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Nanostructured poly(urethane)s and poly(urethane-urea)s from reactive solutions of poly[styrene-*b*-butadiene-*b*-(methyl methacrylate)]-triblock copolymers

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ABSTRACT

Poly[Styrene-*b*-Butadiene-*b*-(Methyl Methacrylate)], SBM triblock copolymers have been incorporated in different polyurethane, PU formulations in order to prepare nanostructured materials. Macrodiols used for PU synthesis were based on a central bis-phenol A, *BPA* unit with two hydroxyl-terminated oligo(oxypropylene), *BPA-PO$_x$* or oligo(oxyethylene), *BPA-EO* chains with varying lengths. The initial solubility of the three blocks and the rheological behavior of the solutions in macrodiols and also in two diisocyanates, isophorone diisocyanate, *IPDI*, and 1,3-xylylene diisocyanate, *XDI* have been first characterized. The PMMA block is the most soluble and its role during the reaction is to stabilize the initial nanostructure or to control the reaction-induced microphase separation.

Block copolymers can be dissolved first in the macrodiol, or preferably in the diisocyanate. With *BPA-PO$_x$* and low SBM content (<10 wt%), transparent linear or crosslinked PU with well dispersed triblock nanoparticles have been prepared, depending on the molar mass of the macrodiol and on the concentration of diblock SB impurities present in the triblock. For high SBM concentrations (>50 wt%), a twin screw extruder had to be used for the blending. Under well-defined conditions, transparent linear PUs and linear segmented polyurethane-ureas have been prepared.

This study confirms that for designing a nanostructured material from a reactive mixture with a triblock additive, one block, called "the nanostructuring block" has to remain soluble up to the end of the reaction.

1. Introduction

Numerous linear thermoplastic polyurethanes (PUs) naturally display nanostructured morphologies, associated with their segmented architecture made of alternating, more or less immiscible soft and hard segments that confer them remarkable mechanical properties (especially an exceptional compromise between abrasion resistance, tear resistance, tensile strength and elongation at break) over a broad temperature range [1]. However, these high-performance materials are not very often optically clear. In contrast, other reactive PU systems based on well chosen miscible components can lead to rigid, perfectly transparent matrices but most of these are rather brittle.

In the past few years, AB-diblock and ABA- or ABC-triblock copolymers have been the subject of numerous studies. Because of favorable/unfavorable thermodynamic interactions between the different blocks, these copolymers can display a wide range of nanostructured morphologies, depending on the architecture (linear, loop, star,

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miktoarm, etc.) and on the absolute and respective lengths (related to their respective volume fractions) of the blocks. These morphologies have been widely studied both from a theoretical and experimental point of view [2–9]. Also in solution, in the case of slightly [10,11] or strongly [12–14] selective solvents, i.e. where at least one block is non-soluble whereas at least one is perfectly soluble, they were shown to be prone to self-organize, often leading to nanostructured micelle dispersions in an appropriate concentration range. If the solvent happens to be a reactive mixture or monomer, and if some specific criteria are met, nanostructured materials can also be obtained after cure, and sometimes these modified materials can display improved mechanical properties such as a better toughness or impact resistance. Finally recently, Zheng et al. demonstrated that it was even not always necessary to start from a self-organized reactive mixture to obtain nanostructured, ordered or disordered, thermosets since this could also be achieved through the "reaction-induced microphase separation" process that involves the microphase separation of some of the blocks of the added copolymer, initially soluble, while other blocks remain soluble throughout the polymerization reaction [15,16].

A lot of literature has been especially devoted to poly[styrene-*b*-butadiene-*b*-(methyl methacrylate)], SBM, triblock copolymers [17–19]. It was demonstrated [20] that SBM copolymers could be added to reactive diepoxide/diamine blends to elaborate nanostructured thermosets: more precisely, the PMMA block was soluble in the diepoxide and in the unreacted blends. During the reaction, due to the decrease in the entropy of the mixture, a macroscopic phase separation could occur. But for diamine hardeners that allowed this block to remain perfectly soluble up to the end of the curing reaction, nanostructured, transparent materials were obtained. In such reactive systems, the PMMA block could thus be viewed as the "nanostructuring block". In contrast when the used diamine was unfavorable for PMMA miscibility, macrophase separation rapidly occurred during curing and flocculated, micrometer size dispersed domains were observed in the final opalescent materials.

The question was then to establish whether the same principle applied to other types of reactive mixtures. More precisely, would it be possible to obtain nanostructured blends by the addition of well-chosen ABC triblock copolymers to one or several polyurethane precursors? Could these blends lead to nanostructured materials by an appropriate controlled curing? And in that way, would it be possible to obtain nanostructured PU matrices that would retain a perfect transparency?

2. Experimental part

2.1. Materials

In a first stage, the polyurethane matrices were mainly obtained from the simple polyaddition reaction of a diisocyanate with an oligodiol. For this purpose two different diisocyanates were used, mainly isophorone diisocyanate, *IPDI*, and occasionally 1,3-xylylene diisocyanate, *XDI*. In order to study the influence of chemical crosslinks on material nanostructuration, a polyfunctional isocyanate containing mainly the trimer of 1,6-diisocyanatohexane, *^{t}HDI*, was also sometimes used. The structure and main characteristics of these 3 compounds are shown in Fig. 1a and Table 1.

