Nanostructured polyamide by reactive blending: 2. Transition from nanovesicles to cucumber-like core-shell nanoobjects

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Abstract

Polyamide 12 (PA 12) has been nanostructured by reactive blending with 20 wt% of a symmetric anhydride end-capped polysty-rene-*b*-polyisoprene (PS-b-PIP-anh) The liposome-like nanovesicles which are originally formed in the polyamide matrix (PA 12) are converted into cucumber-like core-shell nanoobjects upon increasing the volume fraction of PS by addi-j tion of homo PS of a molecular weight lower than the PS block. The key effect of the molecular weight of homoPS with respect to the PS bloc,k has been emphasized. The same nanoobjects can be prepared by direct blending of PA12 with 20 wt% of an asymmetric reactive PS-b-PIP-anh diblock with the same molecular weight and a higher PS content compared to the symmetric diblock. The interesting point is that the thickness of the rubbery envelope of the core-shell nanoobjects changes with the method used for their preparation at constant PA12/ PS/PIP composition, as result of a change in the molecular weight of the shell forming block.

Keywords

Nanostructures Block copolymers Self assembly Reactive blending   Phase morphology

Introduction

The control of the structure of organic materials at the nanometric scale is nowadays one of the most efficient strategies to tune their macroscopic properties. Synthesis and self-assembly of block copolymers is a typical illustration of the implementation of this strategy [1]. The nanometric self-organization of block copolymers is actually predetermined by the volume fraction of the constitutive blocks and the strength of their mutual repulsion. The same rules also hold for the structure of the micelles formed by block copolymers in a solvent selective for one block. In an extreme case, the selective solvent can be a homopolymer selectively miscible with one block. The phase behavior also depends on the relative length of the homopolymer chains and the parent block [2] Polymer matrices have been nanostructured by diblock copolymers either by solvent-casting polymer/ copolymer blends in an appropriate solvent [2] or' by dissolving the copolymer in a reactive liquid precursor of the matrix, followed by polymerization [3] or curing [4] of this liquid. Because the upscaling of these strategies is not straightforward, some of us have proposed to form the block copolymer in situ by reactive melt blending of a precursor with the matrix [5]. In a preliminary experiment, a polystyrene-13-polyisoprene-*b*-polyamide12 (PS-b-PIP-b-PA12) copolymer with a symmetric composition has been formed by reactive melt blending of 20 wt% of an anhydride end-capped polystyrene-*b*-polyisoprene (PS-b-PIP-anh) with an amino end-functional polyamide. Within a few minutes at 220 °C, the ABC triblock copolymer is formed in situ and self-assembles into a liposome-like nanostructure. However, a core-shell nanostructure with a cucumber-like core organization is observed when the volume fraction of the PS block is increased, all the other conditions being the same [5] This paper aims at reporting on the transition between these two nanostructures by using only one reactive diblock (the symmetric one) and by increasing the PS volume fraction by addition of homopolystyrene The effect of the relative molecular weight of homo PS and the PS block on the final phase morphology has also been considered.

Experimental section

Materials

Styrene (Sty, Aldrich, 99+%), isoprene (IP, Janssen Chimica, 99%), ethylene oxide (EO, Meisset) and cyclohexane were dried over CaH_2 (Aldrich) and distilled just before use. ses-BuLi (Aldrich, 0,22 mol/1 in hexane), rc-BuLi (Aldrich, 1 mol/l in hexane), dibutylmagnesium (Aldrich, 1 mol/1 in hexane), were used as received and stoied under Ar at -20 °C Trimellitic anhydride chloride (TAC, Fluka, 99%) was stoied and handled in a glove box. Fluor enyllithium (1 mol/1 in toluene) was prepared by reacting s*ec*-BuLi with fluorene (Aldrich) in toluene under Ar. Liquids were tiansfeiied under Argon (Ar, Meisser) by glass syringes or stainless steel capillaries through rubber septa Polyamide 12 was PA12 Rilsan AECHVO from ATOFINA (M_n~20,000 g/mol, M_w/ M_n=18, [NH_2] = 25µ/g).

