



Controlled crosslinking of polybutadiene containing block terpolymer bulk structures: A facile way towards complex and functional nanostructures

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ABSTRACT

The controlled crosslinking of polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (SBT) block terpolymers in their microphase-segregated bulk state is investigated. Two different methods, cold vulcanization and free radical crosslinking as well as its optimized procedure, the thiol-polyene method, are applied for crosslinking the lamellar polybutadiene microdomains within the lamella-lamella (ll) morphology of SBT bulk structures. It was found that the microphase-separated structures of the block terpolymers react very sensitively towards the addition of swelling solvents and crosslinking agents. The changes in the microphase-segregated morphologies are followed at all stages with transmission electron microscopy to give an in-depth view of the nanoscopic transformations. These partially unexpected changes in the morphologies make a careful adjustment and optimization of the reaction conditions necessary. For cold vulcanization, i.e. the reaction of double bonds with sulphur monochloride, several swelling solvents and concentrations of crosslinking agents are explored. In the case of free radical crosslinking, it is found that an increase of the radical initiator concentration above 5 wt% does not lead to an increase of insoluble material as radical chain cleavages occur as side reactions, thus limiting the amount of the desired gel fraction. However, the addition of a trifunctional thiol can further increase the desired network formation. By means of this procedure and a subsequent homogenization, it is possible to create novel disc-like Janus particles. Dynamic light scattering and scanning force microscopy are used to highlight the flat nanoparticle structure and to demonstrate the influence of the crosslinker on the formed structures.

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1. Introduction

Widespread research in polymer science has been devoted to the field of block copolymers in the past decades. Block copolymers represent a fascinating class of materials as they can combine the properties of several different polymers in a unique fashion. Block copolymers have found applications in nanoelectronics, biotechnology and industry. Due to the mutual incompatibility of different polymers with each other, block copolymers exhibit microphase-segregated morphologies in the bulk. The appearance of a certain morphology is mainly determined by the following parameters: the Flory–Huggins interaction parameter between the blocks (χ), the volume fractions and the degree of polymerization. The phase diagrams of diblock copolymers are theoretically and experimentally well explored [2,4–6].

Generally, several structural transitions can be observed when increasing the volume fraction of one block from 0 to 50%, starting

from a mixed system, via a spherical phase, a cylindrical phase, a gyroidal phase and finally ending up in a lamellar phase. In addition, perforated lamellar structures were found in some diblock copolymer systems between the gyroidal and the lamellar phase [7–9].

However, upon introduction of a third block to the block copolymer system, the situation becomes fairly complicated and much more morphologies can be found. Furthermore, the prediction of the stability of a certain morphology is difficult as all interactions between the different blocks must be considered [10–12]. Pioneering work in the field of block terpolymers was done by Stadler et al. [14,16], who performed in-depth investigations of the polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) system. The phase diagrams of SBM block terpolymers and other block terpolymers comprise a multitude of fascinating phase-segregated structures on the nanometer scale [17].

It was found that even a slight variation in the volume fractions, or a simple change in the interaction parameters between the different blocks, e.g. by hydrogenation of the inner polybutadiene block, can result in significant changes of the microphase-segregated morphologies found. For instance, an increase of the inner PB fraction, while keeping the endblocks of PS and PMMA symmetric,

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can already lead to five different morphologies. Low fractions of PB lead to spherical domains of PB at the lamellar interface of PS and PMMA (so-called lamella–sphere, *ls*), which are followed by PB cylinders (lamella–cylinder, *lc*) upon further increase. A complete lamellar phase with alternating layers of PS, PB and PMMA (lamella–lamella, *ll*) is present for fully symmetric SBM block terpolymers. For SBM block terpolymers, having PB as major component, cylindrical and spherical domains of PS and PMMA can be found in a PB matrix.

Clearly, given the wide variety of complex structures formed by block copolymer systems, it would be desirable to be capable of stabilizing those in order to be able of transferring those complex architectures into solution. First attempts for crosslinking a block copolymer domain were performed by Ishizu et al. [18,19], who reported about the successful synthesis of polymer microspheres. For this purpose they crosslinked the spherical domains of a polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP or SV) and of a polystyrene-*block*-polybutadiene (PS-*b*-PB or SB) diblock copolymer using 1,4-dibromobutane [18] or sulphur monochloride [19]. Decker et al. reported on the aspects of the radical crosslinking of SB and SBS block copolymers [20–24]. The focus of these investigations was drawn to the kinetic and mechanistic aspects and not to the potentially resulting nanostructures.

Concerning the crosslinking of ABC block terpolymer nanostructures towards the preparation of functional nanostructures, the literature is limited to a few approaches. Certainly, the strategy by Liu et al., utilizing the UV crosslinking of cinnamoyl moieties, is worth mentioning. By means of this process it was for example possible to generate PS-PHEMA-PAA (polystyrene-*block*-poly(2-cinnamoyloxy-ethyl methacrylate)-*block*-poly(*tert*-butyl acrylate)) core-shell-corona nanofibres [25]. For this purpose, block terpolymer films, exhibiting core-shell cylinders, were irradiated with UV and sonicated. Morphological rearrangements are unlikely as the UV irradiation proceeds within the rigid block terpolymer nanostructure and does not involve further chemical additives. However, one of the major drawbacks of this process is the chemistry involved. The introduction of the cinnamoyl moieties requires the synthetically demanding polymerization of silyl-protected HEMA, the deprotection of it and the polymer analogues' modification with cinnamoyl chloride. Furthermore, the monomer choice is limited according to the reactivity behaviour of monomers in anionic polymerization.

In contrast, polybutadiene or polyisoprene may serve as alternatives as they are extremely easy to polymerize in a wide variety of solvents and furthermore, a large amount of microphase-segregated structures of its block copolymers is already known. A few attempts of crosslinking SBM block terpolymers with lamella–sphere and lamella–cylinder morphologies have already led to fascinating spherical and cylindrical Janus particles [26–28].

Janus structures are colloids which possess two phase-segregated compartments of different chemistry or polarity. Their preparation on the nanometer scale is very difficult and has so far most convincingly been accomplished via the selective crosslinking of SBM block terpolymer nanostructures.

Janus structures are an intense field of our research due to the fact that they exhibit unique self-assembly behaviour and may serve as future surfactants, owing to their high surface activities predicted. However, a detailed investigation of the crosslinking process itself and the precautions required to carry it out in the fragile environment of block terpolymer bulk nanostructures is lacking. Since additives need to be co-casted while the film formation or swelling agents and reactive chemicals are necessary, morphological rearrangements are most likely.

Herein we report on the controlled crosslinking of polybutadiene microdomains of a series of polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) block terpolymers.

The compositions of the block terpolymers were tailored to be at the morphological boundary of the lamella–lamella morphology, as will be shown below. Cold vulcanization, the reaction between S₂Cl₂ and double bonds, and the thermally initiated free radical polymerization, as well as its optimization, the thiol–polyene reaction were employed as crosslinking reactions and thoroughly investigated. These reaction conditions can easily be applied in standard laboratories, in contrast to γ -irradiation with cobalt sources which represents another way of crosslinking polybutadiene.

Several unexpected problems concerning morphological rearrangements encountered during the crosslinking will be discussed in the following. The finally developed procedures can be applied to a large variety of block copolymers and should stimulate further work in the direction of crosslinking block terpolymer bulk structures, containing polybutadiene or polyisoprene, towards internally structured nanoparticles.

Since the crosslinking of the inner polybutadiene layer preserves the preorientation of the PS and PtBMA part, sheet- or disc-like Janus particles can be obtained after a homogenization procedure (see Scheme 1). Some experimental results of the characterization of the Janus discs will be highlighted at the end to show the influence of the different crosslinking methods on the obtained material.

