

The polymerization of carvacrol catalyzed by Mn-porphyrins: obtaining the desired product guided by the choice of solvent, oxidant and catalyst

Patrícia Salvador Tessaro,^[a] Alexandre Moreira Meireles,^[a] Adriano Silva Guimarães,^[a]
Bernardo Schmitberger,^[a] Ana Luísa Almeida Lage,^[a] Patrícia Santiago de Oliveira Patrício,^[b]
Dayse Carvalho da Silva Martins,^[a] and Gilson DeFreitas-Silva^{[a]*}

[a] P. S. Tessaro, A. M. Meireles, A. S. Guimarães, B. Schmitberger, A. L. A. Lage, D. C. S. Martins and G. DeFreitas-Silva

Departamento de Química – Instituto de Ciências Exatas – Universidade Federal de Minas Gerais

Belo Horizonte - MG, 31.270–901, Brazil

E-mail: gilsonufmg@ufmg.br

[b] P. S. O. Patrício

Departamento de Química – Centro Federal de Educação Tecnológica de Minas Gerais

Belo Horizonte – MG, 30.421-169, Brazil

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1.0. Mass balance for carvacrol oxidation reactions

By the data obtained in the oxidation of carvacrol in the control systems or the catalyst/oxidation systems, the oxidation reactions lead to high conversion values with low yields for the products.

Minority products (thymoquinone or other oxidation products) were formed representing a small part of the initial substrate area. To carry out the mass balance, it was considered that the polymerization and/or oligomerization reaction is taking place, forming chemical species with high molar mass, here they are referred to as products not detectable (PND) by gas chromatography. These species were quantified by comparing the chromatographic peak areas of products to the consumed substrate:

$$A_{\text{PND}} = A_0 - \sum A_{\text{rp}}$$

A_0 = Initial substrate area

$\sum A_{\text{rp}}$ = Sum of reaction product areas including minority products.

2.0. Time dependence of carvacrol conversion in the PhIO/Cat1 system in dimethyl carbonate as solvent

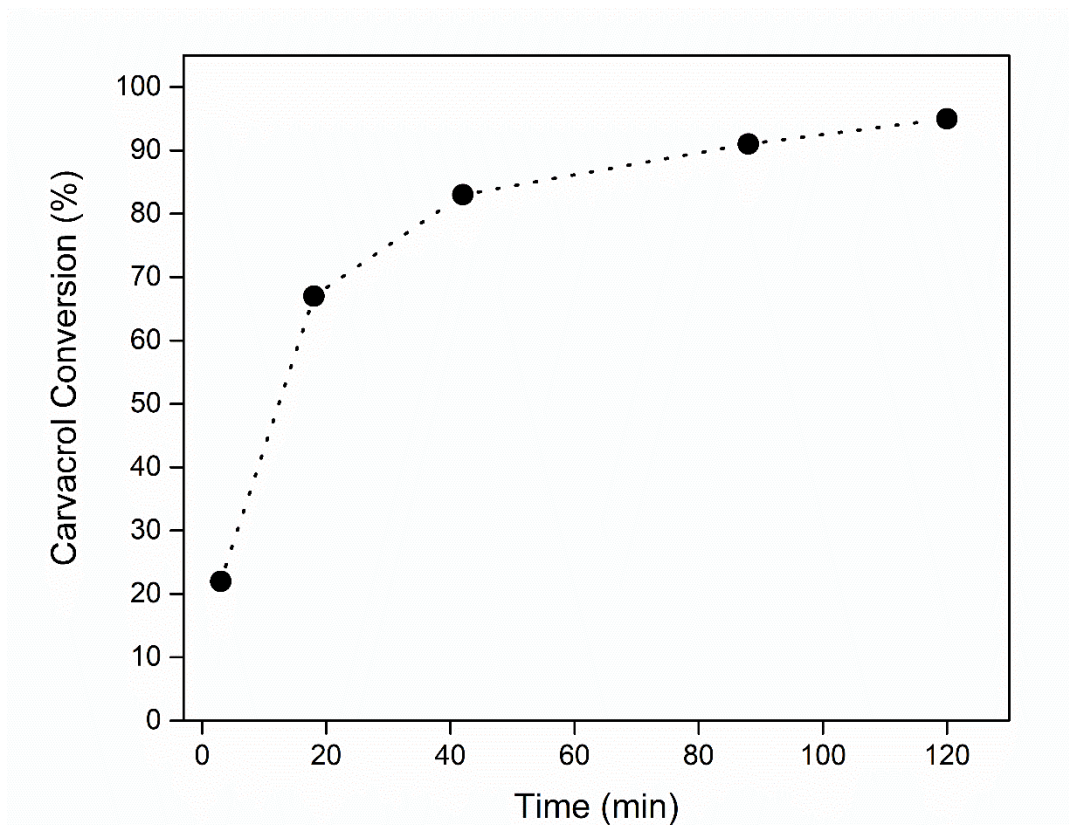


Figure S1. Follow-up of carvacrol oxidation by PhIO catalyzed by (Cat1) in dimethyl carbonate.