Synthesis of the reactive PS-b-PIP-anh diblocks

PS-b-PIP block copolymers were prepared by sequential anionic polymerization of styrene and isoprene, initiated by s*ec*-BuLi in cyclohexane in order to promote the c*is*-1,4 addition of the isoprene units. The glass reactor was dried by flaming under reduced pressure Solvent and monomers were transfer red through previously flamed stainless steel capillaries A sample of diblock was picked out and deactivated by degassed methanol for characterization Finally, ethylene oxide was added to the polymerization medium, followed by a mixture of HCl/methanol/isopropanol (5/ 70/25 in volume) in order to end-cap the chains by a hydroxyl group (PS-b-PIP-OH) In a second step, the PS-b-PIP-OH chains were reacted with a large excess of tiimellitic anhydride chloride (>30 equivalents) in dry THF, in order to have the chains end-capped by a phthalic anhydride as repotted elsewhere [5, 6] This anhydride end-functionalization was confirmed by FTIR The absorption characteristic of the anhydride was observed at 1787 cm^{-1}. The anhydride functionality was quantified by *H NMR at 400 MHz. More details about the copolymer synthesis and characterization were published in a previous paper [5]. Two diblocks were prepared as reported in Table 2.

Characterization

Size exclusion chromatography (SEC) was performed in THF (flow rate of 1 ml/min) at 40 °C using a HP1090 liquid chromatograph equipped with a HP1037A dual refractive index/UV detector (columns HP PL gel 5 µm, 10^5, 10^4, 10^3, 100 A) and calibrated with polystyrene standards (Polymer Labs). ^{1}H NMR spectra were recorded with a Brucker AM 400 MHz spectrometer at 25 °C Infrared spectra were recorded with a Per kin Elmer 1720X spectrometer for polymer films solvent cast on a NaCl disk.

Melt blending

Melt blending was carried out in a 5-cm^3 DSM miniextruder at 220 °C under nitrogen, at 200 rpm for 2 min. The matrix was first added followed by 20 wt% of the diblock (or triblock). In an alternative procedure, the reactive diblock and homo PS were dissolved in THF and co-precipitated in methanol After drying at room temperature in a vacuum oven, the preblend was added to the mini extruder and melt reacted under the aforementioned conditions.

Transmission electron microscopy (TEM)

The phase morphology of the blends was observed with a Philips CM 100 transmission electron microscope. A Reichtert-Jung ultra-cryomicrotome equipped with a diamond knife was used to prepare ultrathin samples at -78 °C in the direction perpendicular to the extrudate. The PIP phase was selectively stained by OsO_4.

