



## Effect of Ionizing Radiation on the Chemical Structure and the Physical Properties of Polycaprolactones of Different Molecular Weight

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**Figure S1.** Molecular weight in the peak maximum ( $M_P$ ) of the size exclusion chromatography (SEC) curve vs molecular weight as reported by the supplier ( $M_n$ ) of polycaprolactones.





Figure S2. Tensile stress-strain curves for the polycaprolactones.



Figure S3. Tensile stress and strain results for the polycaprolactones.



**Figure S4.** Crystallinity percentage for the polycaprolactones in the pellets and after recrystallization from the melt for 30 min and 10 days.



**Figure S5.** Calculated crosslink efficiency (*q*<sub>0</sub>/*p*<sub>0</sub>) vs PCL molecular weight.



Figure S6. Calculated minimum dose for gelation (*d*<sub>0</sub>) vs PCL molecular weight.



Figure S7. SEC curves for PCL 80 K.

l / a.u.

|/a.u.



Figure S8. SEC curves for PCL 50 K.



PCL 43K

Figure S9. SEC curves for PCL 43 K.







Figure S11. Weight average molecular weight  $(M_w)$  vs dose for the irradiated PCLs.





**Figure S12.** Proton nuclear magnetic resonance (NMR) spectra for PCL 50 K non irradiated (black line) and for the soluble part of the PCL 50 K irradiated at 500 (red line) and 1000 kGy (blue line).



Figure S13. Expanded view of the spectra in Figure S12.





**Figure S14.** Proton NMR spectra for PCL 50 K non irradiated (black line) and for the soluble part of the PCL 50 K irradiated at 500 (red line) and 1000 kGy (blue line) derivatized with trifluoroacetic anhydride.



**Figure S15.** Differential Scanning Calorimetry (DSC) traces for PCL 80 K irradiated with electron beam at a dose of 200 kGy.



**Figure S16.** Melting point ( $M_P$ ) for PCL 50 K (in red) and for PCL 80 K (in blue) in the first heating run (open symbols) and in the second heating run (filled symbols).



**Figure S17.** Melting enthalpy for PCL 50 K (in red) and for PCL 80 K (in blue) in the first heating run (open symbols) and in the second heating run (filled symbols).





Figure S18. Glass transition temperature (*T*g) for PCL 50 K (in red) and for PCL 80 K (in blue).



Figure S19. Crystallization enthalpy for PCL 50 K (in red) and for PCL 80 K (in blue).

	PCL 32 K		PCL 43 K		PCL 50 K		PCL 80 K	
Dose	Ts	Eb	Ts	Eb	Ts	Eb	Ts	Eb
(kGy)	(MPa)	(%)	(MPa)	(%)	(MPa)	(%)	(MPa)	(%)
0	$23.7\pm1.8$	$1010 \pm 100$	$39.0 \pm 1.0$	$1590\pm60$	$48.4\pm0.9$	$2250\pm80$	$48.0^{*} \pm 1.5$	1900*± 70
10	$18.3\pm0.4$	$44 \pm 13$	$33.5\pm0.7$	$1360\pm30$				
25	$18.5\pm0.5$	$29.5 \pm 1.1$	$30.4 \pm 1.1$	$1250\pm60$				
50	$18.3 \pm 1.1$	$20 \pm 3$	$20.4\pm1.1$	$800 \pm 60$	$37 \pm 2$	$1410\pm90$	$46 \pm 2$	$1660 \pm 100$
100			$18.9\pm0.7$	$46 \pm 17$	$27 \pm 2$	$1090\pm70$	$43 \pm 2$	$1460 \pm 100$
150					$18.6\pm0.5$	$610 \pm 40$	$34 \pm 3$	$1200 \pm 80$
200					$18.6\pm0.2$	$44 \pm 12$	$17.9 \pm 0.5$	$600 \pm 50$
250					$18.3 \pm 0.1$	$21.4 \pm 1.9$	$17.4 \pm 0.2$	$300 \pm 200$

**Table S1.** Values for tensile stress at break ( $T_s$ ) and strain at break ( $\varepsilon_b$ ) of PCLs when irradiated with electron beam at several doses.

\* Samples escaped from the grips.

**Table S2.** Values for tensile stress at break ( $T_s$ ) and strain at break ( $\varepsilon_b$ ) of PCLs when irradiated with gamma rays at several doses.

	PCL 32 K		PCL 43 K		PCL 50 K		PCL 80 K	
Dose	Ts	Eb	Ts	Eb	Ts	Eb	Ts	Eb
(kGy)	(MPa)	(%)	(MPa)	(%)	(MPa)	(%)	(MPa)	(%)
0	$23.7 \pm$	$1010 \pm$	39.0 ±	1590 ±	$48.4 \pm$	$2250 \pm 80$	48.0*±	1000*+ 70
	1.8	100	1.0	60	0.9		1.5	1900°±70
25	$18.3 \pm$	$48 \pm 15$	$30 \pm 2$	$1240 \pm$	42 + 2	1580 ± 130	47*± 2	2070*±
	0.4			90	$42\pm 3$			100
50	17.2 ±	$13.5 \pm 0.6$	$18.7 \pm$	$630 \pm 70$	32 ± 2	$1200 \pm 60$	$48 \pm 4$	2100 + 200
	0.2		0.4					$2100 \pm 200$
75	$16.1 \pm$	$10.2 \pm 0.8$	$18.5 \pm$	$50 \pm 20$	$24 \pm 3$	960 ± 130	$44.8\pm1.9$	$1630 \pm 140$
	0.9		0.3					
100	13.5 ±	$7.6 \pm 0.7$	18.3 ±	$24 \pm 4$	22.8 ±	$950 \pm 30$	$38 \pm 5$	$1400 \pm 200$
	0.9		0.7		0.7			
150					16.7 ±	01 + 2	01.0 + 1.4	
					0.2	$21 \pm 3$	$21.3 \pm 1.4$	$850 \pm 80$
200	10.6 ±	$5.7 \pm 0.4$	14.9 ±	$10.8 \pm$	$16.4 \pm$	17 + 2	$16.8 \pm 0.2$ $70 \pm 40$	70 + 40
	0.6		0.5	0.4	$0.2$ $17 \pm 3$	$17 \pm 3$		$70 \pm 40$

\* Samples escaped from the grips.



**Figure S20.** Retention of the stress at break vs dose for PCL 50 K (red circles), PCL 80 K (blue circles), PA-6 (green squares), PET (black triangles) and for an aliphatic polyurethane (magenta diamonds).



**Figure S21.** Retention of the strain at break vs dose for PCL 50 K (red circles), PCL 80 K (blue circles), PA-6 (green squares), PET (black triangles) and for an aliphatic polyurethane (magenta diamonds).



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