

Supplementary Materials

# Reinforcement of Styrene Butadiene Rubber Employing Poly(isobornyl methacrylate) (PIBOMA) as High $T_g$ Thermoplastic Polymer

Abdullah Gunaydin<sup>1,2</sup>, Clément Mugesana<sup>1</sup>, Patrick Grysan<sup>1</sup>, Carlos Eloy Federico<sup>1</sup>, Reiner Dieden<sup>1</sup>, Daniel F. Schmidt<sup>1</sup>, Stephan Westermann<sup>1</sup>, Marc Weydert<sup>3</sup> and Alexander S. Shaplov<sup>1,\*</sup>

<sup>1</sup> Luxembourg Institute of Science and Technology, Materials Research and Technology Department, 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg

<sup>2</sup> Department of Physics and Materials Science, University of Luxembourg, 2, Avenue de l'Université, L-4365 Esch-sur-Alzette, Luxembourg

<sup>3</sup> Goodyear Innovation Center Luxembourg, L-7750 Colmar-Berg, Luxembourg

**Table S1.** Free radical polymerization of IBOMA (reaction conditions: [AIBN] = 1.0 wt%, duration: 6h, [IBOMA] = 50 wt%).

Entry	Solvent	Initiator	T [°C]	$M_n$ (g mol <sup>-1</sup> ) <sup>a</sup>	$M_w/M_n$ <sup>a</sup>	Yield [%]
1 <sup>b</sup>	DMF	AIBN	60	715800 <sup>c</sup>	1.6	29
				59250	2.2	
2	Toluene	AIBN	60	73600	2.4	44
3	THF	AIBN	60	59500	2.2	74
4	Cyclohexane	AIBN	60	151800	2.3	41
5	1,1,2-TCA	AIBN	60	68400	2.7	71
6	1,1,2-TCA	ACHN	88	43600	2.4	77
7 <sup>d</sup>	1,1,2-TCA	ACVA	69	89000	2.1	75
8	1,1,2-TCA	VAm-110	110	82900	3.1	80
9 <sup>e</sup>	1,1,2-TCA	VAm-110	110	283000	1.9	70
10	Cyclohexane	ACHN	88	74300	2.6	49

<sup>a</sup>Molecular weight and  $M_w/M_n$  determined by GPC in THF at 40°C with calibration by PMMA standards. <sup>b</sup>The precipitation of PIBOMA was observed. <sup>c</sup>Bimodal distribution. <sup>d</sup>ACVA was found to be insoluble in 1,1,2-TCA. <sup>e</sup>Concentration of [AIBN] = 0.5 wt%.

Polymer	Solvents <sup>b</sup>												
	DCM	Chloroform	TCA	THF	DMF	DMAc	Cyclohexane	Toluene	NMP	Et <sub>2</sub> O	ACN	MeOH	Acetone
PIBOMA	+	+	+	+	+	+	+	+	-	+	-	-	-

**Table S2.** Solubility of PIBOMA<sup>a</sup>

<sup>a</sup> Solubility: soluble at room temperature (+), soluble at 80°C (+<sup>t</sup>), insoluble even on heating (-). <sup>b</sup> DCM - dichloromethane; TCA - 1,1,1-trichloroethane; THF- tetrahydrofuran; DMF - N,N-dimethylformamide; DMSO - dimethyl sulfoxide; DMAc - N,N-dimethylacetamide; NMP - N-methyl-2-pyrrolidone; Et<sub>2</sub>O - diethyl ether; ACN - acetonitrile; MeOH - methanol.

