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SAXS patterns were obtained with the detector placed at two different sample-to-detector distances (S2DD) to be able to measure scattering over a wider q-range. Long distance measurements were able to span a q-range of 0.04505 nm^{-1} to 0.99899 nm^{-1}; short distance measurements a q-range of 0.04104 nm^{-1} to 5.30263 nm^{-1}.

The following report describes an attempt to match the SAXS patterns obtained in separate but similar experiments with different sample-to-detector distances.

Description of samples

Poly(3-hexylthiophene) (P3HT) with M_n = 50 kg mol^{-1} PDI of 2.1 and regioregularity of 99% (OS2100, Plexcore, Plextronics) was mixed with toluene in the required concentration by stirring at high temperature (70C).

The sample was placed in a temperature controllable liquid cell closed off by mica windows and with an optical path length of 1 mm.

Background measurement: TOLUENE

The results are represented in a logarithmic plot of q (nm^{-1}) vs. scattered intensity in arbitrary units. The results from toluene are used to determine the q-range in which meaningful overlap between both sets of experiments can be expected.

The largest overlap in q-values between two toluene SAXS patterns was obtained between a long distance pattern recorded at 11C (A56) and a short distance pattern of 25C (B01). In this case, the q-range in which overlap could be reached is from approximately 0.25 (0.3) nm^{-1} up to 1 nm^{-1}. Overlap is reached by dividing the scattered intensity values at the short distance by a value of 51. This is allowed since the scattering intensities are not absolute. Figures 1 to 3 show respectively the overlap of these SAXS patterns, the overlap attempt between B01 and a long distance pattern at 64C (A52) and one between B01 and the average of A52 and A56. In Table 1, the recorded toluene SAXS patterns and their specifications are listed.

Table 1. Recorded SAXS patterns for toluene with specifications.

Name		Acquisition Temperature [C]	q-range [nm-1]	Exposure Time [s]
Long Distance	A52	64	0.04505 - 0.99899	30
	A56	11	0.04505 - 0.99899	30
Short Distance	B01	23	0.04104 - 5.30263	30

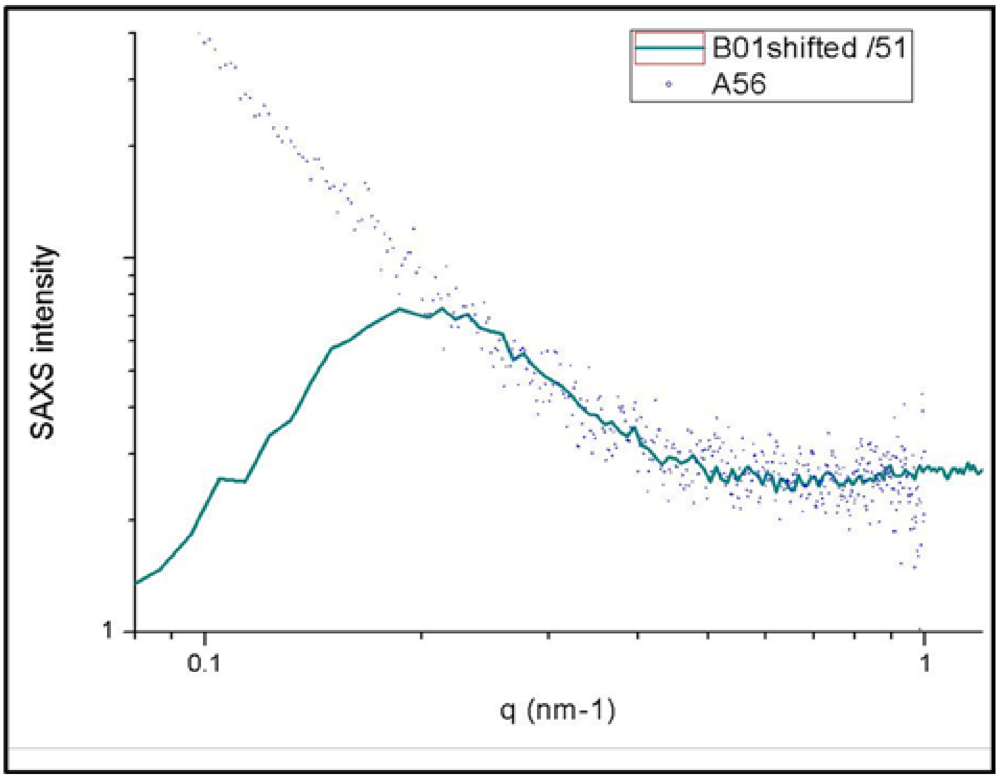

Figure 1. SAXS patterns A56 and B01 in logarithmic plot.

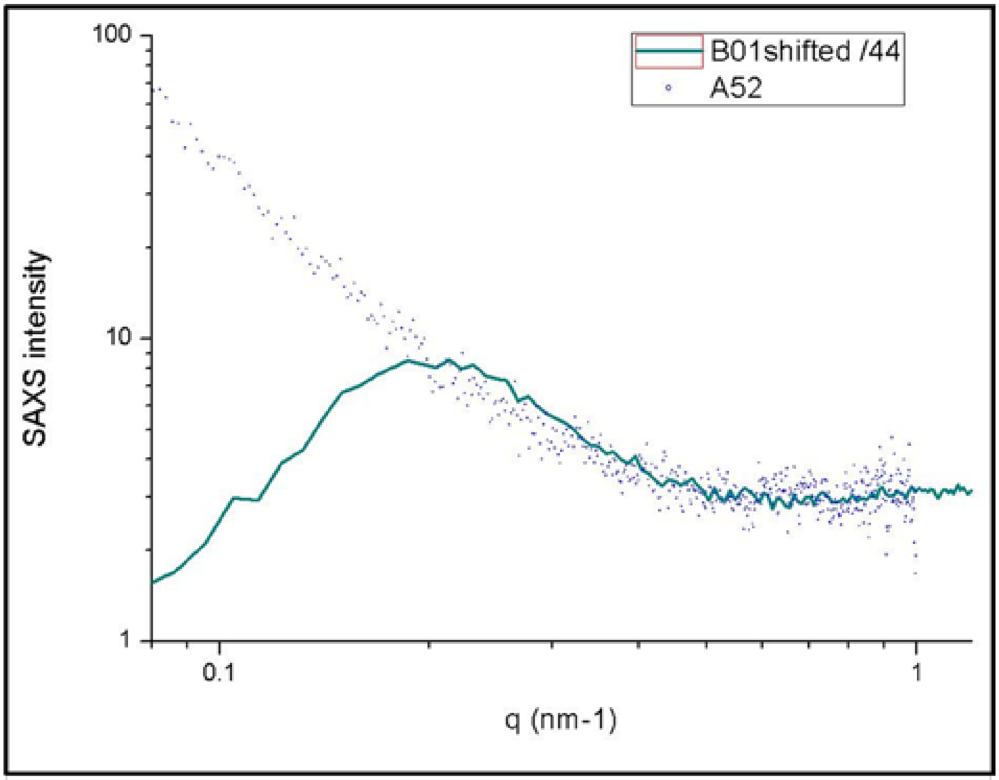

Figure 2. SAXS patterns A52 and B01 in logarithmic plot.

