

*Electronic supplementary information for*

***How cyclic chain topology can reduce the crystallization rate of Poly(3-hexylthiophene) and promote the formation of liquid crystalline phases in comparison with linear analogue chains***

*Jon Maiz<sup>\*a</sup>, Guoming Liu<sup>b</sup>, Fernando Ruipérez<sup>a</sup>, Nicolas Delbos<sup>c</sup>, Olivier Coulembier<sup>c</sup>, Dujin Wang<sup>b</sup>, Alejandro J. Müller<sup>\*a,d</sup>*

<sup>a</sup>POLYMAT and Polymer Science and Technology Department, University of the Basque Country UPV/EHU, Paseo Manuel de Lardizabal 3, 20018 Donostia-San Sebastián, Spain.

<sup>b</sup>CAS Key Laboratory of Engineering Plastics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China.

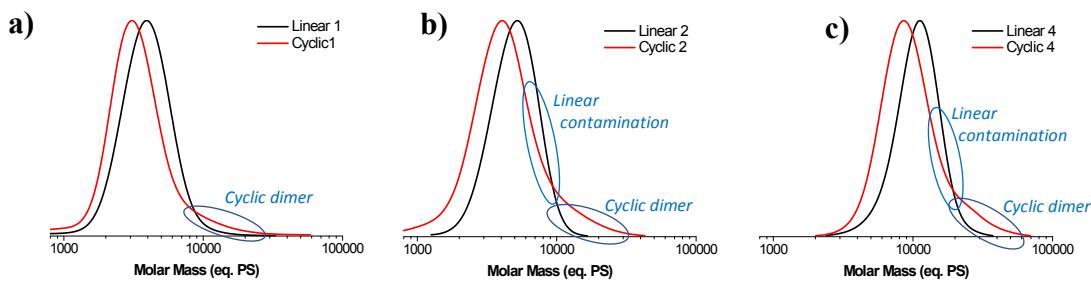
<sup>c</sup>Laboratory of Polymeric and Composite Materials, Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Avenue Maistriau 19, B-7000 Mons, Belgium

<sup>d</sup>IKERBASQUE, Basque Foundation for Science, Bilbao, Spain.

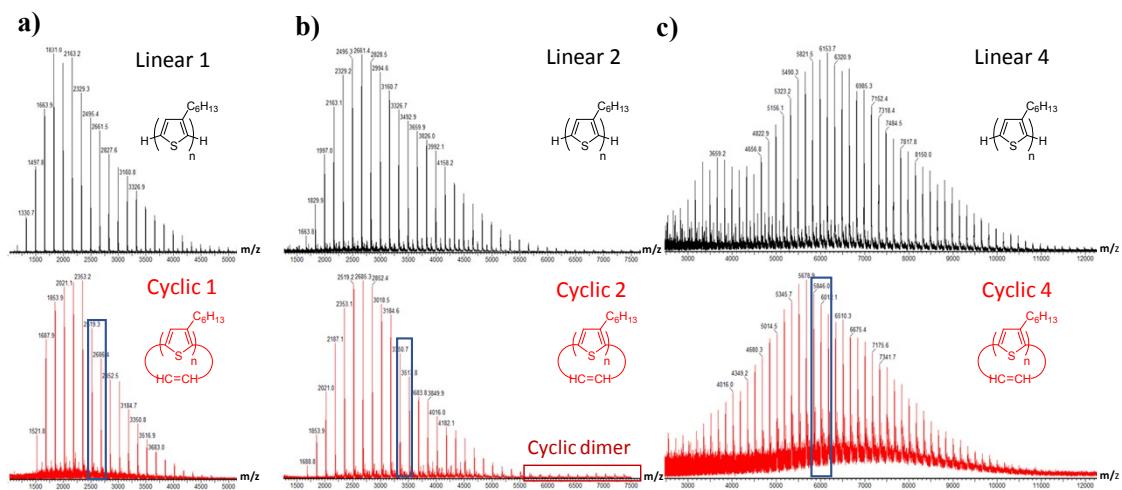
**Corresponding Authors**

\* E-mail [jon.maiz@polymat.eu](mailto:jon.maiz@polymat.eu) (J.M).

