methylene terminated products [14].

The molecular weight of products may be controlled by changing the ratio CTAs to butadiene units (**Table 2**, entries 5 - 7 and 10 - 12). **Figure 2** shows GPC chromatogram of products obtained via cross-metathesis degradation of SB-1 in the presence of mandarin oil ($[C = C]/[CTA] = 10:1$ molar ratio) (**Table 2**, entry 7).

The cross-metathesis degradation of copolymers was also investigated using citrus oils as green solvents. **Table 3** demonstrated the results of cross-metathesis degradation of SB-1 by catalyst **I** using mandarin, lemon and orange oils, 1,2-dichloroethane and chlorobenzene as solvents. It is seen that the copolymer degradation in

organic solvents and in mandarin, lemon and orange oils proceeded with similar efficiency and resulted in the same molecular weight butadiene oligomers. **Scheme 2** shows the composition and yields of butadiene oligomers according to GS/MS (EI) analysis (**Table 2**, entry 4). As seen from **Scheme 2** the products of this reaction were A_m (52%), B_m (23%), and C_m (15%). **Figure 3** presents the mass-spectrum of the major product A_m with $m = 1$ ($m/z = 190$, 43%). Interestingly, that in the case of natural rubber cross-metathesis with *d*-limonene the formation of oligomers with terpene terminated groups in both side (series C_m) did not detected [15]. These results point out that the metathesis reaction, in particular the cross-metathesis degradation of natural rubber in the presence of *d*-limonene as a CTA proceeded via the formation of less substituted intermediate in a transition state.

Computational modeling of natural rubber metathesis

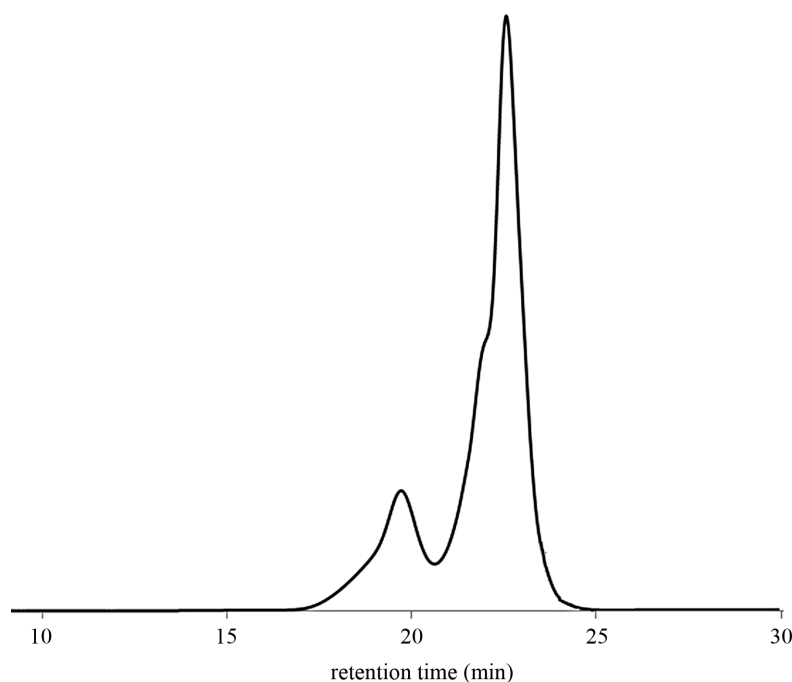
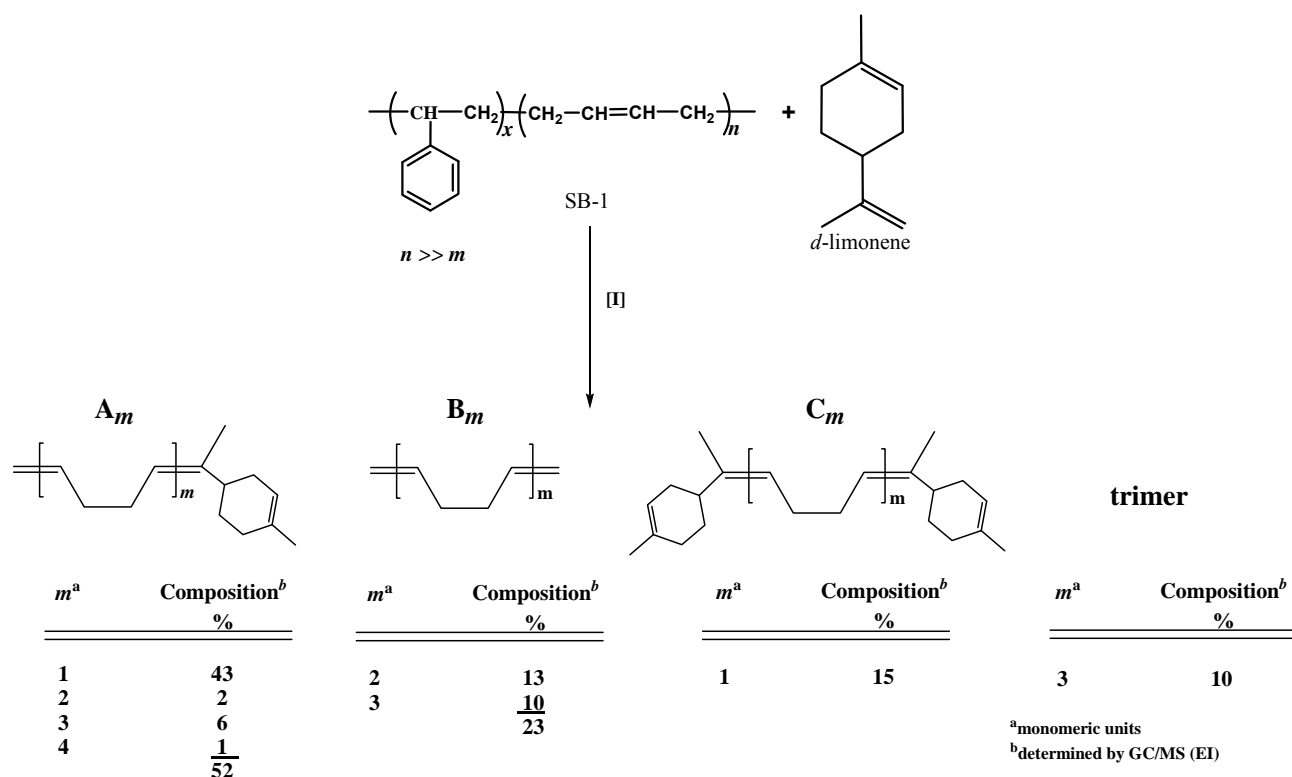