Results and discussion

Figure 1 shows TEM micrographs for the polyamide matrix (80 wt%) after reactive melt blending with a PS-b-PIP-anh copolymer of a symmetric composition (SI-1 in Table 1) Liposome-like vesicular objects are observed in the PA12/PIP/PS ternary blend of a 80/10/10 wt composition. Actually a PA12-b-PIP-b-PS triblock copolymer is formed in situ, that consists of blocks of approximately the same molecular weight (Mn PA12=20 K; Mn PIP= 18 K; Mn PS= 16 K) The self assembly of this triblock in the PA 12 matrix occurs under shear and leads to vesicles with a double layered shell, as discussed elsewhere [5]. However, when the composition of the reactive diblock (20 wt%) is changed at the benefit of PS (SI-2 in Table 1; wt% PS) at constant molecular weight, the nanoobjects formed in PA 12 change from vesicles to core-shell particles with a cucumber-like substructure for the core [5b] (Fig 2). The relative length of the constitutive blocks of the in situ formed triblock has changed (Mn PA12=20 K; Mn PIP = 7 K; MnPS=31 K) and the wt composition of the ternary blend (PA12/PIP/PS = 80/3.6/16.4), as well. These two examples show that the nanoobjects formed in PA12 (80 wt%) can be changed remarkably by tuning the relative length of the constitutive blocks of the end-reactive diblock at constant molecular weight and content (20 wt%). It would however be more convenient to trigger the transition from vesicular to core-shell nanostructures by using only one reactive diblock (i.e., the symmetrical one that generates vesicles) and to adapt the composition of the final ternary blend to the composition at which the core-shell nanostructure is observed. This strategy is easily implemented by increasing the PS content in the 20 wt% of copolymer blended with PA12. Indeed substitution of a SI-1/homo PS blend of a 35/65 wt composition for neat SI-1 in the blend with PA12, restores the blend composition for which core-shell nanostructures are formed (Fig. 2). The key condition is however that the homo PS spontaneously accumulates in the PS nanodomains of the trilbock, which means that the molecular weight of this homoPS is of a prime importance.
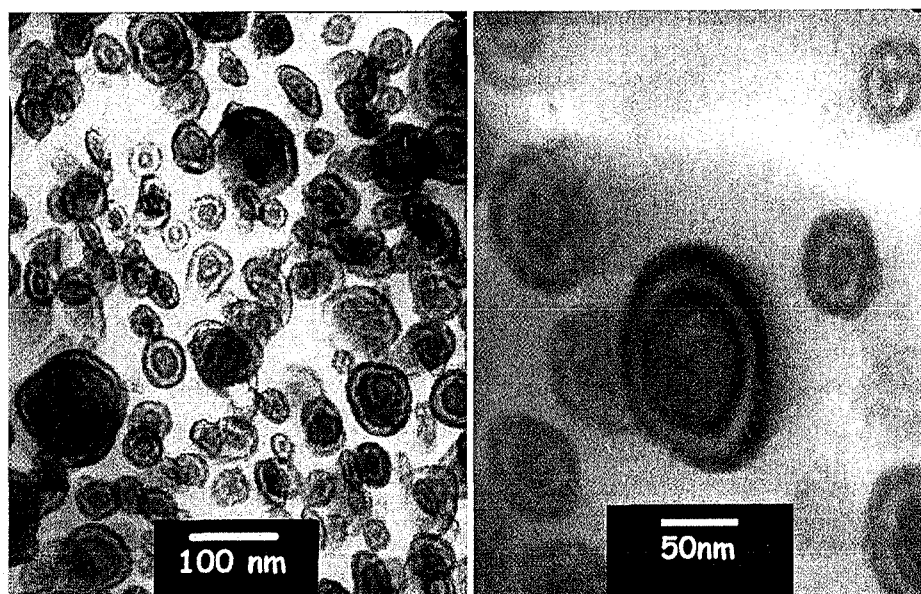

Fig. 1 TEM micrographs for the PA12/SI-1 (80/20) blend with a vesicular morphology, at two different magnifications
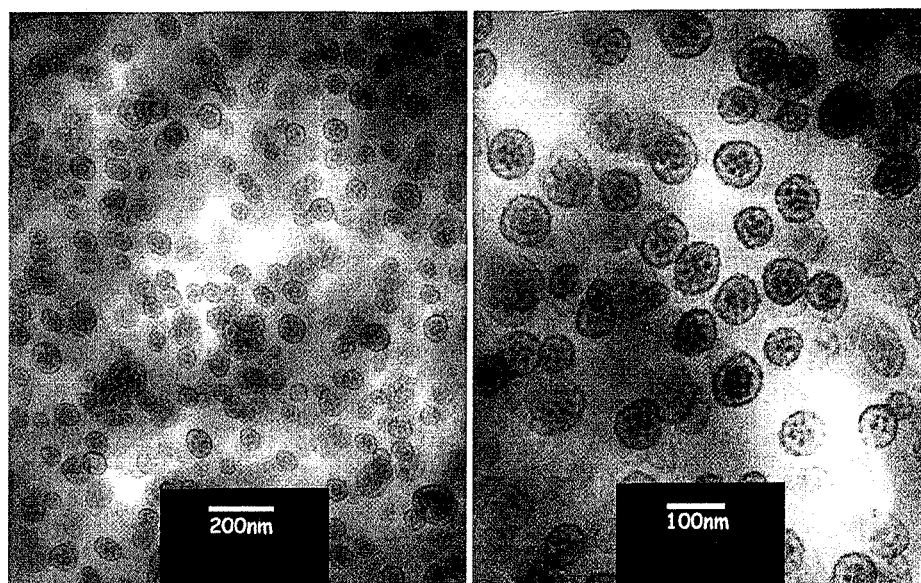
Fig. 2 TEM micrographs for the PA12/SI-2 (80/20) blend with a cucumber-like core-shell morphology, at two different magnifications

