

## Electronic Supplementary Information

### **Aqueous cationic homo- and co-polymerizations of $\beta$ -myrcene and styrene: a green route toward terpene-based rubbery polymers**

Maksim I. Hulnik,<sup>a</sup> Irina V. Vasilenko,<sup>a</sup> Alexei V. Radchenko,<sup>b</sup> Frédéric Peruch,<sup>b</sup> Francois Ganachaud<sup>c</sup> and Sergei V. Kostjuk<sup>a,c,d,e,\*</sup>

<sup>a</sup> *Research Institute for Physical Chemical Problems of the Belarusian State University, 14 Leningradskaya st., 220006 Minsk, Belarus. E-mail: [kostjuks@bsu.by](mailto:kostjuks@bsu.by) or [kostjuks@rambler.ru](mailto:kostjuks@rambler.ru).*

<sup>b</sup> *Laboratoire de Chimie des Polymères Organiques, UMR 5629 CNRS/UB1/IPB University of Bordeaux, 16 avenue Pey Berland, 33607 Pessac Cedex, France.*

<sup>c</sup> *INSA-Lyon, IMP, CNRS, UMR5223, 20 Boulevard Einstein, F-69621 Villeurbanne, France.*

<sup>d</sup> *Sechenov First Moscow State Medical University, Institute for Regenerative Medicine, Moscow, 119991, Russia.*

<sup>e</sup> *Department of Chemistry, Belarusian State University, 14 Leningradskaya st., 220006 Minsk, Belarus*

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**Table S1.** Cationic polymerization of  $\beta$ -myrcene under different conditions<sup>a</sup>

Entry	T (°C)	Time (h)	Conv. (%)	$M_n$ (g mol <sup>-1</sup> )	$M_w/M_n$
1	40	19	95	164000	4.2
2 <sup>b</sup>	40	19	0	-	-
3	30	19	0	-	-

<sup>a</sup>  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ : 0.21 g;  $\text{H}_2\text{O}$ : 3.5g;  $\beta$ -myrcene : 1.5 mL; DBSNa: 0.78 g.

<sup>b</sup> Without  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ .

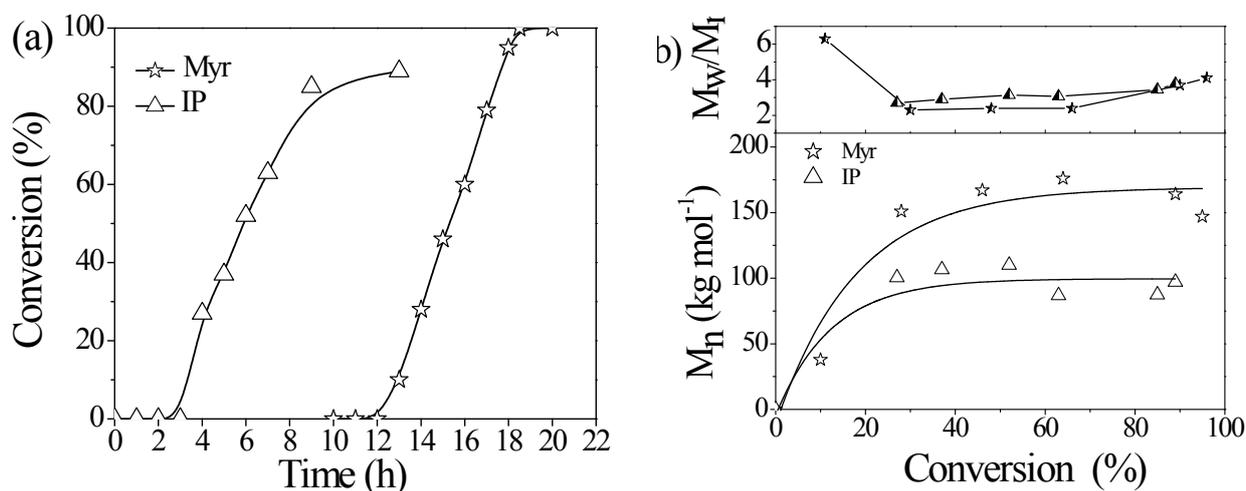
**Table S2.** Copolymer composition for copolymerization of  $\beta$ -myrcene with styrene at 40°C and at different monomer conversions <sup>a</sup>

Entry	Time (h)	Conv. (%)	Myr:St (mol%) <sup>b</sup>
1	12	28	82:18
2	12.5	74	79:21
3	13	99	75:25