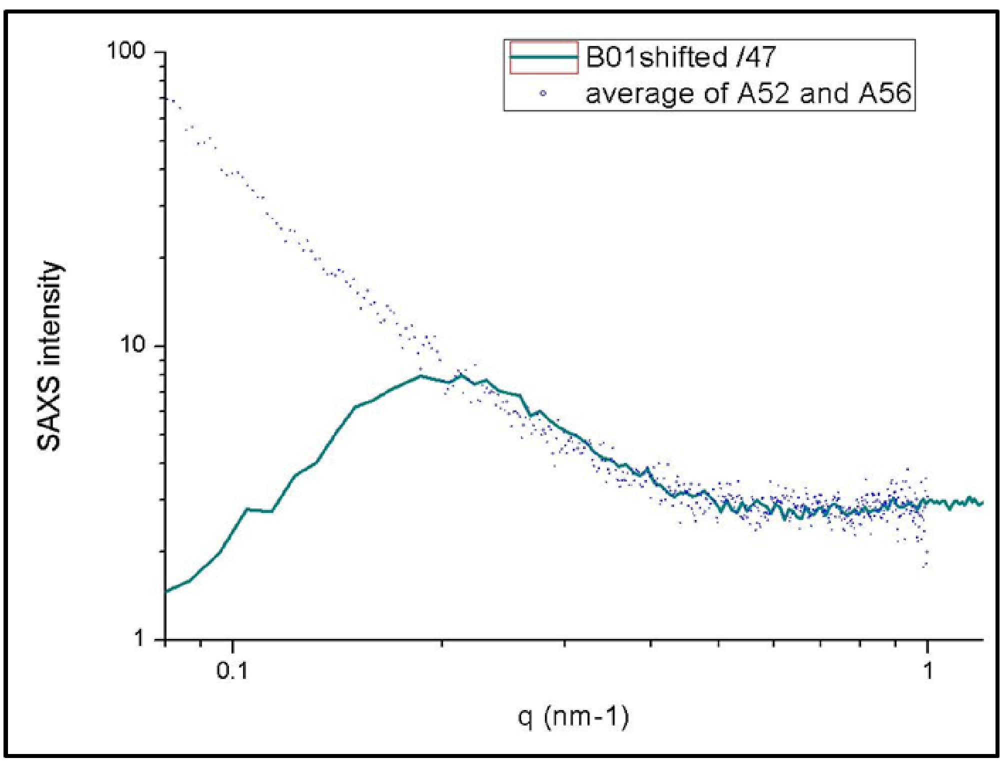

Figure 3. SAXS patterns of the average of A52 and A56; and B01 in logarithmic plot.

Independent of the used toluene results, the overlap between the 2 sets of data (long and short distances) is satisfactory. The difference between long and short distances in the low q-range can be explained as follows: the intensities measured at low q ($q < \sim 0.2\ nm^{-1}$) are at the short S2DD situated very closely to the beam stop and cannot be accurately measured at this short S2DD.

We expect that temperature dependent series of SAXS patterns for different solution samples can be matched in a similar way. Below, this is illustrated for the following samples: 1%, 2% and 5% P3HT in toluene.

Issues with temperature:

The actual temperature of the sample at a certain frame is not monitored accurately in the experiment. In the experiment the sample is cooled by a certain rate from a starting to an ending temperature. It is hoped for that by using the same heating/cooling rates that the temperatures of the different frames will match. However, this is not absolutely certain. The sample temperature per frame was estimated by the temperature profile which was set up during the experiment (as will be indicated below).

1% P3HT in Toluene

Sample information: 8.3 mg P3HT (OS2100) was mixed with 0.830 g toluene at elevated temperature and while stirring, resulting in effective sample concentration of 1%.

The temperature program followed started at 35C and cooled down to 5C at a rate of 1C/min and consecutive isothermal period at 5C, as is shown in Figure 4.

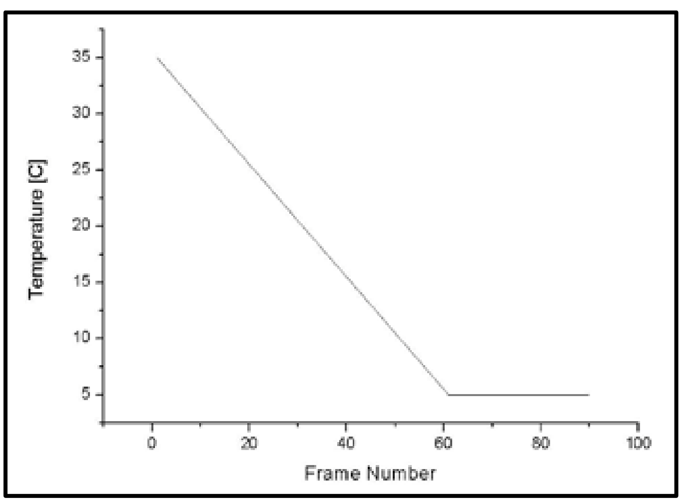

Figure 4. Imposed temperature profile and expected connection with frame numbers.

In Table 2 the recorded SAXS patterns for the 1% sample are listed.

Table 2. List of recorded SAXS series for 1% P3HT in toluene.

Name		Acquisition Temperature [C]	q-range [nm-1]	Exposure Time [s]
Long Distance	A60	35 to 5 (1C/min), isotherm at 5	0.04505 - 0.99899	30
Short Distance	B09	35 to 5 (1C/min), isotherm at 5	0.04104 - 5.30263	30

To compare the overall signal evolution in long distance and short distance experiments on the same sample, the invariant of the long distance series and the scattering intensity evolution at q 0.5 nm^{-1} for short distance will be plotted together. The invariant of the short distance experiments could not be used for this, as can be understood when looking at their representation in Figure 5. What causes the shape of this invariant in contrast to the invariant of the long S2DD experiments is not clear.