It is only in the wet-brush regime that the homoPS chains can swell the interfacial PS brush of the copolymer, i.e.., whenever the homoPS molecular weight is lower than the one of the PS block of the triblock copolymer. This requirement has been confirmed by considering the behavior of three homoPS of increasing molecular weight. First, the reactive diblock has been pre-blended with a homoPS (S-l), whose the molecular weight is half that of the PS block of the reactive copolymer (see Tables 1 and 2). Figure 3A shows that the cucumber-like core-shell morphology is observed in contrast to the vesicles expected for the neat symmetric copolymer (Fig 1). The actual content of PS in the blend is now 16.4%, which corresponds to 82 wt% in the SI-1/S-1 preblend added at a rate of 20 wt%. This is actually the composition of the asymmetric reactive diblock that promotes the cucumber-like morphology (Fig. 2). The bulk morphology of this preblend has been observed by TEM as reported in Fig. 4A.

Table 1 Reactive diblock copolymers used in this study

Code	Type	M_n (10^{-3} g/mol)	M_w/M_n[a]	PS (wt%)	$f(\%)$[c]
SI-1	PS-b-PIP-anh	16 (PS)[a]-18 (PIP)[b]	1. 05	47	93
SI-2	PS-b-PIP-anh	31 (PS)[a]-7 (PIP)[b]	1.03	82	92

[a] *SEC with PS standards*
[b] *400 MHz ^{1}H NMR analysis*
[c] *Anhydiide functionality measured by SEC-UV analysis*

Table 2 Homopolystyrene used in this study

Code	Type	(10^{-3} g/mol)[a]	M_w/M_n[a]
S-1	PS	7	1 03
S-2	PS	16	1 02
S-3	PS	35	1 02

[a] *SEC with PS standards*

The phase morphology is at the border between spheres and perforated lamellae in line with a PS content of 82%, in contrast to the lamellar phase morphology observed for the neat copolymer with 47% PS (Fig. 4B). The key observation is that PA12 can be provided with the same nanostructure by reactive melt blending with a constant amount of an additive (20 wt% in this work) that consists of either a mutually reactive diblock (e.g.. PS-PlP-anh) of a well-defined composition or a preblend of a reactive diblock of the same molecular weight but different composition and a parent homopolymer (PS or PIP) such that the composition of the additive remains unchanged This flexibility allows for the characteristic sizes of the nanoobjects to be changed. Comparison of the core-shell particles observed in Figs. 2A and 3A and magnified in Fig 3B,C, illustrates that the thickness of the PIP rubbery shell is approximately two times larger in case of the two-component PA12/SI-2 (80/20) reactive blend compared to the three-component PA12/(SI-1 + S-l) (80/20) blend (with SI-1 /S-1 = 3.5/65), as result of $Mn PIP = 7 K$ in the former blend and $Mn PIP = 18 K$ in the latter one This methodology is thus effective in tuning, e.g., the shell thickness of thermoplastic core-rubber shell particles, which may be of great interest to understand better the rubber toughening of thermoplastics by this type of core-shell additive.