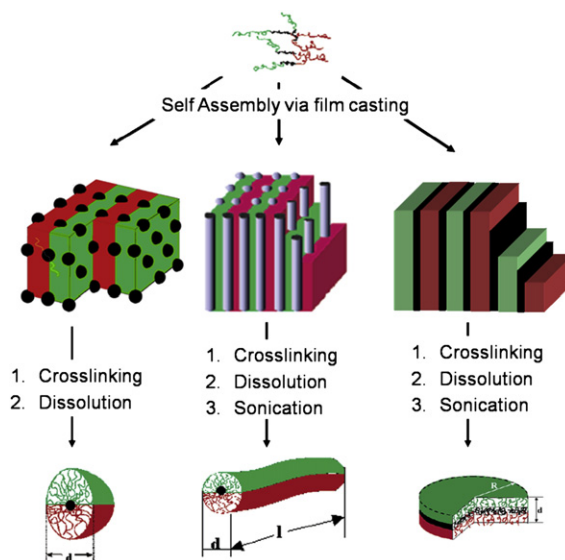
2. Experimental section

2.1. Materials

All solvents and reagents were obtained from Merck or Aldrich in p.a. grade and used without further treatment except for the following ones. Decane (p.a., Aldrich) and isooctane (p.a., Aldrich) were treated with *sec*-butyl lithium and distilled. THF (p.a. Merck) was treated with *sec*-butyl lithium at low temperatures and distilled. Cyclohexane (Merck) and acetonitrile (Aldrich) were obtained in HPLC grade and used directly.

2.2. Synthesis

The anionic polymerization of the polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (SBT) block



Scheme 1. Overview of the pathway for the preparation of different Janus particles via selective crosslinking of microphase-segregated structures of block terpolymers.

terpolymers was conducted in a similar way as reported elsewhere [29,30].

2.3. Crosslinking with AIBN/thiol–polyene process

AIBN (5 wt%, relative to the mass of the SBT block terpolymer), trimethylolpropane mercaptopropionate (TRIS, 0–5 wt%) and SBT block terpolymer were dissolved in CHCl_3 and the film casting process was allowed to take place in a solvent vapour filled desiccator for about two weeks, yielding films with thicknesses between 0.5 and 2 mm. Afterwards, the film was dried in vacuo at RT for 24 h and crosslinked at 80 °C for 48 h. Subsequently, the film was purified by Soxhlet extraction with THF for 24 h yielding a soluble fraction and an insoluble fraction. The insoluble fraction was subjected to a sonication treatment.

2.4. Cold vulcanization

A solvent-cast film (typical thickness between 0.5 and 2 mm) was introduced into the reaction vessel and swollen in solvent (decane or isooctane) for a certain period of time (typically 12–48 h). Afterwards, the calculated amount of S_2Cl_2 (typically 1.5–5 vol%) was introduced with a syringe and the crosslinking was allowed to take place for 12–48 h at room temperature. After the reaction, the film was washed with several aprotic non-solvents, e.g. acetonitrile and isooctane. Subsequently, the film was purified by Soxhlet extraction with THF for 24 h yielding a soluble fraction and an insoluble fraction. The insoluble fraction was subjected to a sonication treatment.

2.5. Sonication

The product underwent ultrasonic treatment using a Branson model-250 digital sonifier, equipped with 1/8 in diameter tapered microtip, at various amplitudes (200 W at 100% amplitude). For this purpose, a dispersion of insoluble crosslinked material ($c = 0.3$ – 1 mg/mL) in THF was allowed to stand at room temperature for several hours to ensure good swelling of the material. Afterwards, it was subjected to the sonication treatment in a temperature controlled cell. The on/off cycle times were typically in the range of 2 s / 2 s and 2 s / 10 s, depending on the amplitude used.

2.6. GPC viscosity

GPC viscosity measurements were conducted using the following column and detector setup: 5 μ PSS SDV gel, 10^3 , 10^5 and 10^6 Å, 30 cm each; Shodex-RI-71 refractive index detector; Jasco Uvidec-100-III UV detector ($\lambda = 254$ nm); Viscotek viscosity detector H 502B. The molecular weights were determined by the universal calibration principle [31] using the viscosity module of the PSS-WinGPC scientific V 6.1 or V 7.12 software package. Linear PMMA standards (PSS, Mainz) were used to construct the universal calibration. Prior to measurements the samples were filtrated using 3 μ m PTFE filters.

2.7. GPC-MALS

GPC-MALS measurements were performed at room temperature using a GPC equipped with a Wyatt Technology DAWN DSP-F multi-angle light scattering detector (He–Ne laser; $\lambda = 632.8$ nm) and a Shodex-RI-71 refractive index detector. Three 30 cm PSS SDV columns (10^4 , 10^5 , and 10^6 Å) were used with THF as eluent at a flow rate of 1 mL/min. Data evaluation was performed with the Astra Software package.

2.8. NMR

^1H and ^{13}C NMR spectra were obtained on a Bruker AC 250 at an operating frequency of 250 and 62.5 MHz, respectively. Various deuterated solvents (Deutero GmbH) were used depending on the solubility of the samples. As an internal standard, the residual proton signal of the deuterated solvent was used.

2.9. Transmission electron microscopy (TEM)

The bulk morphologies of the SBT triblock terpolymer were examined using TEM. Films (around 1 mm thick) were cast from 5% (w/w) solutions in CHCl_3 and allowed to evaporate slowly for 2 weeks. The as-cast films were dried for 1 day in vacuum at room temperature and then annealed at 80 °C for 1–5 days. Thin sections were cut at room temperature using a Reichert-Jung Ultracut E microtome equipped with a diamond knife. To enhance the electron density contrast between the three blocks, the sections were exposed to OsO_4 vapour for 60 s, which leads to a preferential staining of the polybutadiene block appearing black. Bright-field TEM was performed on Zeiss CEM 902 and LEO 922 OMEGA electron microscopes operated at 80 and 200 kV, respectively.

2.10. Scanning force microscopy (SFM)

SFM images were taken on a Digital Instruments Dimension 3100 microscope or on a Veeco Multimode operated in Tapping Mode. Standard silicon nitride probes were driven at 3% offset below their resonance frequencies in the range of 250–350 kHz. According to the distributor of the tips, the normal tips possess finite tip sizes with radii of 10–20 nm. Offline data processing was done using the Nanoscope Software (V 5.13r10sr1 and V6r2.1).

3. Results and discussion

3.1. Synthesis and characterization of SBT block terpolymers

Several polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) (SBT) block terpolymers were prepared by living anionic polymerization in THF using the sequential monomer addition technique. The weight fractions of the different blocks were targeted towards symmetric fractions of the endblocks in order to form lamellar microphase-separated structures in the bulk. Due to the synthetic pathway in THF in the presence of lithium counterions, the block terpolymers are constituted of a high 1,2-butadiene content. From the ^1H NMR spectra (see Fig. 1) the exact weight fractions of the three blocks, as well as the fraction of 1,2-butadiene can be calculated.

All three SBT block terpolymers possess a 1,2-vinyl content of 90–95%, a controlled molecular weight distribution and an almost symmetric composition regarding the endblocks. The polybutadiene fraction was varied in a range from 4 to 10 wt%. A high 1,2-vinyl content of the polybutadiene is preferred as it facilitates the latter radical crosslinking process using AIBN. The molecular characteristics of all the three SBT block terpolymers used in this study are summarized in Table 1.