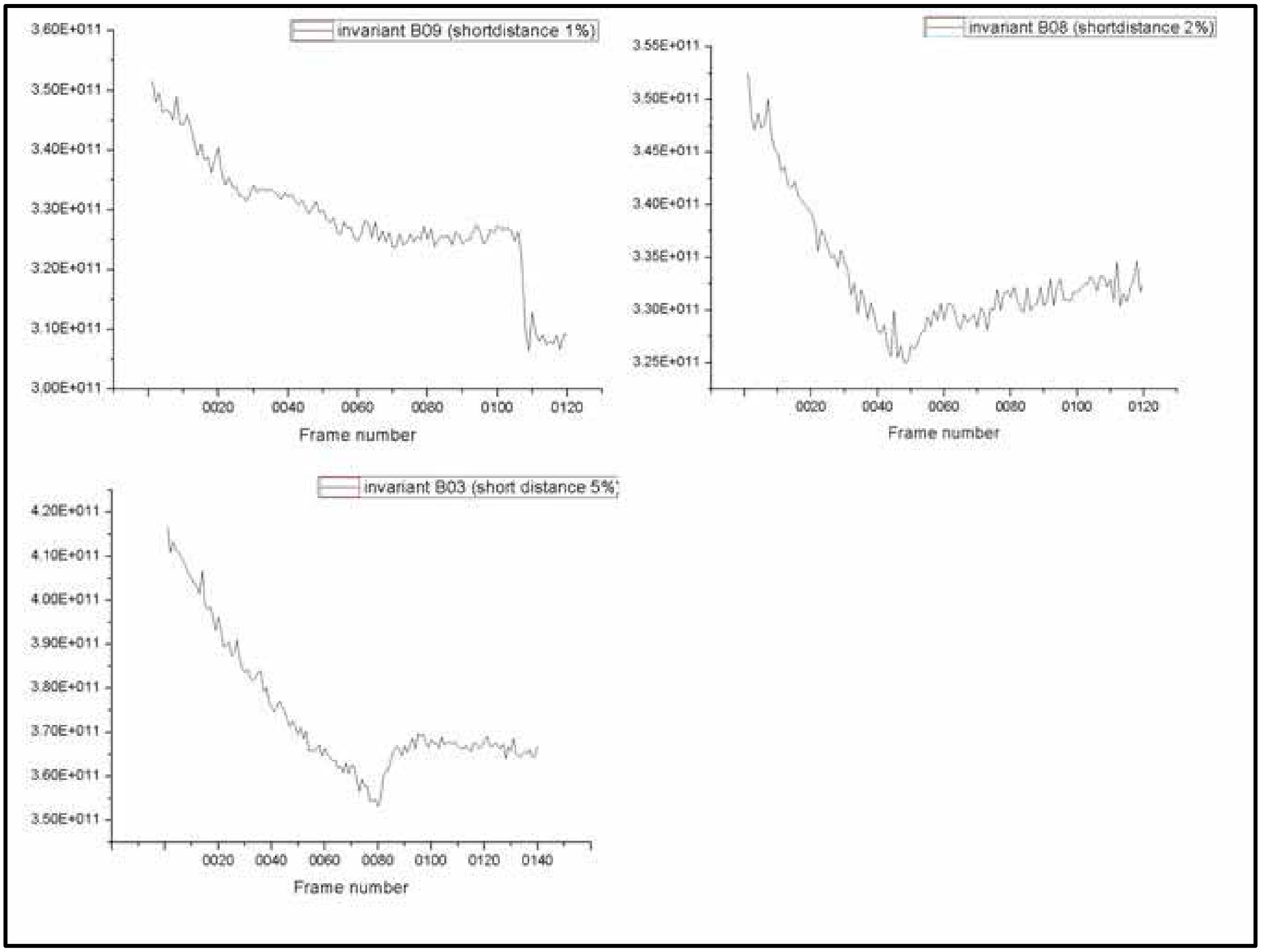

Figure 5. Plots of the invariant of short S2DD measurements for the different samples (1%, 2%, 5%).

Figure 6 shows the overall evolution of the SAXS signal throughout the recorded series on the 1% P3HT sample. For long distance measurements the invariant is shown (black circles) while for short distance the signal evolution at a q-value of 0.5 nm^{-1} is plotted (red triangles).

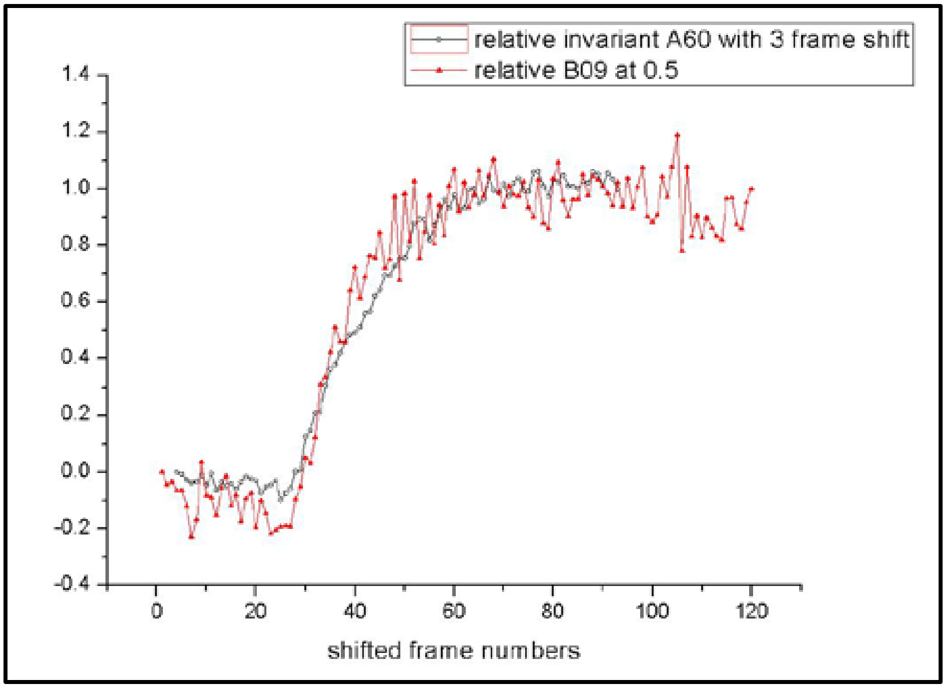

Figure 6. Relative signal evolution in long distance (black, invariant) and short distance (red, scattering intensity at q 0.5 nm-1) experiments for the 1% P3HT in toluene sample.

When matching the frame numbers in both series by the last frame before the (fairly sudden) signal increase, a small offset of approximately 3 frames can be detected. The frame numbers are matched by this 3-frame offset. Four pairs of frames which are chosen are located in different parts of the temperature series, assuring that overlap is investigated for all frames in the experimental series. Figure 7 shows a plot of the 4 frames of each series which are overlapped by shifting the SAXS curves of B09 by dividing through a value of 44. Frames A60_1 and B09_4 are plotted in black, frames A60_30 and B09_33 in red, frames A60_46 and B09_49 in green and frames A60_90 and B09_93 in blue. From Figure 7 it can be observed that for all frames acceptable overlap can be found in the q-range of 0.3 nm^{-1} to 1 nm^{-1}. The difficulty of finding good overlap is more pronounced in the samples with higher concentrations of P3HT, as will be shown in the following sections.