When the molecular weight of homo PS is increased up to that of the PS block (S-2, Table 2), the phase morphology changes as illustrated by Fig. 5A. The TEM micrograph shows that core-shell structures persist with however a modified internal substructure and a bimodal distribution of the particle size In all the cases, the PS cores are stabilized in the PA matrix by an interfacial monolayer of the in situ formed PS-b-PIP-b-PA copolymer PS-b-PIP diblocks seem now to form cylindrical micelles in the PS domains as result of the dry brush regime at the interface as reported by Thomas et al. [2] and more recently by Chen et al. [7].
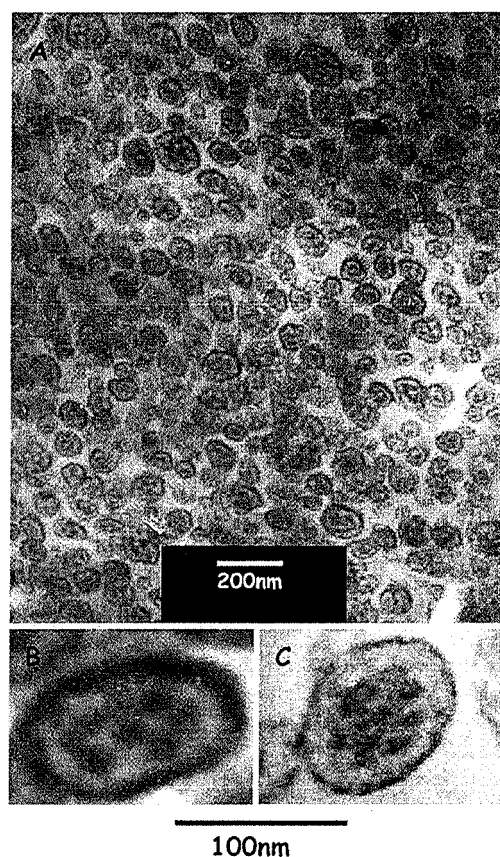

Fig. .3 A TEM micrograph for the PA12/(SI-1/S-1) (80/20(35/65)) blend with a cucumber-like core-shell morphology, B The same at higher magnification. C The counterpart shown in Fig 2 Emphasis: has to be placed on the change in the shell thickness (dark shell of PIP)

These authors observed indeed the same phenomenon for AB/hA blends in which the homo A (hA) is the matrix and the molecular weight ratio, M_{nA}/ M_{nhA}, is close to one. Finally, when the molecular weight of homo PS is much higher than that of the PS block (S-3, Table 2), the same morphology as in the previous case persists (comparison of Fig. 5A,B), except that the diblock cannot form micelles

anymore in the PS microdomains Any diblock excess tends then to accumulate at the PS/PA 12. interface, which is thicker by approximately a factor of 2 (TEM observation) compared to the previous blend in which only the triblock would be at the interface. From the magnification of the shell layer (Fig 5A',B'), it appears that the apparent thickness is uneven and that TEM is not reliable enough to measure the shell thickness.
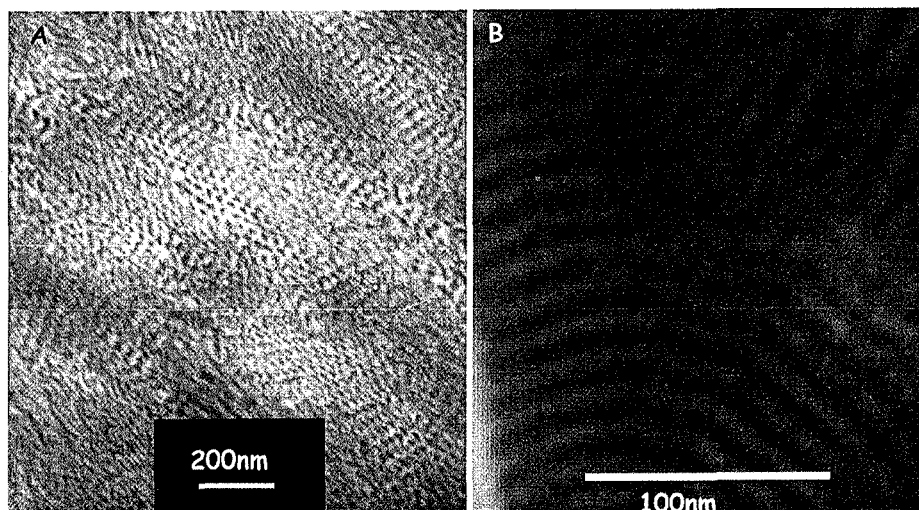

