

Supplementary Information for:  
Ring opening metathesis polymerizations in d-  
limonene: a renewable polymerization solvent  
and chain transfer agent for the synthesis of  
alkene macromonomers

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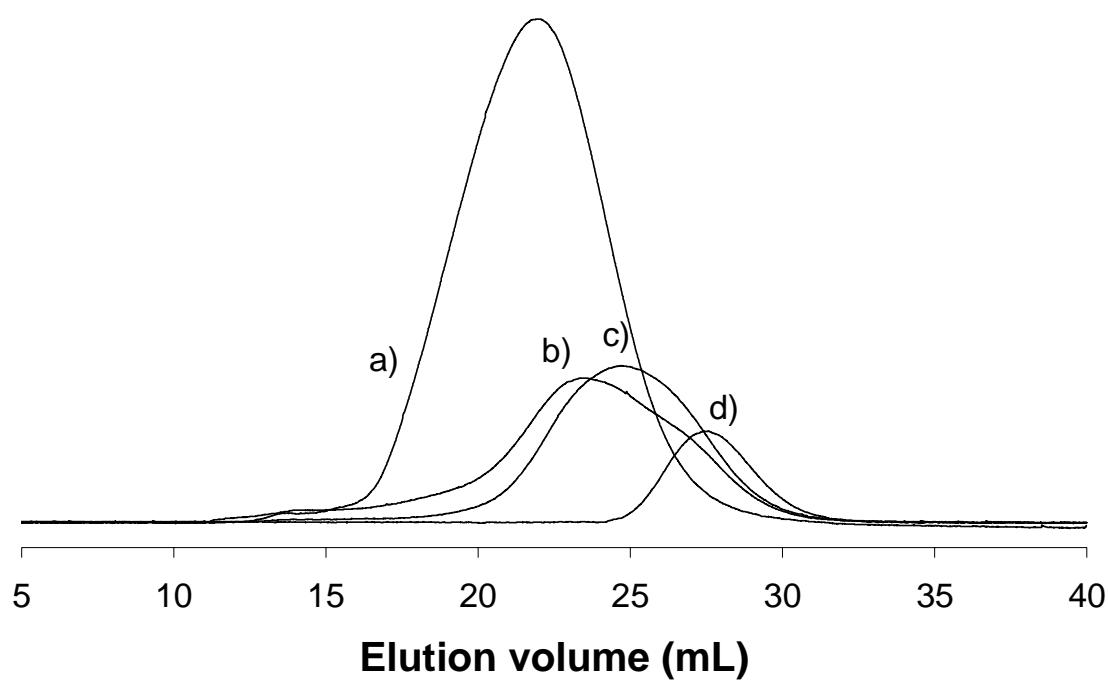
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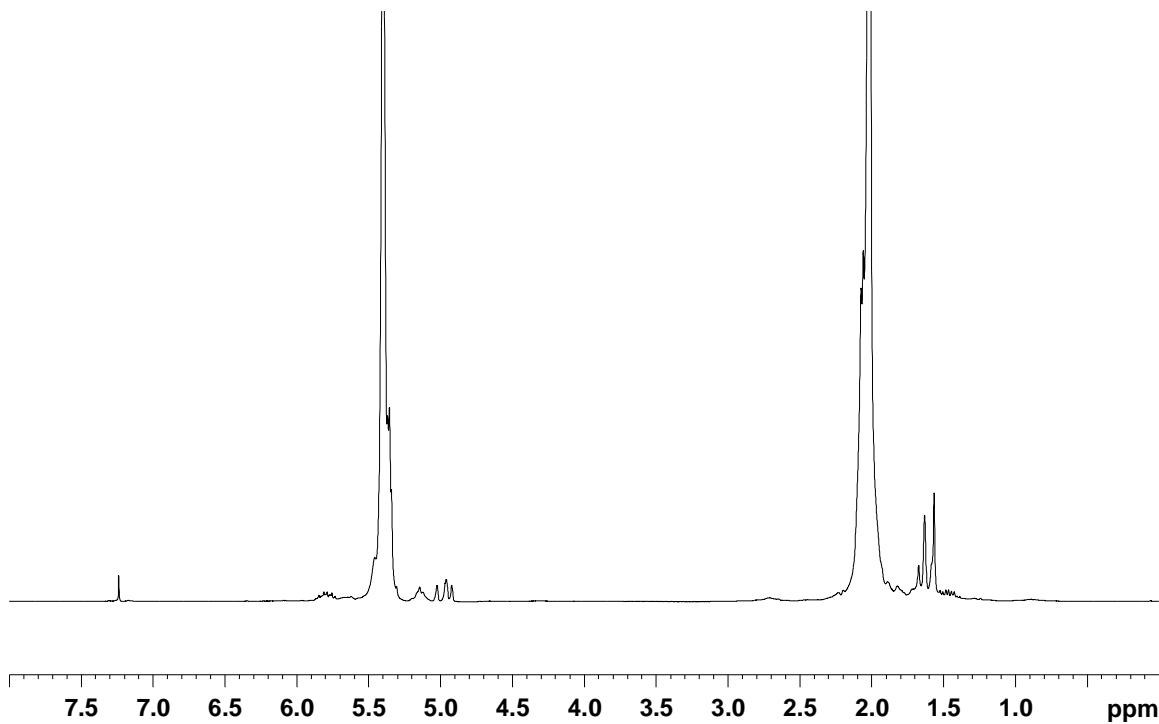
**Table S1.** GC/MS data for the products resulting from the oligomerization of 1,5-hexadiene (HD) in d-limonene.<sup>a</sup>