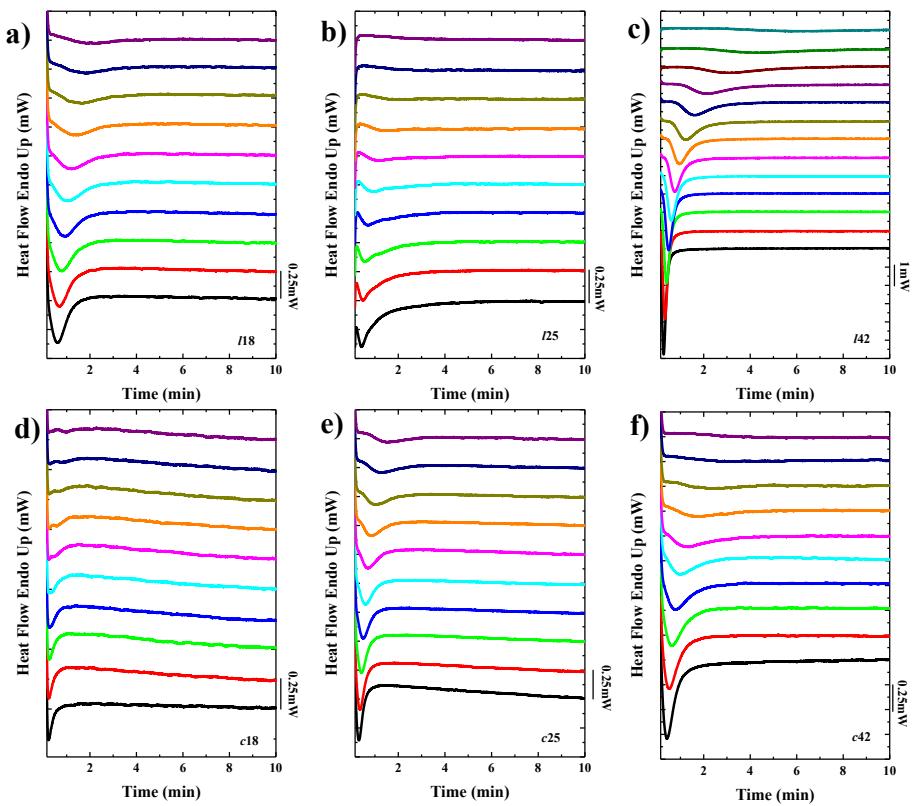
\* E-mail [alejandrojesus.muller@ehu.es](mailto:alejandrojesus.muller@ehu.es) (A.J.M).



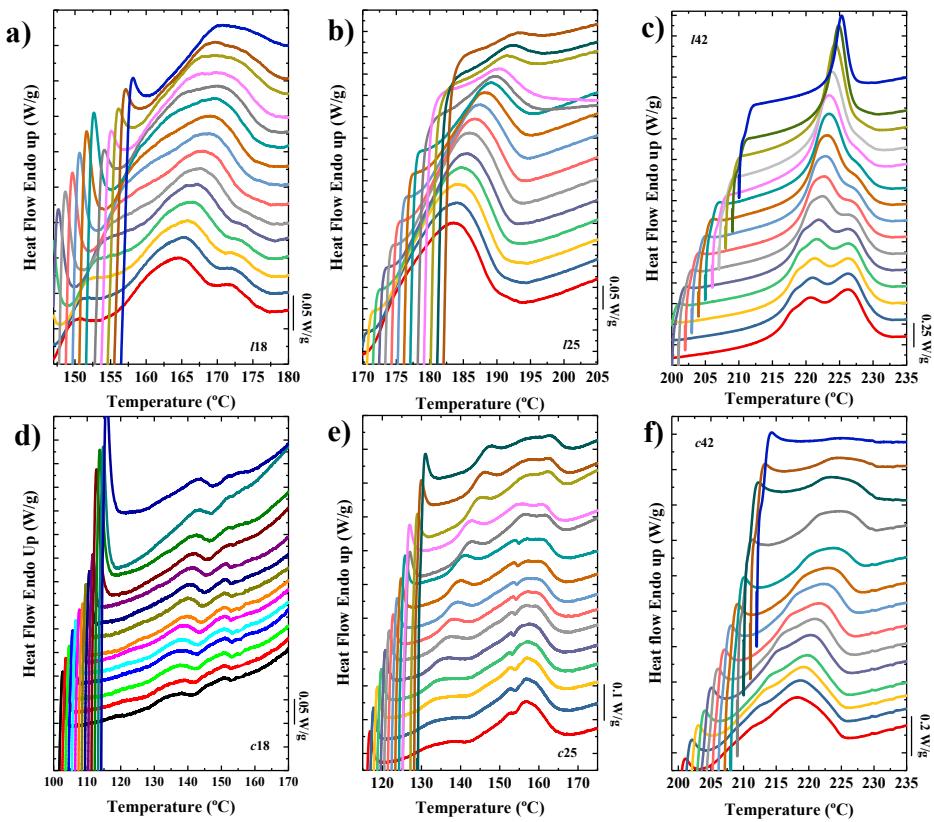
**Figure S1.** GPC profile of Linear (black) and Cyclic (red) polymers. Detection by refractive index plotted with Molar Mass of equivalent polystyrene standards for P3HT samples, a) c18, b) c25 and c) c42.