The oligodiols, *BPA-POx*, were based on a central bisphenol A, *BPA*, unit with two hydroxyl-terminated oligo(oxypropylene) chains with varying lengths. An equivalent molecule bearing 2-hydroxyethoxy groups (i.e. 1 ethylene oxide unit) on each end of the BPA moiety, *BPA-EO1*, was used for comparison. These oligodiols were precisely described in a previous paper [21]. Again a trifunctional compound, here a polycaprolactone triol, *PCL^{t}OH*, was sometimes used to investigate the effect of crosslinking on nanostructuration. All the hydroxylated compounds are depicted in Fig. 1b and Table 1. In a second stage, segmented poly(urethane-urea)s were obtained by use of the previously described oligodiols as soft segment precursors, and of 4,4′-methylene bis(3-chloro-2,6-diethylaniline) (Lonzacure M-CDEA, *MCDEA*, also shown in Fig. 1b and Table 1) as chain extender. All the precursors were used as received.

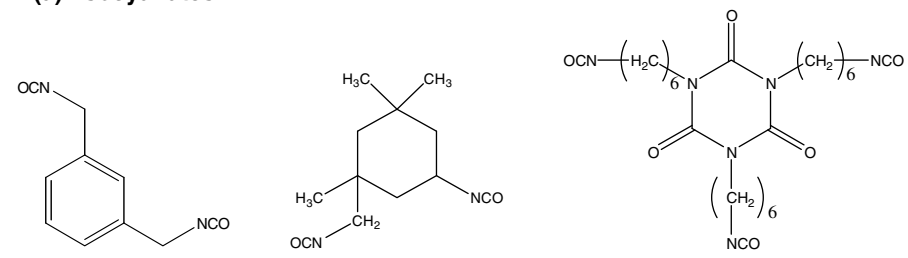
The triblocks used were asymmetric poly[styrene-*b*-butadiene-*b*-(methyl methacrylate)], SBM, copolymers synthesized anionically at pilot scale by Arkema [22,23], and their synthesis and characterization were already described in previous works [20,24]. The PMMA blocks are highly syndiotactic (>70%), and the PB structures are more than 85% 1,4. Because of the synthesis process, some SB diblock copolymers are present in the initial product. In this paper, the nomenclature used for SBMs is similar to that proposed by Stadler et al. [9]: $S_t^xB_uM_v$ with *t*, *u*, and *v* corresponding to the mass percent of blocks determined by ^{1}H NMR and *x* to the PS block number–average molar mass in kg mol^{-1}, determined by SEC. For the initial block copolymers containing "impurities", the nomenclature is $S_t^xB_uM_w$-SB*o* with *o* the weight percentage of diblock SB, and $S_t^xB_uM_w$-SB*o*-S*p* if eventually some residual PS homopolymer is also present.

Several poly[styrene-*b*-butadiene-*b*-(methyl methacrylate)] triblock copolymers were used and compared for the synthesis of nanostructured polyurethanes, differing by the weight proportions of the blocks, by their length and also by the amount of residual SB diblock copolymer or even polystyrene homopolymer. All the triblock copolymers used in this study are described precisely in Table 2. When necessary, these SBM-triblock copolymers were sometimes purified using a previously described dissolution–precipitation technique [20].

Before adding SBM-triblock copolymers to the diisocyanate–oligodiol reacting mixtures, the miscibility of model homopolymers displaying about the same molar masses and chemical microstructure as the three blocks was evaluated with the various precursors. The main characteristics of these homopolymers are displayed in Table 3.

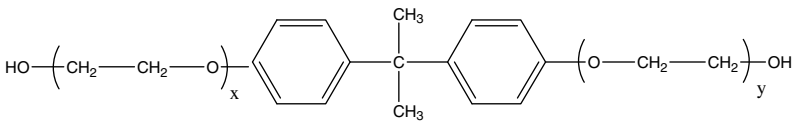
The blending conditions of the various studied systems will be described in the Results part. The materials modified with low amounts of SBM triblock copolymer were prepared by simple casting. In contrast, the blends of the various precursors with high amounts of SBM were too viscous and therefore these materials were processed with

(a) isocyanates:

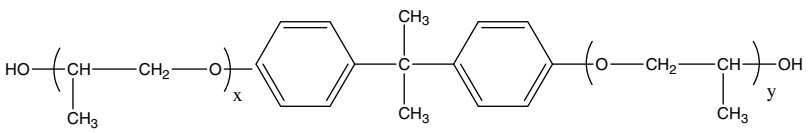


XDI *IPDI* *^{t}HDI*

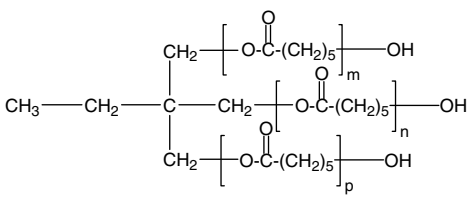
(b) alcohols and diamine:



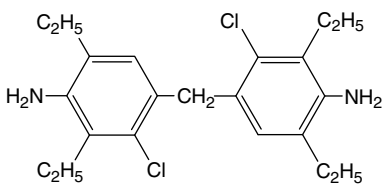
BPA-EO



BPA-PO



PCL^{t}OH



MCDEA

Fig. 1. Chemical structures of the polyurethane precursors.

the help of a twin-screw microcompounder with co-rotating conical screws, recirculation channel and six controlled heating zones (DSM Xplore 15 ml Micro-Compounder).