Figure 2. GPC chromatogram of products after the degradation of SB-1 in the presence of mandarin oil ($[C = C]/[CTA] = 10:1$ molar ratio).

Table 3. Degradation of SB-1 using essential oils, 1,2-dichloroethane and chlorobenzene as solvents. $\{[C = C]/[I] = 1000$ molar ratio, $T = 50^\circ\text{C}$ and $t = 24$ hrs $\}$.

Entry	Solvent ^a	$[C = C]^b/[CTA]$	Yield ^c %	M_n^d (¹ H-NMR)	M_n^e (SEC)
poly(styrene-co-butadiene) (styrene, 30 wt%) (SB-1)				1.7×10^5	
1	1,2-dichloroethane	1:1	95	295	330
2	Chlorobenzene	1:1	94	303	345
3	Mandarin oil	-	94	281	309
4	Lemon oil	-	93	284	317
5	Orange oil	-	94	293	324

^aInitial SB-1 concentration $[M_0] = 1$ mol/L; ^bMolar ratio of $[C = C]$ to mandarin oil as CTA; ^cYields of the butadiene oligomers; ^d M_n determined by ¹H-NMR, end groups analysis where one unit of *d*-limonene contained in the essential oils is attached to the end-group of the butadiene oligomeric chain; ^eNumber-average molecular weights (M_n) of the butadiene oligomers were determined by size exclusion chromatography (SEC) in THF with polystyrene calibration standards. M_n of polystyrene blocks were calculated by gel permeation chromatography (GPC) (THF as eluent with polystyrene calibration standards) and SEC.



Scheme 2. Composition and yields of butadiene oligomers obtained during the cross-metathesis of SB-1 with *d*-limonene.

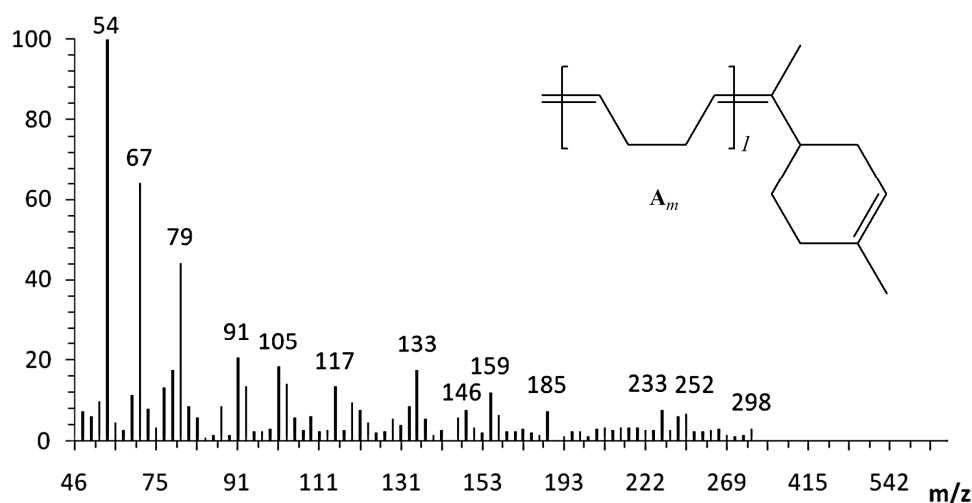


Figure 3. The mass spectrum of the A_m product with $m = 1$ ($C_{14}H_{22}$, $m/z = 190$, 43%).

using the first (I) and second (II) generation Ru-alkylidene catalysts revealed that the highly substituted metal-cyclobutane intermediate will show the elevated activation energy compared to unsubstituted or less substituted intermediates [24]. The cross-metathesis degradation of copolymers is accompanied by the intramolecular cyclization reactions of butadiene units to form the cyclic trimers *trans,trans,trans*-1,5,9-cyclododecatriene as the most thermodynamically favored among the all cyclic and linear products [27,28] (Scheme 2).

4. CONCLUSION

The cross-metathesis degradation of polybutadiene in block copolymers in the presence citrus oils and *d*-limonene as chain transfer agents (CTAs) using I and II catalysts was described. Catalysts I and II showed high efficiency in the cross-metathesis SB-1 and SB-2 copolymers providing the formation of limonene terminated butadiene oligomers with the low molecular weight values around $M_n = 276 - 335 \text{ g}\cdot\text{mol}^{-1}$ and yielded ranging from 91% - 95%. The cross-metathesis degradation

of copolymers using organic solvents and citrus oils proceeded with similar efficiency and resulted in the same molecular weight butadiene oligomers. The limonene-terminated butadiene oligomers of the series A_m with $m = 1$ unit were the major product (43%) in the degradation of SB-1.

5. ACKNOWLEDGEMENTS

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