Cat1 = 2.0×10^{-6} mol; PhIO = Carvacrol = 2.0×10^{-5} mol; 25 °C; magnetic stirring.

3.0. UV-Vis monitoring of carvacrol oxidation reaction by Cat2/PhIO system in dichloromethane

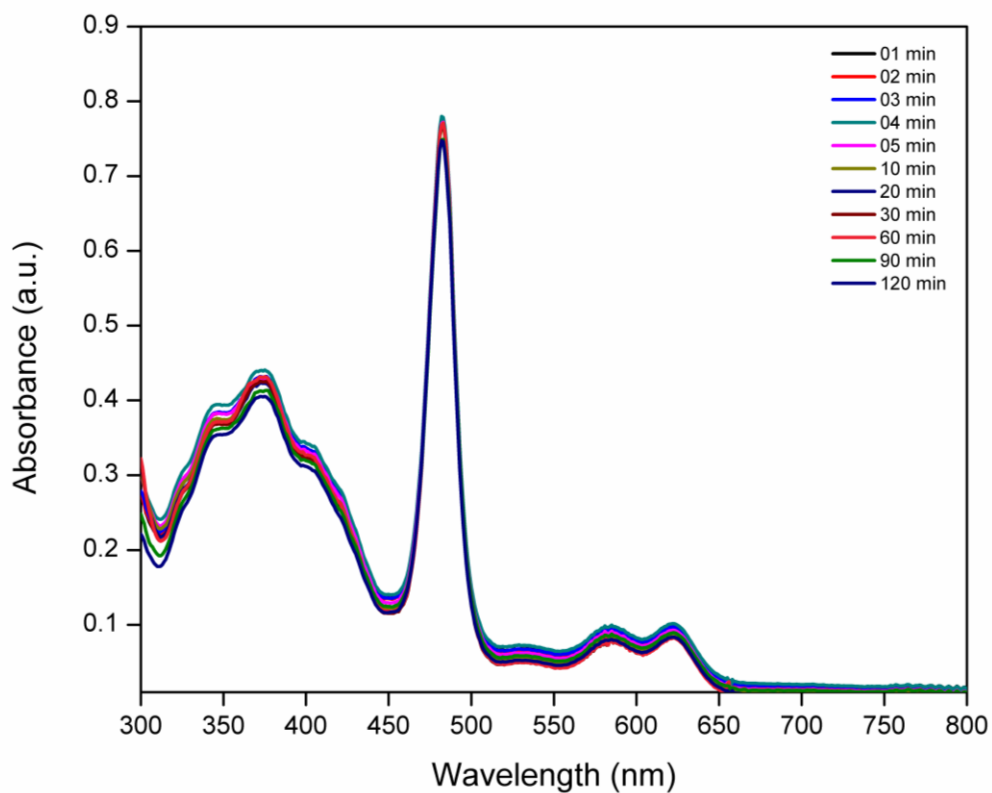


Figure S2. Evolution of the UV–Vis absorption spectrum of the carvacrol oxidation catalyzed by **Cat2** in the presence of PhIO and dichloromethane.