3.2. Microphase structure

Since this study aims at the controlled crosslinking of lamella-lamella block terpolymer morphologies towards the preparation of sheet- or disc-like Janus structures, it is important to ensure the presence of fully lamellar morphologies of the SBT block terpolymers in the bulk. Transmission electron microscopy is a powerful technique for investigating the microphase separation of block copolymers and was hence used in this study. In order to enhance

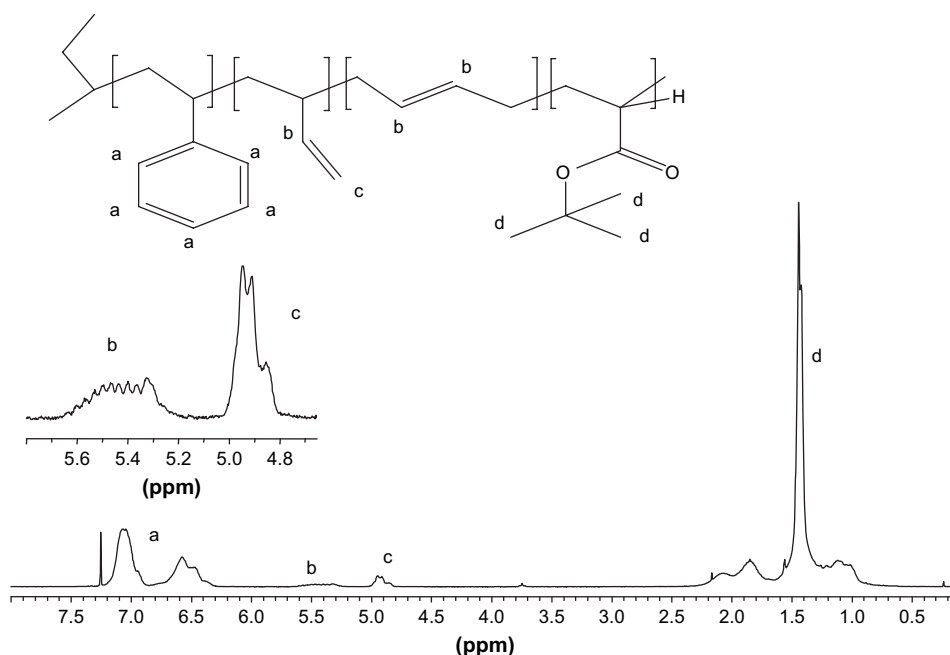


Fig. 1. ^1H NMR spectrum of an SBT block terpolymer, recorded in CDCl_3 . All unassigned peaks of the backbone are located in the broad peak area ranging from 0.7 to 2.4 ppm.

Table 1
Molecular characterization of the SBT block terpolymers

	Composition ^a	$10^3 \times M_n$ (M_w/M_n)	$10^3 \times M_n$, MALS (M_w/M_n)
SBT-1	S ₄₂ B ₁₀ T ₄₈	138 (1.09) ^b	133 (1.06)
SBT-2	S ₄₅ B ₅ T ₅₀	134 (1.07) ^b	133 (1.03)
SBT-3	S ₄₆ B ₄ T ₅₀	171 (1.06) ^b	171 (1.06)

^a Weight fractions of the three blocks as calculated from the ^1H NMR spectra (S = polystyrene, B = polybutadiene, T = *tert*-butyl methacrylate).

^b Calculated value for the number average molecular weight, M_n , based on calculation of the exactly determined M_n of the polystyrene precursor and the determined weight fractions of the blocks. The M_n of the PS precursor and the polydispersity of the block terpolymers were evaluated with standard THF GPC and calibration against linear PS standards.

the electron density contrast of the material, the measured ultrathin sections were stained with OsO_4 prior to measurement. This method preferentially stains the polybutadiene domains, leading to a black appearance in the bright-field imaging mode. Fig. 2 shows TEM micrographs of SBT-1, prepared by solution casting from a chloroform solution.

A continuous polybutadiene layer (black) can be clearly seen between the polystyrene (grey) and the poly(*tert*-butyl methacrylate) (white) lamellae, indicating the presence of a fully lamellar morphology. Interestingly, the SBT block terpolymer forms still a fully lamellar (II) morphology despite the low fraction of polybutadiene. In the case of SBM block terpolymers of similar composition, the lamella–lamella phase is not stable for PB contents smaller approximately 25 wt%. This reflects nicely the earlier mentioned strong influence of the interaction parameters between the different blocks.

The thickness of the inner polybutadiene phase can be calculated to be ca. 6 nm. This value may, however, be slightly overestimated as the incorporation of the staining agent can lead to an increase of the volume fraction. The polybutadiene layer is only visible on one side of the polystyrene lamella in Fig. 2, which is probably due to a tilting of the structure with respect to the cut of the ultrathin section. This is a quite frequently observed phenomenon in TEM images for block copolymer structures with very thin features [32].

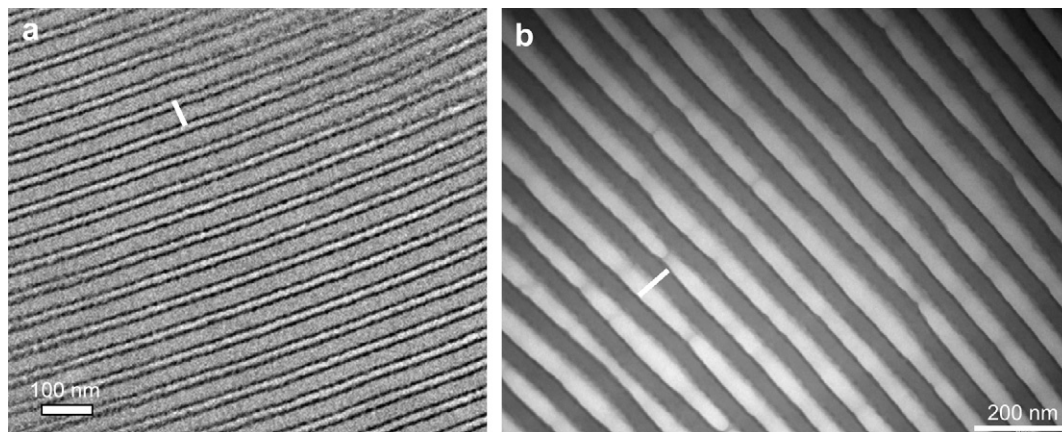


Fig. 2. Transmission electron micrographs of ultrathin sections of an SBT-1 film after staining with OsO_4 . The ultrathin film was imaged using a normal (a) and a carbon coated (b) TEM grid. The white bars indicate the long period of the periodicity of the structure.

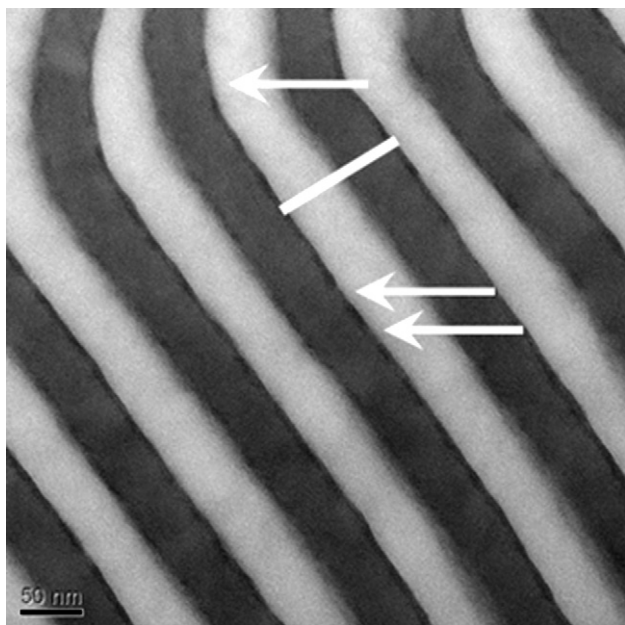


Fig. 3. Transmission electron micrograph of an ultrathin section of an SBT-2 film after staining with OsO_4 . The ultrathin film was imaged using a carbon coated TEM grid. The white bar indicates the long period of the periodicity of the structure.

