Blends of Block Copolymers

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SUMMARY: The formation of superlattices in blends of lamellar ABC triblock and AC diblock copolymers is investigated for two systems with A being polystyrene (S), B being polybutadiene (B) and C being poly(methyl methacrylate) (M) or poly(tert. butyl methacrylate) (T). While in the SBM/SM blends either macrophase separation between the two block copolymers or a cylindrical superlattice was found, in the blend of SBT/ST a non-centrosymmetric periodic lamellar superlattice was obtained.

Introduction

The morphology of microphase separated block copolymers can be controlled by the choice of the repeating units, their relative composition, the degree of polymerisation and temperature. An additional way to control morphology is blending of block copolymers with different relative compositions. This has been demonstrated first by Hadziioannou and Skoulios for various block copolymers of polystyrene and polyisoprene. 1) Later work in this field mostly was devoted to blends of binary block copolymers, i.e. block copolymers composed of two chemically different monomers. 2-7) In this contribution we will focus on blends of lamellar ABC triblock copolymers with lamellar AC block copolymers. The interest in these blends came from the basic question of one of us (R.S.), if it is possible to obtain periodic non-centrosymmetric superlattices via the self-assembling of such block copolymers in a common blend, while these block copolymers by themselves self-assemble into centrosymmetric lamellae.8) Such periodic non-centrosymmetric materials may have interesting properties due to their inherent polarisation, such as piezo- or pyroeletcricity. It is not obvious that a periodic non-centrosymmetric lamellar array $(ABC\ CA)_n$ will be formed rather than macrophases of the type $(ABC\ CBA)_n$ and $(AC\ CA)_n$. On the examples of polystyrene-block-polybutadiene-block-poly(methyl methacrylate) (SBM) with polystyrene-block-poly(methyl methacrylate) (SM) and polystyrene-block-polybutadiene-block-poly(tert. butyl methacrylate) (SBT) with polystyrene-block-poly(tert. butyl methacrylate) (ST) a few general questions of block copolymer blends will be addressed.

Experimental

All block copolymers have been obtained via living sequential anionic polymerisation. The

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details of the synthesis has been described elsewhere.[8,9] Table 1 gives the characteristics of the block copolymers. The blends of these block copolymers were obtained by slow casting from solution in chloroform over several weeks. The samples were further dried at 180°C for 6h in vacuum (in the case of films containing T the annealing temperature was kept at 150°C for 6h). These temperatures are well above the glass transition temperatures of all components. Transmission electron micrographs were obtained from a ZEISS 902 transmission electron microscope operating at 80kV in the bright field mode. Ultrathin sections of the samples were obtained using a Reichert ultramicrotome equipped with a diamond knife. Vaporous OsO_4 was used for staining the samples. In the transmission electron micrographs the B domains appear dark, the S domains appear grey and the M and T domains remain unstained.

Table 1. Characteristics of the triblock and diblock copolymers

Triblock Copolymer [a)]	$S_{34}B_{34}M_{32}^{57}$	$S_{33}B_{34}M_{33}^{153}$	$S_{33}B_{34}T_{33}^{160}$
M_w/M_n [b)]	1.04	1.04	1.04

Diblock Copolymer [a)]	$S_{49}M_{51}^{20}$	$S_{50}M_{50}^{38}$	$S_{50}M_{50}^{52}$	$S_{49}M_{51}^{116}$	$S_{47}T_{53}^{103}$
M_w/M_n [b)]	1.07	1.08	1.1	1.04	1.03

a) Subscripts denote the weight fractions and superscripts give the number averaged molecular weight in kg/mole.
b) Polydispersity was obtained by size exclusion chromatography calibrated with polystyrene standards

Results and Discussion

In Fig. 1 a blend of $S_{33}B_{34}M_{33}^{153}$ with $S_{49}M_{51}^{116}$ is shown, which macrophase separates. This is a quite common result when blending different polymers. A way to increase miscibility between polymers in general is to reduce their molecular weights.