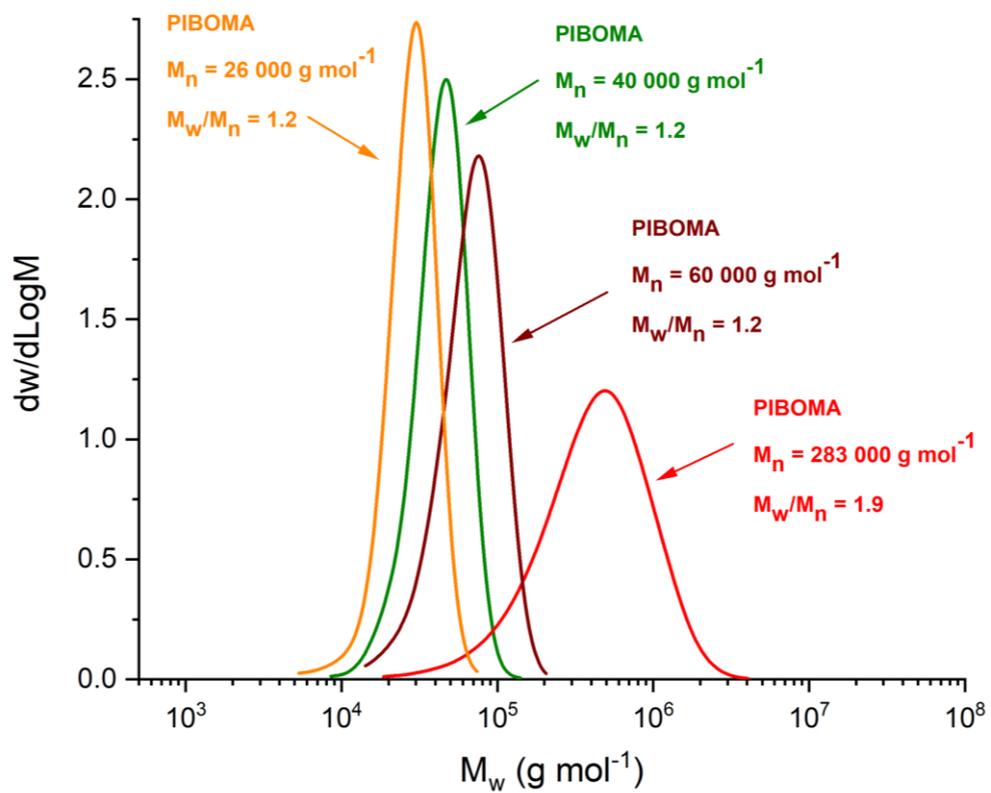


Figure S1. GPC traces of PIBOMA samples obtained via RAFT and free radical polymerization.