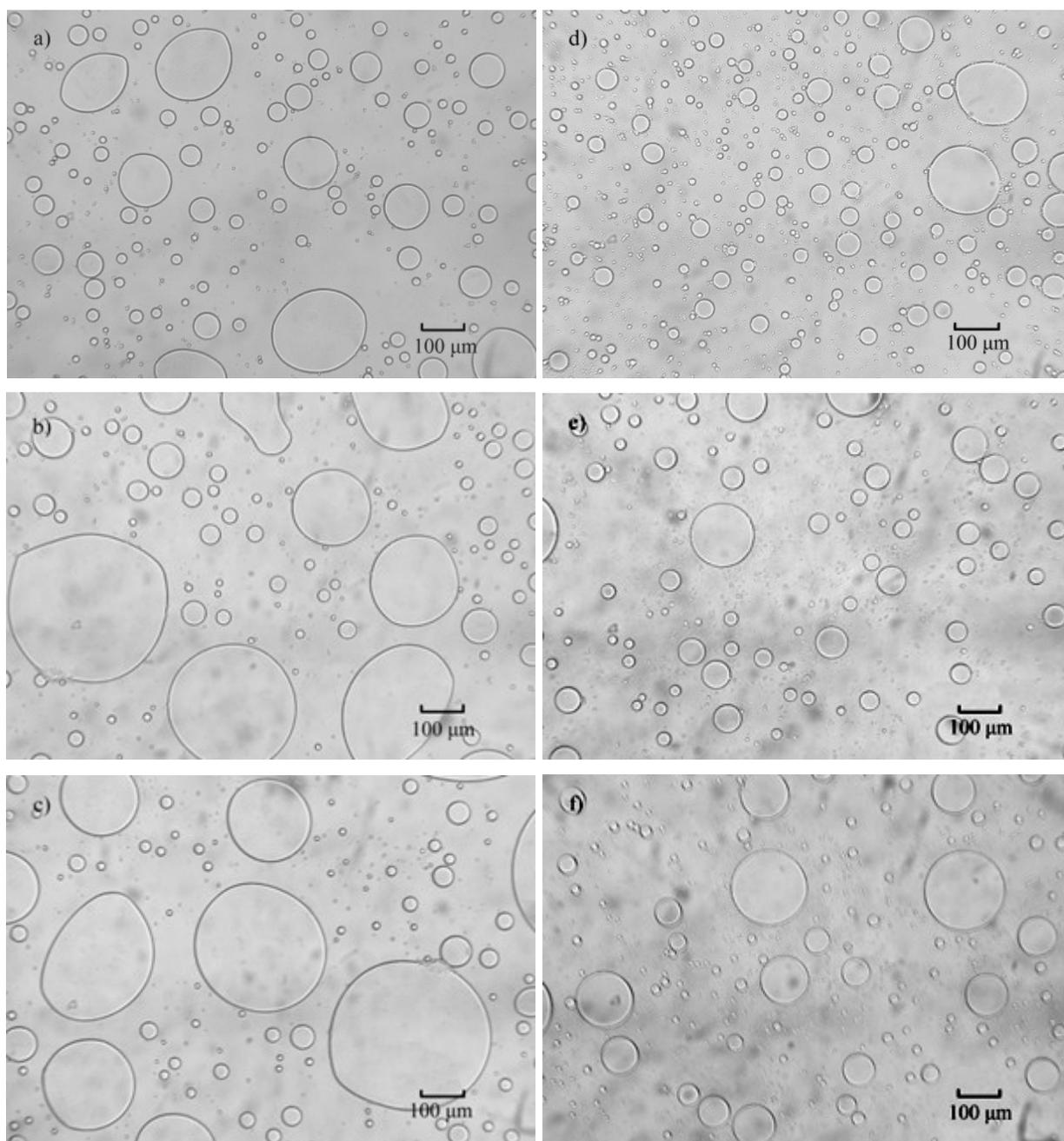
<sup>a</sup>  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ : 0.21 g;  $\text{H}_2\text{O}$ : 3.5g; monomers: 1.5 mL; DBSNa: 0.78 g;

Myr: St =50:50 (in comonomers feed).

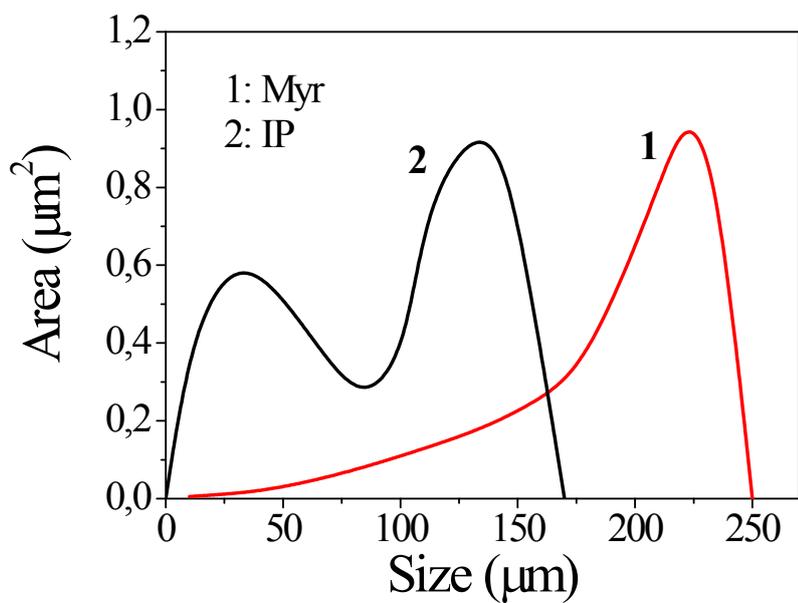
<sup>b</sup> In copolymer, determined by <sup>1</sup>H NMR spectroscopy.

**Fig. S1.** (a) Conversion vs. time and (b)  $M_n$ ,  $M_w/M_n$  vs. conversion plots for  $\beta$ -myrcene (Myr) and isoprene (IP)<sup>1</sup> polymerization at 40°C in the presence of LASC prepared from  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  and branched DBSNa:  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ : 0.21 g;  $\text{H}_2\text{O}$ : 3.5 g; monomer: 1.5 mL; DBSNa: 0.78 g.

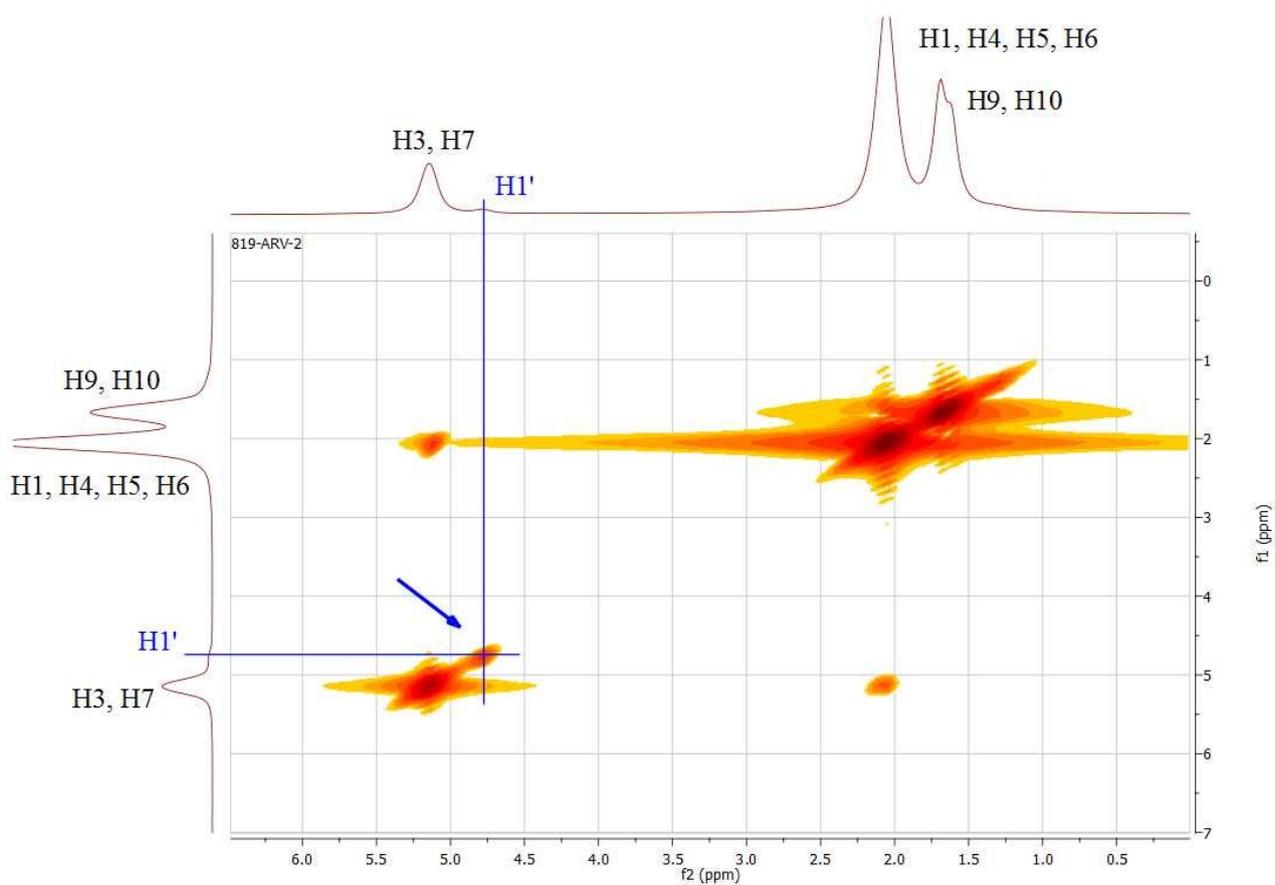
<sup>1</sup> I. V. Vasilenko, H. Y. Yeong, M. Delgado, S. Ouadad, F. Peruch, B. Voit, F. Ganachaud, and S. V. Kostjuk, *Angew. Chem., Int. Ed.* 2015, 54, 12728.