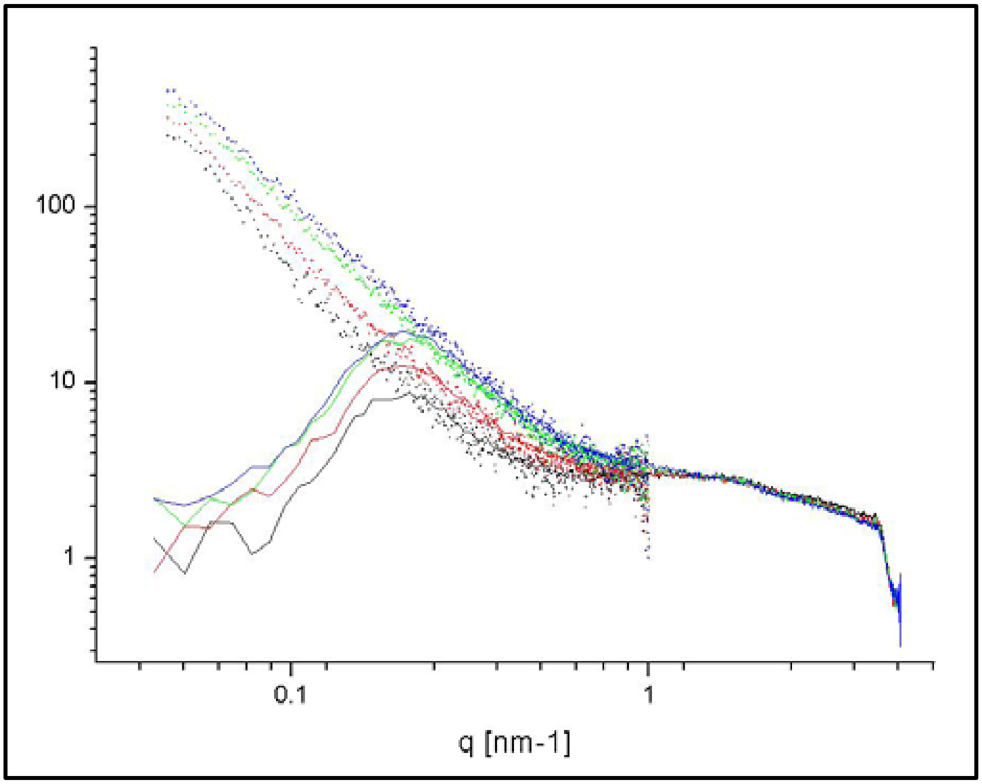

Figure 7. Overlapping SAXS patterns for 1% P3HT in toluene. Frames A60_1 and B09_4 in black, frames A60_30 and B09_33 in red, frames A60_46 and B09_49 in green and frames A60_90 and B09_93 in blue, with long S2DD represented in scatter and short S2DD by solid lines and shifted by division through a value of 44.

2% P3HT in Toluene

Sample information: 20.7 mg P3HT (OS2100) was mixed with 1.001 g toluene at elevated temperature, resulting in a effective sample concentration of 2.07%.

The temperature program followed started at 35C and cooled down to 5C at a rate of 1C/min and consecutive isothermal period at 5C, as shown above in Figure 4.

In Table 3 the recorded SAXS patterns for the 2% sample are listed.

Table 3. List of SAXS series recorded for 2% P3HT in toluene with specificatons.

Name		Acquisition Temperature [C]	q-range [nm-1]	Exposure Time [s]
Long Distance	A61	35 to 5 (1C/min), isotherm at 5	0.04505 - 0.99899	30
Short Distance	B08	35 to 5 (1C/min), isotherm at 5	0.04104 - 5.30263	30

Figures 8 shows the overall signal evolution throughout the temperature program for long distance (invariant of A61) and short distance (SAXS intensity at q 0.5nm^{-1} for B08) experiments. A significant frame shift was observed and in order to achieve overlap between the intensity evolution of both experiments, the series obtained at long S2DD was shifted by 35 frames, notwithstanding the attempt to impose an identical temperature profile to the sample in both experiments. Question remains as to what causes this large offset and what the resulting temperatures are of the recorded scattering patterns.

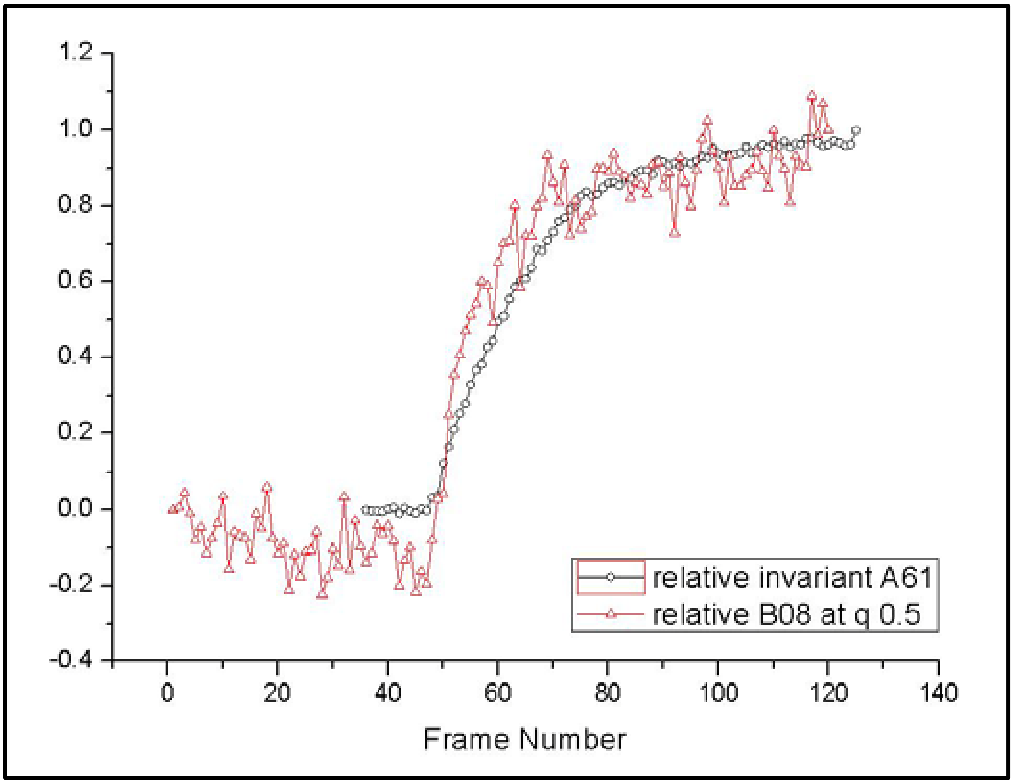

Figure 8. Plot overlaying the relative signal evolution of long S2DD (black, invariant) and short S2DD (red, scattering intensity at q 0.5 nm^{-1}) distance for 2% P3HT in toluene with a 35 frame shift to find reasonable overlap.

In an attempt to find overlap with a single shift factor for these series, frames of both series are matched according to the 35 frame offset described above, resulting in pair wise comparison as listed in Table 4. The shift factor was chosen such that the overlap is maximal for the first pair (A61_5 and B08_40) and results in a division by 39. The curves are shown in Figure 9.

Table 4. Pair wise matching of frames of the series at long distance and short distance, with indicated color with which each pair is portrayed in Figure 9.

	A61	B08	color in Figure 9
Frame Number	5	40	cyan
	15	50	blue
	20	55	green
	35	70	red
	60	95	black