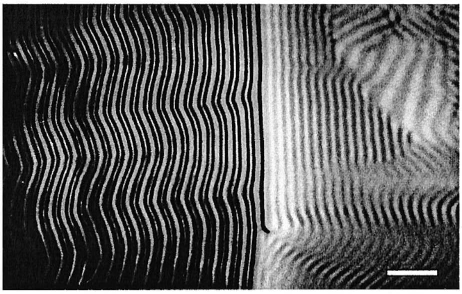

Fig. 1: Macrophase separation in a blend of $S_{33}B_{34}M_{33}^{153}$ with $S_{49}M_{51}^{116}$. Both block copolymers self-assemble into centro-symmetric double layers. On the left side is the triblock copolymer, on the right side is the diblock copolymer. Scale bar corresponds to 250 nm.

A similar blend which differs from the first one only by a reduction of the molecular weights shows a different behaviour. Fig. 2 shows blends of $S_{34}B_{34}M_{32}^{54}$ and $S_{50}M_{50}^{38}$ at various compositions. This system shows cylindrical domains of the B phase, although in the corresponding pure SBM triblock copolymer has a lamellar structure. The formation of these cylindrical domains can be explained by a mixing of the M and S domains of the two block copolymers on a molecular level. By that selective swelling the volume fractions of the outer blocks of the triblock copolymer are increased with respect to the centre block. As a result, no longer B lamellae can be formed, but they break up into cylinders. This morphological transition is comparable with the transition between the lamellar and the "cylinder at lamellar interface" morphology in pure SBM triblock copolymers.10) While at other compositions there are rather disordered mixed superlattices visible, blends with a composition in a range between approximately 25% and 33% of diblock copolymer show mostly a regular mixed cylindrical superlattice. From the TEM micrographs it may be concluded that the cylinders are arranged on a orthorhombic or tetragonal lattice, which could be explained by a lamellar interface between S and M. In a homogeneously mixed matrix a hexagonal packing of the B cylinders would be expected. However, no S and M phases can be distinguished in the TEM micrographs and so this interpretation is not proofed yet.

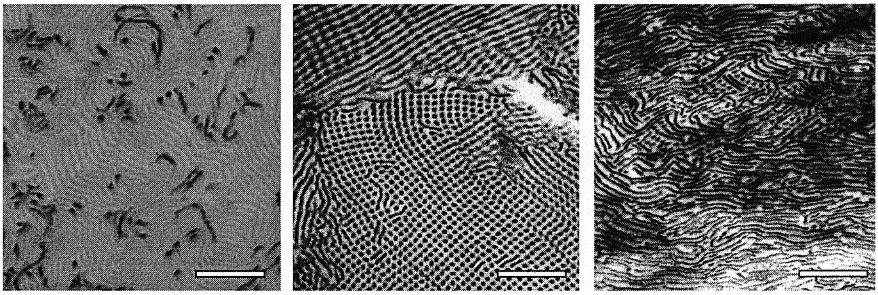

Fig. 2: Formation of cylindrical B-domains in blends of $S_{34}B_{34}M_{32}^{54}$ with $S_{50}M_{50}^{38}$ at various compositions (from left to right: 10%, 66%, 90% $S_{34}B_{34}M_{32}^{54}$). Scale bars correspond to 250 nm.

Varying the molecular weight of the diblock copolymer at a constant blend composition leads to the same morphology. The ordered superlattice in blends with diblock copolymers having longer blocks than the corresponding triblock copolymer blocks are only observed when the solvent is evaporated very slowly (several weeks). In the case of shorter diblock copolymers ordered superlattices form also when the solvent is removed within shorter times (several days).

In order to achieve a lamellar superlattice formed by a lamellar ABC triblock copolymer and a lamellar AC diblock copolymer a parallel orientation of the two block copolymers must be suppressed. A parallel orientation might lead to the cylindrical cases discussed before. An antiparallel orientation of the two different block copolymer chains is necessary, because in that case the lamellae formed by the middle block will not compete with the direct interface between A and C introduced by the AC diblock copolymer. Both situations are shown schematically in Fig. 3.

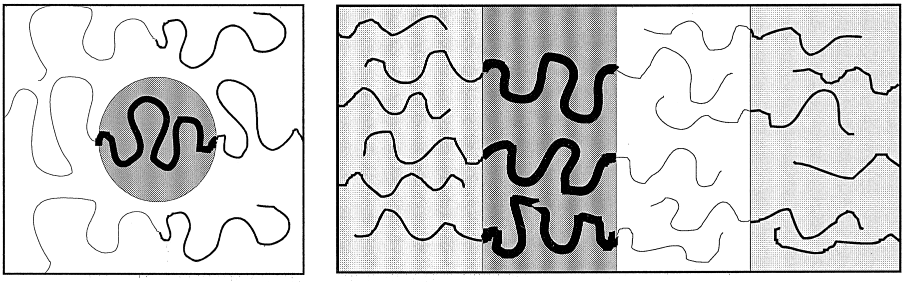

Fig. 3: Schemes of (left) a parallel and (right) an antiparallel chain orientation in blends of ABC triblock copolymers with AC diblock copolymers.