An interesting peculiarity is the observation of two different long periods, depending on the grid type used. The smaller long period in Fig. 2a (53 nm) in contrast to the longer one, observed in Fig. 2b (80 nm), can be explained by a shrinkage of the structure. For block copolymers containing poly(methyl methacrylate) as one phase, the apparent micrograph does not necessarily reflect the real dimensions of the specimen, i.e. the thickness of the lamella is underestimated from the micrograph. This is due to the easy degradation of poly(meth)acrylates upon exposure to an electron beam. On the contrary, aromatic structures, like polystyrene, are much less sensitive to radiation damage as they undergo delocalized excitations [34]. The standard TEM grid (holey Cu-grid) is unable of providing sufficient mechanical stability to the film and thus the structures shrink, which as consequence results in a wrong representation of the actual volume fractions of the two endblocks, PS and PtBMA. In Fig. 2b, the volume fractions are represented as expected and the herein determined long period is closer to the real value, which can, e.g. be determined by SAXS.

In contrast to the clear lamellar (II) morphology of SBT-1, the SBT block terpolymers with polybutadiene fractions smaller 6 wt%, SBT-2 and SBT-3, show slightly different microphase-segregated

structures. Fig. 3 shows a TEM image of SBT-2, in which localized discontinuities of the butadiene lamella can be observed (highlighted by the arrows).

These discontinuities seem to be randomly distributed and do not exhibit any higher three-dimensional (3D) order or periodicity. A clear transition to the lamella–sphere (ls) or lamella–cylinder (lc) morphology cannot be observed. This morphology is thus best described as an irregularly perforated lamella (ipl). Perforated lamellar structures of diblock copolymers, such as the hexagonally perforated lamella (hpl), are considered to be metastable long-living transition states [35–37]. Consequently, the ipl structure found here will certainly react very sensitive to the presence of crosslinking and swelling agents. The thickness of the polybutadiene lamella is less than 5 nm and the long period can be calculated to be 86 nm.

Despite the discontinuities, this SBT block terpolymer may still serve as a material for the synthesis of flat Janus particles. The perforations may only act as a kind of desirable predetermined breaking point, leading to a decrease of the duration of the homogenization procedure using sonication.

A transmission electron microscopic investigation of the third SBT block terpolymer, SBT-3, with an even lower content of polybutadiene (4 wt%) reveals a clear break-up of the II morphology. The TEM images in Fig. 4 show comparable morphologies, mainly independent of the solvent used for the film casting.

In all cases, only short cylinders or elongated spheres can be seen at the interface of PS and PtBMA. The morphologies itself are not very well developed in the complete samples, indicating a strong competition of the chain conformational entropy and the interfacial energies of the system. Due to the small domain size of the polybutadiene, SBT-3 is not suitable for the synthesis of Janus discs. However, a clear transition to a defined lamella–cylinder or lamella–sphere morphology does not take place, which unfortunately prevents the usage of this block terpolymer for the synthesis of spherical Janus micelles as well. Even the polar solvent dioxane cannot induce the clear transition to a lamella–sphere morphology.

In consequence of the microphase-separated structures found, only SBT-1 and SBT-2 were investigated for the controlled crosslinking as only those bulk nanostructures may result in disc-like Janus particles.

3.3. Crosslinking of the SBT block terpolymer bulk nanostructures

Two strategies were employed for the crosslinking of the SBT block terpolymer morphologies. Cold vulcanization, radical crosslinking using AIBN and its optimization – the thiol–polyene procedure – have proven to be effective routes for crosslinking

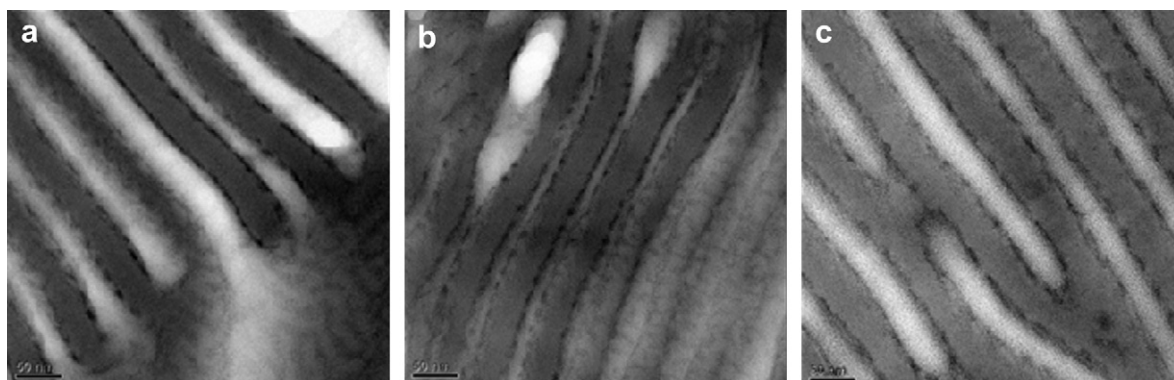


Fig. 4. Transmission electron micrographs of ultrathin sections of SBT-3 films after film casting from different solvents, dichloromethane (a), dioxane (b) and 2-butanone (c). The ultrathin sections were stained with OsO_4 and imaged using standard TEM grids.

polybutadiene microdomains. Cold vulcanization is the reaction of double bonds with sulphur monochloride (S_2Cl_2) in the swollen state and leads to the coupling of two vinyl moieties. In contrast to the free radical crosslinking via, e.g. AIBN, this reaction leads to a significant volume increase of the crosslinked material. The agent does not react in a chain reaction, but in a defined molar ratio.

3.4. Cold vulcanization with sulphur monochloride (S_2Cl_2)

As a first step, the swelling ability of several solvents in combination with the SBT block terpolymer films needs to be analyzed. The choice of solvents is limited to aprotic solvents, because protic solvents react with S_2Cl_2 and thus prevent crosslinking. The conditions were optimized for the SBT-2 block terpolymer, as this polymer was expected to react more sensitively to changes in solvent quality. This assumption is based on the fact that perforated lamellar structures may not be in full thermal equilibrium, as mentioned above. The investigations revealed that only a small number of organic solvents are able to swell the polymer film under retention of the desired morphology. Many solvents from polar to non-polar tend to dissolve the polymer film completely, which is probably due to the high solubility of the poly(*tert*-butyl methacrylate). Fig. 5 shows the corresponding TEM images of the swollen block terpolymer films after one day of swelling, subsequent rapid drying, microtome cutting and staining with OsO_4 .

Among the suitable solvents only decane and isooctane can be used as they do not alter the microphase-separated structure in any undesired fashion. Whereas the discontinuities remain in the polybutadiene layer upon swelling with decane (Fig. 5b), a continuous lamella can be observed when using isooctane as swelling agent (Fig. 5a). The latter solvent promotes “healing” of the perforations of the polybutadiene layer, which is due to the good swelling of the polybutadiene in isooctane. In contrast, a mixture of acetonitrile with 5 vol% THF induces an undesired transition of the lamella–lamella morphology to a microphase-segregated structure with small cylindrical or disc-shaped domains of polybutadiene at the interface. This is caused by the high polarity of acetonitrile, leading to a minimization of the surface area of the polybutadiene domains. Consequently, the latter solvent combination is not suitable for the preparation of large disc-shaped Janus particles with high aspect ratios. These results confirm the expected sensitivity of the irregularly perforated lamella towards a change in the solvent quality and show how carefully the solvent choice needs to be done. The differences in the morphologies, which develop upon swelling in the three different solvents, have an influence on the kind of Janus particles, which can be created during the cold vulcanization.