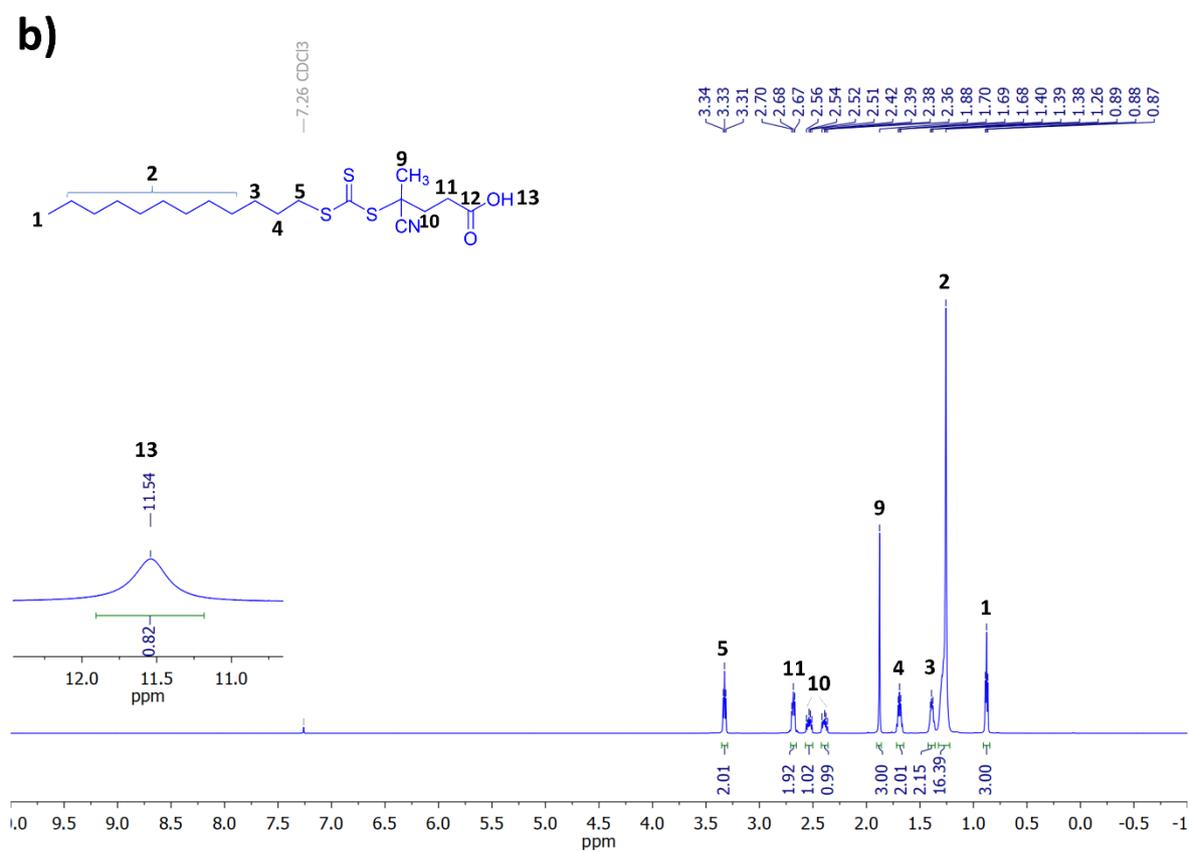
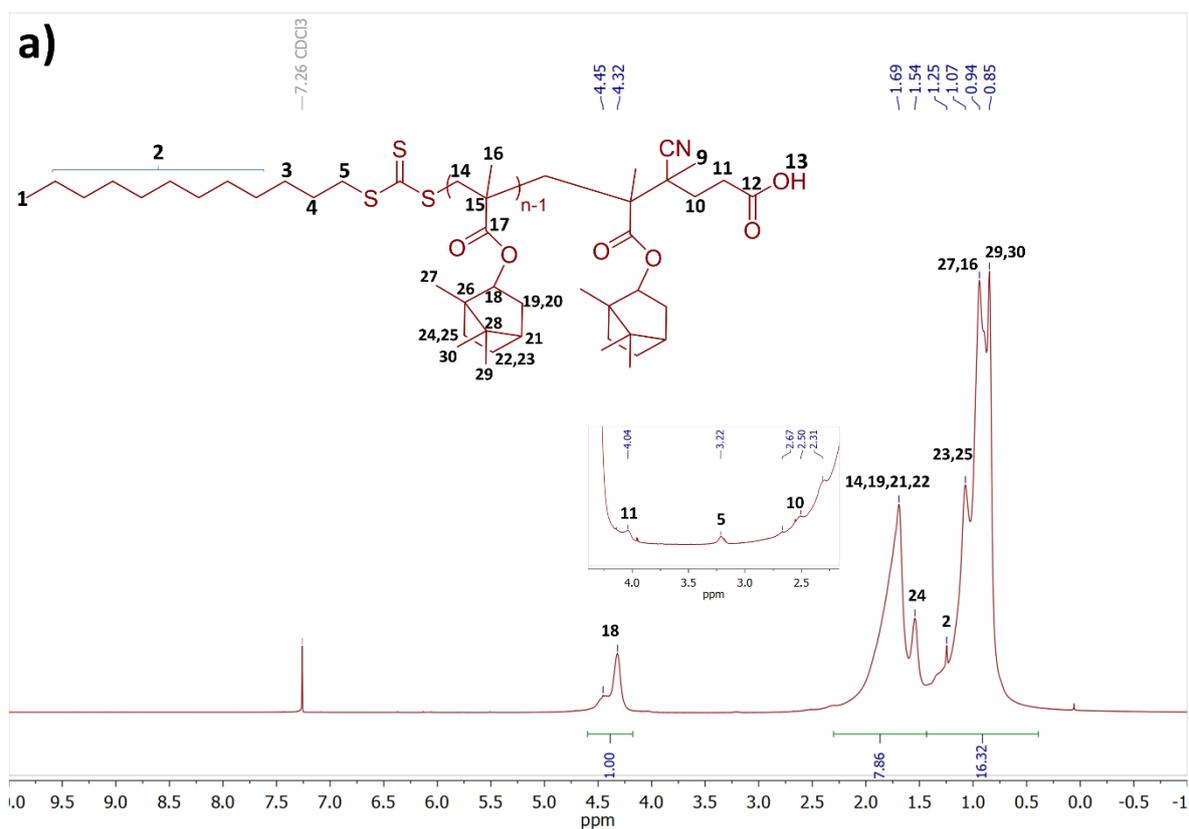


Figure S2.  $^1\text{H}$  NMR of PIBOMA 26K (a) and CDTPA RAFT agent (b) (25 °C,  $\text{CDCl}_3$ ).