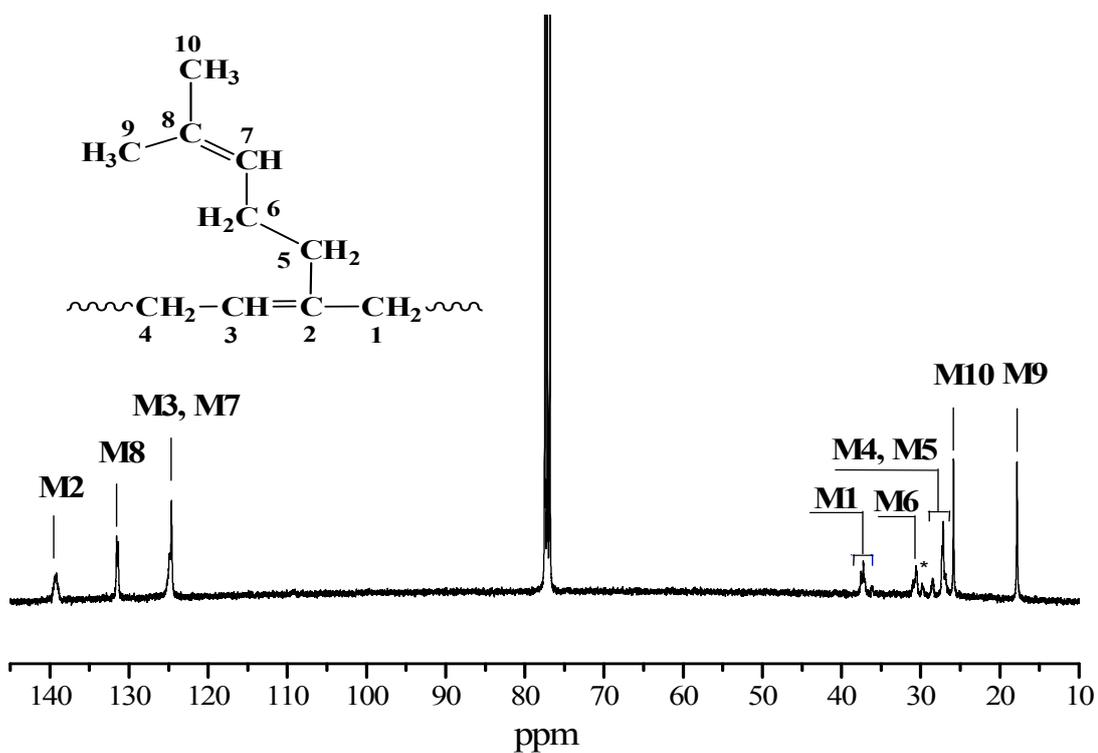
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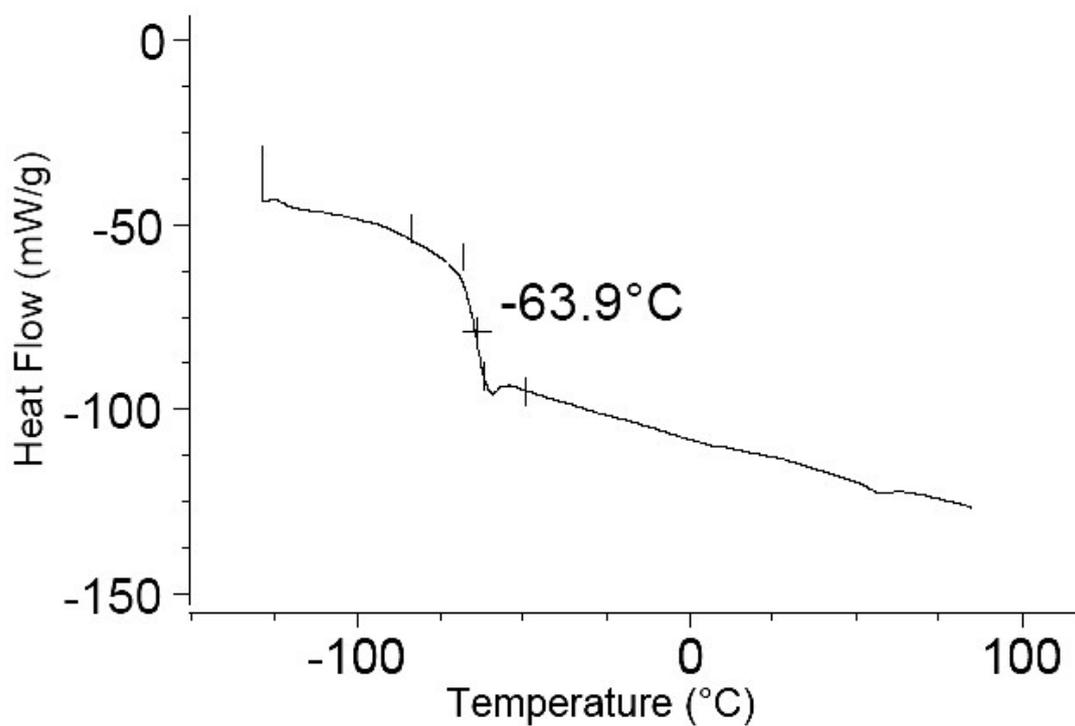
**Fig S3.** Size distribution of emulsion of  $\beta$ -myrcene or isoprene as determined by optical microscopy and image analyses (see main text for details).



