ESRF	**Experiment title:** Time-resolved SAXS/WAXS/DSC of stereocomplex formation in an amphiphilic block copolymer melt	**Experiment number**: SC3098
Beamline: BM26	**Date of experiment**: from: 1/10/10 to: 4/10/10	**Date of report**: 27/1/11 *Received at ESRF:*
Shifts: 9	**Local contact(s)**: G. Portale, D. Hermida-Merino	

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Report:

The thermal properties, and crystallization kinetics of amphiphilic poly(D-lactide)-*b*-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) (PDLA-*b*-PDMAEMA) and poly(L-lactide)-*b*-poly(*N*,*N*-dimethylamino-2-ethyl methacrylate) (PLLA-*b*-PDMAEMA) copolymers and their stereocomplexes were studied by differential scanning calorimetry (DSC) and compared to that of the corresponding poly(lactide) homopolymers. The morphology of these materials was determined using atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). Additionally the crystalline structure was investigated using wide angle X-ray scattering (WAXS). Finally particle-like structures formed by the stereocomplexes were observed with AFM and the thermal properties were analysed by DSC. The copolymers exhibit cold crystallization behavior, and a lower melting temperature than the homopolymers. The crystallization kinetics was affected due to the presence of the PDMAEMA block. The majority of the copolymers are miscible in the melt, and only DL_{65}-b-$\mathrm{DMAEMA}_{35}^{15.9}$ (the subscripts denote the compositions in wt%, the subscript indicates the total M_n in kg mol^{-1}) has a heterogeneous melt. The difference in the melt morphology (homogeneous *vs*. heterogeneous has an important influence on the crystallization kinetics. Stereocomplexes were obtained despite the presence of the PDMAEMA block, additionally an important influence of the molecular weight was found. For the low molecular weight stereocomplexes the particles have a disk-shape, on the other hand for high molecular weight sample, the particle has a star-like shape. This work has led to a submitted paper.[1]

Small- and wide-angle X-ray scattering (SAXS and WAXS)experiments were performed on station BM26B (DUBBLE), ESRF, Grenoble, France. A modified DSC Linkam hot stage was employed that allows the transmission of X-rays through mica windows. At first the samples was heat from 25°C to 110 °C at 20 °C/min, after that the sample was heated at 20°C/min to 175 °C. After 5 minutes the samples were cooled at 5 °C/min to 25 °C. The wavelength employed was λ=1.24Å and the sample-detector distance was 3.75 m. The wavenumber $q = 4\pi \sin \theta/\lambda$ scale for SAXS was calibrated using collagen and NBS silicon.

The key evidence to ascertain the structure of the melt was obtained by SAXS and is shown in Figure 1. SAXS studies demonstrate that the blocks are miscible in the melt, for the majority of the copolymers, since no maximum in the SAXS profile (determined at a temperature where all samples are in the melt) was observed in Figure 1(a). However, for copolymer DL$_{65}$-*b*-DMAEMA$_{35}^{15.9}$ we were able to observe a small peak in the SAXS data (see arrow in Figure 1(b)) suggesting structural heterogeneity in the melt.

The blocks in the sample LL$_{64}$-*b*-DMAEMA$_{34}^{16.5}$ are miscible in the melt while those within DL$_{65}$-*b*-DMAEMA$_{35}^{15.9}$ are weakly segregated according to the SAXS evidence. Both can form spherulites since the first will crystallize from a homogeneous melt while the second can undergo break-out from its weakly segregated heterogeneous structure. This difference in melt structure is unexpected because of the similar chemical structure of both copolymers. The only difference between these two copolymer samples is the presence of PLLA in the first and PDLA in the second, since the molecular weight of the blocks are nearly identical (so *N* is identical). One could speculate that the way the blocks interact are different (or in other words the segregation strength is different) because this stereochemical variation in their structure is producing a slightly different χ value.

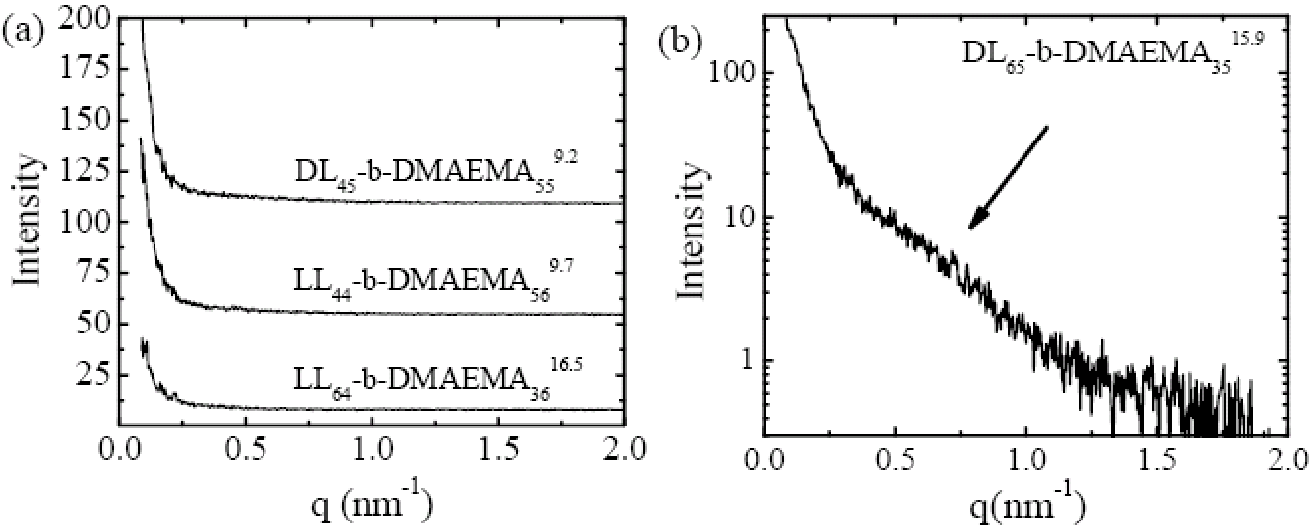

Fig.1. SAXS patterns obtained at 175 °C for the PLA-b-PDMAEMA copolymers indicated.

References

1. Michell, R. M.; Müller, A. J.; Spasova, M.; Dubois, P.; Hermida-Merino, D.; Burattini, S.; Greenland, B. W.; Hamley , I. W.; Cheval, N.; Fahmi, A.; Mendoza, C. E. *Submitted* 2011.