2.2. Characterization

The miscibility or non-miscibility of various mixtures was evaluated with the help of a home-made light transmission device [25]. For non-reactive systems, binary polymer/solvent blends were placed in a test tube and heated until a clear mixture was obtained. After a few minutes, the samples were cooled at 1 K/min. The cloud point temperature, T_{cp}, was taken when the intensity of the transmitted light began to decrease. In the case of initially miscible reactive blends, their isothermal polyaddition was run *in situ* in the test tube once again until the intensity of the transmitted white light began to decrease. This moment was considered as the cloud point time, t_{cp}.

Transmission electron microscopy analyses were carried out at the "Centre Technologique des Microstructures de l'Université Claude Bernard Lyon1" on a Philips CM120 microscope operating at 80 kV. Ultrathin sections (thickness: 60 nm) were obtained using two different techniques:

(1) The sample was cut using an ultramicrotome equipped with a diamond knife, to obtain 60 nm-thick ultrathin sections. Then, the sections were stained on nickel grids with osmium tetraoxide vapors during 2 h.
(2) For samples with rigidity not high enough to prepare high quality ultrathin sections at room temperature, a pyramid-shaped piece was cut and treated with a 4% aqueous solution of osmium tetraoxide during 1 week. Ultrathin sections were then microtomed on the flat top of the pieces.

Considering the applied staining conditions, in the micrographs PB appears black, PS gray, and PMMA whiter than the polyurethane network.

Table 1
Main characteristics of the isocyanate precursors and hydroxylated precursors used in this study

Isocyanate precursors used in this study Monomer	Chemical nature	M_n (kg/mol)	Eq_{NCO} (mol/kg)	n_{20}^{D} [a]	δ (MPa$^{1/2}$)[b]	Supplier
IPDI (isophorone diisocyanate)	diisocyanate	222.2	8.978	1.483	21.6	Crenova
XDI (1,3-xylylene diisocyanate)	diisocyanate	188.2	10.602	1.542	25.4	Mitsui Chemicals, Inc.
^{t}HDI (1,6-diisocyanatohexane trimer, Tolonate HDT®)	triisocyanate	/liquid, T_g = −68 °C	5.157	1.505	24.0	Rhodia

Hydroxylated precursors used in this study Monomer	Chemical nature	M_n (kg/mol)	T_f or $T_{gmidpoint}$ (°C) ΔC_p (J K^{-1} mol^{-1})	n_{20}^{D} [a]	δ (MPa$^{1/2}$)[b]	Supplier
BPA-PO1 (Dianol 320®)	macrodiol	345 (x + y)[c] = 2	T_g = 0 (±1) 0.62 (±0.02)	1.544	21.7	Seppic
BPA-PO2 (Dianol 340®)	macrodiol	465 (x + y)[c] = 4.1	T_g = −29 (±1) 0.56 (±0.02)	1.528	21.1	Seppic
BPA-PO3.5 (Simulsol BPMP®)	macrodiol	625 (x + y)[c] = 6.8	T_g = −44 (±2) 0.55 (±0.04)	1.503	20.2	Seppic
BPA-EO1 (Dianol 220®)	macrodiol	321 (x + y)[c] = 2	T_g = −5 (±1) 0.56 (±0.04)	–	22.4	Seppic
PCLtOH (polycaprolactone, Desmophen VPLS 2249/1®)	macrotriol	319	T_g = −61 (±3) 0.71 (±0.04)	1.467	24.5	Bayer
MCDEA (4,4′-methylenebis (3-chloro-2,6-diethylaniline))	diamine	380	T_f = 88–90	–	22.0	Lonza

[a] Refractive index (20 °C).
[b] Hildebrand solubility parameter.
[c] See Fig. 1.

Table 2
Structure and composition of the triblock copolymers used in this study

Composition	Weight proportions	Nomenclature	Designation
Purified triblock copolymer PS 9200 – PB 8500 – PMMA 24200 *41 900 g/mol*	Purified triblock copolymer 22% PS 20% PB 58% PMMA As-received triblock copolymer 90 % SBM 10 % SB	$S_{22}^{9.2}B_{20}M_{58}$ $S_{22}^{9.2}B_{20}M_{58}$-SB*10*	SBM01
Purified triblock copolymer PS 9200 – PB 10600 – PMMA 20500 *40 300 g/mol*	Purified triblock copolymer 23% PS 26% PB 51% PMMA As-received triblock copolymer 80 % SBM 20 % SB	$S_{23}^{9.2}B_{26}M_{51}$ $S_{23}^{9.2}B_{26}M_{51}$-SB*20*	SBM02
Purified triblock copolymer PS 6800 – PB 10550 – PMMA 20510 *37 900 g/mol*	Purified triblock copolymer 18% PS 28% PB 54% PMMA As-received triblock copolymer 48 % SBM 52 % SB	$S_{18}^{6.8}B_{28}M_{54}$ $S_{18}^{6.8}B_{28}M_{54}$-SB*52*	SBM03
Purified triblock copolymer PS 16000 – PB 18500 – PMMA 88600 *123 100 g/mol*	Purified triblock copolymer 13% PS 15% PB 72% PMMA As-received triblock copolymer 80 % SBM 17 % SB 3 % S	$S_{13}^{16}B_{15}M_{72}$ $S_{13}^{16}B_{15}M_{72}$-SB*17*-S*3*	SBM04