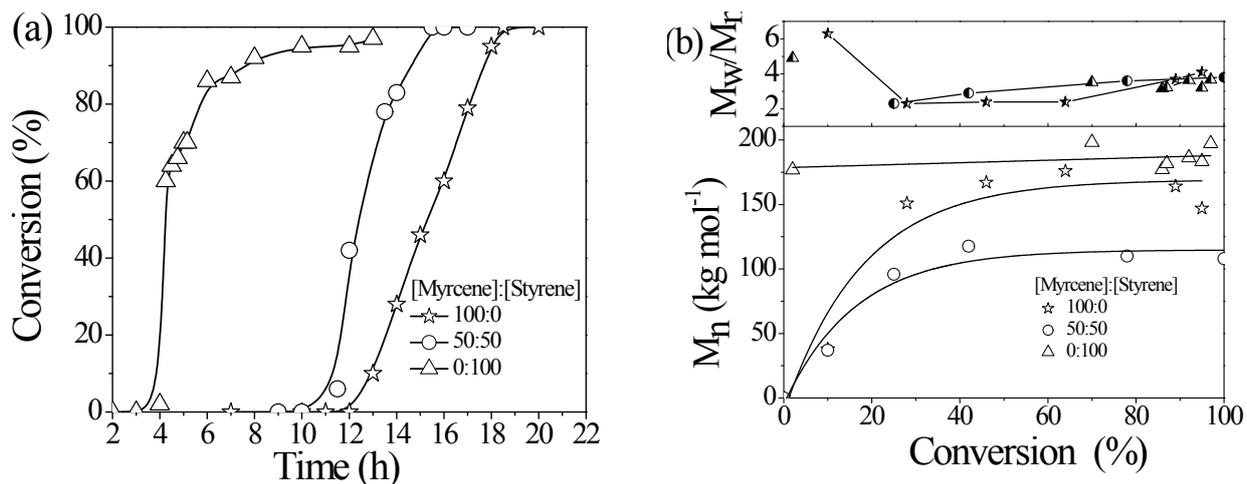
**Fig. S4.**  $^1\text{H}$  -  $^1\text{H}$  COSY 2D NMR spectrum of synthesized poly( $\beta$ -myrcene) ( $M_n=164,000 \text{ g mol}^{-1}$ ;  $M_w/M_n=2.7$ ).



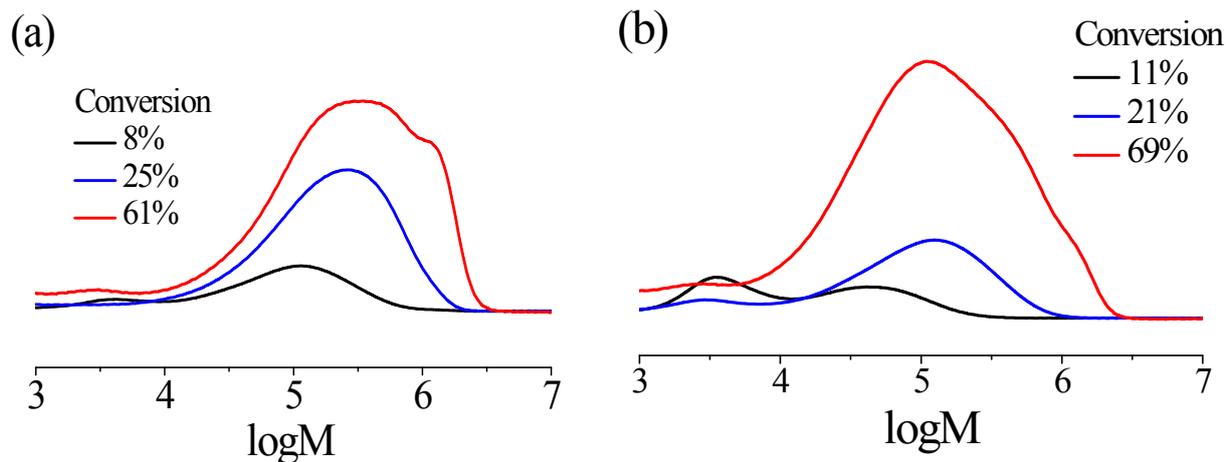
**Fig. S5.**  $^{13}\text{C}$  NMR spectrum of synthesized poly( $\beta$ -myrcene) ( $M_n=164,000 \text{ g mol}^{-1}$ ;  $M_w/M_n=2.7$ ).



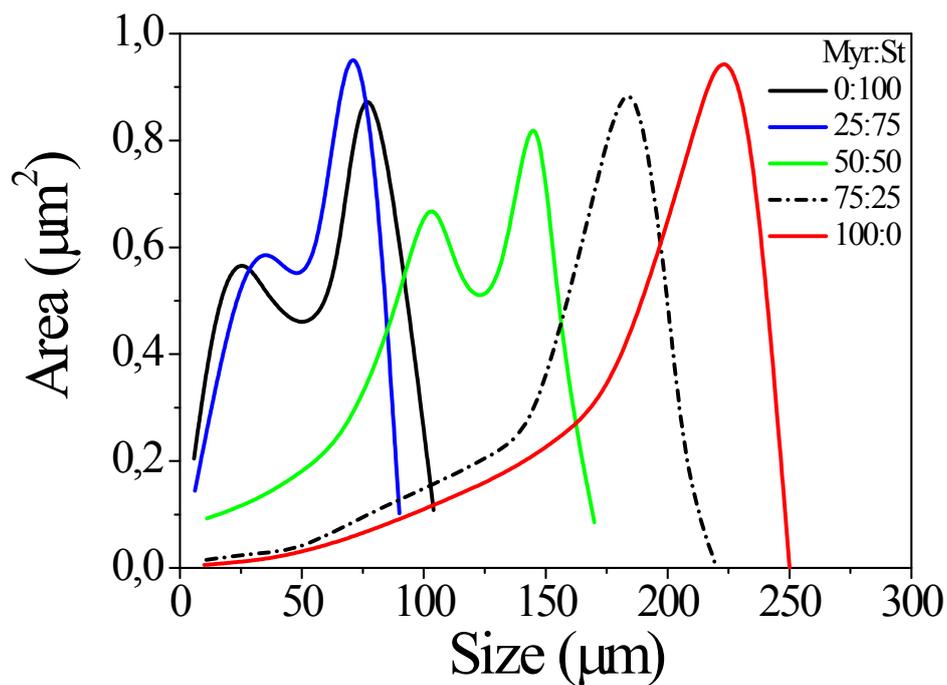
**Fig. S6.** DSC thermogram of poly( $\beta$ -myrcene) obtained via LASC mediated emulsion polymerization of  $\beta$ -myrcene (see Table 1 for details).



