Supporting Information

The influence of chain primary structure and topology (branching) on crystallization and thermal properties; the case of polysulfides

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1.1SI. Materials

All chemicals were used as received from suppliers unless otherwise stated. Ethylene sulphide (ES), propylene sulfide (PS), ethyl 2-bromoacetate, sodium methoxide, tributylphosphine, acetyl chloride, potassium chloride, tetrabutylammonium bromide, allyl bromide, thioacetic acid and 2,2′-(ethylenedioxy)diethanethiol were purchased from Sigma-Aldrich (Gillingham, UK). Dichloromethane, dimethylformamide (DMF), methanol and tetrahydrofuran (THF) were purchased from Fisher Scientific UK Ltd (Loughborough, UK). Azobisisobutyronitrile (AIBN) was purchased from Fluka (Gillingham, UK) and recrystallized from warm methanol before use.
1.2SI. Polymer synthesis

Copolymers of propylene sulfide and ethylene sulfide, with different architectures were synthesized according to a literature protocol,\textsuperscript{12} which was recently applied to the preparation of branched chains.\textsuperscript{13}

*Synthesis of initiators.* The initiators were prepared as thioacetates and then deprotected *in situ*; the referenced literature provides the details of the synthetic procedures for the bifunctional \((S,S'-(\text{ethane-1,2-diylbis(oxy)})\text{bis(ethane-2,1-diyl)})\) diethanethioate) (DOD),\textsuperscript{12} the tetra- and octafunctional (respectively tetrakis(3-thioacetyl propanoxy) pentaerythritol and octakis(3-thioacetyl propanoxy)bis) and the 10-, 15- and 20-armed combs, as per previous works\textsuperscript{13} which briefly, were synthesised firstly from the polymerization of thioglycidyl propargyl ether from the bifunctional DOD initiator to produce an oligoalkyne with an average of 10, 15 and 20 alkyne groups per chain, followed by a the [3+2] Cu-catalysed Huisgen reaction with S-(3-azidopropyl)thioacetate to convert alkyne groups into thioacetates.

*Synthesis of polysulfides.* The same procedure was adopted for all monomers. 1 mL of degassed DMF containing 1.8, 0.9 or 0.6 mmol of the thioacetate initiators were added to 9 mL of degassed DMF, then adding 2.66, 1.33 or 0.89 mL of tributylphosphine (always corresponding to 6 equiv.s per thioacetate) for the degree of polymerization (DP) 10, 20 or 30 polysulfides, respectively. 1.05 equiv.s (per thioacete) of sodium methoxide were added as a 0.5 M methanol solution and allowed to react for 10 minutes before the addition of PS/ES (18 mmol of episulfide with the PS:ES molar ratio corresponding to 1:0, 3:1 or 1:1); the amount of episulfide were added in one injection (one-shot addition method) or two injections of 9 mmol episulfide with the second injection 45 minutes after the first injection (repeated addition method). 1 hour after the
last monomer addition, 3 equiv (per thioacetate) of ethyl 2-bromoacetate were added and allowed to react for a further 3 hours. The mixtures were then concentrated in vacuo using a Genevac EZ2 Elite centrifugal evaporator and the residues were dissolved into 40 mL of dichlromethane and extracted against 7 mL of half-saturated brine (x3). The organic phase was separated, dried over Na$_2$SO$_4$, filtered and concentrated as above. The resulting oils were then precipitated into 6 mL of methanol three times, decanted and dried under high vacuum for 24 hours in the Genevac EZ2 evaporator followed by a further 24 hours in the vacuum oven at 40 °C.

1.3SI. Solution characterization

$^1$H NMR spectra were recorded on 1.5 wt%. polymer solutions in deuterated chloroform using a Bruker Avance 300 MHz spectrometer.