Table 3
Structure of the model homopolymers

Homopolymer	M_n[a] (kg/mol)	I_p[a]	Microstructure[b]	$T_{gmidpoint}$ (°C)[c] ΔC_p ($J\,K^{-1}\,mol^{-1}$)	δ ($MPa^{1/2}$)[d]	Supplier
Polystyrene (PS)	98.9	1.25	heterotactic	106 (±1) 0.30 (±0.04)	18.5	Arkema
Polybutadiene (PB)	5.1	1.05	80% 1,4-*PB*, 20% 1,2-*PB*	−97 (±1) 0.55 (±0.06)	16.9	Aldrich
Poly(methyl methacrylate) (PMMA)	88.6	1.66	10% iso, 36% hetero, 54% syndio	115 (±1) 0.25 (±0.02)	19.1	Lucite International

[a] From Size Exclusion Chromatography.
[b] From ^{1}H NMR.
[c] From Differential Scanning Calorimetry.
[d] Hildebrand solubility parameter.

Rheological measurements were run using a stress-controlled AR1000 apparatus (TA Instruments). The linear viscoelastic domain was determined at first, at the lowest temperature studied with a given frequency. The measurements were then carried out under forced-stress conditions, on 1 mm-thick samples placed between two parallel circular plates (diameter: 60 mm). These samples were at first heated up to a high enough temperature (especially above their order–disorder transition whenever it existed), then cooled back slowly to room temperature or slightly below (~0 °C) before the measurement was started. G′ and G″ were then monitored at 1 rad/s as a function of temperature, while heating at 2 K/min.

3. Results and discussion

In previous works devoted to the modification of polyepoxide networks with SBM triblock copolymers [20,24], the initial morphology of the reactive blends with the triblocks could be rather easily observed and could therefore be directly compared with that of the final material, allowing a quite precise description of the microphase separation mechanism. In reactive epoxide–diamine blends modified with a thermoplastic, the evolution of the morphology could even be followed by TEM throughout the reaction [26]. In the present work, the reactivity of the diisocyanate-based reactive blends made such studies impossible; therefore only non-reactive blends based on homopolymers or triblock copolymers and one of the precursors were separately examined, keeping in mind that the transposition of their behavior to the case of the complete reactive system should be made cautiously.

3.1. Initial solubilities

3.1.1. Blends of the model homopolymers with polyurethane precursors

Whatever their composition, binary blends of PB with any precursor were always prepared in bulk by heating up to an adequate temperature (50–180 °C, depending on the nature of the second component) where a homogeneous mixture was obtained. PS/solvent or PMMA/solvent blends, containing low polymer amounts (<30 wt%) were also prepared in bulk using the same method. Depending on the mixtures it was necessary to heat up to 100–200 °C in these cases. Finally the systems with more than 30 wt% PS or PMMA homopolymer were too viscous to be prepared in bulk and the use of a co-solvent was necessary. Both components were thus dissolved in chloroform and mixed in proper proportions before the solvent was evaporated at room temperature, first at ambient pressure for 4 days, then one night under a vacuum; the mixtures were finally heated up to 150 °C under ambient pressure until a constant weight could be measured.

Polystyrene is partially miscible with both diisocyanates, *IPDI* and *XDI*. In these two precursors PS displays a UCST (upper critical solubilization temperature)-type behavior as described in Fig. 2, showing that PS miscibility is higher with *IPDI* than with *XDI*, a slightly more polar molecule. In a similar way, PB is partially miscible (UCST behavior, see Fig. 2) with *IPDI* whereas it is totally immiscible with *XDI*. Finally, Fig. 2 clearly shows that PB is also less miscible than PS with *IPDI*. Apart from this, both homopolymers are totally immiscible with ^{t}*HDI*, as well as with all the hydroxylated compounds used in this work.

Model diurethanes were obtained from the end-capping reaction of stoichiometric amounts ([NCO]/[OH] = 1) of *IPDI* or *XDI* with 1-butanol. Both PB and PS were entirely immiscible with these 2 compounds. The increase in the size of the molecule (entropic effect) and/or the change from an isocyanate group to a urethane bond (enthalpic effect) thus seem unfavorable as far as miscibility is concerned. Therefore, it can be assumed that even if they are initially miscible in the reacting mixture, these two blocks

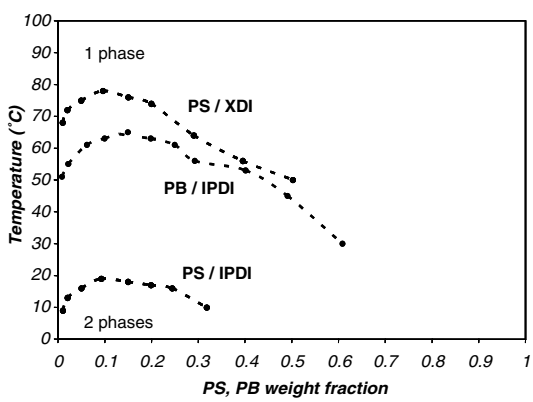


Fig. 2. Cloud point curves measured for partially miscible diisocyanate/(PS or PB) blends.

will probably be expelled shortly from the growing PU chains during the matrix buildup in the presence of a SBM-triblock copolymer.