Another point which needs attention to be paid to is whether the crosslinking agent itself can have an influence on the

microphase-separated structure. Therefore, a detailed TEM investigation was performed after crosslinking the swollen films with different concentrations of sulphur monochloride (see Fig. 6). The images are somewhat blurry, which is related to the fluffy appearance and the related difficulties in cutting the ultrathin sections of the highly swollen and crosslinked films. This is also one of the reasons why the crosslinked polybutadiene layer is not clearly visible in all micrographs. Additionally, the butadiene phase is distributed in an extremely thin lamella and the contrast, evolving from the reaction of the thin crosslinked polybutadiene with S_2Cl_2 layer, is not always high enough to give sufficient contrast during the TEM imaging. A clear dark appearance of the PB phase can, however, be seen for the crosslinked lamella in Fig. 6d (SBT-1). Indications for a crosslinked PB phase can be seen in the magnified inset in Fig. 6b (SBT-2). Reasonably, it is easier to visualize the slight electron density contrast after crosslinking with S_2Cl_2 in isooctane for the block terpolymer with the higher polybutadiene content, i.e. SBT-1 (Fig. 6d). Additional staining of some remaining double bonds with OsO_4 after crosslinking an SBT-1 bulk structure in isooctane gives a clear evidence for the persistence of the lamellar morphology (compare Fig. 6e and f).

Considering the concentration effect of the crosslinking agent on the microphase-separated structure, a dramatic effect can be observed. The TEM image in Fig. 6a (SBT-2, isooctane, 5 vol% S_2Cl_2) shows a break-up of the PS lamella into cylinders and the PtBMA phase becomes continuous. A transition to a core-shell cylindrical morphology occurs. The change in the morphology is definitely induced by the crosslinking agent, S_2Cl_2 , as it was observed earlier that swelling in isooctane does not lead to a break-up of the PS phase (see Fig. 5a). This strong effect was unexpected in the first place, as sulphur monochloride is an extremely reactive chemical and was only used in relatively small quantities (<5 vol%). However, the morphological reorientation acts on a faster time-scale than the crosslinking. Consequently, the crosslinking of complex block terpolymer bulk nanostructures and metastable morphologies needs to be verified at every step of the crosslinking process. A similar transition cannot be observed for the reaction in decane (Fig. 6c), which is due to the unlike solvent quality and the different swelling behaviour of the three block terpolymer phases. Generally, decane is a worse swelling solvent and thus reduces the mobility of the phase towards structural rearrangements. On the other hand, it also limits diffusion of S_2Cl_2 and may thus be not advantageous for a tight crosslinking. In the case of the crosslinking of SBT-1 with 5 vol% S_2Cl_2 in isooctane (Fig. 6d), the break-up of the polystyrene lamella can only be seen for a small part of the imaged sample (hence not shown here), but the major parts remain intact. The ordinary lamellar morphology of SBT-1 obviously exhibits a higher stability towards a change in the solvent quality as it represents the

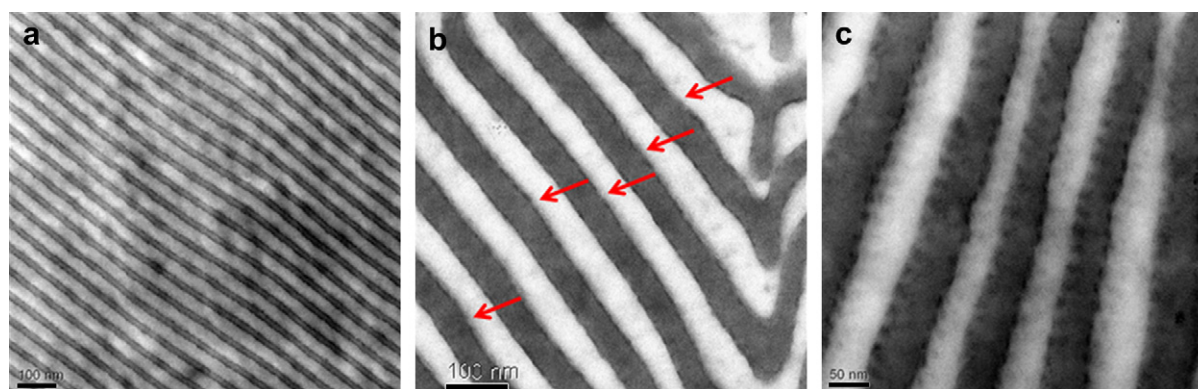


Fig. 5. Transmission electron micrographs of ultrathin sections of SBT-2 films after swelling in isooctane (a), decane (b) and acetonitrile/THF (95/5 vol%), c) and rapid drying. Prior to imaging the films were stained with OsO_4 .

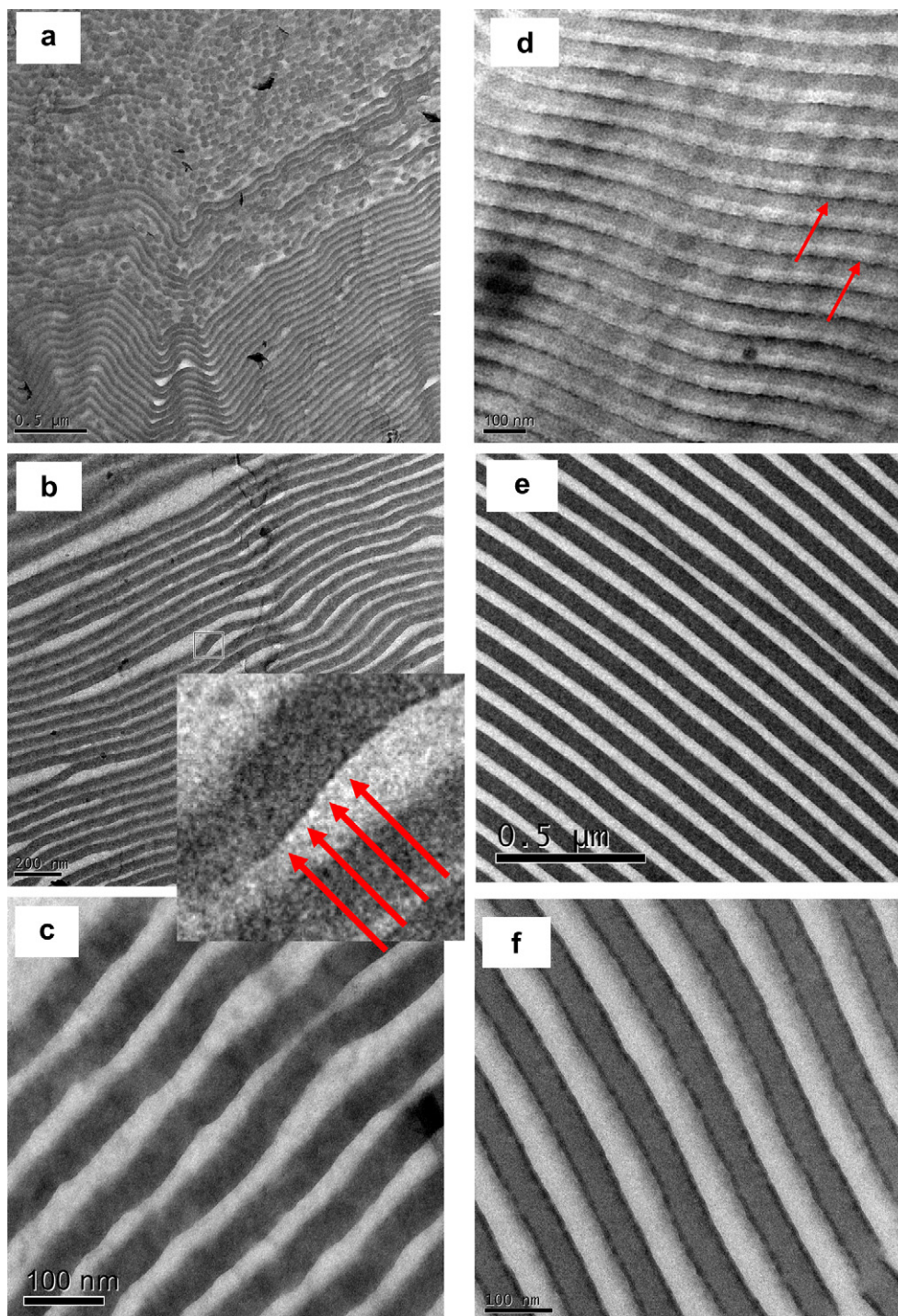


Fig. 6. Transmission electron micrographs of different polymer films after crosslinking with S_2Cl_2 . SBT-2 crosslinked with 5 vol% (a) and 3 vol% (b) S_2Cl_2 after swelling in isooctane. SBT-2 crosslinked with 5 vol% S_2Cl_2 after swelling in decane (c) and SBT-1 crosslinked with 5 vol% S_2Cl_2 after swelling in isooctane (d). SBT-1 crosslinked with 1.5 vol% S_2Cl_2 after swelling in isooctane (e) and after additional staining with OsO_4 (f).

thermodynamic equilibrium structure. Consequently, the crosslinking of the SBT-1 bulk films after swelling with isooctane and crosslinking with 1.5 vol% S_2Cl_2 proceeds smoothly as can be seen in Fig. 6e and f.