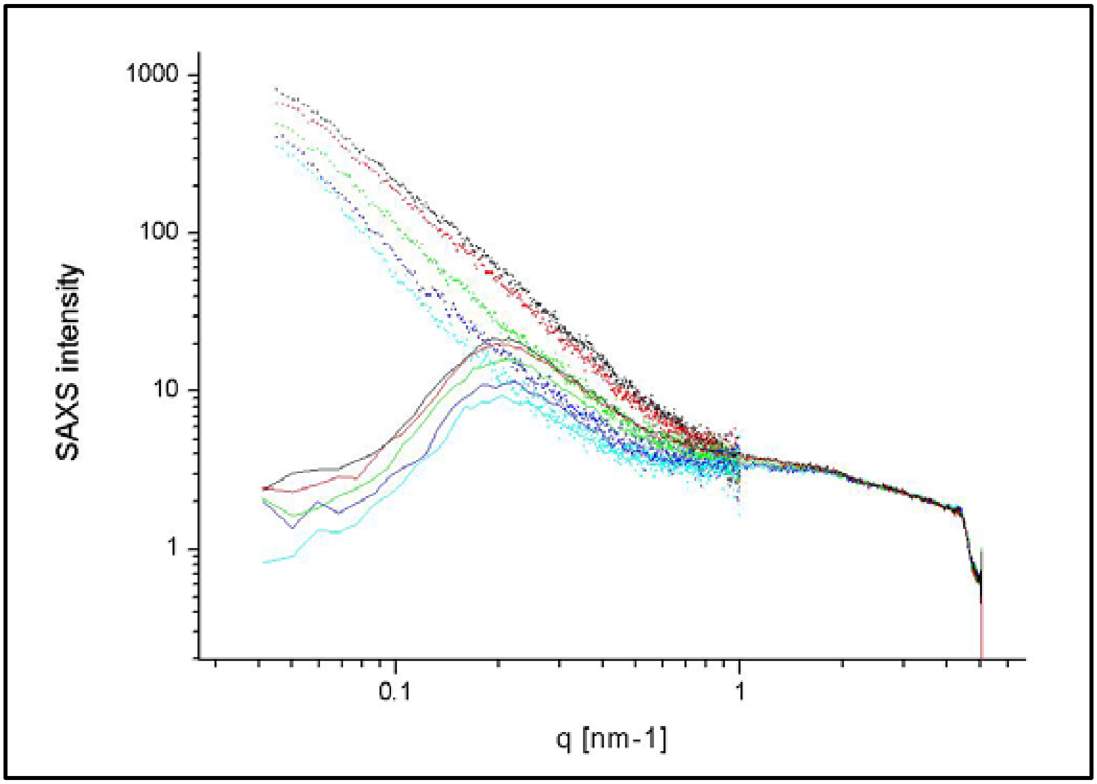

Figure 9. SAXS patterns of A61 (scattered data points with frames 5 in cyan, 15 in blue, 20 in green, 35 in red, 60 in black) and B08 (solid lines with frames 40 in cyan, 50 in blue, 55 in green, 70 in red, 95 in black) shifted in attempt to find overlap by division of B08 data by 39.

When looking only at the first set, frames A61_5 and B08_40, for which overlap is optimized, a q-range similar as the one in the toluene sample and the 1% sample can be matched by shifting. This is shown in Figure 10 for q approximately 0.3 nm^{-1} to 1 nm^{-1}. This range is rapidly decreasing when moving to frames positioned further in the temperature series. It can be noticed however that when looking at both series individually, the evolution of the signal is very comparable between the two experiments, as was expected from Figure 8. In the case of Figure 9, a single shift factor was used for the complete series. In Figures 11 to 15 on the other hand, a different shift factor is used to match each pair individually as well as possible. Figure 16 shows the overlay of these plots.

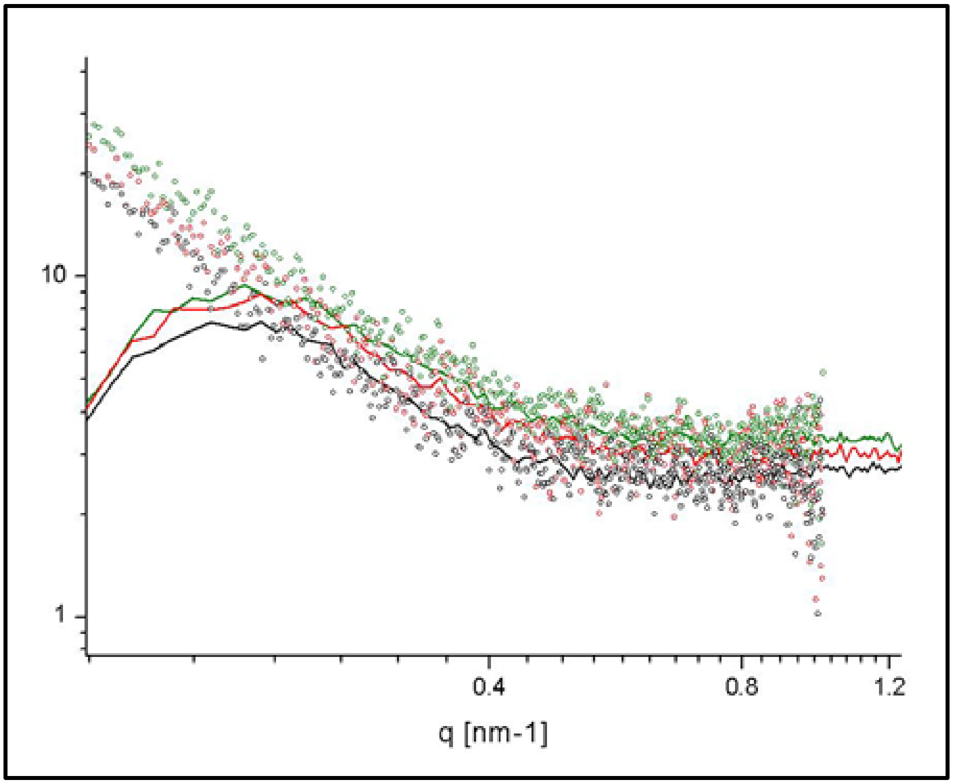

Figure 10. SAXS patterns of toluene, 1% and 2% samples at the highest sample temperature showing similar overlap regions (~0.3 nm^{-1} to 1 nm^{-1}).

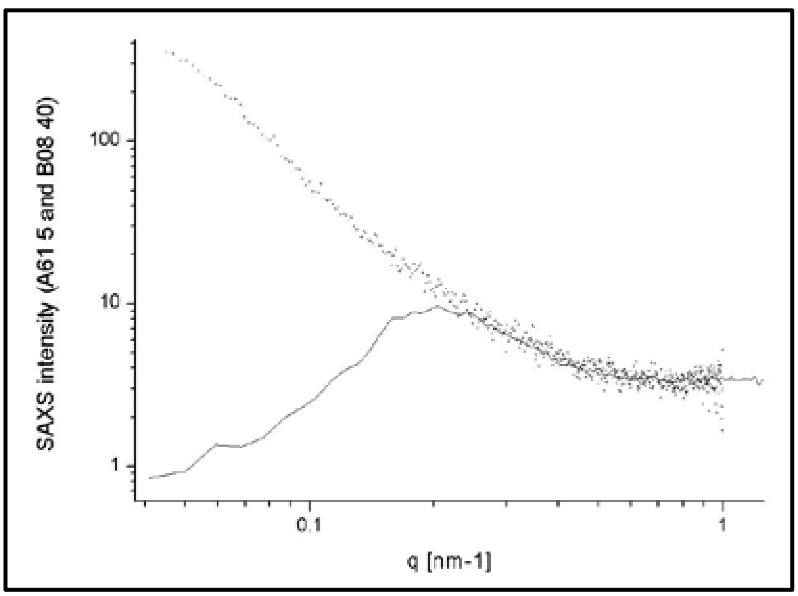

Figure 11. SAXS patterns of A61 frame 5 and B08 frame 40, partially overlapping by shifting B08 by dividing through 38. Overlap was reached in the range of 0.25 nm^{-1} to 1 nm^{-1}.

