Vesicular Nanostructures Prepared by Reactive Melt Blending**

Christian Koulic, Zhihui Yin, Christophe Pagnoulle, and Robert Jérôme*

The toughening of thermoplastics with rubber is one of the most important applications in the rapidly expanding field of polymer blends. The control of the morphology of rubber-modified thermoplastics is, however, the key issue for a successful toughening process.[1] In this respect, micellar structures, such as vesicles, have been recently proposed as toughening agents. Practically, amphiphilic block copolymers are dissolved in a liquid reactive mixture which is the precursor of the matrix to be toughened. They spontaneously form nanostructures, the nature of which depends on their molecular composition and structure. In an example reported by Bates and co-workers,[2c] an epoxidized polyisoprene-*b*-polybutadiene copolymer dissolved in diglycidyl ether bisphenol A, spontaneously self assembles into spherical micelles or vesicles depending on the diblock composition. The epoxy resin is then hardened upon addition of 4,4′-methylenedianiline and the micellar structures are accordingly frozen in. This behavior is general to block copolymer/epoxy systems in which one constitutive block is miscible with the matrix and the other one is an immiscible rubbery block.[2] In the specific case of a vesicular morphology, a drastic increase in fracture toughness was observed at low copolymer content (ca. 2.5 wt %) together with a substantial decrease in modulus.[2e] Meyer and co-workers also investigated the toughening of brittle thermoplastics, such as poly(methyl methacrylate) (PMMA) and polystyrene (PS), by using the same strategy. They successfully preformed micelles of hydrogenated polybutadiene-*b*-poly(methyl acrylate) in methyl methacrylate (MMA) or styrene that were frozen in upon polymerization of the continuous monomer phase. Although the prevention of macrophase separation was confirmed by small-angle X-ray scattering (SAXS) studies, no data for the mechanical properties was made available.[3] Even though micellar nanostructures are promising toughening agents for brittle thermoplastics or thermosets, the two-step strategy based on polymerization (or cure) of the matrix after the nanophase morphology is established is not sufficiently straightforward to be viable on a large scale. Herein we report on the nanostructuration of a block copolymer by the one-step reactive melt blending with the matrix to be toughened. A core–shell morphology with a rubbery shell was targeted in the case of a polyamide matrix. For this purpose, polyamide 12 (PA12) chains, end-capped by a primary amine, were melt blended with 20 wt % of a polystyrene-*b*-polyisoprene (PS-*b*-PIP) copolymer end-capped at the PIP chain end by an anhydride. The aim was to build up a core–shell morphology with a rubbery layer between the PA12 matrix and the PS nanophase.

Previous studies[4] emphasized that the kinetics of the interfacial reaction has a decisive effect on the phase morphology in reactive blending. When all the chains are reactive and the mutually reactive groups are used in the stoichiometric molar ratio, the reaction can go to completion in the case of a high reaction rate and when the chains have a relatively low molecular weight. Since the coupling reaction of the PS-*b*-PIP diblock to PA12 must be as complete as possible, the fast reaction of the primary amine end group of PA12 with the anhydride (anh) end group of PS-*b*-PIP-anh has been considered. The diblock was synthesized by sequential anionic polymerization of styrene and isoprene initiated by *sec*-BuLi, followed by deactivation by ethylene oxide and derivatization of the ω-hydroxy end group into an anhydride.[4d] The expected end capping of the diblock by the anhydride end group was confirmed by FTIR spectroscopy (absorption at 1780 cm^{-1}) and by size-exclusion chromatography (UV detection at 366 nm) after reaction with 9-(methylaminomethyl)anthracene.[5]

Table 1. Polymers used in this study.

Code	Type	M_n($\times 10^{-3}$) [g mol^{-1}]	M_w/M_n	Addition[b]
S1	PS-*b*-PIP	16[a]-18[b]	1.05[c]	1,4: 93 %, 3,4: 7 %
S2	PS-*b*-PIP-anh	16[a]-18[b]	1.05[c]	1,4: 93 %, 3,4: 7 %

[a] Size-exclusion chromatography using PS calibration. [b] By ^{1}H 400 MHz NMR spectroscopy. [c] Size-exclusion chromatographic analysis.