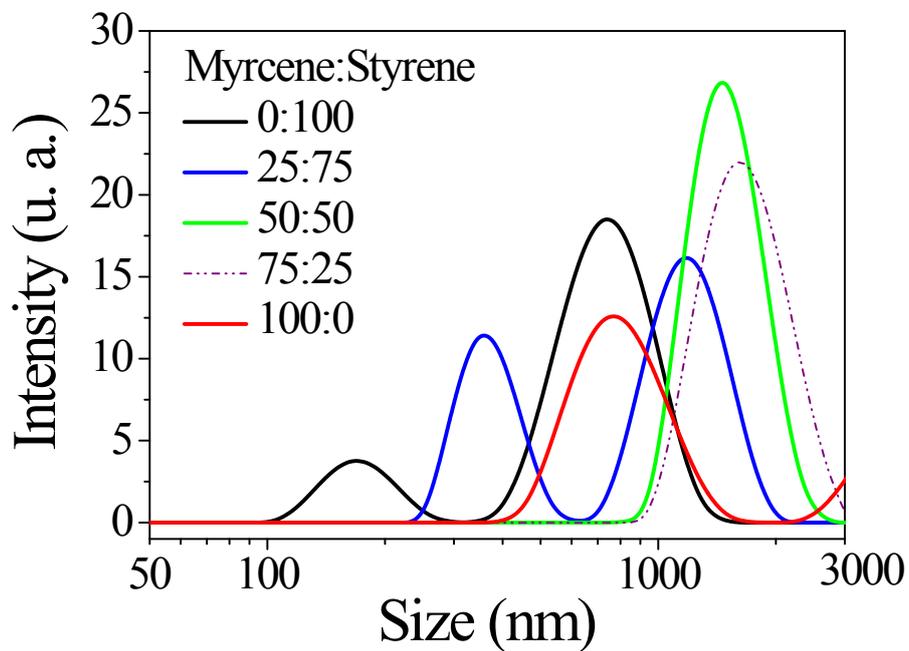
**Fig. S7.** (a) Conversion vs. time and (b)  $M_n$ ,  $M_w/M_n$  vs. conversion plots for homopolymerization of  $\beta$ -myrcene, styrene as well as copolymerization of  $\beta$ -myrcene and styrene (molar monomer content is 50 : 50) at 40°C in the presence of LASC prepared from  $\text{YbCl}_3 \times 6\text{H}_2\text{O}$  and branched DBSNa:  $\text{YbCl}_3 \times 6\text{H}_2\text{O}$ : 0.21 g;  $\text{H}_2\text{O}$ : 3.5g; monomer: 1.5 mL; DBSNa: 0.78 g.



**Fig. S8.** SEC traces of poly( $\beta$ -myrcene-co-styrene) at different (and normalized by) monomer conversions for copolymers synthesized at molar  $\beta$ -myrcene : styrene ratio of (a) 75 : 25 and (b) 25 : 75.

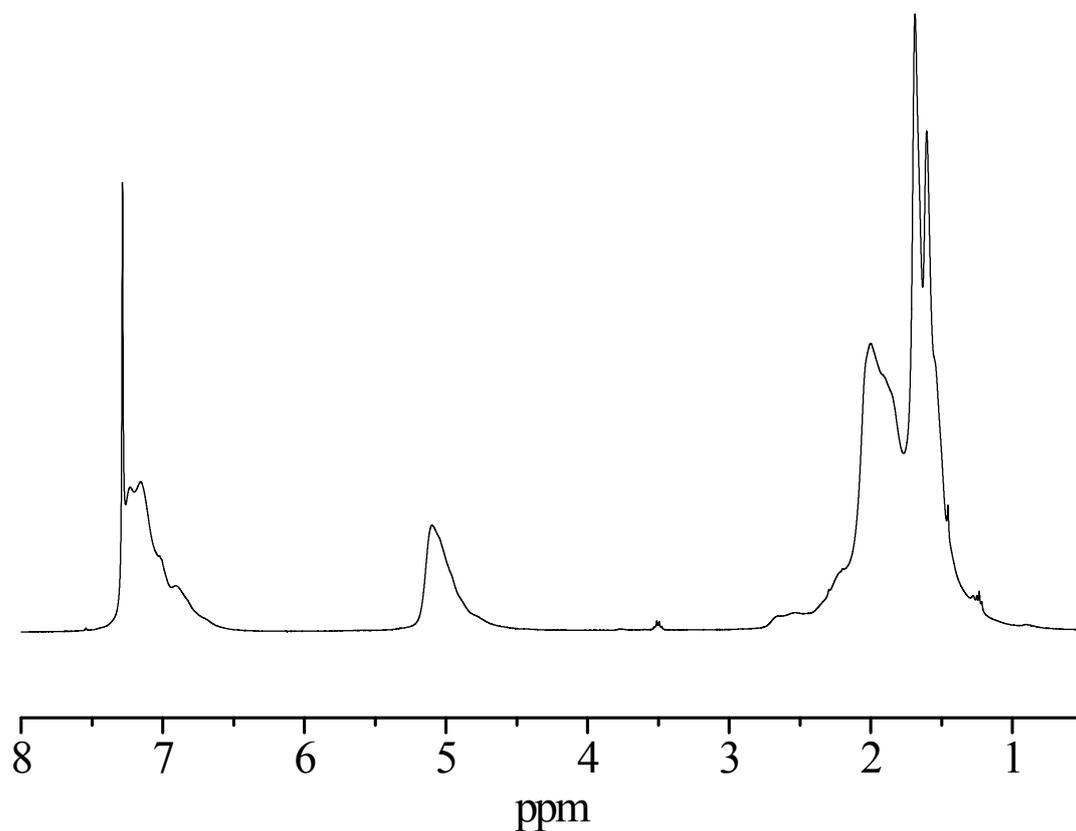


**Fig S9.** Size distribution of emulsions of  $\beta$ -myrcene/styrene mixtures as determined by optical microscopy and image analyses (see main text for details).