Different situations of lamellar superlattices have been discussed in ref. 8. For the formation of a periodic non-centrosymmetric superlattice it is required that both A and C chains of the diblock copolymer prefer the contact with the corresponding chains of the triblock copolymer rather than mixing with similar chains (which would lead to a centrosymmetric array of lamellae). Also a sufficient incompatibility between the A and C block is necessary in order to suppress the break up of the B-lamellae into cylindrical domains leading to a parallel chain orientation of diblock and triblock copolymer. A blend of $S_{33}B_{34}T_{33}^{160}$ and $S_{47}T_{53}^{103}$ fulfils these conditions and Fig. 4 shows a periodic non-centrosymmetric lamellar superlattice formed by an equimolar blend. The sequence of colours follows exactly the sequence (SBT TS SBT)$_n$ (grey-black-white-grey..). An artefact by the experiment can be excluded due to the presence of a particular defect, which arises when grains with antiparallel orientation come together: the dark B-lamellae are broken along that line, while the S and T-lamellae are continuous across the orientation grain boundary. As a reason for the mixing of A (C) chains of ABC with A (C) chains of AC within one lamella different chain stretchings are considered, which are caused by the different topologically neighboured blocks (A-C interface in the diblock copolymer and A-B interface in the triblock copolymer). A net reduction of the elastic energy (caused by chain stretching) is possible under favourable conditions, when differently stretched blocks of the same chemical species interpenetrate each other. This effect is discussed in detail elsewhere.[11)]

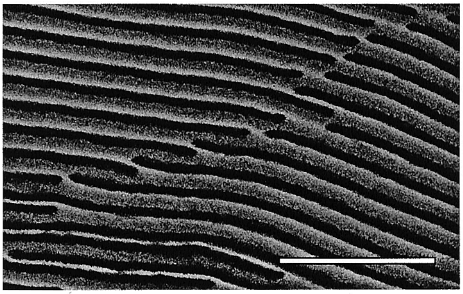

Fig. 4: Periodic non-centrosymmetric lamellar superlattice in a blend of 60% $S_{33}B_{34}T_{33}^{160}$ and 40% $S_{47}T_{53}^{103}$. Scale bar corresponds to 250 nm.

Besides the composition of the block copolymers, their relative amounts and their molecular weights, also the choice of the solvent is important for the structure formation in block copolymer blends. It was shown before that in pure ternary triblock copolymers there may be a large influence of the solvent used for film casting. [12)] Moreover, in a blend the selectivity of the solvent can lead to macrophase separation. Blends of SBT and ST cast from toluene or 2-butanone show macrophase separation. While toluene favours polybutadiene and thus the ST precipitates first, in the case of 2-butanone SBT precipitates first because it is a bad solvent for polybutadiene. Chloroform is less selective for the different blocks and so macrophase separation prior to microphase separation upon evaporation of the solvent can be avoided. Chloroform has also been used in most prior morphological investigations of similar block copolymers [13)]. Besides the quality of the solvent also the conditions during the casting process are important, as discussed for the blends of SBM with SM block copolymers of various molecular weights. It cannot be ruled out that the SBM/SM system is more sensitive towards the solvent than SBT/ST. Therefore the observed macrophase separation in Fig. 1 may also be due to the choice of solvent and the conditions during the casting process.

While in this work only blends of block copolymers with symmetric compositions (all blocks within one block copolymer have equal lengths) were investigated, it is also possible to blend other types of block copolymers. An overview of block copolymer blends will be given elsewhere [14)].

Conclusions

In none of the blends enthalpic interactions favouring the contacts between different block copolymers are present, because only chemically similar blocks form common mircrodomains. The driving force for the formation of these superlattices must be of entropic origin and may be caused by an overall increase of conformational entropy for the blocks in the mixed superlattice.

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