In conclusion, concerning the structural integrity of the micro-phase-segregated structure, decreasing the concentration of the crosslinking agent (1.5–3 vol%) has a positive influence for all samples. A break-up of the polystyrene layer can no longer be observed, neither for SBT-1 nor for SBT-2, allowing the desired crosslinking process in the lamellar morphology to take place.

Isooctane is to be preferred as swelling solvent, as it promotes a desirable continuous layer formation of the polybutadiene phase even at very low volume fractions of PB. Furthermore, the high degree of swelling ensures a fast and efficient crosslinking reaction to take place.

Aside the structural evolution during swelling and crosslinking, the focus was also set on the extent of the crosslinking. Table 2 summarizes the results of the purification of the SBT-2 polymer films after swelling and crosslinking with S_2Cl_2 using three different solvents and varying concentrations of crosslinking agent.

Table 2
Results of the purification after cold vulcanization of SBT-2

Swelling solvent	S ₂ Cl ₂ (vol%)	Fraction of insoluble material (%)	Degree of crosslinking ^{a,b} (%)
Decane	5	89.4	ca. 61
Isooctane	5	94.5	ca. 96
Isooctane	3	93.2	ca. 73
Isooctane	1.5	95.2	ca. 73
ACN/THF 95/5 vol%	5	6.3	Not measured

^a Crosslinking was performed for 24 h, using S₂Cl₂ as crosslinking agent, after swelling of the film in the corresponding solvent for 24 h. Soxhlet extraction was conducted for 24 h using THF as eluent.

^b Based on elemental analysis of the sulphur and/or the chlorine content of the insoluble material after Soxhlet extraction.

The cold vulcanization after swelling in the ACN/THF (95/5 vol%) mixture leads to mainly soluble Janus particles, reflecting the morphological transition to a completely discontinuous polybutadiene layer during swelling. The two other solvents, decane and isooctane, show a small difference for the fractions of insoluble and soluble materials. The major part is insoluble for both procedures. However, the insoluble fraction is always higher using isooctane as swelling solvent, even for low concentrations of sulphur monochloride. The extent of crosslinking, as determined by elemental analysis, indicates a slight difference in the extent of crosslinking for the two methods, meaning that the degree of crosslinked polybutadiene bonds is higher for isooctane. This is due to a higher extent of swelling in the case of isooctane, which facilitates the diffusion of the crosslinking agent into the polybutadiene lamella. The purification results reflect directly the solvent induced changes of the morphologies (see Figs. 5 and 6). Based on the TEM results regarding the structural transitions, the S₂Cl₂ content needs to be reduced in case of isooctane. Nevertheless, its good swelling ability still ensures a high degree of crosslinking and a large fraction of insoluble material. Note that the morphologies and the extent of crosslinking are much more sensitive to the type of solvent and the crosslinking agent used than to the times for swelling and reaction.

In order to obtain flat Janus particles in the end of the process, the cold vulcanization has to be performed in decane or in isooctane with 1.5–3 vol% of crosslinking agent. This ensures the integrity of the microphase-separated structure and the presence and persistence of a lamellar (II) morphology. Isooctane has some advantages as it leads to a “healing” of the holes in the ipl structure of the polybutadiene layer and to a better crosslinking even at lower contents of crosslinking agent.

Concerning an up-scaling of this reaction up to the gram scale, it is recommended performing the cold vulcanization using larger samples with similar thicknesses. Although we did not find differences for the crosslinking of films with thicknesses ranging from 0.5 to 2 mm, some problems could be anticipated if a big bulk plastic sample was introduced. With increasing ratio of volume to surface area, i.e. increased sample size, the diffusion rate of swelling solvent and crosslinking agent starts playing a larger role.

3.5. Crosslinking with AIBN and the thiol–polyene procedure

The radical crosslinking processes using AIBN or the thiol–polyene method have one important advantage over the cold vulcanization, which is the stability of the linking bonds in acidic media. This allows a subsequent facile hydrolysis of the poly(*tert*-butyl methacrylate) part using strong acids for the preparation of novel water-soluble disc-like Janus particles. On the contrary, however, radical crosslinking usually does not proceed with the same efficiency as the cold vulcanization, leading to a lower degree of crosslinking.

According to the work of Decker et al. [20–24], the crosslinking of AIBN in combination with TRIS, a trifunctional thiol, is expected to lead to an increased fraction of insoluble material (thiol–polyene reaction). This is due to the fact that TRIS can act as transfer agent and is also able to react with the 1,4-polybutadiene moieties which are usually not attacked during a normal radical crosslinking. Hence, this additive should lead to a stronger and more complete crosslinking and undesired side reactions, like radical transfer to the polymer backbone and radical chain scission should additionally be decreased due to the high chain transfer constants known for thiols. Therefore, the beneficial influence of this additive was also investigated in the present study.

Before carrying out the crosslinking, TEM images were recorded in order to assure the presence of lamellar morphologies. It can be seen in Fig. 7 that film casting in the presence of AIBN and TRIS has no influence on the development of the lamellar (II) morphology. The morphologies are of long range order and the black polybutadiene layers can be seen nicely in all cases. It is worth noting that a further increase of the TRIS concentration above 10 wt% results in a preferential swelling of the PtBMA phase. Despite the swelling of this phase, the lamellar block terpolymer morphology mainly remains unaffected.

An initially performed variation of the AIBN concentration from 3 to 10 wt% showed only a small influence on the ratio of insoluble to soluble material after purification with Soxhlet extraction (see Table 3). The fraction of insoluble material increases for higher concentrations of AIBN, but reaches a kind of plateau with further increase. It will be seen later that the never occurring complete crosslinking, even at high AIBN concentration, might be due to radical chain cleavages. Therefore, in order to ensure a sufficient crosslinking with an acceptable amount of side reactions, the simple radical crosslinking procedure can be carried out at a concentration of 5 wt% AIBN.

Table 3 also compares the influence of TRIS on the ratio of soluble to insoluble material. It can be seen from entries 2 and 5, as well as 6 and 7, that an addition of 5 wt% TRIS results in a clear increase of the crosslinked insoluble fraction, representing a beneficial influence of this additive. Generally, the fraction of insoluble material is much higher for SBT-1 than that for SBT-2, which is due to the higher content of polybutadiene, facilitating the crosslinking procedure. Unfortunately, it was not possible to determine the exact extent of crosslinking of the polybutadiene bonds, e.g. by infrared spectroscopy, as the content of polybutadiene is too low to allow a sufficient resolution of the signals. However, a rough estimation, also based on NMR spectra, indicates a degree of crosslinking of around 60–80%. The extent of crosslinking is in a similar range compared to the cold vulcanization process.