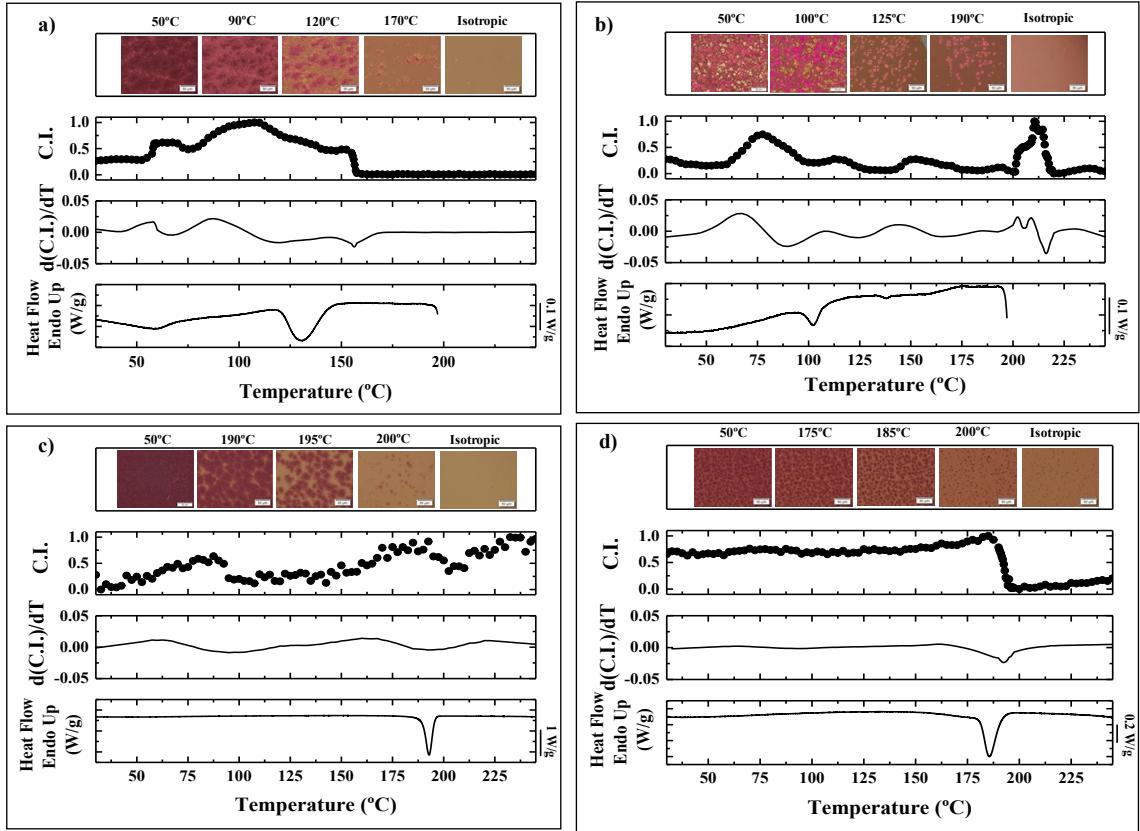
**Figure S2.** MALDI-ToF spectra of linear (black) and cyclic (red) polymers of different molar masses for P3HT samples, a) c18, b) c25 and c) c42.