In this study, a symmetric diblock (Table 1) has been melt blended with PA12 at 220 °C. Observation by transmission electron microscopy (TEM) shows there is a gross phase separation in the case of nonreactive blending (Figure 1). The expected lamellar nanostructure is observed in the microdomains formed by the symmetric diblock. The thickness of the constitutive PS lamellae can be estimated to be approximately 7 nm. A drastic decrease in the particle size occurs when the blending is reactive (Figure 2 A). At higher magnification, the dispersed nanophases exhibit a core–shell structure with a three-layer substructure for the shell (Figure 2 B–

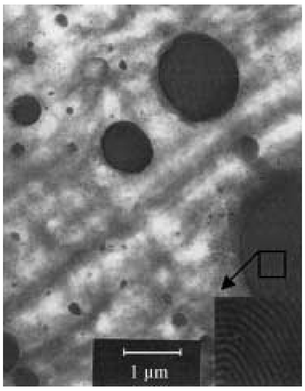

Figure 1. TEM image for the 80/20 (wt/wt) blend of PA12/**S1** (11500 ×). The insert shows a close-up of the lamellar organization of the microphase (105000 ×).

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[*] Prof. R. Jérôme, C. Koulic, Z. Yin, Dr. C. Pagnoulle
Center for Education and Research on Macromolecules (CERM)
University of Liège
Sart-Tilman, B6a, 4000 Liège (Belgium)
Fax: (+32) 4-366-3497
E-mail: rjerome@ulg.ac.be

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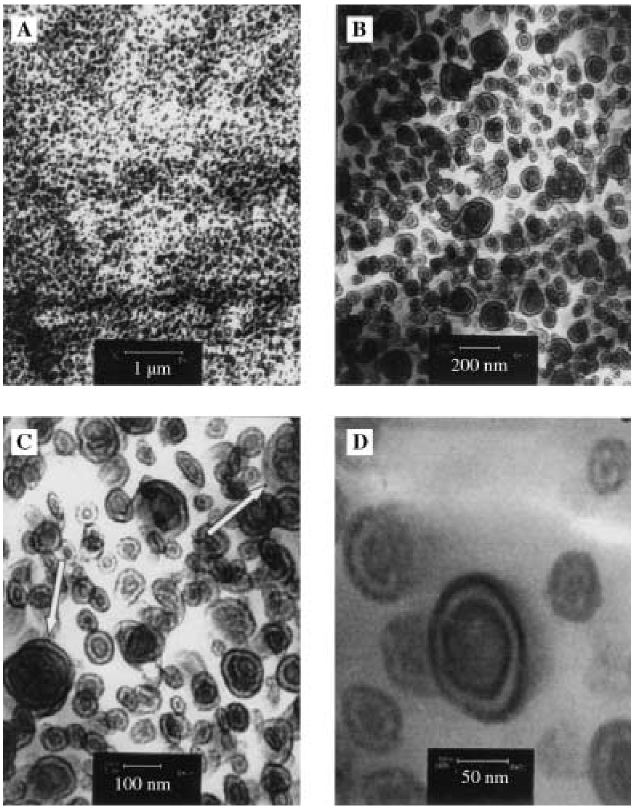

Figure 2. TEM image for the 80/20 (wt/wt) blends of: A) PA12/**S2** (11500 ×), B) PA12/**S2** (39000 ×), C) PA12/**S2** (73000 ×), and D) PA12/**S2** (205000 ×). The white arrows point out larger nanophases with a multicore substructure.