4.0. Mass spectrometry analysis of the Cat1/PhI(OAc)₂/BHT/Carvacrol system

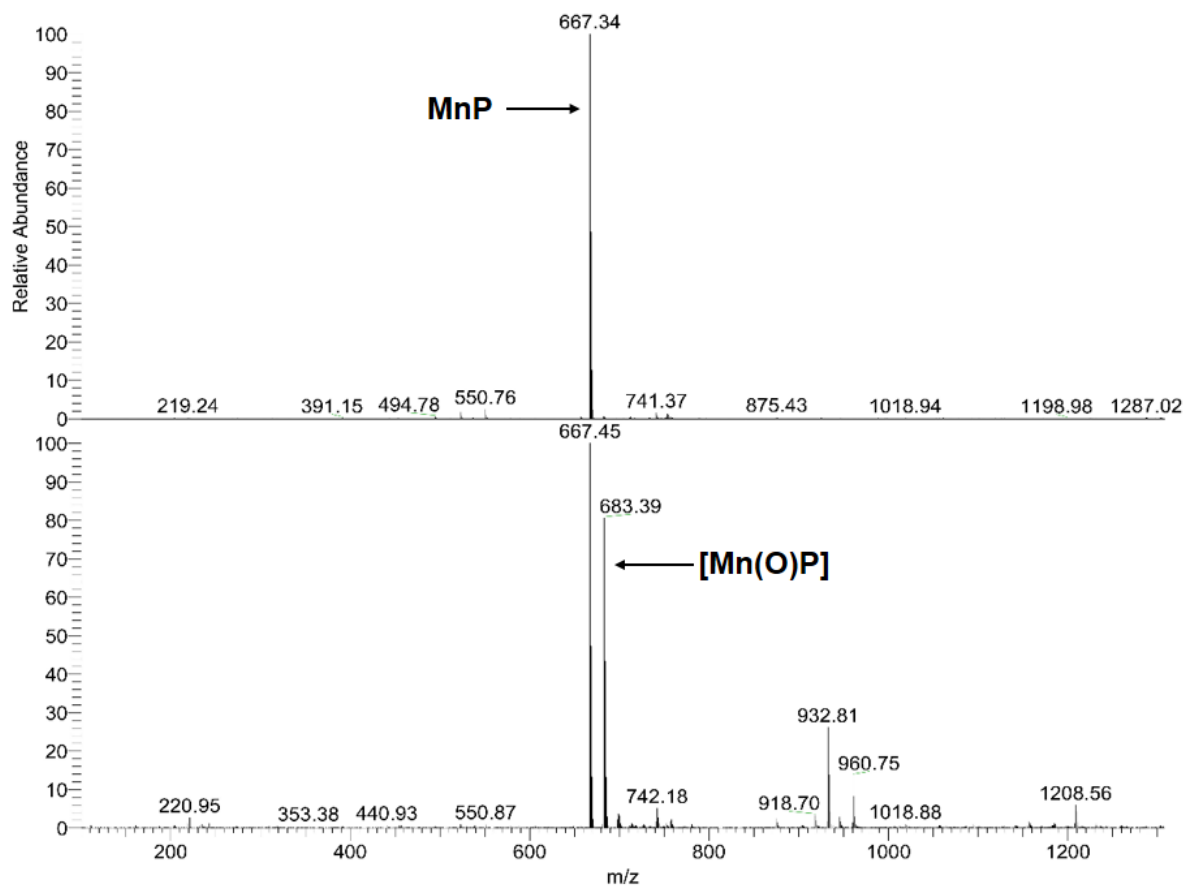


Figure S3. Mass spectrometry analysis of the (a) **Cat1** ($m/z = 667.34$; $[\text{Mn}^{\text{III}}(\text{TPP})]^+$) and (b) Cat1/PhI(OAc)₂/BHT/Carvacrol system ($m/z = 667.45$ $[\text{Mn}^{\text{III}}(\text{TPP})]^+$; and $m/z = 683.39$ $[\text{Mn}^{\text{V}}(\text{O})\text{P}]^+$).

5.0. Carvacrol oxidation reactions in the presence of mannitol and sodium azide (NaN₃) as radical scavengers^a

Table S1. Carvacrol oxidation reactions by PhI(OAc)₂ and PhIO in the presence of mannitol or NaN₃ as radical scavengers, in dichloromethane.

Entry	System	Carvacrol conversion (%) ^b	Entry	System	Carvacrol conversion (%) ^b
1	PhI(OAc) ₂ /Mannitol ^c	98	9	PhIO/Mannitol ^c	100
2	PhI(OAc) ₂ / Cat1 /Mannitol	100	10	PhIO/ Cat1 /Mannitol	100
3	PhI(OAc) ₂ / Cat2 /Mannitol	99	11	PhIO/ Cat2 /Mannitol	100
4	PhI(OAc) ₂ /MnCl ₂ /Mannitol	99	12	PhIO/MnCl ₂ /Mannitol	100
5	PhI(OAc) ₂ /NaN ₃ ^c	100	13	PhIO/NaN ₃ ^c	100
6	PhI(OAc) ₂ / Cat1 / NaN ₃	100	14	PhIO/ Cat1 /NaN ₃	100
7	PhI(OAc) ₂ / Cat2 / NaN ₃	100	15	PhIO/ Cat2 /NaN ₃	100
8	PhI(OAc) ₂ /MnCl ₂ / NaN ₃	98	16	PhIO/MnCl ₂ /NaN ₃	100

^a Conditions: **Cat1** or **Cat2** or MnCl₂ = 2 × 10⁻⁶ mol, PhIO or PhI(OAc)₂ = Carvacrol = radical scavenger = 2 × 10⁻⁵ mol; 25 °C; magnetic stirring; 120 minutes.

^b Substrate-based values.

^c Reactions were carried out in the absence of the catalyst.