Gel permeation chromatography (GPC) was performed using a Polymer Laboratories PL-GPC50 Plus integrated GPC (Polymer Laboratories, UK) assembled with a PLgel 5 μm Guard and two PolyPore 5 μm columns, using triple detection (viscosimetry, refractive index, 2-angle static light scattering). THF was employed as the eluent at a temperature of 30 °C and a flow rate of 1.0 mL.min$^{-1}$. The system was calibrated using polystyrene standards of known molecular weight, intrinsic viscosity and dn/dc.
1.4SI. Self Nucleation

The self-nucleation technique was applied to samples with different chain topology (i.e., linear, stars and combs), as well as different DPs (i.e., DP=10, 20 and 30). Figure S1 shows an example for the linear (a) copolymer, where DSC cooling runs from the applied $T_s$ temperatures are shown, as well as subsequent heating runs. Additionally, the standard DSC cooling and subsequent heating traces are included for comparison purposes.

Figure S1 shows that if $T_s$ is greater or equal to 130 °C, no changes in $T_c$ occurs; hence the polymer is in *Domain I*, or complete melting domain. If a $T_s$ between 120 and 111 °C is employed, a shift in $T_c$ to higher values is observed signalling an increase in nucleation density caused by self-nucleation (see Figure S1A). The polymer is then under *Domain II* (or exclusive self-nucleation *Domain*) since no traces of annealing can be seen in the subsequent melting scans (see Figure S1B). Finally, if the $T_s$ temperature is 110 °C or lower, the sample partially melts and the unmolten crystals are annealed during the 5 min at $T_s$, hence, the polymer falls into *Domain III*. The subsequent melting scans in *Domain III*, reveal three endotherms, two of them were originally present in the standard sample and they are due to the melting of the crystals formed during cooling from $T_s$ melt. The new endotherm is where the annealed crystals melt and it is indicated with arrows in Figure S1B. The melting temperature of the annealed crystals is a linear function of $T_s$, as expected.
Figure S1. Self-nucleation of linear DP30 sample, (A) DSC cooling scans from $T_s$ (after the 5 min isothermal step at $T_s$ was completed) and (B) DSC subsequent heating scans after the coolings shown in (a). Black curves indicate standard scans, blue curves indicate Domain I, green curves indicate Domain II and red curves indicate Domain III. Arrows indicated the annealing peak.

The minimum temperature within Domain II is known as the ideal self-nucleation temperature because it is the $T_s$ value that provokes maximum self-nucleation without annealing. It is denoted: $T_{s, \text{ideal}}$. Based on the SN results, the sample with the highest $T_{s, \text{ideal}}$ value (i.e., $T_{s, \text{ideal}}=111 \, ^\circ\text{C}$) was the linear sample with the largest DP (i.e., linear (a)) with DP of 30). Hence, this $T_{s, \text{ideal}}$ was employed as the starting point for all SSA thermal fractionation experiments.
1.5SI. Morphology by PLOM

All the materials exhibited a granular texture and high nucleation density. Even though we tried to perform crystallization at the highest possible temperatures (conditions that favor low nucleation rates) and for long times, as soon as the material started to crystallize the number of microscopic spherulites (with sizes close to 1 micron) was too large. Hence, for these copolymers we found impossible to determine spherulitic growth rates, as their growth cannot be followed in an optical microscope given that their size is too small and they cease to grow as soon as they impinged on one another. For that reason, we have discussed the evidences from the point of view of nucleation density in the main text of the paper.

![Linear (a)](image1) ![Linear (b)](image2)

**Figure S2.** Polarized light optical micrographs of linear/one-shot (left) and linear/repeated addition (right) copolymers with a fixed DP of 30 (resp. $La_{(PS_{15}-ES_{15})_2}$ and $Lb_{(PS_{15}-ES_{15})_2}$), growing at 30 °C.
Figure S3. Polarized light optical micrographs showing the granular texture of (A) linear; stars of (B) 4 and (C) 8 arms, and combs of (D) 10 (E) 15 and (F) 20 arms samples with a fixed DP of 30 (resp. $La_{(PS_{15}-ES_{15})_2}$, $S_{(PS_{15}-ES_{15})_4}$, $S_{(PS_{15}-ES_{15})_8}$, $C_{(PS_{15}-ES_{15})_{10}}$, $C_{(PS_{15}-ES_{15})_{15}}$ and $C_{(PS_{15}-ES_{15})_{20}}$) growing at 30 ºC.