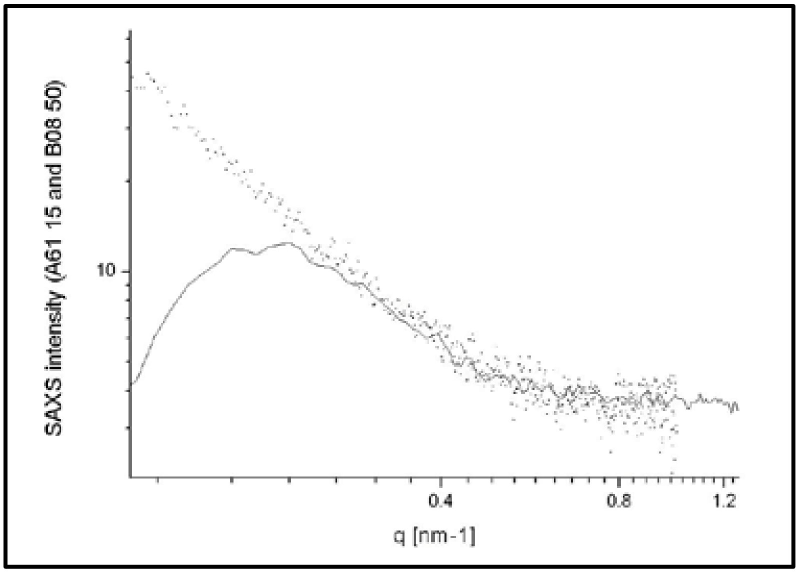

Figure 12. SAXS patterns of A61 frame 15 and B08 frame 50, partially overlapping by shifting B08 by dividing through 36. Overlap was reached in the range of 0.3 nm^{-1} to 1 nm^{-1}.

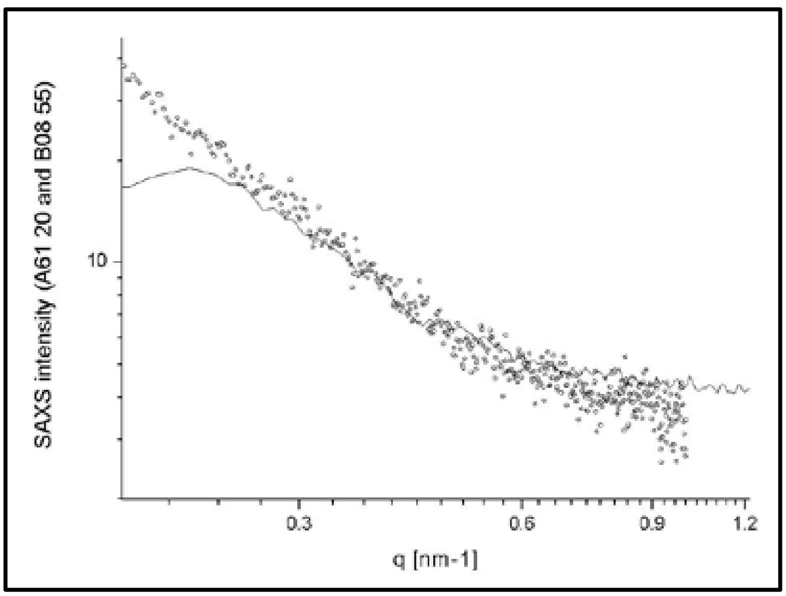

Figure 13. SAXS patterns of A61 frame 20 and B08 frame 55, partially overlapping by shifting B08 by division through 33.

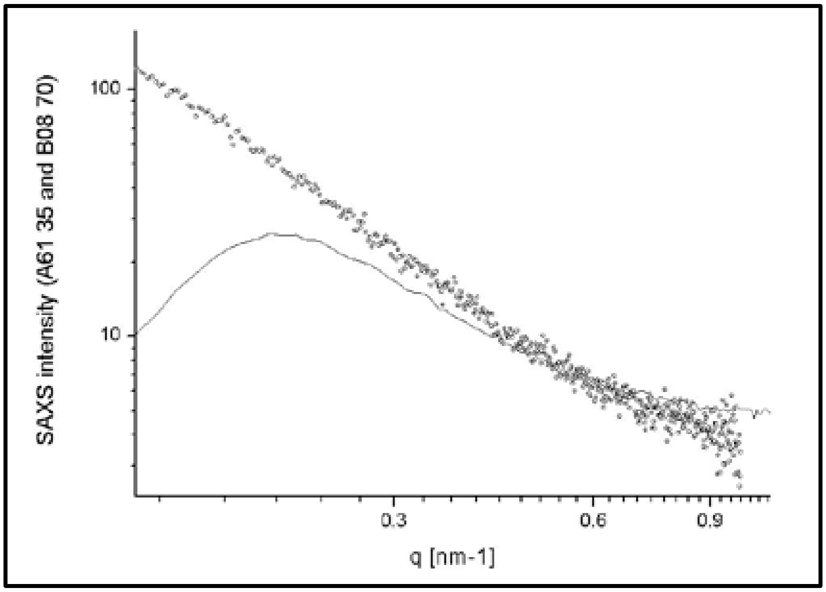

Figure 14. SAXS patterns of A61 frame 35 and B08 frame 70, with B08 shifted by division through 30. Overlap is not possible.

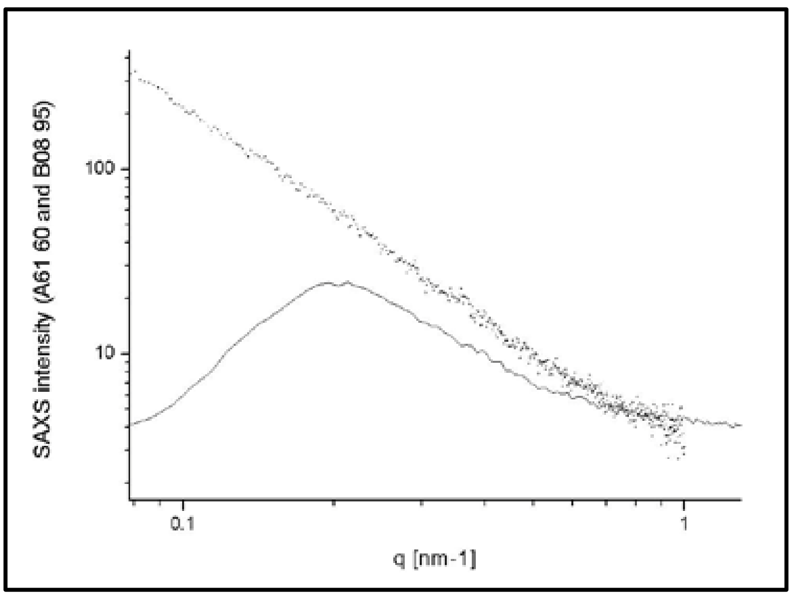

Figure 15. SAXS patterns of A61 frame 60 and B08 frame 95, with B08 shifted by diving through 35. There is no range within the available q-range, where significant overlap could be reached.

For the series of 2% P3HT in toluene, finding good overlap seems more problematic than for the 1% P3HT sample. Not only is it impossible to find overlap with a single shift factor per series over the complete q-range determined for toluene, it is also not possible to find overlap with any shift factor of choice for each pair of SAXS patterns individually. SAXS patterns in the start of the temperature series can still be matched. For the SAXS patterns at lower temperatures matching becomes impossible, as was shown in Figures 14 and 15. This is due to the fact that the slopes of both SAXS patterns of a pair are not the same. The reason for this however is not clear and it was expected that both patterns would be able to simply overlap after shifting. Figure 16 shows all 5 pairs in one overlay plot.