In order to investigate the occurring side reactions during the radical crosslinking procedures, GPC viscosity measurements of the soluble parts were performed (Fig. 8). The measurements revealed the presence of a strong peak at about half of the molecular weight of the block terpolymer precursors. The appearance of this peak is independent of the crosslinking method (AIBN, AIBN + TRIS) as well as of the block terpolymer used. The molecular weight indicates that the chain scission must take place at the inner block segment, i.e. polybutadiene. This may be caused by a radical chain transfer with subsequent chain cleavage. It can be seen that the addition of TRIS cannot fully prevent the radical chain cleavage, as a peak corresponding to roughly half of the molecular weight of the precursor remains. However, since the fraction of soluble material is much lower in the case of the thiol–polyene procedures, the radical chain scission reactions are at least significantly reduced.

At the higher molecular weight side, two shoulders in the range of 10⁶–10⁷ g/mol can be observed for the crosslinking of the SBT-2

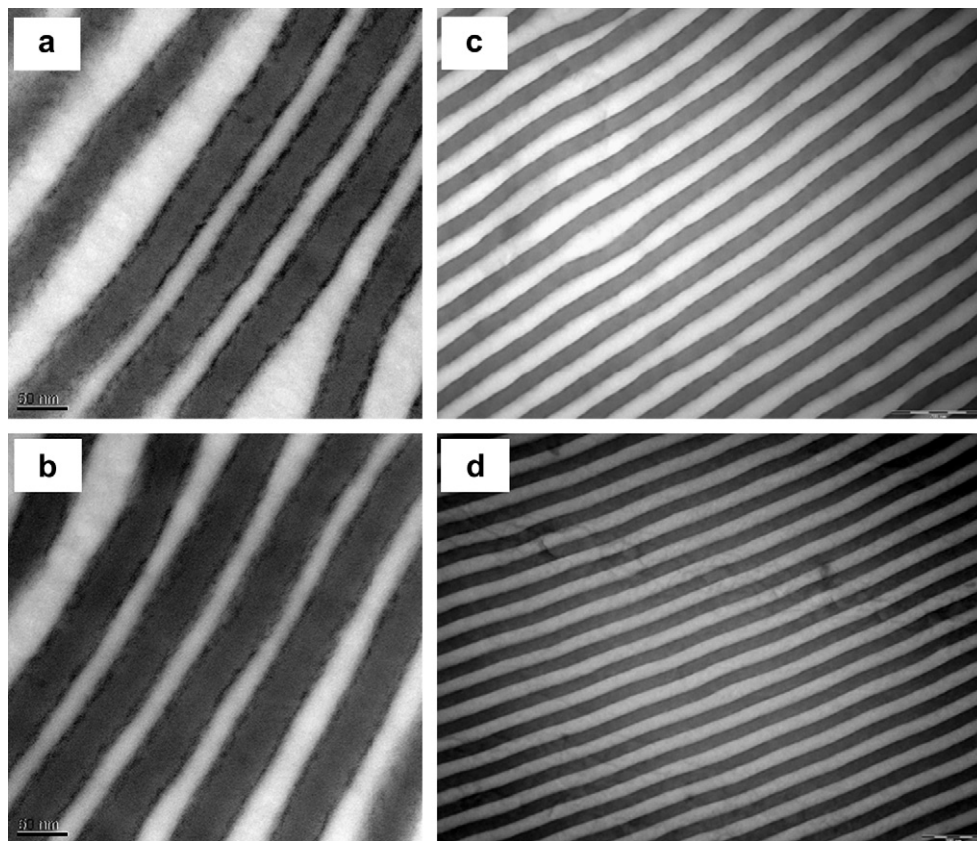


Fig. 7. Transmission electron micrographs after staining with OsO_4 . Ultrathin sections of SBT-2 with 5 wt% AIBN (a), SBT-1 with 5 wt% AIBN and 5 wt% TRIS (b), SBT-1 with 5 wt% AIBN (c) and SBT-1 with 5 wt% AIBN and 5 wt% TRIS (d).

samples, whereas no shoulder is visible for the soluble fraction of the crosslinked SBT-1 sample. The Soxhlet extraction obviously has an estimated molecular weight cut-off of 10^7 g/mol. The absence of high molecular weight shoulders in the latter case is due to the facilitated crosslinking at higher PB content, leading to the rapid formation of high molecular weight gel networks. Comparing the peak values of the two shoulders for the two SBT-2 fractions leads to the conclusion that the crosslinking with the thiol–polyene system leads to higher crosslinked aggregates, whereas the reaction with pure AIBN results in a considerable amount of only lightly crosslinked oligomers of the block terpolymers. The high transfer efficiency of the thiols is responsible for this behaviour as the addition of those introduces trifunctional crosslinking points and thus a more continuous crosslinking. Oligomeric structures are undesired as they can only be considered as fragments of the targeted nanostructures.

In conclusion, two different kinds of crosslinking methods for polybutadiene microdomains were studied. It was clearly proven

that the crosslinking can be accomplished via two ways, the cold vulcanization and the radical crosslinking process in combination with the thiol–polyene process. For performing the cold vulcanization the conditions need to be adjusted carefully as the morphologies react very sensitively to changes in the solvent quality. The addition of the crosslinking agent, sulphur monochloride, has a remarkable and unexpectedly strong influence on

Table 3

Influence of the AIBN concentration and the addition of TRIS on the crosslinking behaviour of SBT block terpolymer films

Entry	Terpolymer	AIBN (wt%)	TRIS (wt%)	Fraction of insoluble material ^a (%)
1	SBT-2	3.2	–	26
2	SBT-2	5	–	48
3	SBT-2	5.9	–	51
4	SBT-2	9.8	–	55
5	SBT-2	5	5	63
6	SBT-1	5	–	72
7	SBT-1	5	5	91

^a Soxhlet extraction with THF for 24 h.

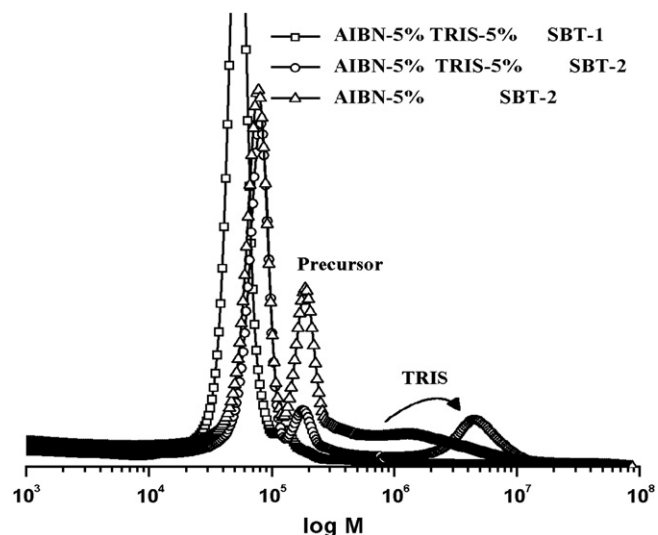


Fig. 8. RI traces for the molecular weight distribution as obtained by GPC viscosity measurements for the soluble fractions after Soxhlet extraction of the crosslinked block terpolymer samples.