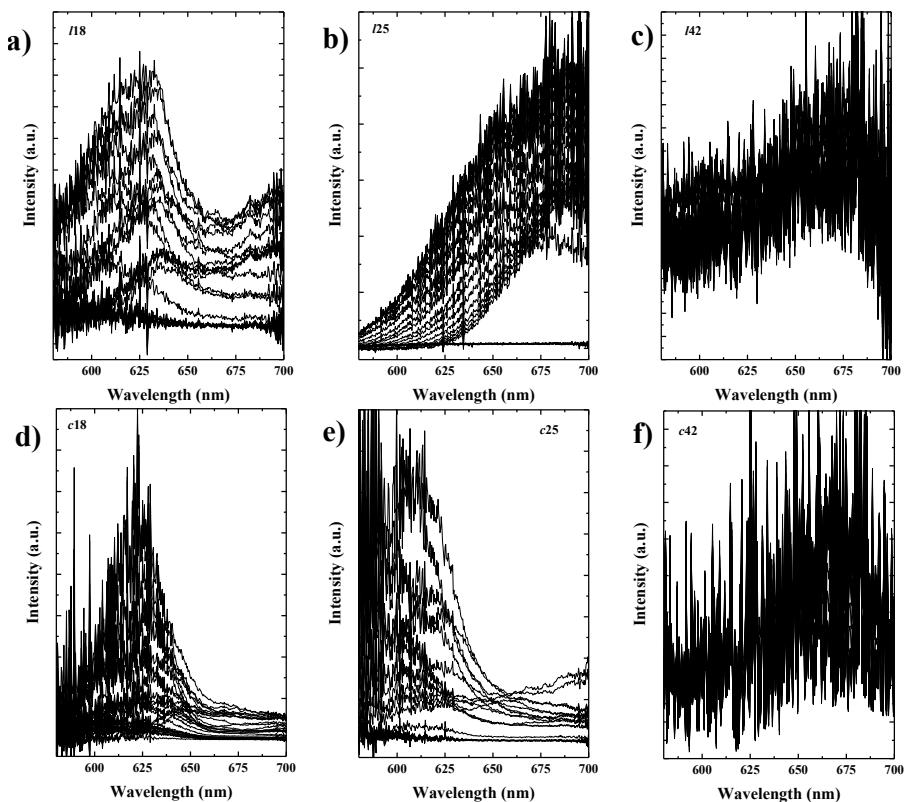
**Figure S3.** Isothermal crystallization experiments as a function of time for P3HT samples, a) *l*18, b) *l*25, c) *l*42, d) *c*18, e) *c*25 and f) *c*42.



**Figure S4.** After isothermal crystallization experiments the observed melting peaks as a function of temperature for P3HT samples, a) *l*18, b) *l*25, c) *l*42, d) *c*18, e) *c*25 and f) *c*42.



**Figure S5.** PLOM-S measurements of the IN transition for a) *l*18 P3HTsample, b) *c*18 P3HT sample, c) *l*42 P3HTsample and d) *c*42 P3HTsample. In each box first, PLOM images from isotropic phase until RT during the transition are shown. The temperatures at which the images were acquired are included in the images. Second, the evolution of the conversion index (C.I., defined as normalized integral value of the transmitted light between 580 and 700 nm) are plotted against temperature. Third,  $d(C.I.)/dT$  from which the TIN are determined as the peak temperatures. Finally, the obtained DSC cooling scans are plotted in order to compare the transitions observed by the two different techniques.



**Figure S6.** The graphs show the relative transmittance spectra recorded during the phase transitions for a) *l18* P3HT, b) *l25* P3HT, c) *l42* P3HT, d) *c18* P3HT, e) *c25* P3HT and f) *c42* P3HT samples.