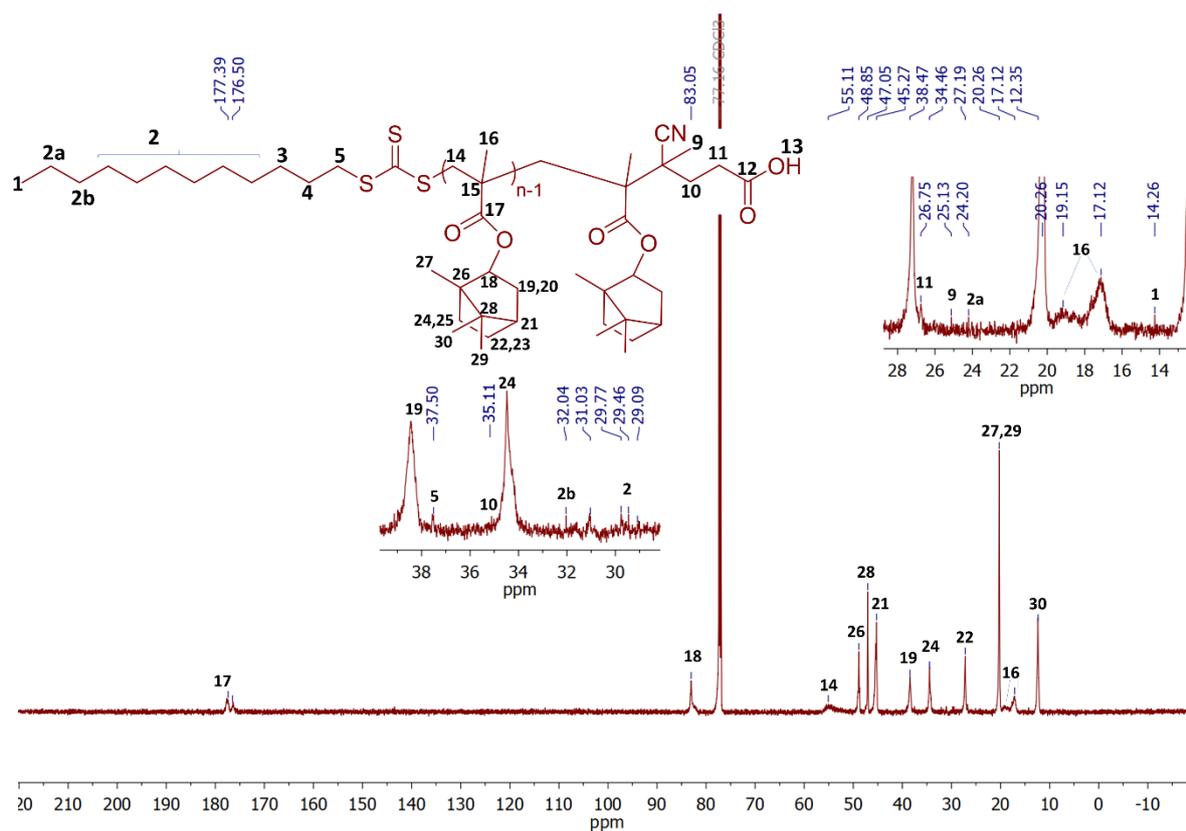


Figure S3.  $^{13}\text{C}$  NMR of PIBOMA 26K (25 °C,  $\text{CDCl}_3$ ).