In contrast, PMMA is entirely miscible with both diisocyanates. Its miscibility with hydroxylated precursors was already thoroughly described in a previous paper [21]: for its blends with all the short *BPA-PO* oligodiols used in this work, as well as with *BPA-EO1*, no phase separation was ever observed. In conclusion, PMMA is the most favorable block considering initial miscibility in the polyurethane precursors, and could also be a good candidate as "nanostructuring block" during the curing reaction.

After polymerization, all the polyurethanes synthesized from the polyaddition of *IPDI* with any of the 4 oligodiols in the presence of 10 wt% PMMA ([NCO]/[OH] = 1) were still perfectly clear, as well as those obtained from the reaction of *XDI* with *BPA-PO2* and *BPA-PO3.5*. Only the materials resulting from the reaction of *XDI* with *BPA-PO1* and *BPA-EO1* with 10 wt% added PMMA were opaque.

In a previous paper, it was shown that it was possible to obtain perfectly transparent, nanostructured thermosets from the polyaddition of diepoxide and diamine precursors in the presence of SBM-triblock copolymers; the only requirement was the solubility of the corresponding PMMA homopolymer with the growing thermosetting polymer during the whole reaction [20]. If the same criterion applies to polyurethane matrices, then the most favorable systems should be those based on *IPDI* and on the first 4 oligodiols described in Table 1b, that therefore have been the subject of most of the studies described hereafter.

3.1.2. Blends of the SBM-triblock copolymers with polyurethane precursors

As shown above, oligodiols are selective solvents for the PMMA block, whereas the PS and PB blocks should micro segregate in these precursors. In contrast, in the diisocyanates and depending on the temperature these last two blocks can be totally or only partially miscible, or even immiscible. This can strongly modify the rheological behavior of the SBM/precursor mixtures and therefore have important consequences on the processing of the reactive blends. The behavior of diblock [27] and triblock copolymers in solvents with different selectivities for each of the blocks has been rather well described in the literature, using both rheological and morphological (especially SAXS) techniques, although most of the studies were rather devoted to systems where the soluble block was the midblock [19,28–32], in contrast with the present work. For example Soenen et al. [28,29] correlated rheological observations with morphologies analyzed by microcalorimetry and SAXS at increasing temperature or during isothermal annealing of SEBS-triblock copolymer solutions in a selective solvent, and the onset of flow observed during heating could be ascribed in that way to the disordering temperature associated with the thermal destruction of a superlattice. The behavior of SBM-triblock copolymers themselves, in a solvent selective for the midblock B, was also recently described by Yamaguchi [19]: at low concentrations, the mixed non-soluble S and M blocks form spherical microdomains in the swollen B matrix, whereas at higher concentrations S and M are segregated in distinct glassy, cylindrical microdomains forming a continuous network and leading to a substantial increase in the storage modulus.

Here in order to appreciate this particular aspect, rheological measurements were conducted on more or less concentrated blends of SBM01 with the various oligodiols and diisocyanates separately. For that purpose the triblock was previously dissolved in the oligodiols at 150 °C, or in the diisocyanates at 100 °C under inert atmosphere, until homogeneous mixtures were obtained.

The rheological behavior of blends of *IPDI* with 13, 20 and 30 wt% SBM01 is depicted in Fig. 3. In this case the model PMMA was entirely miscible whereas PS and PB displayed UCST-type behaviors with maximum precipitation temperatures equal to 19 and 65 °C, respectively. Mixtures with the lowest amounts of SBM01 (13 or 20 wt%) display classical liquid-like behaviors throughout the whole temperature range, while G′ becomes higher than G″ for the blend with 30 wt% triblock below ~20 °C. This could correspond to the onset of precipitation/dissolution of the PS block in *IPDI*, and therefore could be attributed to an order–disorder transition (T_{ODT}), although no special additional phenomenon is detected around 60 °C that could be associated with the precipitation/dissolution of PB blocks; but this last phenomenon might lead only to the formation of individualized disordered micelles.

