SUPPLEMENTARY INFORMATION

# Core-crystalline nanoribbons of controlled length via diffusion-limited colloid aggregation

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## Polymerization mechanisms

The thermal curing step consists of an anionic homopolymerization of epoxy monomers initiated by BDMA. As is well known,[1] the reaction proceeds through alkoxide anions that are the active propagating centers in the anionic polymerization. On the other hand, the photocuring step at room temperature takes place via a photoinitiated cationic ring-opening polymerization.[2] Here, visible-light irradiation of the three-component initiator system ($Ph_2ISbF_6$, CQ and EDMAB) results in a strong Brønsted acid which protonates epoxy groups to generate oxonium ions, that are the active propagating sites in the cationic polymerization. In the presence of the superacid, the residual alkoxide ions of the anionic polymerization are rapidly protonated generating alcohols, which can be incorporated into the cationic propagation scheme through the so-called Activated Monomer (AM) mechanism.[3] Compared to the neat epoxy propagation, known as the Activated Chain End (ACE) mechanism, the AM mechanism describes the reaction of epoxy groups with alcohols leading to the incorporation of alcohol into the network while the epoxy chain is terminated and simultaneously a new epoxy group is activated by a released proton.

[1] I. E. Dell'Erba and R. J. J. Williams, *Polym. Eng. Sci.*, 2006, **46**, 351–359.

[2] I. E. dell'Erba, F. D. Martínez, C. E. Hoppe, G. E. Eliçabe, M. Ceolín, I. A. Zucchi and W. F. Schroeder, *Langmuir*, 2017, **33**, 10248–10258.

[3] S. Penczek, *J. Polym. Sci. Part Polym. Chem.*, 2000, **38**, 1919–1933.

## SAXS profiles of the neat PE-*b*-PEO block copolymer at different temperatures

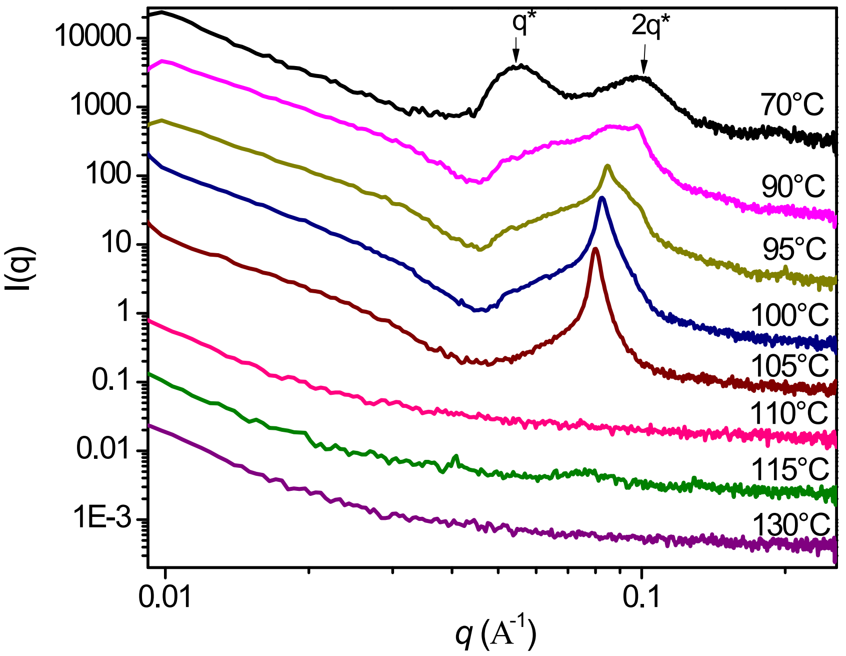

**Figure S1.** SAXS profiles of the PE-*b*-PEO block copolymer ($M_n$ = 1400; 50 wt% PEO, Aldrich Chemical Co.) recorded at different temperatures.