D). As a rule, the size of the nanophases is in the 40- to 80-nm range. Since the first and the third layer of the shell are the darkest domains on staining with OsO_4, they have been assigned to PIP. PS is thought to form the intermediate layer of the shell whose thickness (ca. 8 nm) is consistent with that observed for the lamellar morphology of the PS-*b*-PIP diblock. According to this picture PA12 should be the core-forming component. This hypothetical structure of a bilayer of triblock chains is reasonable because a single core–shell structure cannot be formed by a PA12-*b*-PIP-*b*-PS triblock in which the three constitutive blocks are of a comparable molecular weight ($M_{\mathrm{nPA12}} \approx 25000\ \mathrm{g\,mol^{-1}}$).[6] Indeed, dispersion in the PA12 matrix means the external brush of PA12 is wet, which triggers the curvature of the PA12/PIP and PIP/PS interfaces; the extreme situation is a PS core surrounded by a PIP shell. However, PIP and PS layers of approximately the same molecular weight cannot be accommodated in a classical core–shell structure for steric reasons. In contrast, a double triblock layer (PA12/PIP/PS/PIP/PA12) can account for the observed nanostructuration as unreacted PA12 chains can be accommodated in the core so that steric constraints are relieved, thus forming bilayered vesicular nanostructures. This morphological description also accounts for the high dispersity of the core size (10 to 65 nm), even though the shell dimension remains unchanged. Some larger nanophases (ca. 150 nm) are also observed that apparently result from partial coalescence of smaller particles, as suggested by a multicore substructure (Figure 2C). It must be noted that Thomas and co-workers accounted for the formation of single-layered vesicles in their study of binary mixtures of a diblock AB and a homopolymer A by considering the interface curvature and packing requirements of the blocks in the domain space.[7a] The same criteria were also useful to explain the nonconstant mean curvature (CMC) of the shell in the morphology of a symmetric ABC triblock.[7b]

In conclusion, the reactive dispersion of symmetric PS-*b*-PIP-anh diblock copolymer within a polyamide matrix whose chains are end-capped by a primary amine, spontaneously forms core–trilayer shell nanophases. This morphology is nothing but a dispersion of PIP-PS-PIP vesicles in the polyamide matrix, that is, the counterpart of the vesicular morphology imparted to epoxy resins by a two-step process which is responsible for their high-impact properties. This very first example of nanostructuration of a three-phase polymeric material by reactive blending paves the way for the design of new materials by classical processing techniques and to the establishment of fundamental relationships between morphology of multiphase materials and key properties such as thermoplastics toughening.

Experimental Section

Polystyrene-*b*-polyisoprene was prepared in a glass reactor previously flamed under vacuum. Polymerization of styrene in cyclohexane was initiated by *sec*-BuLi under argon at room temperature. After 4 h, freshly distilled isoprene was added and left to react at 35°C overnight. Living chains were terminated by ethylene oxide (2 equiv with respect to the initiator) followed by the addition of a HCl/methanol/isopropanol mixture (5/70/25).[8] The PS-*b*-PIP-OH diblock was collected by precipitation in methanol, carefully dried under reduced pressure at room temperature, and treated with trimellitic anhydride chloride in dry THF as reported elsewhere.[4d] A nonreactive counterpart of the anhydride end-capped diblock was collected by picking out a sample of the reactive mixture before the addition of ethylene oxide. The living chains were deactivated by degassed methanol, precipitated in methanol, and dried under reduced pressure at room temperature.

Melt blending was carried out in a 5-cm^3 DSM microextruder at 220°C under nitrogen for 2 min at 200 rpm. PA12 was first added followed by 20 wt% of the diblock.

The phase morphology was observed with a Philips CM100 transmission electron microscope. A Reichtert–Jung ultracryomicrotome equipped with a diamond knife was used to prepare ultrathin samples at -78°C. The PIP phase was selectively stained with OsO_4.

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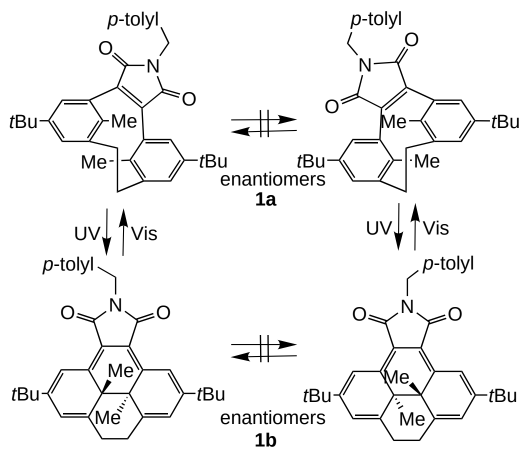
Enantioselective Photochromic Reaction of a [2.2]Metacyclophan-1-ene**