The same behavior was observed in a much more spectacular way for the blends of SBM01 with the less miscible *XDI*. Fig. 4 shows the curves obtained for two SBM01 solutions, both more dilute than all the *IPDI*-based blends described above. In this case the PMMA block is miscible with the diisocyanate, the PB block is entirely immiscible whereas the PS block should become immiscible below a certain temperature (Fig. 2). For the blend with only 5 wt% triblock copolymer, G′ is always lower than G″ and the behavior is that of a liquid in the whole temperature range. In contrast, with 10 wt% SBM01 G′ > G″ at room temperature, and both moduli suddenly drop above 65–70 °C with the curves crossing each other at ~67 °C. The rheological behavior of this particular blend is indeed identical to that of several blends of SBM-triblock copolymers with diepoxide precursors described in a previous work [27]. The crossing temperature can be attributed to a rhe-

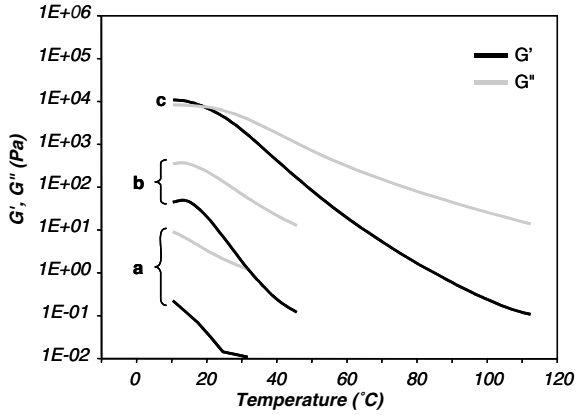


Fig. 3. Conservation (G′) and loss (G″) moduli vs. temperature for blends of *IPDI* with neat SBM01 ($S^{9.2}_{22}B_{20}M_{58}$-SB10); (a) 13 wt% SBM01; (b) 20 wt% SBM01; (c) 30 wt% SBM01 (2 °C/min, 1 rad/s).

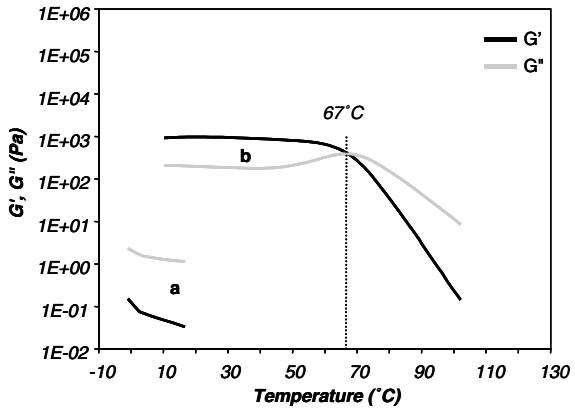


Fig. 4. Conservation (G′) and loss (G″) moduli vs. temperature for blends of *XDI* with neat SBM01 ($S_{22}^{9.2}B_{20}M_{58}$-SB10); (a) 5 wt% SBM01; (b) 10 wt% SBM01 (2 °C/min, 1 rad/s).

ological T_{ODT}, denoting the change from an ordered solution with gel-like behavior to a more disordered state. As the PS block length in the SBM01 copolymer is much lower than that of the model homopolymer described above (Table 3), it can probably dissolve in *XDI* at a lower temperature (67 °C instead of about 78 °C for the model homopolystyrene with $M_n \approx 99$ kg/mol, see Fig. 2), even though the presence of insoluble PB blocks could also hamper this dissolution [27]. Above T_{ODT}, the partial dissolution of PS blocks in *XDI* would finally lead to a disordered dispersion of PB micelles that, given the low amount of added triblock copolymer, would not alter the fluid-like rheological behavior of the blend.

In *BPA-PO* oligodiols, only the PMMA block can be miscible. For the system *BPA-PO2*/SBM01, the G′/G″ vs temperature curves displayed in Fig. 5 look indeed very similar to those obtained for the *XDI*/SBM01 blends. Here the mixture with 5 wt% triblock copolymer has a fluid-like behavior over the whole temperature range, whereas the mixture with 10 wt% displays $T_{ODT} \approx 102$ °C. The threshold concentration

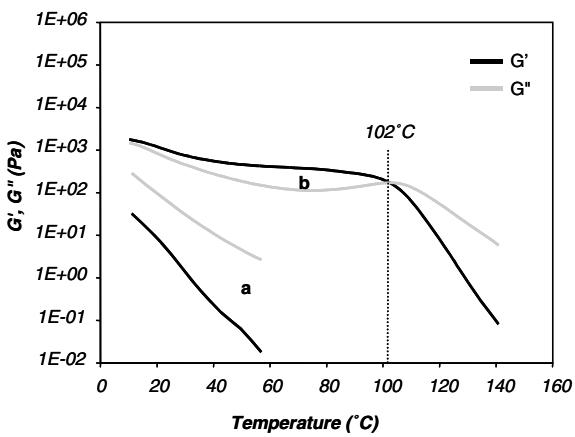


Fig. 5. Conservation (G′) and loss (G″) moduli vs. temperature for blends of *BPA-PO2* with neat SBM01 ($S_{22}^{9.2}B_{20}M_{58}$-SB10); (a) 5 wt% SBM01; (b) 10 wt% SBM01 (2 °C/min, 1 rad/s).

for obtaining a gel-like behavior is therefore rather low, in comparison with blends of a diepoxide with a rather similar SBM-triblock copolymer of higher molar mass [27]. In this particular case the blends were shown to display an ordered state only above 20 wt% copolymer. The reason for this difference can be found in a different aggregation number (number of triblock molecules in a single micelle), related to a different solubility of the 3 blocks in diepoxide and in *BPA-PO* oligodiols [24], or, to a lesser extent, in a different amount of SB-diblock impurities. For a same concentration, larger micelles would indeed favor the formation of a gel. Moreover, it was shown in a previous work that *BPA-PO* oligodiol molecules were self-associated through hydrogen bonds [21]; the degree of self-association of these solvent molecules through their OH terminal groups was mainly determined by their relative sizes. This could be another reason for the occurrence of a gel at lower SBM concentrations in the present study.