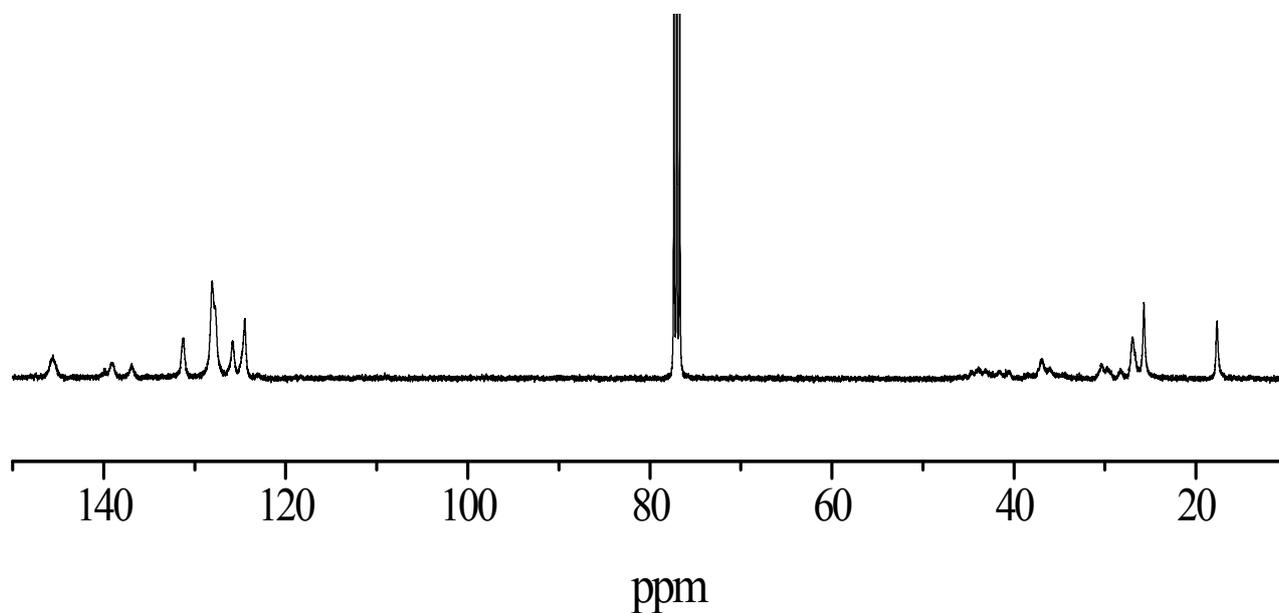


**Fig. S10.** Particle size distributions as determined by dynamic light scattering of emulsions of  $\beta$ -myrcene, styrene and their mixtures with LASC, analyzed during the induction period prior to polymerization.

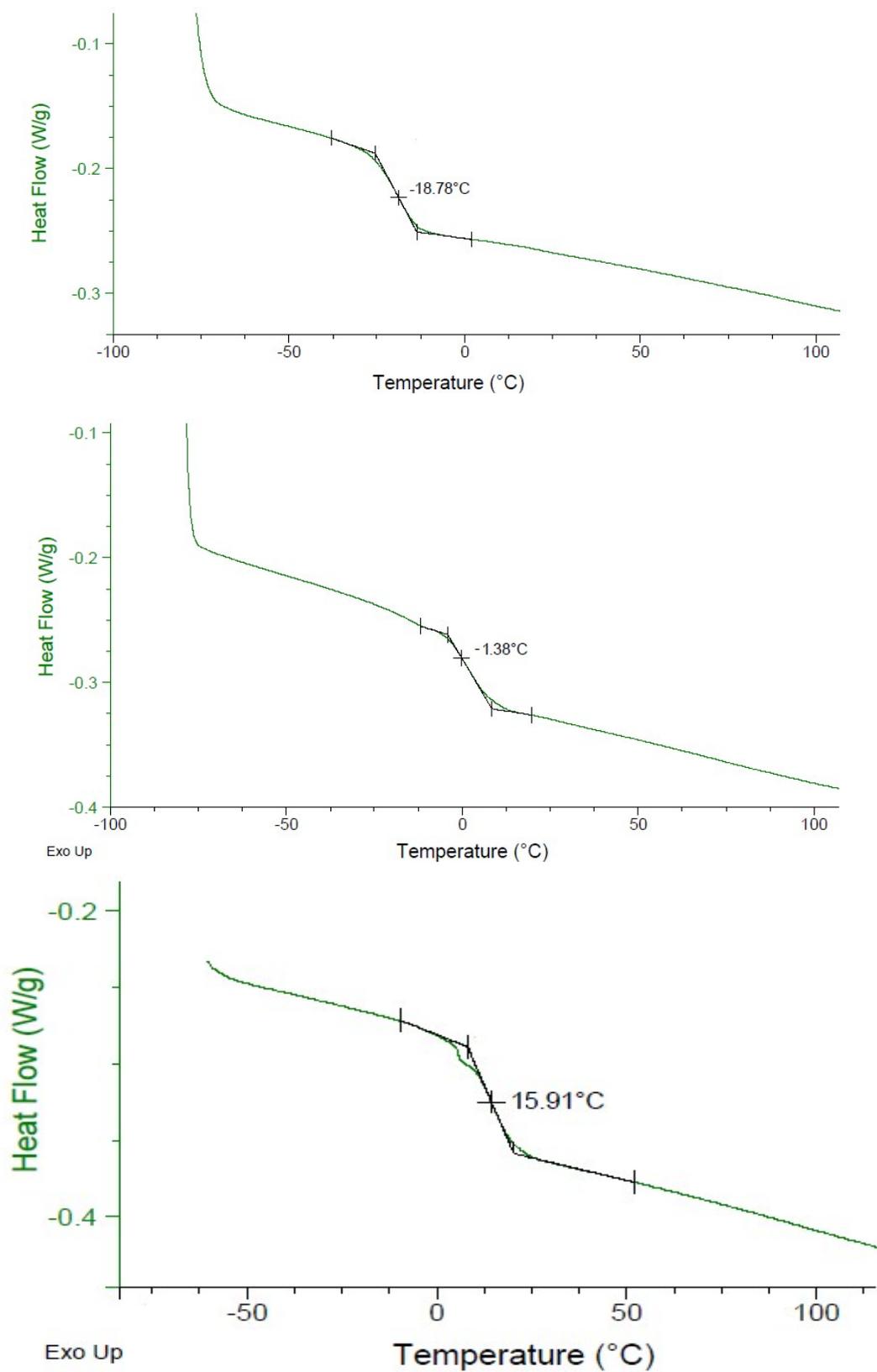




**Fig. S11.** <sup>1</sup>H NMR spectrum of poly( $\beta$ -myrcene-*co*-styrene) obtained at Myr : St ratio of 50 : 50 mol/mol.