Fig. 4 A TEM micrograph of the bulk morphology for the SI-1/S-1 (35/65) pre-blend. B TEM micrograph of the bulk morphology for the SI-1 copolymer
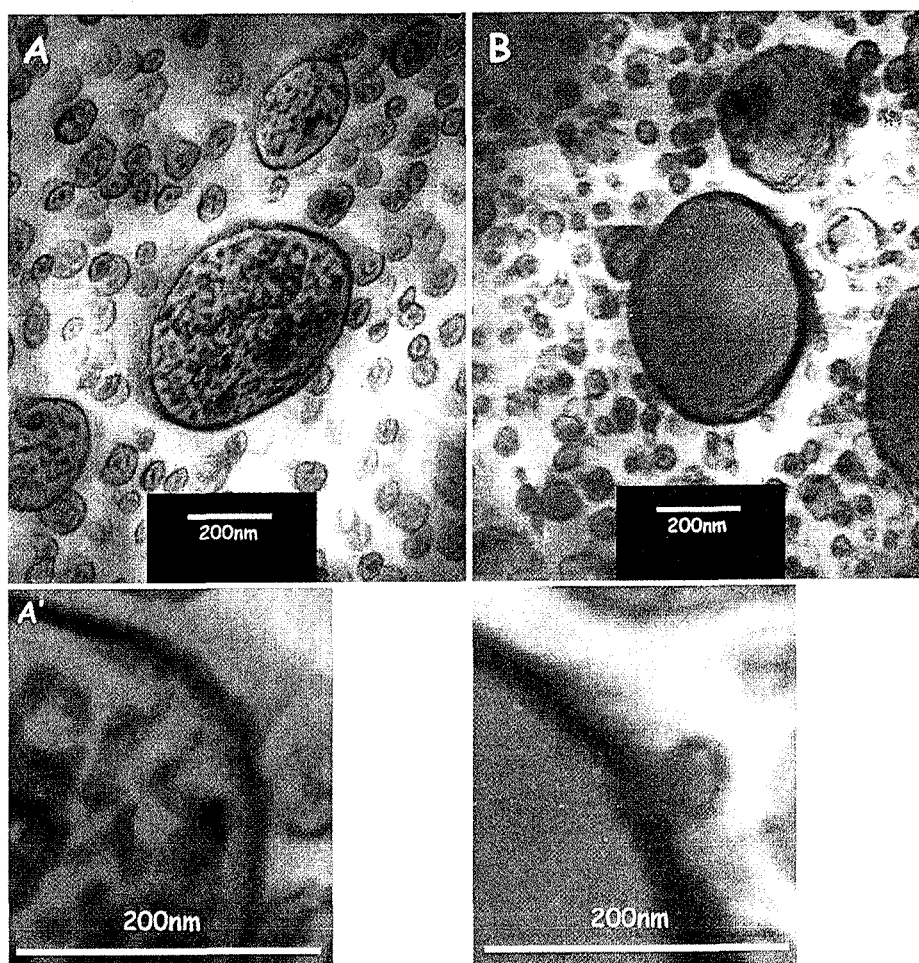

Fig. 5 A TEM micrograph for the PA12/SI-1/S-2 (80/20(35/65)) blend. B TEM micrograph for the

PA12/SI-1/S-3 (80/20(35/65)) blend. A',B' Magnifications of one nanoobject observed in A and B, respectively

Conclusions

In this work, reactive PS-PIP-anh diblocks of different composition and same molecular weight have been melt blended with 80 wt% of mutually reactive PA12 Vesicular nanoobjects are formed in the PA 12 matrix when the diblock is symmetric If PS is the major constitutive block, cucumber-like core-shell nanoobjects are then observed It is however possible to add homo PS with a molecular weight lower than the PS block of the symmetric copolymer for triggering a transition from the vesicular to the core-shell nanostructure The interesting point is that the thickness of the PIP shell has a different thickness depending on the way the core-shell morphology is prepared in relation to the length of the **PIP** block of the reactive diblock The possible tuning of the thickness of this shell is a key issue to study the effect of morphological characteristic features on macroscopic properties, such as the stiffness/toughness balance of thermoplastics.

Acknowledgements

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