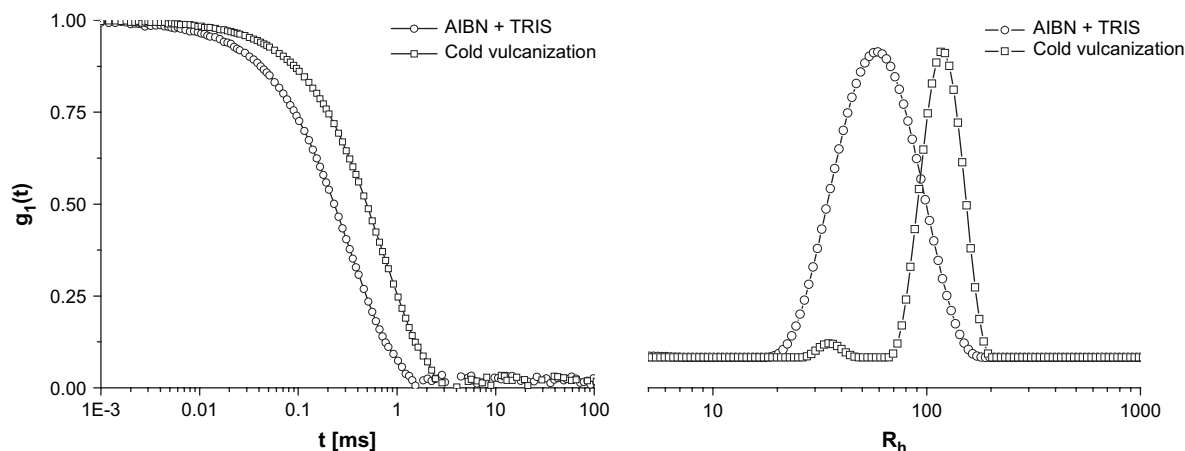


Fig. 9. Normalized field auto-correlation functions (left) and their corresponding CONTIN plots (right) for differently crosslinked SBT-2 bulk structures. The crosslinking method is indicated within the figure. After crosslinking, the samples were sonicated for 5 min at 30% amplitude. The small peak in the CONTIN plot of the sample obtained by cold vulcanization may arise from small fragments, which were cut-off during the homogenization.

the microphase-segregated morphology. The radical crosslinking process and the thiol–polyene process can be performed more easily and the resulting material has the benefit of possessing bonds which are stable to acidic conditions. Therefore, this material is the ideal precursor for the acidic hydrolysis towards amphiphilic water-soluble Janus sheets. On the contrary, the radical crosslinking suffers from some side reactions and generally leads to lower gel fractions. Both methods provide suitably crosslinked material for the preparation of sheet- or disc-like Janus structures.

3.6. Characterization of resulting soluble nanostructures

Soluble internally structured flat nanoparticles can be obtained after sonication of the crosslinked block terpolymer bulk nanostructures (see Scheme 1). As mentioned earlier, these kinds of nanoscopic Janus discs are widely unknown in literature, although theoretical calculations exist, dealing with their remarkable surface activities. Clearly, this demonstrates the limited synthetic accessibility. Detailed investigations concerning size and shape evolution, angular dependent scattering behaviour, supramolecular aggregation and behaviour at oil/water interfaces were recently published by us elsewhere [38]. Therefore, herein a result regarding the influence of the crosslinking method will be highlighted.

Fig. 9 compares the influence of the crosslinking method, cold vulcanization or thiol–polyene process, by means of the particle

sizes obtained by dynamic light scattering. The two differently crosslinked SBT-2 samples were sonicated under exactly the same conditions for 5 min at 30% of the maximum amplitude, leading to the observation of nanometer-sized particles.

It can be seen that the sample, crosslinked with the cold vulcanization, leads to significantly larger particle sizes. The average hydrodynamic radius is larger by a factor of two as compared to the sample, which had been crosslinked via the thiol–polyene method. Consequently, the crosslinking with S_2Cl_2 leads to a more continuous crosslinking throughout the material and may have some advantages if very large structures are required for specific applications. On the contrary, the crosslinking with the thiol–polyene method can experimentally be achieved more easily as it only involves co-casting of the component and simple heating of the microphase-segregated bulk structure. Hence, depending on the requirements, the appropriate crosslinking method can be selected.

The ultimate success of this strategy to prepare flat Janus-type nanostructures can be shown by scanning force microscopy. Fig. 10 shows a representative SFM image with two circular objects. The objects possess disc-like character as can be seen in the high aspect ratios deduced from the section analysis and the 3D surface plot of the larger structure. The particles are indeed completely flat in their centre.

The results convincingly demonstrate how the unique bulk morphologies of polybutadiene containing ABC block

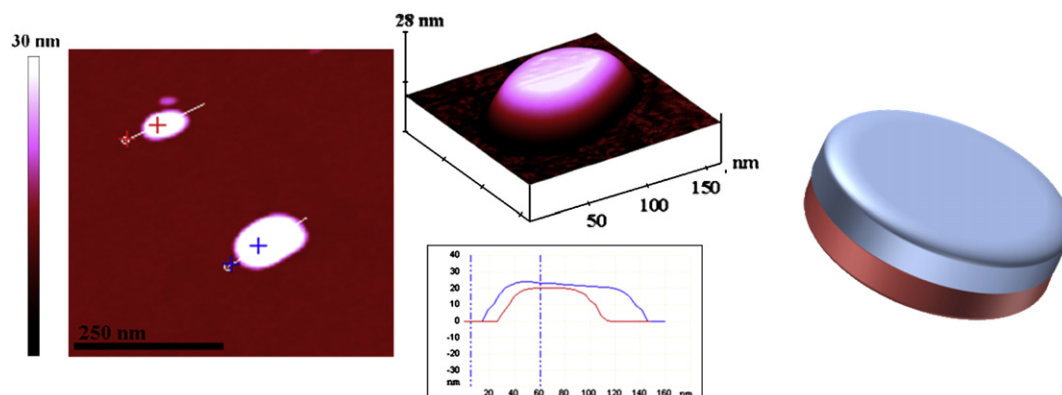


Fig. 10. Scanning force microscopy height image (left) obtained from a dip-coated sample (0.1 mg/L) of Janus discs, based on SBT-2 (crosslinked with S_2Cl_2 and sonicated for 10 min at 30% amplitude). Corresponding section analyses and 3D surface plot (larger particle) are shown in the center. Schematic representation of a Janus disc is shown on the right.

terpolymers can be transformed into novel internally structured nanoparticles.

4. Conclusions

The controlled crosslinking of polybutadiene microdomains of polystyrene-*block*-polybutadiene-*block*-poly(*tert*-butyl methacrylate) block terpolymers has been explored. Despite the low fractions of polybutadiene of only 5–10 wt%, lamellar (II) morphologies are formed, contrary to polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) block terpolymers.

The microphase-segregated morphologies of the block terpolymers react very sensitively towards additives, which are necessary for the crosslinking. This is due to the accompanying instability related to the low PB content. Careful optimization of the conditions is necessary in order to successfully crosslink the desired morphologies. The morphologies developed upon addition of chemicals were thoroughly investigated at all stages of the crosslinking. The addition of swelling solvents and crosslinking agent partially caused severe, unexpected and undesired changes in the bulk morphologies, thus requiring careful adjustment of the crosslinker concentration and the type of swelling solvent. Generally, the cold vulcanization leads to a higher extent of crosslinking and a larger fraction of desired crosslinked material. The free radical crosslinking can be performed more easily and can be improved by the thiol-polyene process, which leads to a higher fraction of crosslinked material. GPC viscosity measurements indicate that radical chain cleavage at the inner block takes place as side reaction. This side reaction prevents a further increase of the fraction of crosslinked material with increasing concentration of radical crosslinker, however, it can be suppressed to some extent by the addition of thiols for the thiol-polyene process.

Both methods, cold vulcanization and radical crosslinking, provide facile and highly effective routes for the crosslinking of polybutadiene containing block terpolymer microphase-segregated structures. Moreover, the shown procedures may serve as guidelines for future investigations for the preparation of functional nanoparticles via crosslinking microphase-segregated block terpolymers in the bulk.

Finally, some properties of the obtained Janus discs are highlighted to demonstrate the effectiveness and usefulness of crosslinking block terpolymer bulk structures towards the preparation of internally structured nanostructures. The size of the resultant nanoparticles was shown to depend on the crosslinking method, i.e. larger structures can be obtained by the cold vulcanization, representing a more continuous crosslinking. Additionally, the flat

shape of the novel Janus discs can be confirmed by scanning force microscopy.

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