

## Supporting Information

### Bioelastomers: current state of development

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**Table S1.** Main bioelastomers based on polyterpenes, polyurethanes and polyesters described in the manuscript and their main characteristics/highlights.

Type	Bioelastomer		Synthesis	Characteristics	Highlights	Ref
Polyterpenes	Polyocimene	Polyocimene	Redox emulsion polymerization	Yields from 15-20%, with molecular weights nearly to 1.5 kDa	Difficult propagation of growing species	35
			Coordination polymerization	Use of titanium complexes give high 1,4- <i>trans</i> microstructure at higher temperatures.	Catalytic systems with a temperature-dependent stereoselectivity.	61
			Cationic polymerization	Triflate esters as initiator.	Produce oligoocimenes at high conversion	64
		Ocimene and styrene	Coordination copolymerization	Catalyst based on titanium complexes promote the copolymerizations.	Range of compositions of styrene from 0.23-0.87.	61
		Polyocimene	Ammonium persulfate and redox-initiated emulsion polymerization	Monomer conversions ranging from 15 to 98% and molecular weights greater than 100 kDa. $T_g$ 's from -70 to 58 °C	The redox emulsion polymerization achieves a maximum conversion of 65% but the polymer obtained contains a configuration preferably 1,4	20, 35
	Myrcene	Polymyrcene	RAFT polymerization	Monomer conversions from 24 to 50% and molecular weights from 2.4 to 9 kDa. $T_g$ 's close to -60 °C	The resulting polymer has 1,4-isomer content greater than 90%	49, 50
			Coordination polymerization	Titanium complexes form polymers with high 1,4- <i>trans</i> isomer content. The use of Lutonium alkyl complexes promote high 3,4-regioselectivity.	Cis-1,4 content higher than 92% can reach with neodymium catalyst.	54, 55, 57, 59, 60, 61
			Cationic polymerization	Oligomyrcenes obtained with triflate esters as initiator. Use of Lewis acid surfactant combined catalyst (LASC) produce	LASC provides a polymer with predominantly 1,4-units.	64, 65

		polymyrcene with $M_n$ up to 150 <i>kDa</i> .		
	Anionic polymerization	Trialkyl aluminum derivatives and <i>n</i> -butyllithium have been used as initiating systems.	Polymers with dispersities from 1.7-2 using trialkyl aluminum and less than 1.2 through butyllithium.	66, 67
Poly(myrcene- <i>co</i> -styrene)	Coordination copolymerization	Range of compositions from 0.14-0.9 of styrene with titanium catalyst.	Catalyst system based on lanthanum produce a polymyrcene of the copolymer with 1,4- <i>trans</i> microstructure >98%.	56, 61, 62
	Cationic copolymerization	Random copolymers with $M_n$ from 60-120 <i>kDa</i> .	Use of LASC and able to recover from the reaction mixture.	65
	NMP copolymerization	Poly(myrcene- <i>b</i> -styrene) exhibit $T_g$ s about -70 and 60°C, brittle behavior, and better thermal stability.	Changing the molar feed compositions of the monomers is possible to obtain poly(myrcene- <i>stat</i> -styrene).	46
Polystyrene- <i>b</i> -poly( $\beta$ -myrcene)- <i>b</i> -polystyrene	RAFT copolymerization	Slightly broad dispersity in the triblock copolymer and PS content from 9.8-51.89 wt%.	Potential alternative biobased to TPEs as SBS and SIS.	51
Polymyrcene- <i>co</i> -polyisoprene	Coordinative copolymerization	Catalyst system based on lanthanum produce maintain the 1,4- <i>trans</i> stereoregularity of the polymerization.	Use of Lutetium catalyst results resulted in random and block copolymerization of myrcene and isoprene.	56, 58
Poly(myrcene- <i>co</i> -isoprene- <i>co</i> -styrene)	Coordinative copolymerization	Monomodal distributions and dispersities around 1.5-1.6 with lanthanum catalyst.	The terpolymer presents high <i>trans</i> -1,4-polymyrcene content.	56
Poly(myrcene- <i>co</i> -ethylene)	Coordinative copolymerization	Use of half-sandwich scandium complexes.	Depend on the ligands is possible to produce diblock myrcene-ethylene, multiblock myrcene-ethylene and alternating myrcene-ethylene copolymers.	63
Poly(styrene- <i>co</i> -ethylene- <i>co</i> -myrcene)	Coordinative copolymerization	Monomodal molecular weight, narrow distribution (1.3-1.6) of the terpolymers with a lanthanidocene catalyst.	Ethylene facilitates the insertion of styrene or $\beta$ -myrcene monomer.	62