entry	[HD] (M)	CDT <sup>b</sup> (%)	<b>B<sub>3</sub></b> (%)	<b>A<sub>1</sub></b> (%)	<b>B<sub>4</sub></b> (%)	<b>A<sub>2</sub></b> (%)	<b>B<sub>5</sub></b> (%)	<b>A<sub>3</sub></b> (%)	<b>C<sub>1</sub></b> (%)	<b>B<sub>6</sub></b> (%)	<b>A<sub>4</sub></b> (%)	<b>C<sub>2</sub></b> (%)	<b>B<sub>7</sub></b> (%)	<b>A<sub>5</sub></b> (%)	<b>C<sub>3</sub></b> (%)
Retention time (min)	6.1	6.9	7.6	11.1	11.7	13.9	14.5	14.9	16.1	16.6	17.1	18.0	18.6	19.2	
1	1.0	6.3	23.7	10.1	17.6	7.8	13.8	5.5	0.5	7.0	3.1	0.2	2.9	1.4	0.1
2	0.6	4.1	15.1	23.9	10.7	16.3	6.6	9.8	2.7	2.9	3.8	1.5	0.9	1.3	0.4
3	0.3	2.3	9.6	40.0	6.7	19.8	3.1	8.6	3.2	0.9	2.8	1.8	0.1	0.5	0.6
4	0.2	1.7	5.2	41.9	3.4	21.9	2.0	8.9	8.6	0.6	2.6	3.2	- <sup>d</sup>	- <sup>d</sup>	- <sup>d</sup>
5 <sup>c</sup>	0.2	1.1	20.9	45.9	8.2	14.7	2.2	4.0	1.3	0.5	0.9	0.3	- <sup>d</sup>	- <sup>d</sup>	- <sup>d</sup>

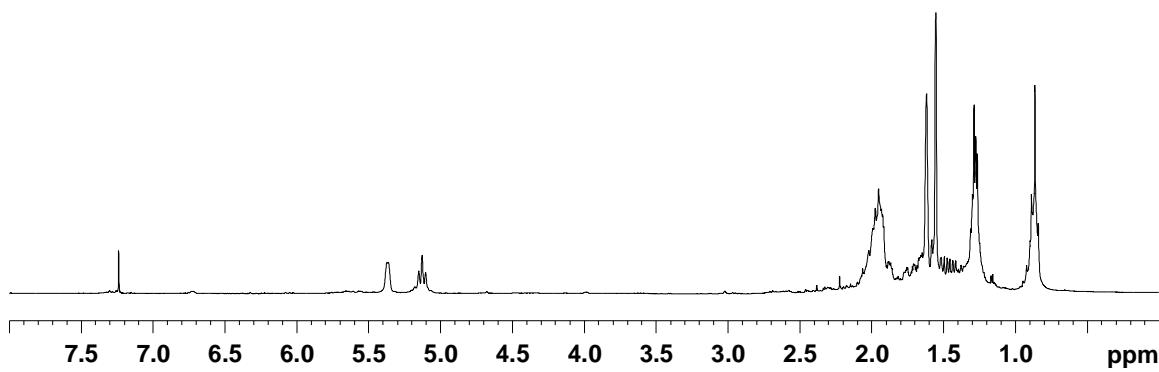
<sup>a</sup>All reactions were run at 45° C for 24 h with 1,5-hexadiene (3.0 mmol), d-limonene and 1 mol % of (1,3-dimesitylimidazolidine-2-ylidene)(tricyclohexylphosphine)benzylidene ruthenium dichloride unless otherwise noted. <sup>b</sup>CDT = cyclododecatriene. <sup>c</sup>Reaction time was 3 h. <sup>d</sup>Not detected.