6.0. Table S2. Oxidation of carvacrol using non-porphyrin compounds as catalysts.

Experiment	Catalyst	[catalyst] / mM	[carvacrol] / mM	Oxidant ([oxidant] / mM)	Solvent	Temp. (°C)	Time (h)	Carvacrol conversion (%)	Thymoquinone yield (%)	Other products	Reference
1 ^a	Fe(III) phthalocyanine	0.005	-	KHSO ₅ (0.15)	ACN	25	1	94	63.3	Non indicated	Milos (2001)[1]
2 ^{a,b}	Fe(III) phthalocyanine	0.005	-	KHSO ₅ (0.15)	ACN	25	1	96	65.1	Non indicated	Milos (2001)[1]
3 ^a	Fe(III) phthalocyanine	0.005	-	H ₂ O ₂ (0.15)	ACN	25	3	36	19.1	Non indicated	Milos (2001)[1]
4 ^{a,b}	Fe(III) phthalocyanine	0.005	-	H ₂ O ₂ (0.15)	ACN	25	3	39	23.6	Non indicated	Milos (2001)[1]
5	Keggin-type tungstoborates ^{c1}	0.012	3	H ₂ O ₂ (9.8)	ACN	~ 82 ^d	4	~ 35	< 5	Benzoquinones as main products	Santos (2003)[2]
6	Keggin-type tungstoborates ^{c2}	0.012	3	H ₂ O ₂ (9.8)	ACN	~ 82 ^d	4	Similar to experiment 5	Similar to experiment 5	Similar to experiment 5	Santos (2003)[2]
7	Cr(salpn)-NaY	-	29	H ₂ O ₂ (29)	ACN	60	5	14.2	13.0	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
8	Cr(salpn)-NaY	-	29	H ₂ O ₂ (87)	ACN	60	5	23.5	17.6	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
9	Fe(salpn)-NaY	-	29	H ₂ O ₂ (29)	ACN	60	5	12.7	11.6	Thymoquinones, thymohydroquinone,	Günes (2006)[3]

										and other benzoquinones	
10	Fe(salpn)-NaY	-	29	H ₂ O ₂ (87)	ACN	60	5	27.6	22.0	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
11	Zn(salpn)-NaY	-	29	H ₂ O ₂ (29)	ACN	60	5	11.0	11.0	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
12	Zn(salpn)-NaY	-	29	H ₂ O ₂ (87)	ACN	60	5	6.7	6.7	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
13	Ni(salpn)-NaY	-	29	H ₂ O ₂ (29)	ACN	60	5	7.9	7.9	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
14	Ni(salpn)-NaY	-	29	H ₂ O ₂ (87)	ACN	60	5	5.9	5.9	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
15	Bi(salpn)-NaY	-	29	H ₂ O ₂ (29)	ACN	60	5	3.2	3.2	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
16	Bi(salpn)-NaY	-	29	H ₂ O ₂ (87)	ACN	60	5	4.9	4.9	Thymoquinones, thymohydroquinone, and other benzoquinones	Günes (2006)[3]
17	Fe(III) phthalocyanine	1.0	0.3	KHSO ₅ (1.2)	Methanol:Water (8:1 v/v)	RT ^e	0.5	100	19.7	Poly(5-isopropyl-2-methyl-1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]

18	Fe(III) phthalocyanine	1.0	0.3	KHSO ₅ (0.9)	Methanol:Water (8:1 v/v)	RT ^e	0.5	99.6	26.3	Poly(5- isopropyl-2-methyl- 1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]
19	Fe(III) phthalocyanine	1.0	0.3	KHSO ₅ (0.6)	Methanol:Water (8:1 v/v)	RT ^e	0.5	99.0	31.3	Poly(5- isopropyl-2-methyl- 1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]
20	Fe(III) phthalocyanine	1.0	0.3	KHSO ₅ (0.45)	Methanol:Water (8:1 v/v)	RT ^e	0.5	94.3	24.3	Poly(5- isopropyl-2-methyl- 1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]
21	Fe(III) phthalocyanine	1.0	0.3	KHSO ₅ (0.3)	Methanol:Water (8:1 v/v)	RT ^e	0.5	82.0	12.7	Poly(5- isopropyl-2-methyl- 1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]
22	Fe(III) phthalocyanine	0.5	0.3	KHSO ₅ (0.6)	Methanol:Water (8:1 v/v)	RT ^e	0.5	96.0	32.3	Poly(5- isopropyl-2-methyl- 1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]
23	Fe(III) phthalocyanine	1.0	0.15	KHSO ₅ (0.6)	Methanol:Water (8:1 v/v)	RT ^e	0.5	98.9	30	Poly(5- isopropyl-2-methyl- 1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]
24	Fe(III) phthalocyanine	1.0	0.45	KHSO ₅ (0.6)	Methanol:Water (8:1 v/v)	RT ^e	0.5	92.4	21.3	Poly(5- isopropyl-2-methyl- 1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]
25	Fe(III) phthalocyanine	1.0	0.6	KHSO ₅ (0.6)	Methanol:Water (8:1 v/v)	RT ^e	0.5	60.0	10.5	Poly(5- isopropyl-2-methyl- 1,3-phenylene oxide) (Polymer) and others	Günay (2016)[4]

^a Carvacrol was oxidated in an oregano essential oil. ^b Co-catalyst CH₃COONH₄ added.

^{c1} (TBA)₄H₂[Mn(H₂O)BW₁₁O₃₉]·H₂O, ^{c2} (HDTMA)₄H₂[Mn(H₂O)BW₁₁O₃₉]·10H₂O. ^d Reflux conditions. ^e Room temperature (RT).