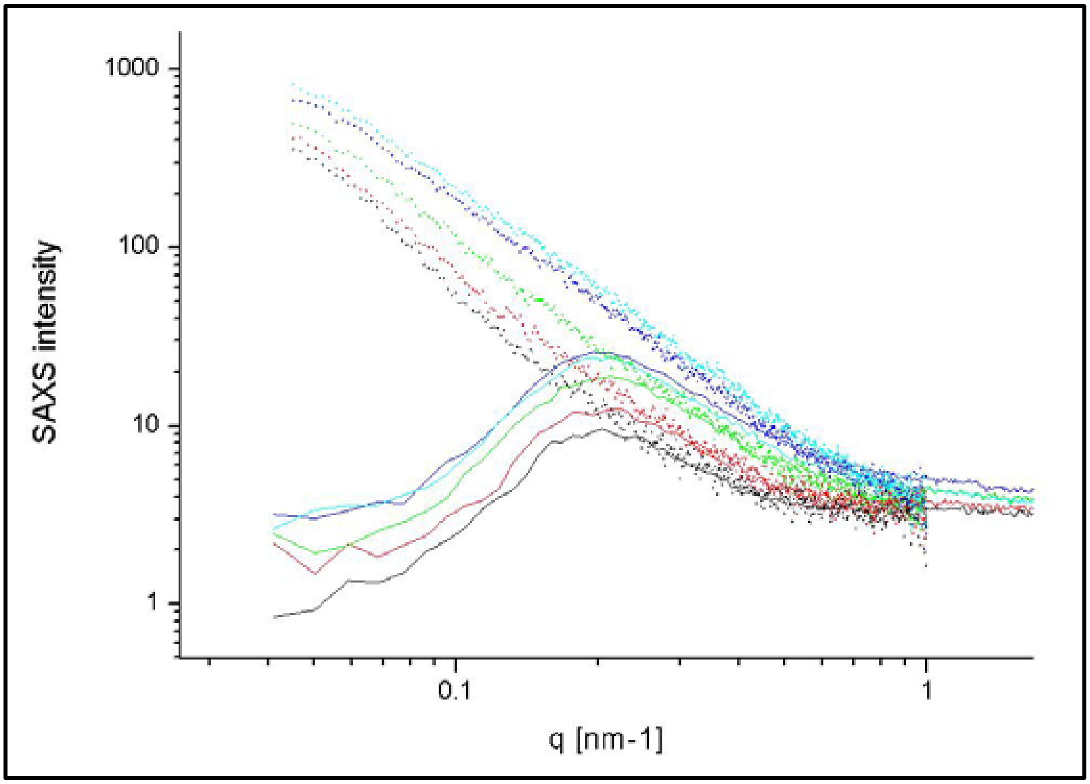

Figure 16. Overlay of Figures 11 to 15.

5% P3HT in Toluene

Sample information:

Long distance: 27.6 mg P3HT (OS2100) was mixed with 0.5518 g toluene at elevated temperature, resulting in an effective sample concentration of 5.00%.

Short distance: 29.2 mg P3HT (OS2100) was mixed with 0.5916 g toluene at elevated temperature, resulting in an effective sample concentration of 4.94%.

The temperature program followed started at 70C and cooled down to 10C at a rate of 1C/min and consecutive isothermal period at 10C, as shown in Figure 17.

In Table 5 the recorded SAXS patterns for the 5% sample are listed.

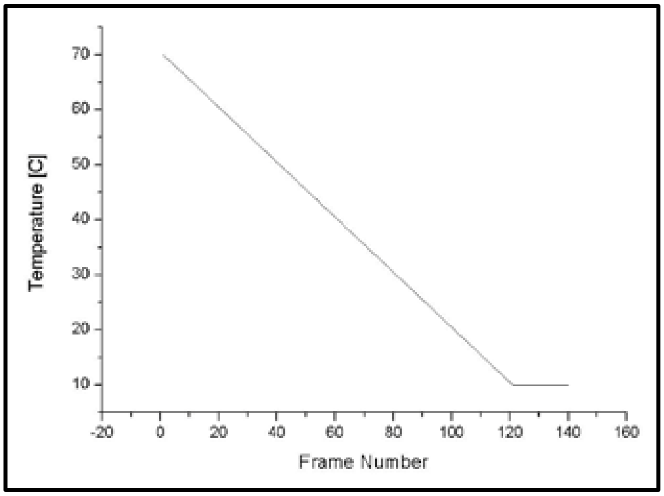

Figure 17. Imposed temperature profile according to frame numbers.

Table 5. List of SAXS series recorded for 5% P3HT in toluene with specifications.

Name		Acquisition Temperature [C]	q-range [nm-1]	Exposure Time [s]
Long Distance	A47	70 to 10 (1C/min), isotherm at 10	0.04505 - 0.99899	30
Short Distance	B03	70 to 10 (1C/min), isotherm at 10	0.04104 - 5.30263	30

To compare the signal evolution from the two separately recorded SAXS series, the relative SAXS intensity signals are plotted in Figure 18 with a frame shift of 9 frames for the series recorded at long S2DD (A47) in order to match both series.

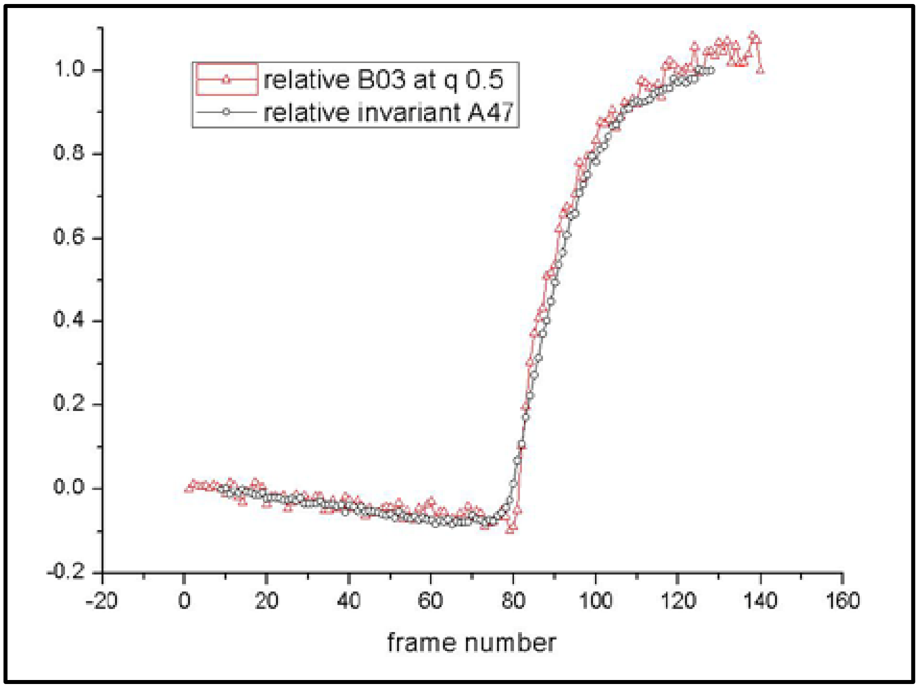

Figure 18. Relative SAXS signal evolution of the 5% sample: Long S2DD invariant (black) and short S2DD scattering intensity at q 0.5 nm-1 (red).

In the 5% series, where the P3HT concentration is considerably higher as in any of the previous samples (1% and 2%), it is troublesome to find good overlap between the two individually recorded SAXS series. Shift factors were optimized for individual pairs and the best possible overlapped results are shown in Figure 19.