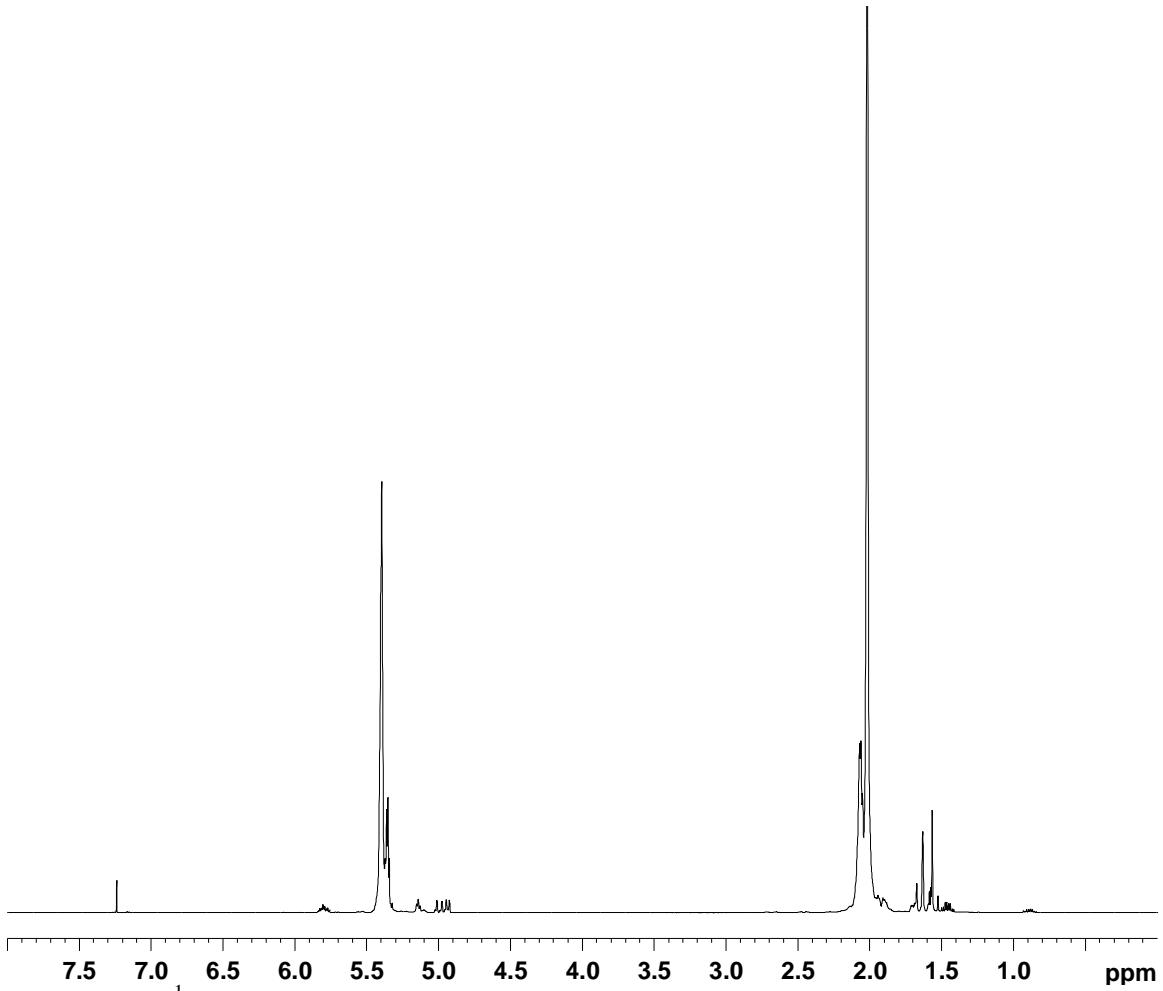
**Figure S1.** Size exclusion chromatography data (90° lighting scattering detector) for the ring opening metathesis polymerization of 1,5-cyclooctadiene (1.3 M) in d-limonene at 23°C for a) 1 h, b) 3 h, c) 6 h and d) 20 h.



**Figure S2.** <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 300 MHz) spectrum for product resulting from the ring opening metathesis polymerization of 1,5-cyclooctadiene (1.3 M) in d-limonene at ambient temperature after 20 h.