## Conversion of epoxy groups as a function of time

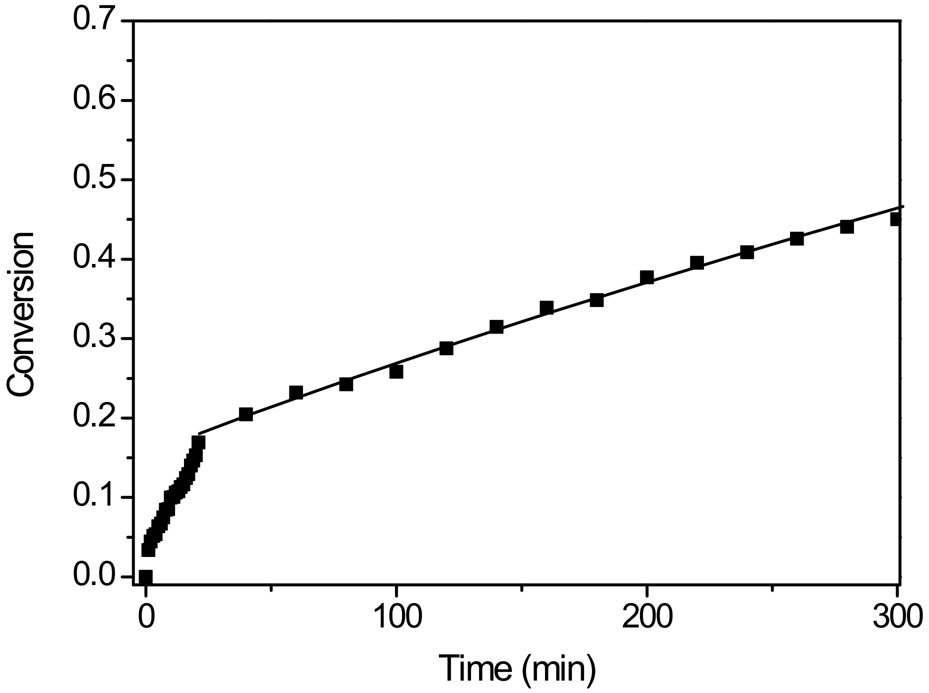

**Figure S2.** Conversion of epoxy groups as a function of time for a mixture containing 10 wt% BCP polymerized through a protocol of two consecutive thermal- and photo-curing steps. In the figure, the first 4.5 h of photocuring are shown.