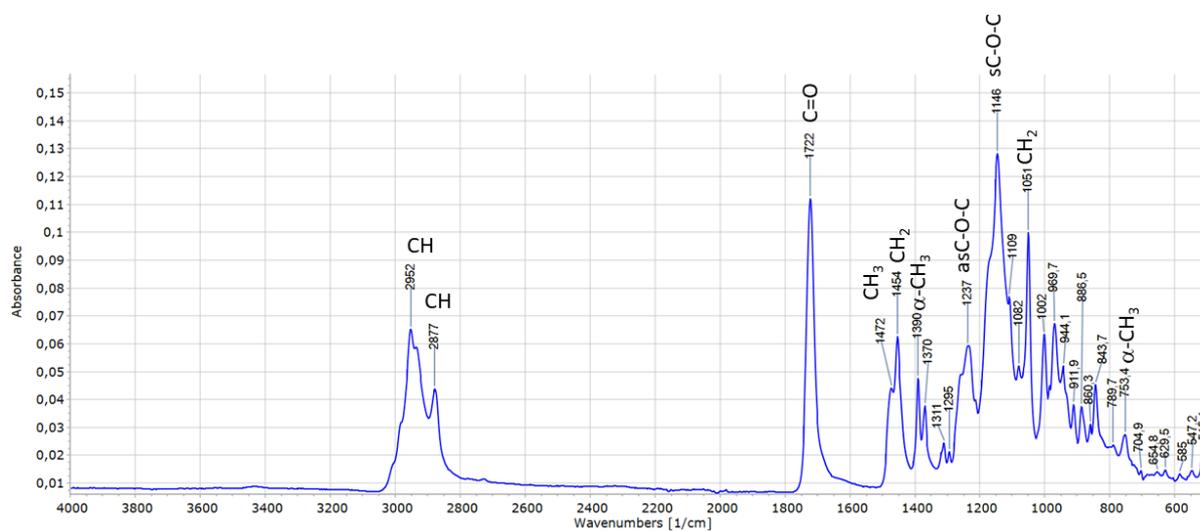
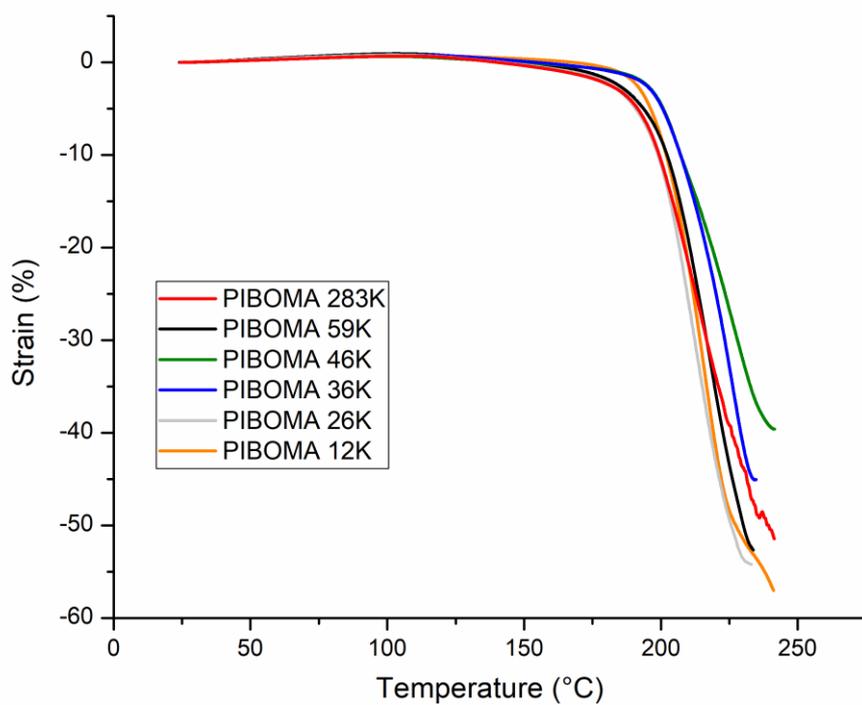
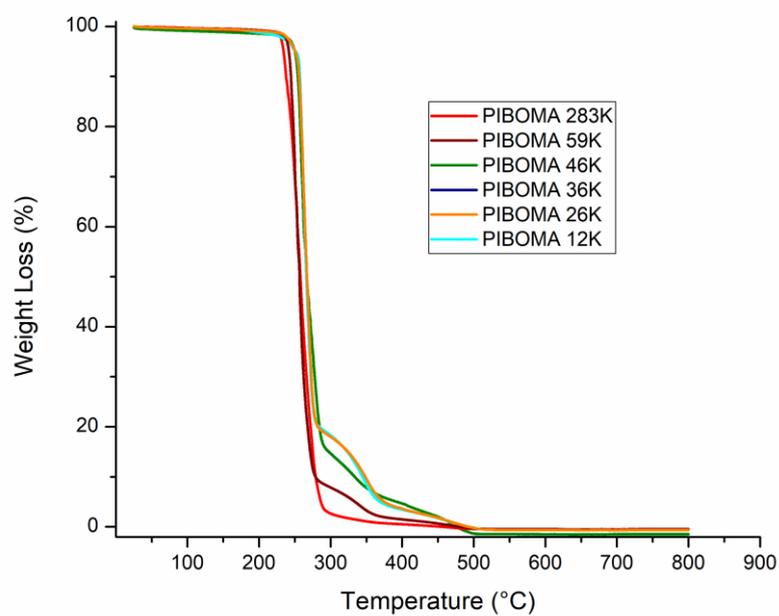