7.0. Carvacrol's polymer characterization

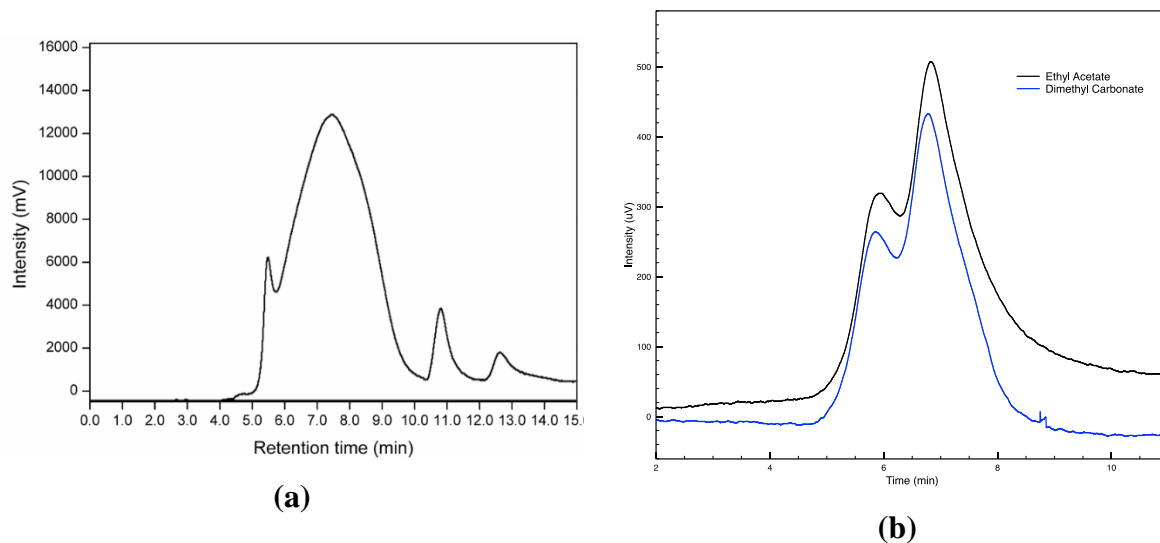


Figure S4. GPC chromatogram of the synthesized polymer. (a) Dichloromethane. (b) Ethyl acetate (black line) and dimethyl carbonate (blue line).

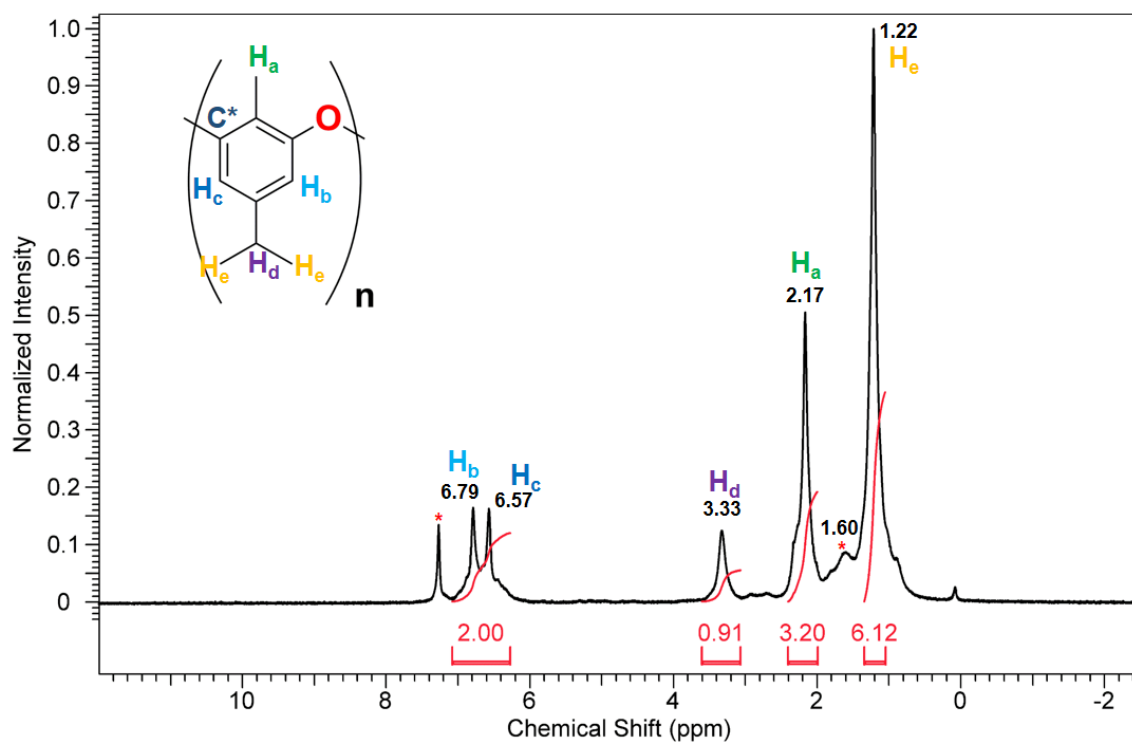


Figure S5. ^1H NMR spectrum of carvacrol's polymer in CDCl_3 (400 MHz, TMS) at 25 °C. The signals assigned with * are referent to the non-deuterated solvent and/or impurities of the solvent.