		Poly(myrcene-co-ethylene-co-propylene)	Coordinative copolymerization	High activity, unimodal and narrow molecular weight distribution with half-sandwich scandium complexes.	New generation of myrcene-based ethylene-propylene-diene rubbers (EPDM).	63
		Myrcene and glycidyl methacrylate (GMA)	NMP copolymerization	The copolymers obtained have low dispersity and the molar fraction of GMA incorporated range from 0.10 to 0.90.	Copolymerization resulted in a statistical copolymer.	47
		Poly(myrcene-co-isobornyl methacrylate)	NMP copolymerization	Possible gradient myrcene/iBOMA copolymer with compositions of molar fraction from 0.10-0.90	Thermoplastic elastomers from partially bio-based raw material to replace conventional TPEs	48
		Poly(myrcene)- <i>b</i> -poly(methyl methacrylate)	Coordinative copolymerization	Neodymium based catalyst	Versatility to copolymerize myrcene with a polar vinyl monomer.	60
	Polyfarnesene	Polyfarnesene	Redox emulsion polymerization	Yields from 20-24% and molecular weights around to 3.2 kDa	Side chain length impacts in the polymerization reaction	35
Coordination polymerization			Iron complexes as catalyst.	According to the ligand can be obtained trans-1,4 or cis-1,4 polyterpenes.	55	
Poly(farnesene-co-glycidyl methacrylate)		NMP copolymerization	Depend on the initiator used in the synthesis can be obtained poly(farnesene- <i>stat</i> -GMA) and poly(farnesene- <i>b</i> -GMA)	Functional groups into methacrylate can be used to compatibilized the polymer matrix with fillers or immiscible polymer blends.	49	
Poly(styrene-co-farnesene)		Coordinative copolymerization	Lanthanidocene catalyst allow to produce an incorporation of 2.5 to 9.8 mol% of $\beta$ -farnesene in the copolymer.	Essentially the microstructure consists of 1,4 and 3,4-polyterpene units.	62	
Polyurethanes	Diphenylmethane diisocyanate (MDI) and poly(lactide-co-caprolactone)	Two-Step polymerization process	Poly(lactide-co-caprolactone) segment improve the thermal stability and mechanical properties.	Display shape memory and biocompatibility. Promising applications if biomedical field.	87	
	Succinic acid (SU), sebacic acid (SA), fumaric acid (FA), 1,3-propanediol (PDO), 1,4-butanediol (BDO) and MDI	Melt polycondensation	Elongation at break > 800% and 30MPa of tensile strength with a	Environmentally friendly and biodegradable TPUs	89	

			macrodiol composition of 60%.		
	Poly(1,3-propylene succinate) glycol (PPS), MDI and BDO	One-pot solvent-free polymerization	The use of PPS with high molecular weight in the TPU exhibit better mechanical properties.	Fully biobased TPU with thermo-induced shape memory.	<sup>90</sup>
	Tall oil (TO)based polyol, soybean oil (SO)-based polyol, rapeseed oil (RO)-based polyol, poly(ethylene adipate (PEA), MDI, ethylenglycol (EG) and dicyandiamide (DYDI)	One-step method	Macrodiols based on tall and rapeseed oil lead to materials with better fire resistance properties.	PU with TO polyols have lower emission of carbon monoxide than the reference material.	<sup>91</sup>
	Polytetramethylene ether glycol (PTMEG), MDI, BDO and isosorbide.	Pre-polymer method	The isosorbide content affects thermal and mechanical properties.	Use of isosorbide as biobased chain extender.	<sup>92, 93</sup>
	Polycarbonate diol (PCD), isosorbide and hexamethylene diisocyanate (HDI).	One-step condensation polymerization	$T_g$ of the TPU depend on the isosorbide/PCD ratio.	TPU display biocompatibility and flexibility.	<sup>94</sup>
	Isosorbide, MDI and rapeseed oil-issued polyester polyol	Two-step synthesis	The presence of isosorbide results in a slight increase of hardness and shape retention	Do not increase the water absorption by the presence of isosorbide significantly	<sup>95</sup>
	Azealic acid, isosorbide, MDI and BPO		The polyester polyol was synthesized by esterification of azelaic acid and isosorbide	Properties are dependent on the content of diisocyanate	<sup>96</sup>
	Poly(tetra-methylene ether glycol), MDI and Isosorbide or isomannide	Pre-polymer method	Display reversible properties that allow reprocessability at mild temperatures	The presence of isosorbide or isomannide as chain extender improve the self-healing features.	<sup>97</sup>
	Poly(propylene succinate)s, MDI, BPO and 1,3-propanediol (PDO)	Pre-polymer method	Elongation at break up to 550% and tensile strength of 30 MPa	Biobased thermoplastic polyurethane elastomers with low stiffness and good damping capacity	<sup>98</sup>
	Biobased diisocyanate (bio-DIC), BPO, HDI and $\alpha$ , $\beta$ -oligo(ethylene-butylene adipate) diol	Pre-polymer method	Tensile strength from 6.5 to 33.3 MPa with a content of 50% of bio-DIC	Content of the bio-DIC affects thermal and thermomechanical properties.	<sup>99</sup>
Polyesters	Poly(L-lactide- <i>b</i> - $\epsilon$ -decalactone- <i>b</i> -L-lactide)	ROP	$M_n > 30 \text{ kDa}$ $\text{Đ} \leq 1.5$	Copolymers with a $T_g$ of -50°C to compositions of mol% of 40/60 and 80/20 of LLA/ $\epsilon$ DL, respectively	<sup>107, 108</sup>