**Figure S3.** <sup>1</sup>H NMR ( $\text{CDCl}_3$ , 300 MHz) spectrum for product resulting from the cross metathesis of d-limonene and 1-hexene. The reaction was catalyzed with 2 mol % of (1,3-dimesitylimidazolidine-2-ylidene)(tricyclohexylphosphine)benzylidene ruthenium dichloride

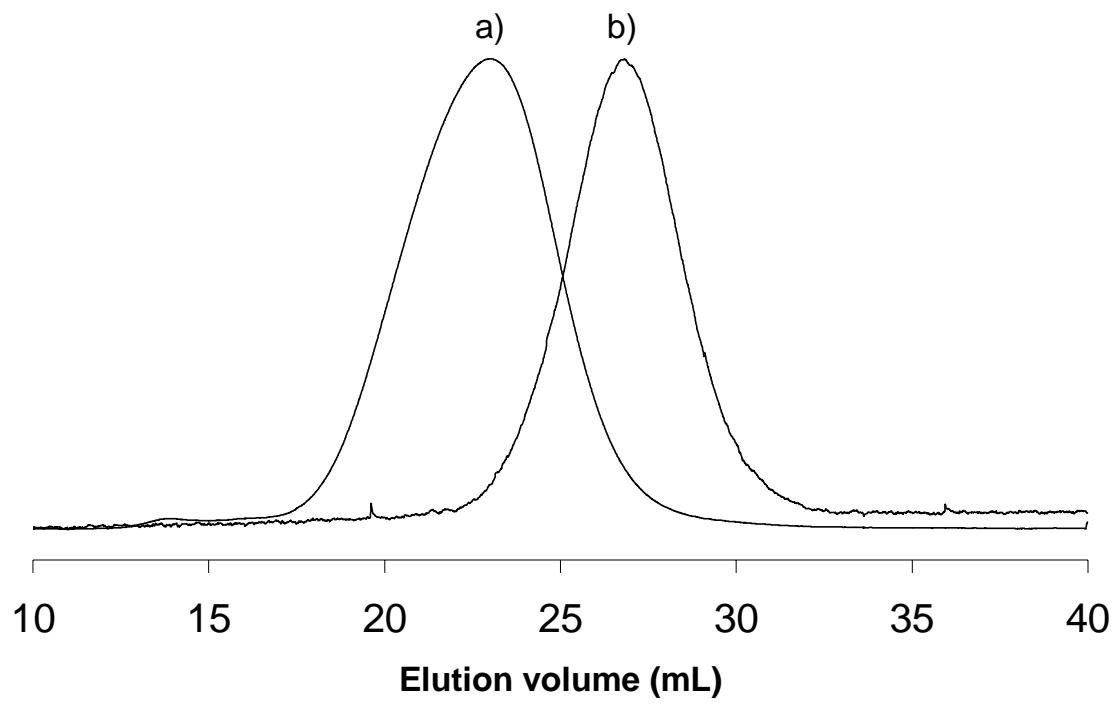


**Figure S4.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz) spectrum for product resulting from the ring opening metathesis polymerization of 1,5-cyclooctadiene (1.3 M) in d-limonene at  $70^\circ\text{C}$  after 1 h.

**Table S2.** Effect of time and temperature on the ring opening metathesis polymerization of 1,5-cyclooctadiene (1.3 M).<sup>a</sup>

Entry	Solvent	Temp (° C)	Time (h)	Yield (%)	M <sub>w</sub> (g/mol)	M <sub>w</sub> /M <sub>n</sub>
1	toluene	23	1	51	57900	2.64
2	d-limonene	23	1	83	11100	2.38
	hydrogenated					
3	d-limonene	23	1	66	56100	2.0
4	d-limonene	23	3	91	4920	1.65
5	d-limonene	23	6	84	3860	1.55
6	toluene	23	6	71	49900	2.94
7	d-limonene	23	20	76	1740	1.19
8	d-limonene	70	1	56	1120	1.05
9	d-limonene	70	3	37	970	1.09
10	d-limonene	70	6	37	910	1.09
11	d-limonene	70	20	20	870	1.05

<sup>a</sup>All polymerizations were run with 4.0 mmol monomer, 0.005 mmol (1,3-dimesitylimidazolidine-2-ylidene)(tricyclohexylphosphine)benzylidene ruthenium dichloride and 3.0 mL solvent.



**Figure S5.** SEC lighting scattering data ( $90^\circ$  detector) for the ring opening metathesis polymerization of 1,5-cyclooctadiene (1.3 M) at  $23^\circ\text{ C}$  for 3 h in a) hydrogenated d-limonene and b) d-limonene.