1.6SI. Standard DSC scans

In Figure S4, combs of 10, 15 and 20 arms with a fixed DP of 30 are compared. Additionally, the influence of the variation of DP is analysed for the comb with 15 arms. For comparison purposes, the linear sample (DP=30) is also included in Figure S4.
**Figure S4.** DSC (A) cooling and (B) heating scans for linear and comb copolymers with different number of arms (i.e., 10, 15 and 20) and a fixed DP of 30. A variable DP (i.e., 10, 20 and 30) is presented for the comb with 15 arms.

It is interesting to compare the linear and comb samples in Figure 5. The linear sample has a higher onset crystallization temperature and a higher final melting temperature than any of the combs. It should be remembered that DP values are reported per arm.

**1.7SI Wide Angle X-ray Scattering (WAXS)**

WAXS patterns were taken at RT for all the samples (linear, star and combs) with a fixed DP of 30.
As we mentioned in the article, the WAXS patterns of all the samples show similar diffraction peaks at 2θ of 20 and 24°. The increase of the number of arms do not shift significantly these peaks.

In order to study the thermal behaviour of these peaks, temperature-dependent X-rays study was performed.

Figure S6 shows the WAXS patterns at selected temperatures for the linear (see Figure S6A), 8 arm-star (see Figure S6B) and 15-arm comb (see Figure S6C) copolymers. Figure S7 shows the WAXS patterns at selected temperatures (the experiments were performed in the ALBA synchrotron) for the La sample, in order to elucidated the origin of the multiple peaks observed in the DSC experiments.
**Figure S6.** WAXS patterns of the samples taken at the indicated temperatures for (A) linear (a); (B) star-4 arms and (C) comb 15-arms copolymers with DP of 30.

![WAXS patterns taken during heating](image1)

**Figure S7.** Top. WAXS patterns taken during heating (at 20 ºC/min) the copolymer sample \( L_a(PS_{15}-ES_{15})_2 \) after cooling from the melt at 20 ºC/min. Bottom. Normalized height of the main peak as a function of the temperature.

![Normalized Height of the peak](image2)
Figure S6 shows a decrease of intensity with the increase of the temperature, which is related with the decrease on the $X_c$ of the samples, because part of the crystals start to melt. The $2\theta$ and $d$ spacings calculated by Bragg’s law are list in Table S1.

WAXS and SAXS experiments (Figure S7 and S9, respectively) were performed at the ALBA synchrotron during heating of the samples at the same rate employed in our DSC experiments. These WAXS pattern show reflections from only one type of unit cell. If the intensity of the main peak is plotted as a function of temperature, a monotonic reduction in intensity is observed, that would be characteristic of a single type of unit cell melting. As the degree of crystallinity is too low, totally ruling out simultaneous melting and recrystallization processes is difficult, but these processes are certainly not apparent in the collected data. (see Figure S7). DSC experiments were also performed as a function of cooling rate and the trends did not reveal any reorganization process during the heating scan. From DSC, SAXS and WAXS we conclude that melting and reorganization during the heating scan if present is not very significant and the origin of the double melting peak reflects a wide range of crystallizable sequences with a distribution that tends to bimodality.