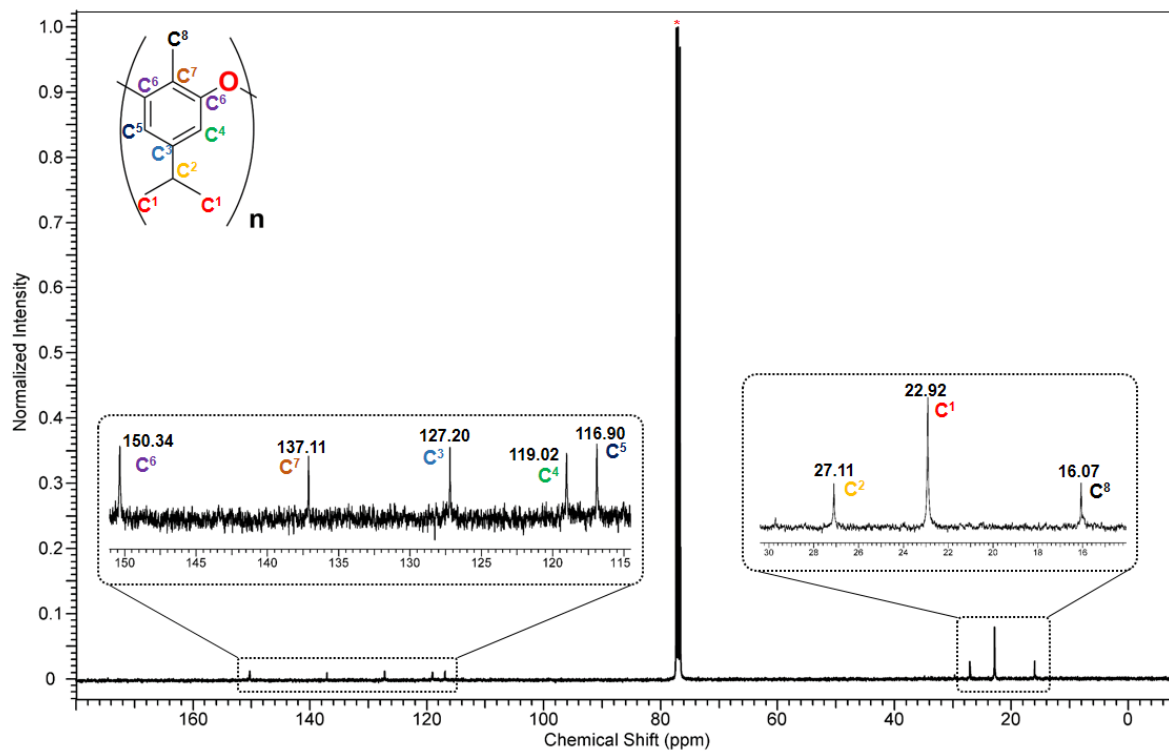


Figure S6. ^{13}C NMR spectrum of carvacrol's polymer in CDCl_3 (400 MHz, TMS) at 25 °C. The signals assigned with * are referent to the non-deuterated solvent.