## TEM image of a material with $x_t = 0$

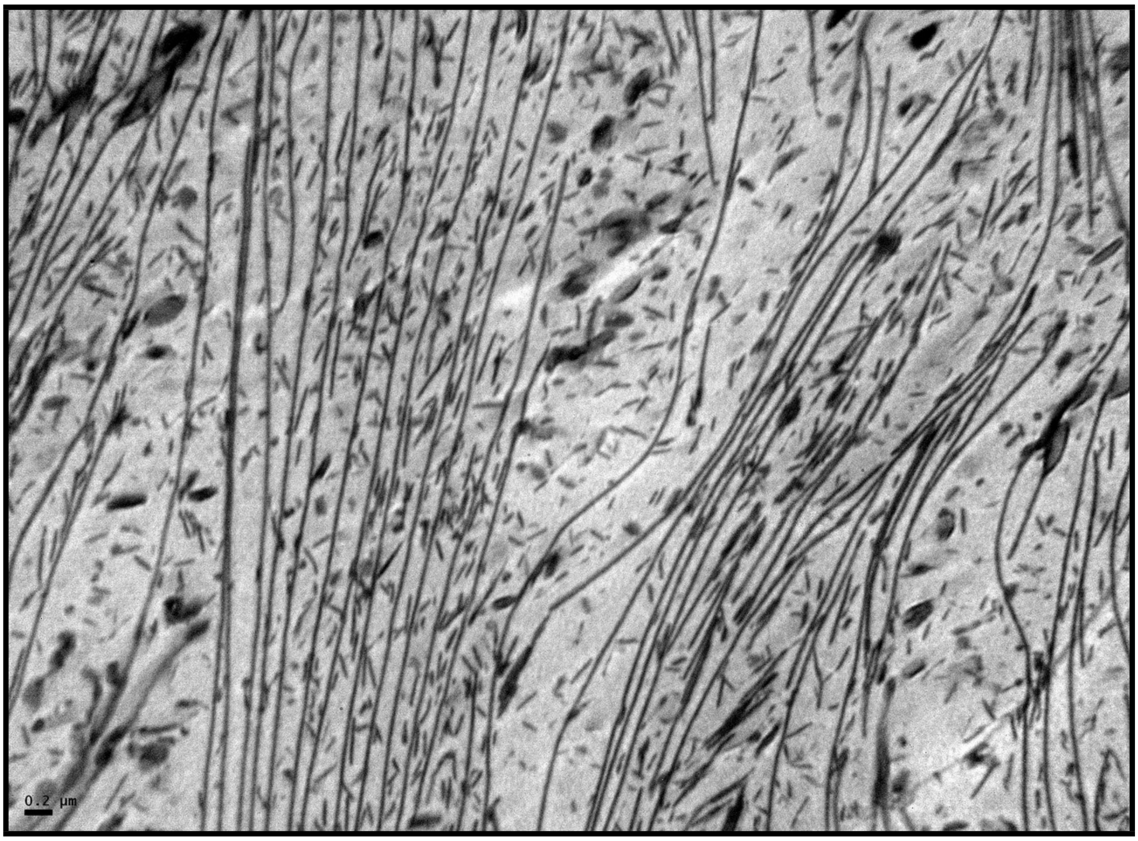

**Figure S3.** TEM image of a fully photocured material ($x_t = 0$).

## TOM micrographs of the sample with 10 wt % BCP before curing

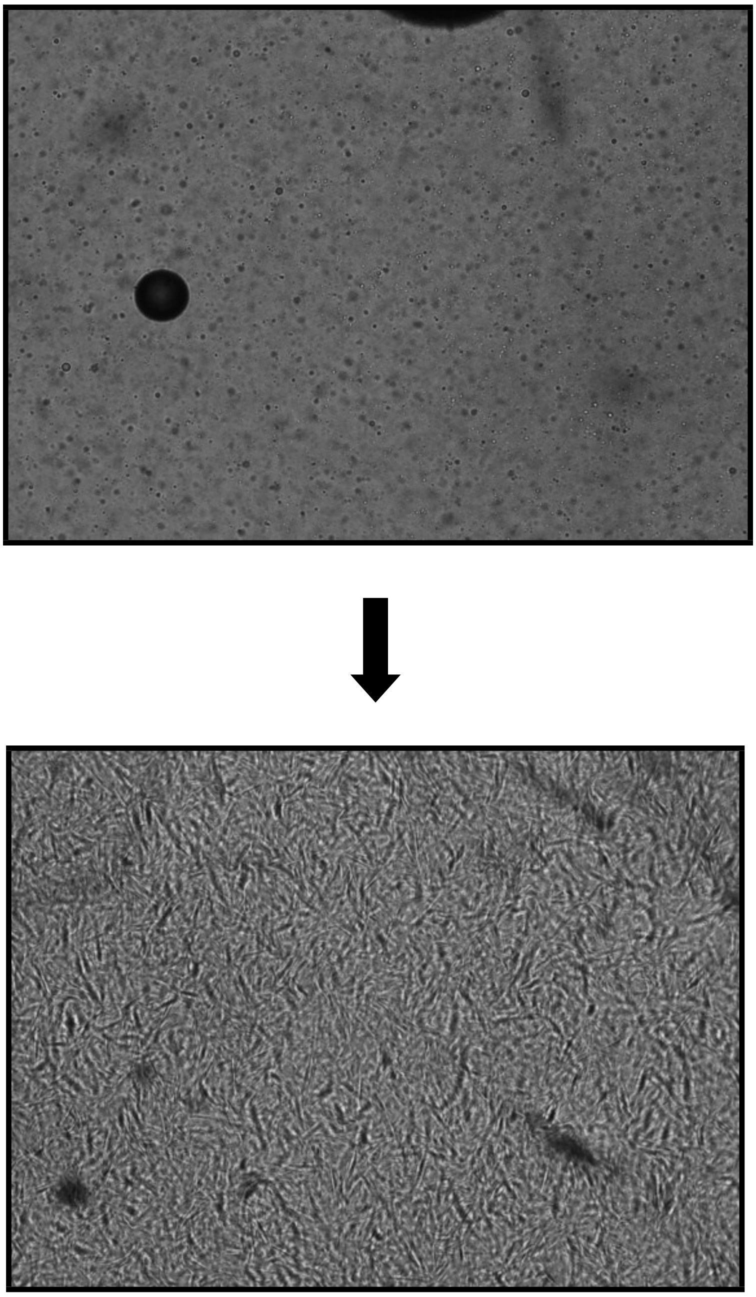

**Figure S4.** TOM micrographs of the sample with 10 wt % BCP before curing: upper image at 120ºC, lower image at room temperature. Micrographs were acquired with a Leica DMLB microscope equipped with a hot stage (Linkam THMS 600).

## Fitting results of SAXS data

SAXS data was fitted using the SASfit software package in the *q*-region from 0.08 to 0.5 nm$^{-1}$. The models used are implemented into the SASfit package and were used without modification (*Kohlbrecher, J. SASfit: A program for fitting simple sructural models to small angle scattering data.* https://kur.web.psi.ch/sans1/SANSSoft/sasfit.pdf. All the scattering were modeled with the HomogeneousXS algorithm, assuming the presence of elongated planar objects. The polydispersity distribution of the length of the objects was included as a LogNormal-distribution. For the case of the scattering profiles corresponding to the samples with $x_t = 0$, 0.3, 0.51 and 0.76 a structure factor (Paracrystalline model) was needed to to account for the correlation maxima observed. The fitting results for the sample containing 10 wt% PE-*b*-PEO are summarized in Table S1.

**Table S1.** Fitting results of SAXS data corresponding to samples obtained with different $x_t$ values.

| **$x_t$** | **Thickness (nm)** | **Stacking Separation (nm)** |
|---|---|---|
| **0** | 8.11 | 24.55 |
| **0.30** | 8.35 | 23.93 |
| **0.51** | 9.08 | 30.23 |
| **0.76** | 8.58 | 31.49 |
| **0.85** | 7.62 | ---- |
| **1.00** | 7.74 | ---- |