**Table S1.** Calculated diffraction spacings ($d$) according to the Bragg’s law for linear (a), star 4-arms and comb samples of 10, 15 and 20 arms at different temperatures.

| Temperature (°C) | 2θ (º) | d (nm) |
|-----------------|--------|--------|
|                 | 2      | 4      | 10     | 15     | 20     | 2      | 4      | 10     | 15     | 20     |
| RT              | 20.2   | 20.0   | 19.9   | 20.3   | 19.8   | 0.439  | 0.445  | 0.446  | 0.437  | 0.448  |
|                 | 24.0   | 23.9   | 23.9   | 24.2   | 24.1   | 0.371  | 0.373  | 0.372  | 0.367  | 0.369  |
| 140             | -      | -      | 18.4   | 18.7   | 18.8   | -      | -      | 0.482  | 0.474  | 0.471  |
| -40             | -      | -      | 20.2   | 20.3   | 20.2   | -      | -      | 0.439  | 0.437  | 0.439  |
|                 | 23.9   | 24.1   | 24.0   |        |        | 0.372  | 0.369  | 0.370  |        |        |
| 30              | 20.2   | 20.1   | -      | -      | -      | 0.439  | 0.442  | -      | -      | -      |

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| Temperature (°C) | / | / | / | / | / | / | / |
|-----------------|---|---|---|---|---|---|---|
| 40              | 19.2 | - | - | - | - | - | 0.462 |
|                 |     |   |   |   |   |   | 24.6 |
| 45              |     |   |   | 20 | 19.9 | - | - | 0.443 |
|                 |     |   |   |     |       |   |   | 24 | 24.2 |
| 50              | 20.5 | 20.1 | - | - | - | 0.434 | 0.441 |
|                 |     |   |   |     |     |   |   | 24.3 | 23.8 |
| 70              | 19.7 | 19.6 | - | - | - | 0.451 | 0.452 |
|                 |     |   |   |     |     |   |   | 24.3 |     |
| 90              | 19.4 | 19.3 | - | - | - | 0.458 | 0.461 |
| 110             | 18.9 | 19.1 | 18.5 | 18.9 | 19.2 | 0.480 | 0.464 | 0.479 | 0.469 | 0.462 |
| post            | 20.2 | 20.1 | - | - | - | 0.440 | 0.441 |
|                 |     |   |   |     |     |   |   | 24.1 | 24.0 |

1.8SI. Temperature Dependent SAXS

Temperature-dependent SAXS experiments were performed with a similar protocol to those used in the temperature-dependent WAXS experiments.

Figure S8 shows a decrease in the intensity of the higher q value SAXS maximum. It is expected that the $d^*$ values, which are labelled in Figure S8 increase with the increase of temperature due to annealing effects. However, the viscosity of the sample could generate deviations of the expected behaviour.

Figure S8F shows an example of the original data ($I$ vs $q$), which is equivalent to Figure S8A (represented as $Iq^2$ as a function of $q$)
**Figure S8.** SAXS patterns of (A) linear (a); (B) star 4-arms; (C) comb 10-arms and (D) comb 15-arms copolymers with DP of 30 taken at the indicated temperatures. The $d^*$-value obtained from the maximum is labelled. (F) $I$ vs $q$ curve (original data after background corrections) taken for the linear sample with DP 30 (this data was transformed into $Iq^2$ vs $q$ in Figure S8A).

The SAXS patterns reveal a very wide reflection (i.e., wide peak) at low temperatures, indicating that a wide distribution of long periods exists in the sample. This wide peak disappears as temperature is increased (see Figure 2), due to the lack of crystalline lamellar staking when the amorphous content in the sample increases. Note that lamellar stacks are the responsible for generating the long period signal. The SAXS patterns shown in Figure 2 are compatible with a wide distribution of long periods, that also reflect a wide distribution of lamellar thickness (typical of a copolymer with a wide
distribution of crystallizable sequence lengths), hence the wide distribution of melting points.

Figure S9. SAXS patterns taken during heating of the L_a_(PS_{15}-ES_{15})_2 after cooling down the samples at 20 °C/min.