Unlike *XDI*/SBM blends, the model PS homopolymer is entirely immiscible with *BPA-PO* diols. However the molar mass of the PS block in SBM01 (<10 kg/mol) is so much lower than that of the model (∼99 kg/mol) that it could still allow a partial dissolution of the PS blocks in *BPA-PO2*, in the same way as with *XDI*, but only at a higher temperature, hence the higher T_{ODT} observed in this case.

The results were almost the same for the blends of SBM01 with *BPA-PO1*, except for the value of T_{ODT} that was found 40° higher ($T_{ODT} \approx 142$ °C). This could be due to a higher degree of self-association of the oligodiol (*BPA-PO1* is shorter than *BPA-PO2*, and therefore has a higher concentration of terminal OH groups), although *BPA-PO1* was also shown to be a better solvent for the PMMA block than *BPA-PO2*.

As a first conclusion, only the blends with less than 10 wt% SBM01-triblock copolymer seem likely to be processed by simple casting in view of the rheological behaviors observed for the various precursor/SBM mixtures. Using this particular technique, it should be easier to dissolve the triblock copolymer in the diisocyanate than in the oligodiol since the former is a less selective solvent towards the different SBM-blocks. In so doing, the dissolution should be faster and it should be possible to dissolve higher amounts of copolymer in the diisocyanate while keeping a fluid behavior.

3.2. Linear Polyurethanes modified with low amounts of SBM-triblock copolymer (<10 wt%)

Ideally, the best way to account for the formation of the final morphologies of the SBM-modified PU materials would be to be able to study those of the initial reactive mixtures oligodiol/diisocyanate/triblock copolymer. However, in most cases the high temperatures required to prepare as homogeneous as possible ternary mixtures make such studies impossible without interference from the polyaddition reaction. As suggested above, for the preparation of nanostructured polyurethanes with low amounts of SBM the latter was first dissolved in the diisocyanate at 100 °C under inert atmosphere, until a homogeneous mixture was obtained. After the addition of the proper amount of oligodiol ([NCO]/[OH] = 1), the non-catalyzed system

was stirred at 100 °C for 30 min in the same vessel, then cast in a mold and finally allowed to polymerize for 15 h at 130 °C.

In some cases, dibutyl tin dilaurate (DBTDL, 0.01 wt%) was used as a catalyst. If so, DBTDL was preferably dissolved in the oligodiol, the initial mixing stage was run only for 5 min and the polymerization step was also much shorter (about 30 min at 130 °C).

Finally when SBM had to be dissolved in the oligodiol, a higher temperature was necessary for an efficient mixing of the reactive blend components. The system was thus stirred for 5 min at 140 °C, then 30 min at 100 °C before the polymerization stage (130 °C, 15 h). No catalyst was used in this case.

3.2.1. IPDI/BPA-PO1

For this formulation, no catalyst was ever used and the SBM-triblock copolymer was always dissolved in the diisocyanate. With 5 wt% SBM01, entirely nanostructured, transparent materials were obtained. The TEM micrographs depicted in Fig. 6 show dispersed micelles with a diameter ≈30 nm. Looking more into details, these micelles appear to have a core-shell morphology, with a black PB shell and a gray PS core, quite similarly to what was observed for a SBM-modified polyepoxide matrix [24]. For SBM01, the phase ratio PB/PS is sufficiently high to allow the PS phase to be completely covered by a continuous PB layer.

No special order or periodicity appears in the micrographs, suggesting that the polyaddition began in a disordered state. This would be consistent with the great fluidity presented by the initial reactive blend at the reaction temperature, and should also apply to all the systems with low amounts of SBM (<10 wt%): even if they sometimes have a gel-like behavior at room temperature, all these systems are very fluid at the higher temperatures used for polymerization. Two criteria might therefore be essential for the final morphology of the material, i.e. (1) the temperature and (2) the proportion of SBM incorporated in the blend, since T_{ODT} should increase with increasing the amount of triblock copolymer [27]. In other words, for every given polymerization temperature there would be a critical amount of SBM-triblock copolymer above which the reaction would start in a more or less ordered state, and therefore could probably lead to a better defined morphology. It is hard to tell whether PB and PS are initially miscible or immiscible with the reactive blend at the considered temperatures (100, 130 or even 140 °C); however they are both totally immiscible with the final PU, whereas PMMA should remain entirely miscible throughout the reaction. Polyaddition could thus simply result in the freezing of the initial morphology, not depending on the kinetic or thermodynamic features of the curing process, but the possibility of a reaction-induced microphase separation process cannot be totally dismissed either.

