## **Double-crystalline PLLA-***b***-PVDF-***b***-PLLA triblock copolymers:** preparation and crystallization

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## **Electronic Supplementary Information**



**Figure S1.** <sup>1</sup>H-NMR spectrum of bromine-terminated PVDF<sup>18</sup> in acetone-*d6*. Signals corresponding to PVDF backbone are designated with "V".



Figure S2. <sup>19</sup>F-NMR spectra of bromine-terminated PVDF<sup>18</sup> in acetone-*d6*.



**Figure S3.** Maldi-ToF spectrum of alkyne-terminated PLLA<sup>3</sup>. Sodium ions were used for cationization.



**Figure S4.** WAXS patterns of (a)  $L_{24}V_{52}L_{24}^{36}$  cast from DMF solution and (b)  $L_{24}V_{52}L_{24}^{36}$  crystallized from melt.

**Table S1.** m/z values corresponding to high intensity mass distribution in Figure S3. Suggested chemical structure:



m/z <sub>exp</sub>	m/z <sub>theor</sub> <sup>a</sup>	$\Delta_{m/z}$
1562.6	1562.1	-
1706.6	1706.2	144.0
1850.6	1850.3	144.0
1994.6	1994.4	144.0
2138.6	2138.5	144.0
2282.6	2282.6	144.0
2426.6	2426.7	144.0
2570.6	2570.8	144.0
2714.6	2714.9	144.0
2858.6	2859.0	144.0
3002.7	3003.1	144.1
3146.7	3147.2	144.0
3290.8	3291.3	144.1
3434.9	3435.4	144.1
3579.0	3579.5	144.1
3723.0	3723.6	144.0
3867.0	3867.7	144.0
4011.1	4011.8	144.1
4155.1	4155.9	144.0
4299.1	4300.0	144.0

 ${}^{a}m/z_{theor} = 98.1$  (mass initiator rest) + 23.0 (mass sodium ion) + 144.1 (mass repeating unit) \* n (number of repeating units). **Table S2.** m/z values corresponding to low intensity mass distribution in Figure S3. Suggested chemical structure:

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m/z <sub>exp</sub>	$m/z_{theor}$ <sup>a</sup>	$\Delta_{m/z}$
1634.5	1634.2	-
1778.5	1778.3	144.0
1922.5	1922.4	144.0
2066.5	2066.5	144.0
2210.5	2210.6	144.0
2354.5	2354.7	144.0
2498.5	2498.8	144.0
2642.5	2642.9	144.0
2786.6	2787.0	144.1
2930.7	2931.1	144.1
3074.7	3075.2	144.0
3218.8	3219.3	144.1
3362.9	3363.4	144.1
3506.9	3507.5	144.0
3651.0	3651.5	144.1
3795.0	3795.6	144.0
3939.1	3939.8	144.1
4083.2	4083.9	144.1
4227.2	4228.0	144.0

 ${}^{a}m/z_{theor} = 98.1$  (mass initiator rest) + 23.0 (mass sodium ion) + 144.1 (mass repeating unit) \* n (number of repeating units) + 72.1 (mass 1/2 repeating unit).