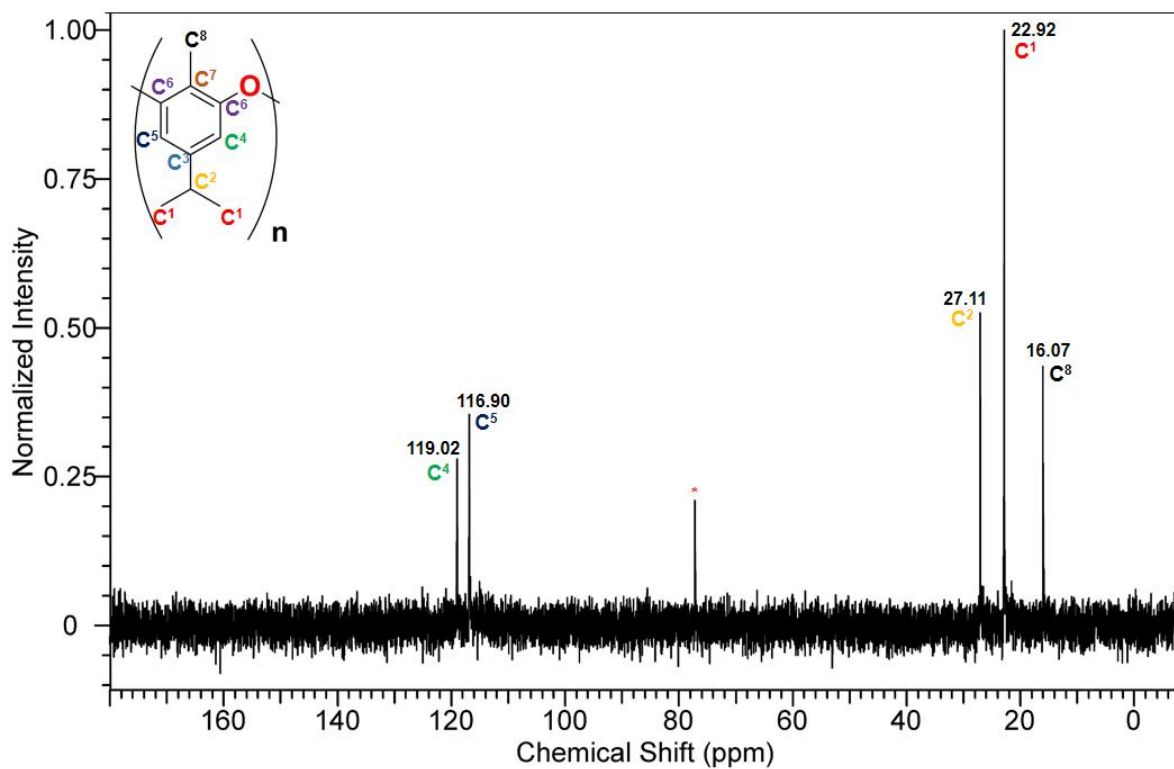


Figure S7. DEPT-135 spectrum of carvacrol's polymer in CDCl_3 (400 MHz, TMS) at 25 °C. The signals assigned with * are referent to the non-deuterated solvent.

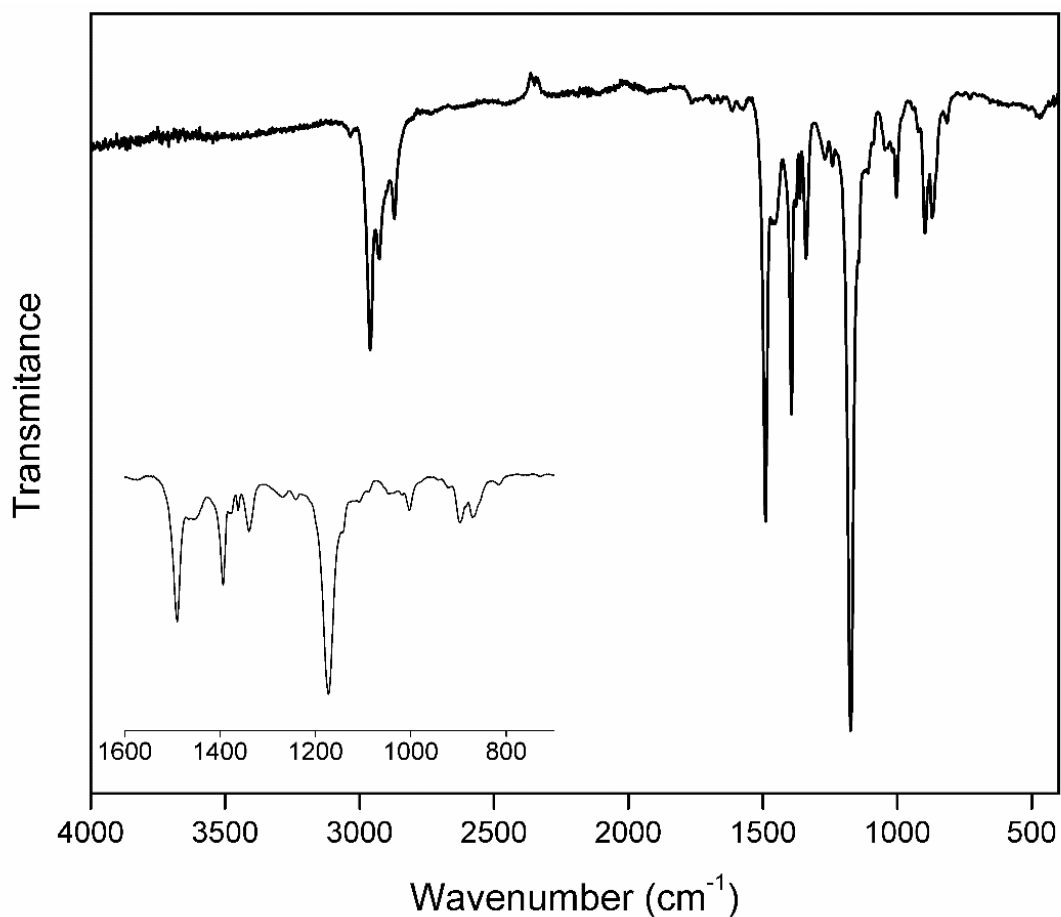


Figure S8. FTIR-ATR spectrum from carvacrol's polymer.

Table S3. Functional groups and vibration modes from polymer associated to bands by FTIR.