**Fig. S12.** <sup>13</sup>C NMR spectrum of poly( $\beta$ -myrcene-*co*-styrene) obtained at Myr : St ratio of 50 : 50 mol/mol.



**Fig. S13.** DSC thermograms of poly( $\beta$ -myrcene-*co*-styrene)s obtained at different Myr : St molar ratios (from top to bottom): 75 : 25; 50 : 50, 40 : 60 and 25 : 75.

N (S) (2018) 13:38 09.07.18  
 Number of observed lines: 51 Kp Cu 2 $\theta$ min= 5.0° 2 $\theta$ max= 75.0° error: .2°  
 Searched phases: inorganic Zs [Zz...], where Zs - any element

Fitting parameters:

PD	PDD	PDI	LD/LW	SKALA	I/Ic	Q	Card #	Chemical formula (mineral name)
.84	1.36	.34	33/40	1.00	1.80	*	24-1132	Na2 S O4
1.29	1.34	.44	26/28	.54	1.50	*	5- 631	Na2 S O4 THENARDITE SYN

Measured Pattern	24-1132 Na2 S O4	5- 631 Na2 S O4	Residual Pattern
18.50	4.796 5	4.762 9	-4
19.00	4.670 31		-10
19.76	4.493 2	4.484 4	-2
22.55	3.943 33	3.922 35	-2
23.12	3.846 6		-5
23.55	3.778 38	3.846 11	8
25.49	3.494 30	3.774 30	5
27.98	3.189 21		-6
28.95	3.085 16	3.175 27	-8
31.75	2.818 100	2.809 100	0
32.06	2.792 52		-2
33.86	2.648 57	2.639 45	-15
36.34	2.472 1	2.463 2	-1
37.75	2.383 18	2.375 20	-2
38.56	2.335 13		2
40.16	2.244 3	2.237 4	-1
40.72	2.214 2		-1
	unmatched	2.183 2	
42.32	2.134 5	2.132 6	-1
43.04	2.100 2	2.101 6	-4
43.27	2.089 4	2.088 7	-3
43.79	2.066 4	2.062 5	-1
46.12	1.967 18	1.965 20	-2
47.28	1.921 1		-1
48.24	1.885 9	1.883 9	-2
48.72	1.868 16	1.868 16	0
49.34	1.846 2	1.842 3	-1
	unmatched	1.832 1	
50.58	1.803 2	1.799 2	0
	unmatched	1.770 1	
	+	1.751 15	
52.41	1.744 20	1.742 20	-15
53.87	1.701 1	1.695 2	-1
54.50	1.682 6		-1
55.14	1.664 4	1.681 7	0
56.65	1.623 3	1.651 4	-4
	-	1.623 3	
	-	1.621 4	
57.30	1.607 2	1.613 3	-4
58.13	1.586 8	1.585 9	-3
58.98	1.565 9	1.563 10	-1
59.39	1.555 7		2
60.32	1.533 3	1.531 3	-1
61.17	1.514 1	1.513 1	0
61.82	1.500 2	1.497 3	-1
	unmatched	1.493 1	
62.67	1.481 1	1.479 2	-1
	unmatched	1.464 1	
63.95	1.455 8	1.453 9	-1
64.53	1.443 1	1.443 2	-1
65.18	1.430 2		-1
66.55	1.404 3	1.403 4	-1
67.42	1.388 1		-1
68.06	1.376 2	1.376 3	-1
	unmatched	1.337 1	
	unmatched	1.330 2	
71.14	1.324 3	1.325 2	1
71.47	1.319 1	1.318 3	-2
	unmatched	1.314 2	
72.89	1.297 5	1.294 3	-1
73.95	1.281 2	1.279 3	-1
74.48	1.273 1	1.271 2	-1

(S)