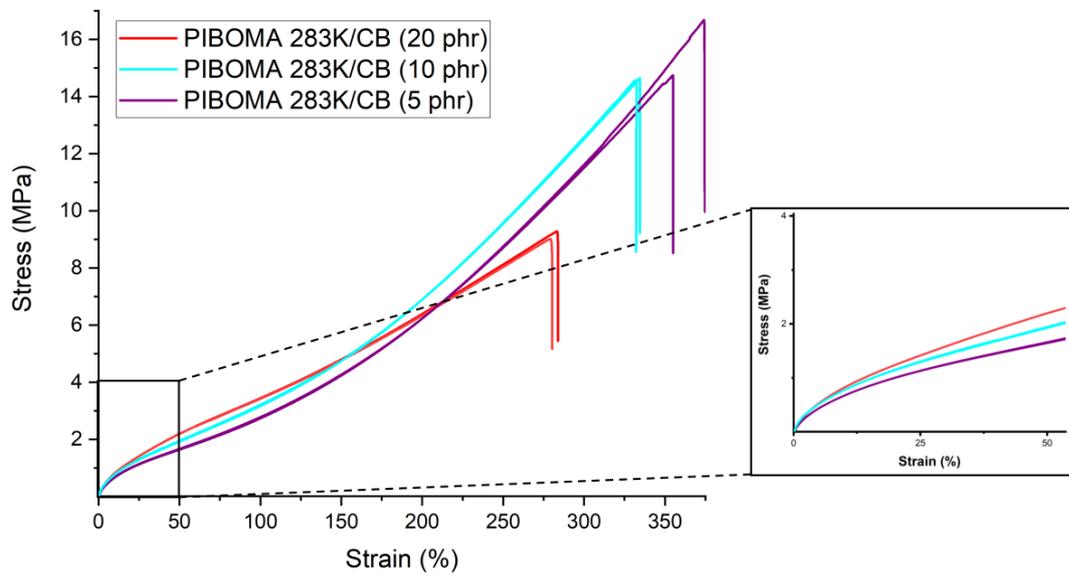
Figure S4. FT-IR spectrum of PIBOMA 26K.



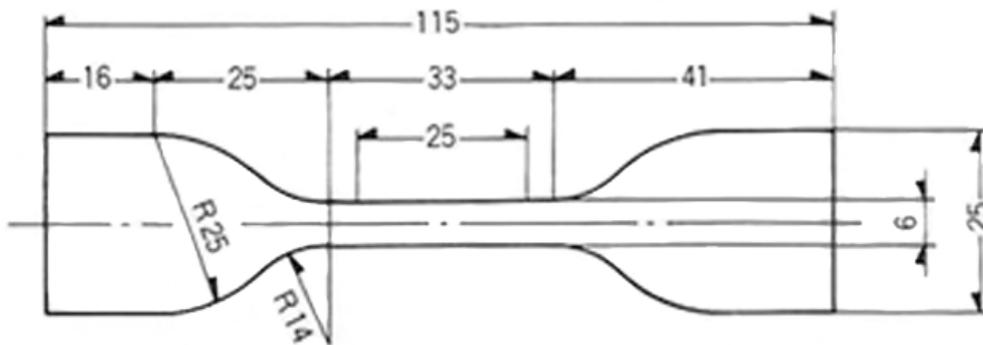
**Figure S5.** TMA traces of PIBOMA having different molar masses.



**Figure S6.** TGA traces of PIBOMA having different molar masses (TGA was performed in air with a heating rate of  $5^{\circ}\text{C min}^{-1}$ ).



**Figure S7.** Stress–strain curves of SBR compounds containing 50 phr of CB and filled with increasing content of PIBOMA283K.



**Figure S8.** Specimen dimensions used in tensile testing (correspond to Type V in ASTM D638-14).