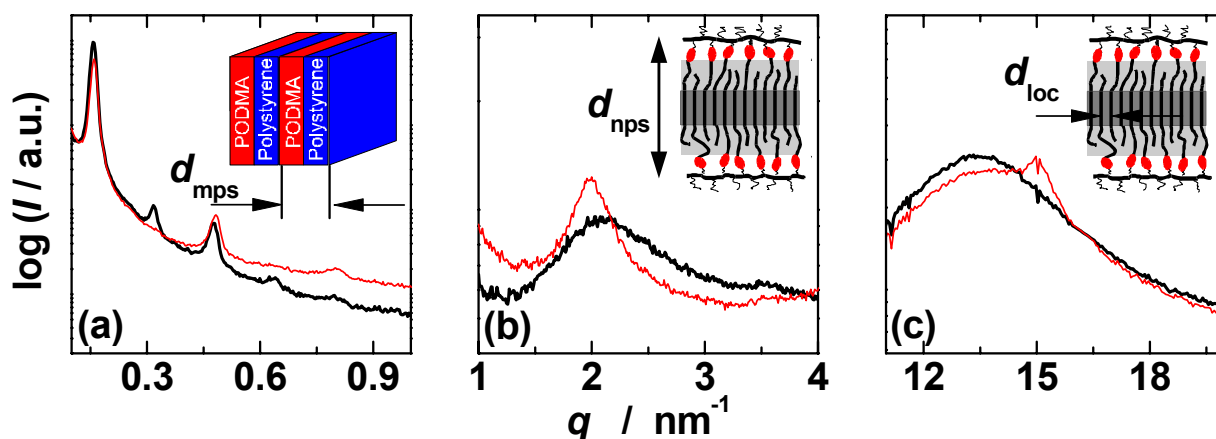


Aim of this proposal was to study the crystallization of long alkyl groups in the side chain of poly(*n*-octadecylmethacrylate) [PODMA] under confinement. The isothermal crystallization process in five microphase-separated poly(styrene-*b*-octadecylmethacrylate) block copolymers [P(S-*b*-ODMA)] containing PODMA lamellae or cylinders with sizes in the range between 10 and 25nm has been investigated. A PODMA homopolymer was studied for comparison. A central question was whether or not the structure of semi-crystalline PODMA survives in small PODMA domains surrounded by glassy polystyrene. Moreover, we were interested to understand further details of the side chain crystallization process. Based on results from calorimetric and X-ray measurements in our labs it was predicted that side chain crystallization in P(S-*b*-ODMA) block copolymers occurs in a strong confinement, i.e. without significant change of the block copolymer morphology and that the side chain crystallization in PODMA lamellae is nearly unaffected while significant confinement effects occur in case of PODMA cylinders with a diameter <15nm [1]. This picture has been nicely confirmed by the scattering data measured at different stages of the isothermal crystallization process of P(S-*b*-ODMA) block copolymers on beam line BM26B. Further details of the side chain crystallization process could be puzzled out.

The results of isothermal crystallization experiments on P(S-*b*-ODMA) block copolymers in Grenoble confirm that side chain crystallization occurs in strong confinement [3]. The block copolymer structure does not change during crystallization (Fig.1). The disappearance of the even orders of the lamellar pattern seems



**Fig.1.** Scattering data for a lamellar P(S-*b*-ODMA) block copolymer containing about 44vol% ODMA measured during isothermal crystallization (thick black line:  $t_c=1\text{min}$ ; thin red line:  $t_c=20\text{min}$ ) at  $T_c=27^\circ\text{C}$  on beam line BM26B at the ESRF in Grenoble. Different structures are indicated in different  $q$  ranges: (a) microphase separation of PS and PODMA blocks with  $d_{mps}\sim 40\text{nm}$ , (b) nanophase separation of main chain and alkyl side chains in the PODMA domains with  $d_{nps}\sim 3.1\text{nm}$ , (c) local structure of crystalline parts of the alkyl groups with  $d_{loc}\sim 0.41\text{nm}$ .

to indicate that we are close to a symmetric situation in case of semi-crystalline PODMA domains. The peaks at larger  $q$  values can be understood based on the findings for PODMA homopolymers. The occurrence of the prepeak at  $q\sim 2\text{nm}^{-1}$  in the melt indicates the nanophase separation of incompatible main and side chain parts in the PODMA domains. Position and shape of this prepeak change during side chain crystallization. The shift of the prepeak shows that the main chain-to-main chain distance increases slightly consistent with the increasing trans content of the alkyl groups. The reduced peak width indicates an increase of the correlation length. Parallel to the changes in the prepeak a sharp reflex develops at  $q\sim 15\text{nm}^{-1}$  on top of the amorphous halo incorporating in case of the block copolymers contributions of both components (PODMA & PS). The sharp reflex is related to the hexagonally packed part of the alkyl groups within the PODMA domains and occurs at the same position like in PODMA homopolymers. DSC data show that the degree of crystallinity  $D_c$  in PODMA lamellae is comparable to that for homopolymers. Temperature-dependent half times  $\tau_c$  from DSC as well as from synchrotron scattering indicate that the crystallization kinetics in PODMA lamellae is slowing down only slightly. Altogether the results show that structural features as well as parameters describing the side chain crystallization in small PODMA lamellae are similar to those for homopolymers since the lamellar block copolymer morphology fits to the lamellar morphology of semi-crystalline PODMA. Significant confinement effects have been observed in case of small ( $<15\text{nm}$ ) PODMA cylinders which can crystallize in a glassy PS matrix:  $D_c$  is  $\sim 50\%$  reduced, the crystallization kinetics slows dramatically down and the isothermal transformation interval broadens significantly (Avrami coefficient  $n\sim 1$ ). The strength of these confinement effects decreases if the diameter of the PODMA cylinders increases. Obviously, the curved PS-PODMA interfaces in block copolymers with cylindrical morphology do not fit so well to the structure of semi-crystalline PODMA. However, a basic feature of PODMA homopolymers survives even under these extreme conditions. The existence of the prepeak (and a second order peak at  $q\sim 4\text{nm}^{-1}$  indicating lamellar packing like in homopolymers) shows that nanophase separation still occurs. Thus, the alkyl groups can still crystallize. This shows that our P(S-*b*-ODMA) block copolymers are systems with a hierarchy of length scales in the nanometer range. Speculative pictures for the internal structure of PODMA lamellae and cylinders have been proposed [3]. In lamellar block copolymers the PODMA main chains are assumed to be basically perpendicular and the alkyl groups are expected to lie parallel to the PODMA-PS interfaces. The picture for the PODMA cylinders assumes that main chain rich regions and alkyl nanodomains are stacked. Further work to qualify these pictures based on oriented samples is in progress.

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