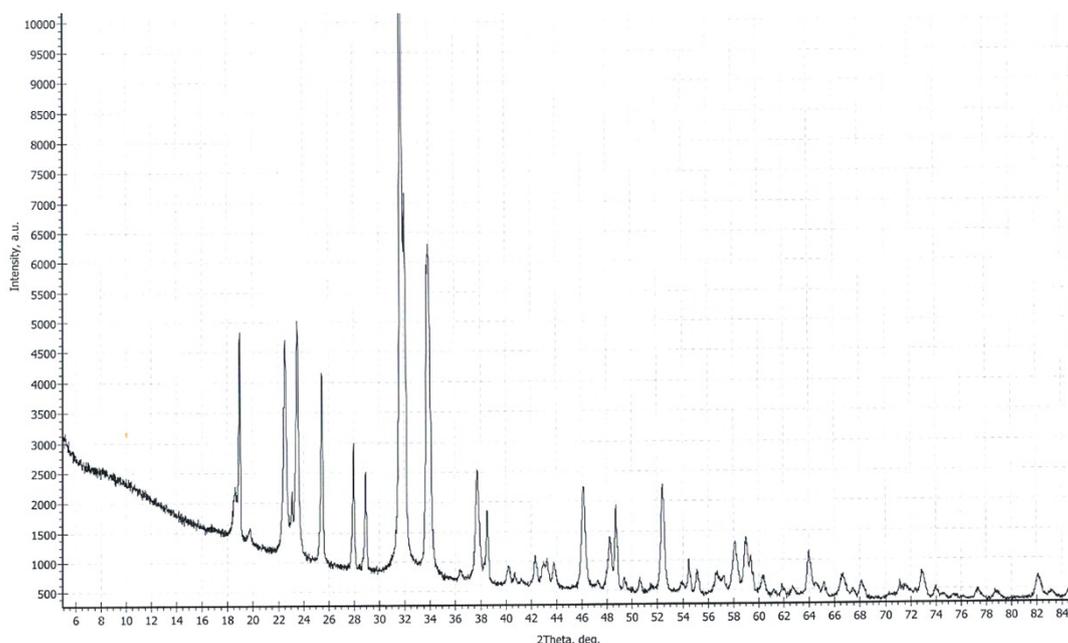
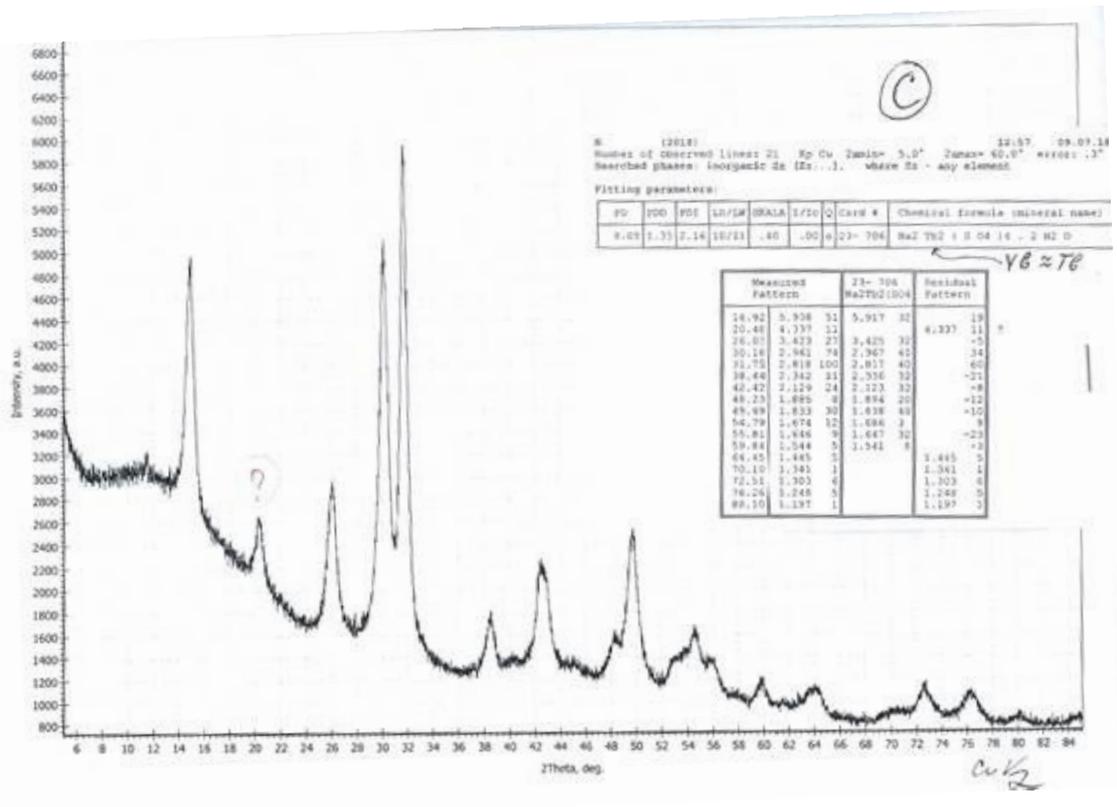
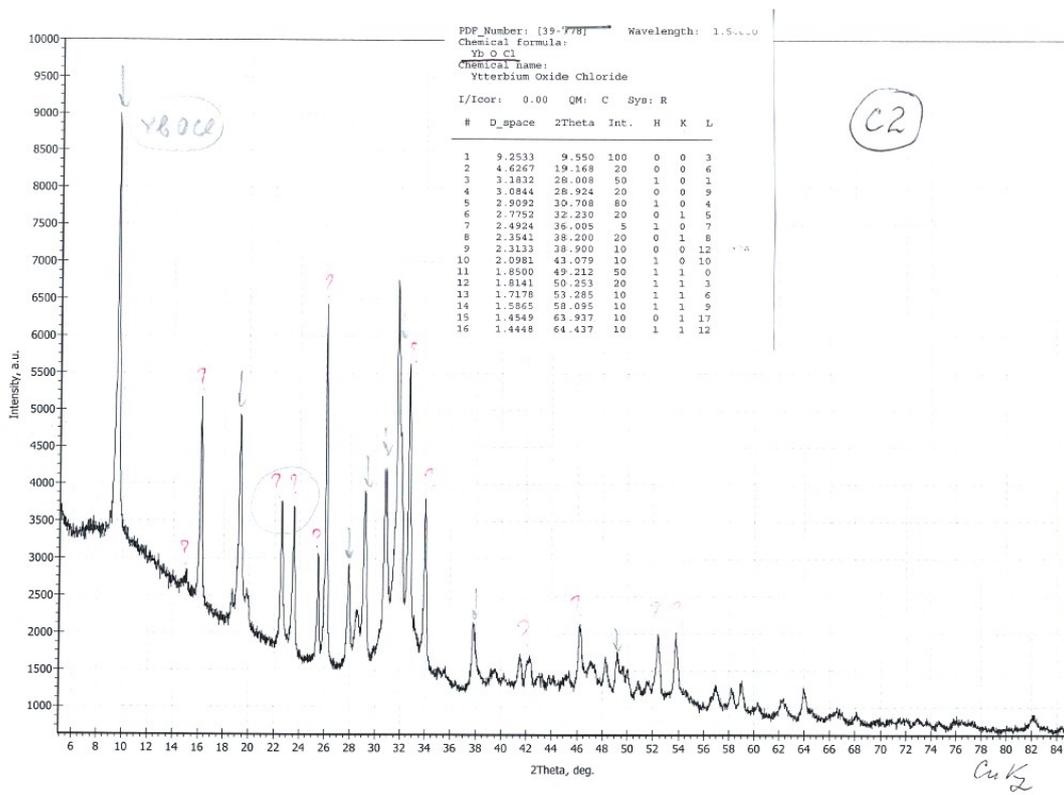


Fig. S14. X-ray diffraction pattern of inorganic salt contained in DBSNa.



**Fig. S15.** X-ray diffraction pattern of ytterbium salt after its recovery from reaction mixture and treatment by aqueous HCl (run R3\*, Table 3).



**Fig. S16.** X-ray diffraction pattern of ytterbium salt after its second recovery from reaction mixture (run R2, Table 3).