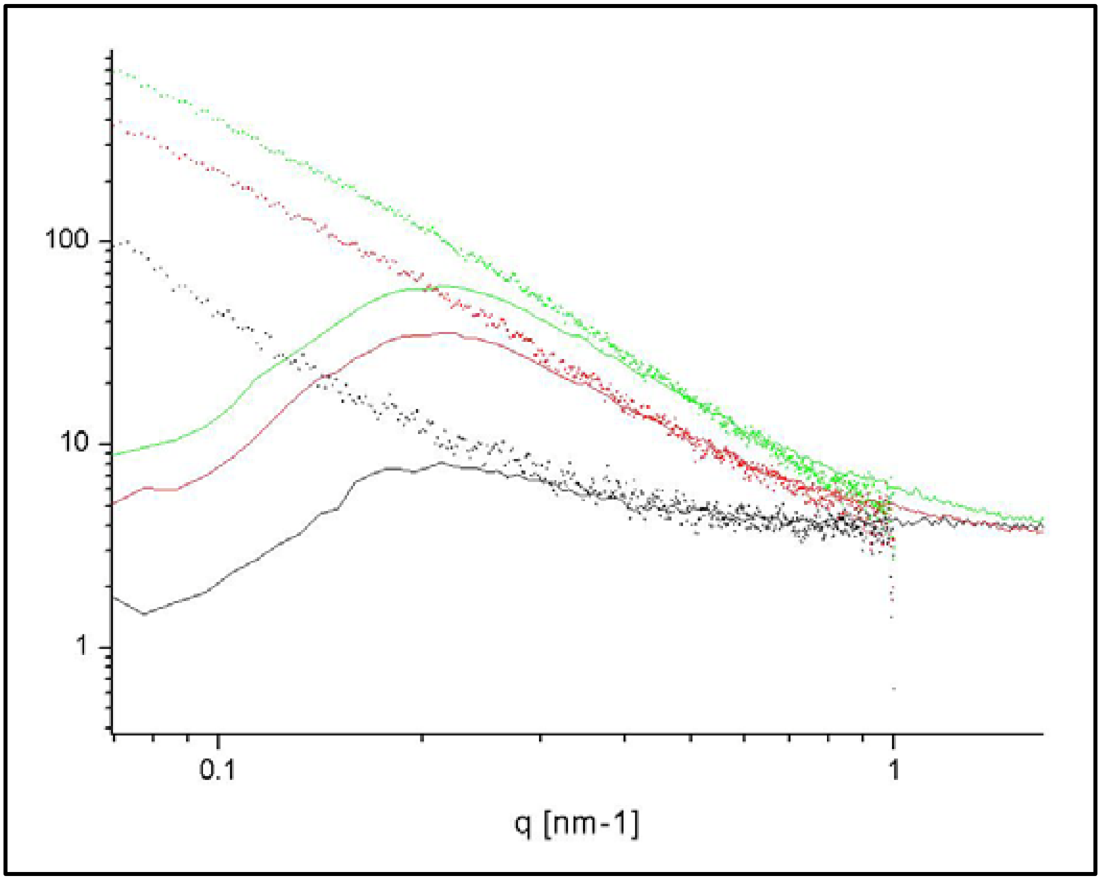

Figure 19. SAXS patterns of 5% P3HT in toluene long distance (A47, scatter) and short distance (B03, solid lines) series. Frames A47_31 and B03_40 (shift 36) in black, A47_81 and B03_90(shift 38) in red and A47_111 and B03_120 (shift 34) in green.

Also here it can be clearly seen that the overlap region decreases as we progress into the temperature series to lower temperatures until there is no overlap possibility left.

Conclusions

When comparing the 4 different samples which were measured (toluene, 1% P3HT in toluene, 2% and 5%) and the temperature induced behavior of each of them, the following can be concluded.

The best overlap can be found at higher temperatures and lower P3HT concentrations. Starting at concentrations of 2% and when decreasing the temperature, overlap becomes problematic. It is not clear why both SAXS series do not follow similar patterns upon temperature changes. The short S2DD series was initially recorded to be able to detect a signal which should be situated at approximately 4 nm^{-1} and would be a measure for crystallinity within our sample. This signal was not detected, as can be clearly seen in Figure 20 (lowest temperature for the 5% sample).

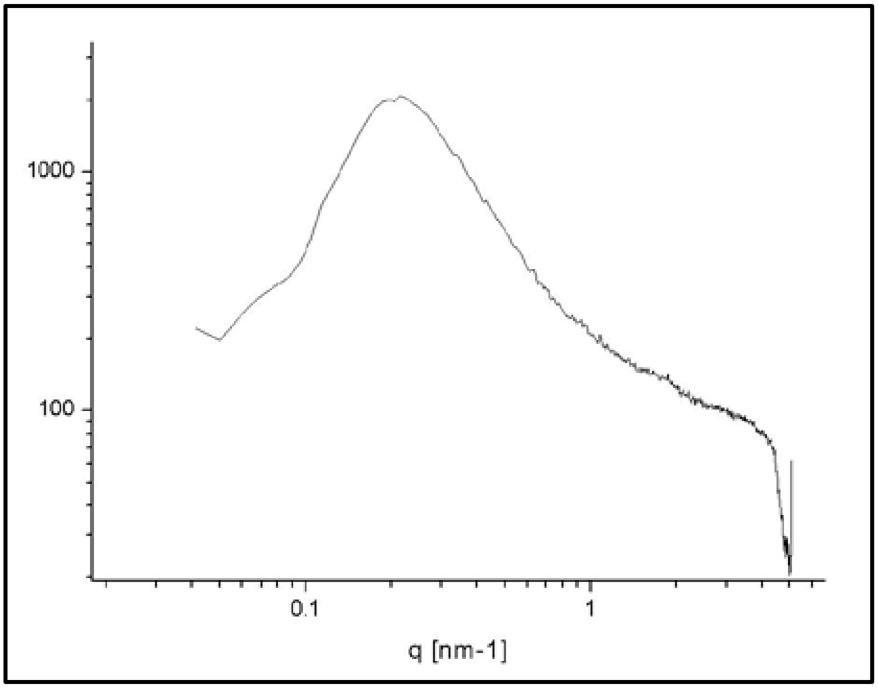

Figure 10. SAXS pattern of short distance measurement on the 5% sample at low temperature (10C) showing no peak at approximately 4 nm^{-1}.

Additionally, the overlap problems pose a question as to which of both series of signals has to be taken into account as the one on which analysis can be built.

Remaining questions and discussion points

- Can we understand why in the overlap region between the 2 S2DD measured we see changes in slope when structure formation occurs at that length scale and with increasing concentration? We were expecting to have the same scaling behavior in that region.
- We think to understand the low q-differences (at the short S2DD) the low q signal is all buried close to the beamstop region, making the signal at the short S2DD not accurate at the small q range.
- At high q-range we would value the short S2DD data more highly and take those as representative. The high q-data of the long S2DD distance are very noisy due to bad sample to noise ratio so not accurate either.
- There are problems with the intermediate q-range where both data sets should coincide better. In the liquid state the agreement is still OK to acceptable for all compositions, but with the formation of the structure significant deviations start to set in.
- When shifting the SAXS patterns, it is not clear if it is reasonable to use different shift factors within a single experimental series (e.g. 2% and 5%, for 1% this was not necessary).
- The invariant for the short S2DD (as shown in Figure 5) shows both a decrease and an unexpected shape.