Wavenumber (cm ⁻¹)	Vibration Mode	Intensity
2964	ν C-H symmetric and asymmetric	medium
2924		
2871		
1602	ν C=C (aromatic ring)	weak
1573		weak
1487		strong
1388	δ C-H (isopropyl methyl group)	strong
1360		medium
1173	δ R ₂ C=CH ₂ (1:2:5-substitution)	strong
996		medium
896		strong
863	δ C-H bending	strong
810	δ C-H out-of-plane (aromatic ring)	weak

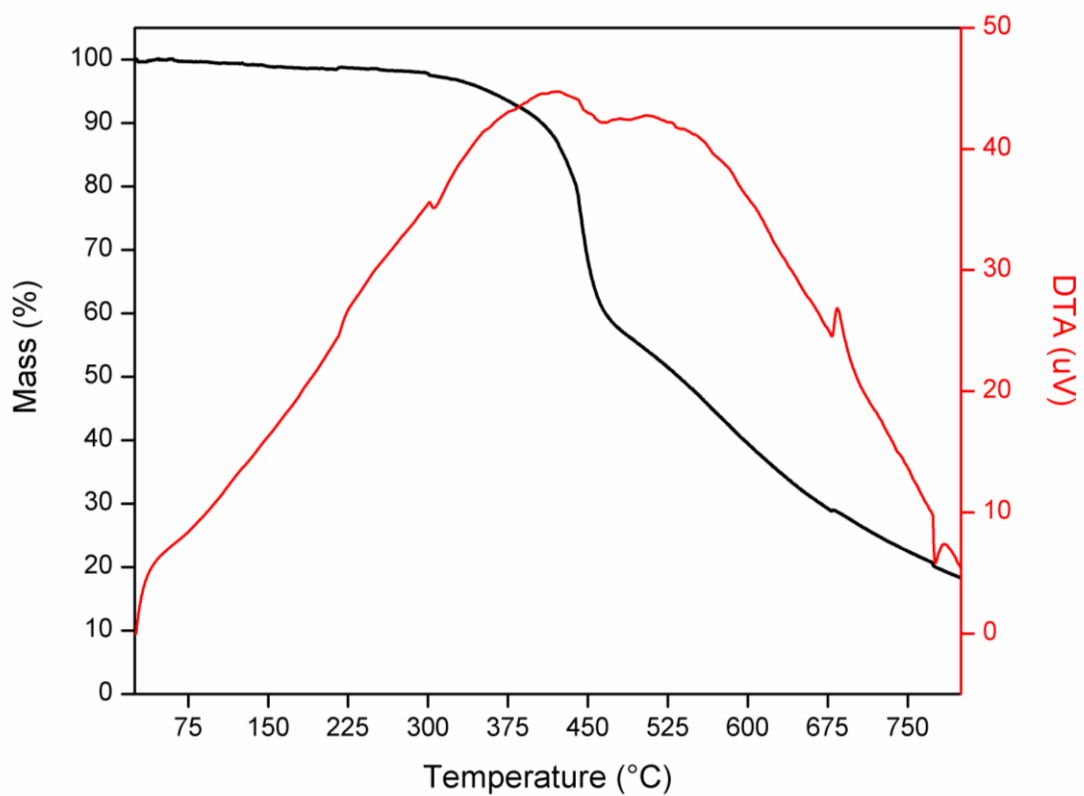


Figure S9. TG curve from carvacrol's polymer, under N₂ atmosphere at a heating rate of 10 °C min⁻¹.

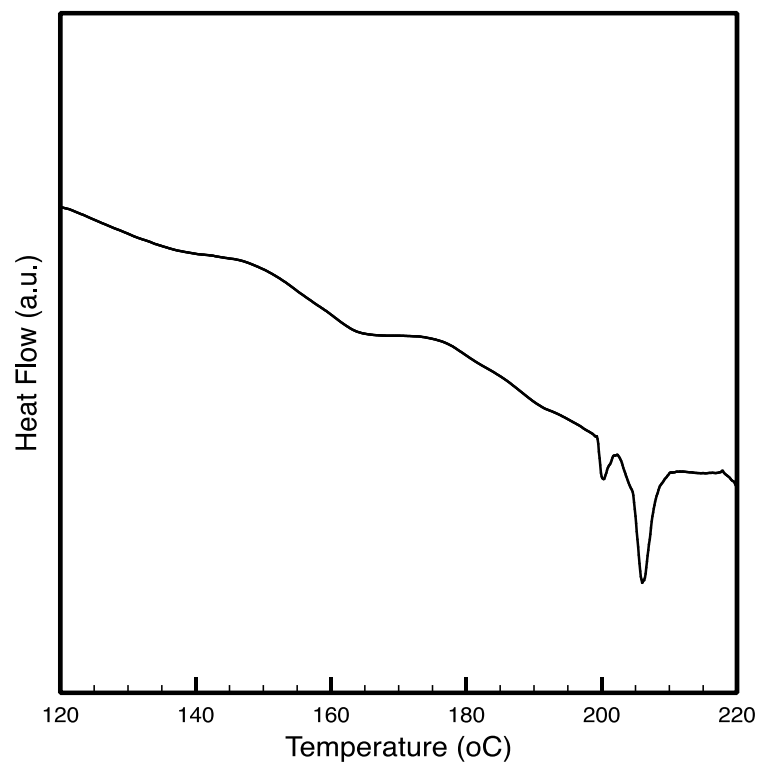


Figure S10. DSC curve (2nd run) from carvacrol's polymer.

8.0. References

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