Michinori Takeshita* and Takehiko Yamato

Photochromic compounds have been extensively studied owing to their potential as photomemory and photoswitching materials.[1] Photochromic compounds reversibly change their absorption spectra (color) upon photoirradiation. However, reading the photomemory by changes in the absorption spectrum causes the destruction of the memory, since photoirradiation results in excitation of photochromic compounds.[1] Therefore, various attempts at nondestructive readout have been reported,[1] for example, by locking one of the photoisomers by the addition of chemical substances[2] or by electrooxidation (gated photochromic reaction).[3] Reading the change in chiral information originated in photochromic reactions is one of the most promising systems, since chiral information can be read without excitation of photochromic compounds.[4, 5] In photocyclization systems, for example, diarylethenes,[5a] fulgides,[5b] and spiropyrans,[5c] the enantiomers of the photochromic compounds undergo diastereoselective photocyclization. In these systems, one should be aware of the diastereoselectivity of the cyclization, since such selectivity is altered by the conditions (e.g. temperature, medium, etc). This fact encouraged us to study enantiomeric photocyclization, that is, a photochromic reaction between two enantiomers in which no racemization takes place.

We chose 1,2-disubstituted [2.2]metacyclophan-1-enes (MCP-1-enes),[6] which we recently reported,[7] as the enantiomeric photocyclization system (Scheme 1). It is well known that ring inversion of the phenyl groups in the *anti* 8,16-dimethyl[2.2]metacyclophane system is forbidden because of the steric hindrance between the inner methyl groups and the opposite phenyl groups.[8] For similar reasons, ring inversion of MCP-1-enes does not occur, and MCP-1-enes are chiral molecules because no mirror symmetry exists in the molecule. Therefore, one can expect that racemization of the enantiomers of MCP-1-enes does not take place. MCP-1-enes show photochromism,[6, 7] and tetrahydropyrenes (THP) formed from MCP-1-enes by UV irradiation are also chiral. It is expected that no racemization occurs, even during the photochromic reaction, and that the photochromic reaction takes place with both enantiomers.



Scheme 1. Enantioselective photochromic reaction of [2.2]MCP-1-ene **1a** and THP **1b**.

We have designed and synthesized some MCP-1-enes and found that the enantiomers of maleimide-type MCP-1-ene **1a** are easily separated.[9] MCP-1-ene **1a** was synthesized from 1,2-dicyano[2.2]MCP-1-ene[7] in three steps.[10] Figure 1 shows the changes in the absorption spectrum of a solution of **1a** in hexane upon irradiation with 313-nm light. The pale yellow solution of **1a** changed to violet upon UV irradiation, and irradiation with visible light returned the spectrum to its initial form. The violet color shows the formation of THP **1b**.[11] The photostationary state at 313 nm was analyzed with HPLC (silica gel, hexane/AcOEt 10:1, 385 nm (isosbestic point)) and contains 35 % of MCP-1-ene **1a** and 65 % of THP **1b**.

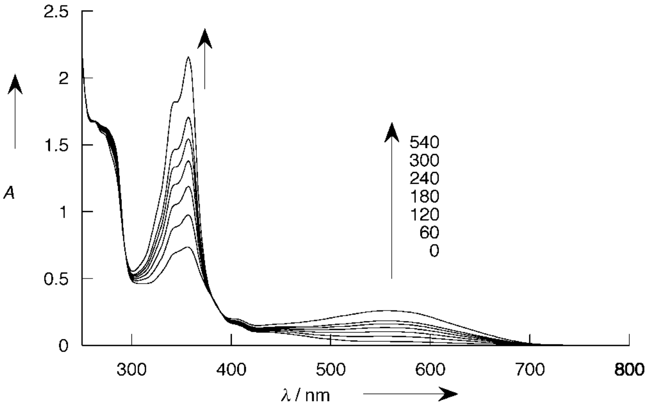


Figure 1. Changes in the absorption spectrum of **1a** (0.16 mM in hexane) upon irradiation with 313-nm light. Numbers indicate the irradiation time (s).

Figure 2 shows a chromatogram of the racemic mixture of **1a** (HPLC on a chiral column).[9] Three peaks were found and these peaks were assigned to one enantiomer of MCP-1-ene

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[*] Prof. M. Takeshita, Prof. T. Yamato
Department of Applied Chemistry
Faculty of Science and Engineering, Saga University
Honjo-machi 1, Saga, 840-8502 (Japan)
Fax: (+81) 952-28-8862
E-mail: michi@ce.saga-u.ac.jp

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