Poly(L-lactide- <i>b</i> - $\delta$ -decalactone- <i>b</i> -L-lactone)	ROTEP	Display elastomeric behavior with wax appearance.	Develop of new sustainable copolymers.	110
Poly(lactide- <i>co</i> -polymenthide- <i>co</i> -poly(lactide)	ROTEP	Elastomeric behavior, Young's module of 26.8 $\pm$ 2.1 MPa and strain at break of 765 $\pm$ 40%	Develop to replace the commercial styrenic block polymers	109
Poly(ethylenglicol- <i>b</i> - $\epsilon$ -decalactone) and poly( $\epsilon$ -decalactone- <i>b</i> -ethylenglicol- <i>b</i> - $\epsilon$ -decalactone)	ROP	Amphiphilic block copolymers with self-assemble into micelles. Elastomeric properties not mentioned.	Potential biomedical applications due its low cytotoxicity and biodegradability	111
Poly(lactide)- <i>b</i> -poly(caprolactone- <i>co</i> - $\epsilon$ -decalactone)- <i>b</i> -poly(lactide)	ROTEP	Good control over composition and narrow relation between composition and mechanical behavior.	Attractive TPE due its tunable mechanical properties.	112
Poly( $\gamma$ -methyl- $\epsilon$ -caprolactone)	ROP	Cross-linked with $\beta$ -lactone (4,4-(ethane-1,2-diyl)bis(oxetan-2-one)	Promising removable and biodegradable elastomers.	113
Poly(lactide)- <i>b</i> -poly( $\gamma$ -methyl- $\epsilon$ -caprolactone)- <i>b</i> -poly(lactide)	ROTEP	The use of isotactic PLA that is semicrystalline there a increase in strength and toughness	ABA block polymers as replace conventional TPEs	114
Poly( $\beta$ -myrcene)-graft-poly(L-lactide)	ROP	Copolymers with high molecular weights and narrow distributions.	Fully biobased TPE with tunable mechanical properties according to the PLLA/PMy content.	118
Poly(limonene carbonate)- <i>b</i> -poly( $\epsilon$ -caprolactone)- <i>b</i> -poly(limonene carbonate)	ROP and LO/ CO <sub>2</sub> ROCOP	Hard compositions from 21-63 wt% of poly(limonene carbonate). Tensile strength of 21.2 MPa and elongation at break around of 400%	Fully biobased ABA triblock polymer and able to be chemically recycled.	115
Poly(hexamethylene 2,5-furanodicarboxylate)- <i>b</i> -poly(tetrahydrofuran)	Transesterification and melt polycondensation	Present shape-memory polymer behavior induced by temperature.	The predominance of poly(tetrahydrofuran) segments improves the recovery properties.	116
Poly(1,4-butylene 2,5-furandicarboxylate)-PBSS	Transesterification and melt polycondensation	PBBS soft segment could tuning the	Potential biomedical applications due the copolymers are nontoxic, thermally	117

			mechanical properties.	stable and renewable	
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