3.2.2. IPDI/BPA-PO2 or BPA-PO3.5

When the same experiment was carried out using *BPA-PO2* or *BPA-PO3.5* as the starting oligodiol, analogous disordered, 30 nm-diameter micelle dispersions were recovered after polymerization in the presence of 5 wt% SBM01; but in this case some large onion-like particles were also observed, as shown in Fig. 7. The final materials were opaque. As the initial mixtures were also slightly hazy, these large structures were in fact most probably present from the start.

The increase in the molar mass of the starting oligodiol is accompanied by a dilution of the reactive groups (OH and NCO), compared with the *BPA-PO1*-based sys-

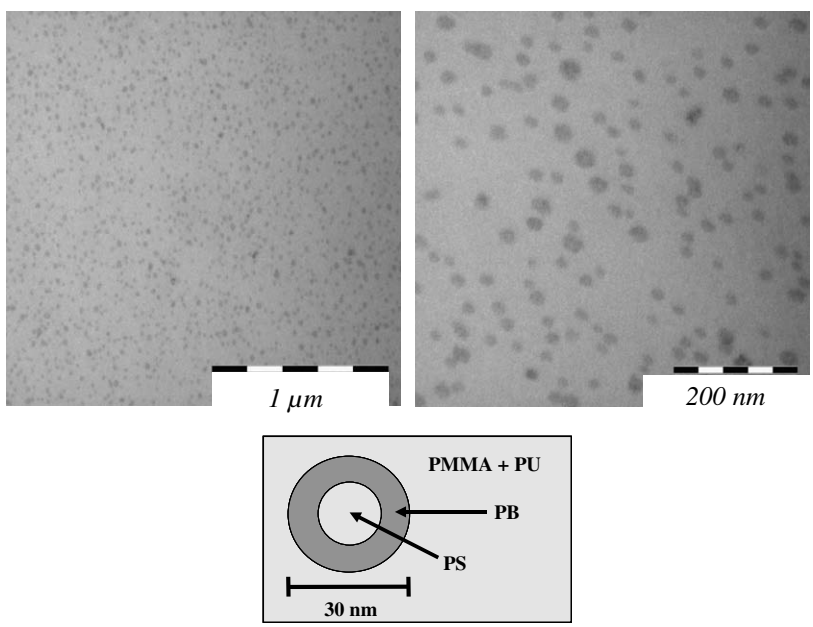


Fig. 6. TEM micrographs and proposed morphology for the polymerized blend ([*IPDI*/*BPA-PO1*]/5 wt% neat SBM01) stained with osmium tetroxide.

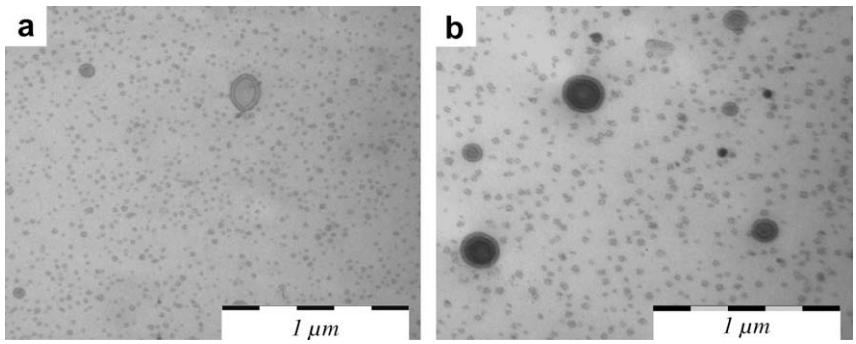


Fig. 7. TEM micrographs of the polymerized blends (a) ([*IPDI*/*BPA-PO2*]/5 wt% neat SBM01) and (b) ([*IPDI*/*BPA-PO3.5*]/5 wt% neat SBM01), stained with osmium tetroxide.

tem. This apparently results in a poorer miscibility of the SBM-triblock copolymer, or presumably rather in a destabilizing of its residual diblock impurities: once again for SBM-modified polyepoxide matrices the literature showed that part of this diblock could remain incorporated in the triblock structure, leading to multi-shell particles, while the excess part was definitely expelled in a separate phase [24]. In order to confirm this explanation, the same polyurethanes were synthesized in the presence of either 5 wt% neat or purified SBM01 $S_{22}^{9.2}B_{20}M_{58}$; the resulting morphologies are shown in Fig. 8. Using the purified triblock copolymer, all the large particles disappear, and perfectly clear materials are obtained. Diblock impurities, although in low proportion (10 wt% with respect to the triblock), are thus in sufficient amount to account for the generation of micron-size onion-like particles in the materials modified with the neat SBM01. Moreover, the experimental procedure (dissolution in *IPDI* or in the oligodiol) had no strong influence on the final morphology, showing that although the structure of the initial solutions might be different, both of them were very fluid and the mixing time before casting (30 min) was sufficient to reach the thermodynamic equilibrium for the ternary diisocyanate/oligodiol/SBM blend.

Finally, and depending on the desired application it sometimes may be necessary to adjust the glass transition temperature, T_g, of the matrix. The polyurethanes based on *IPDI* and *BPA-POx* have almost the same chemical nature but varying T_g's (between 115 °C for that based on pure

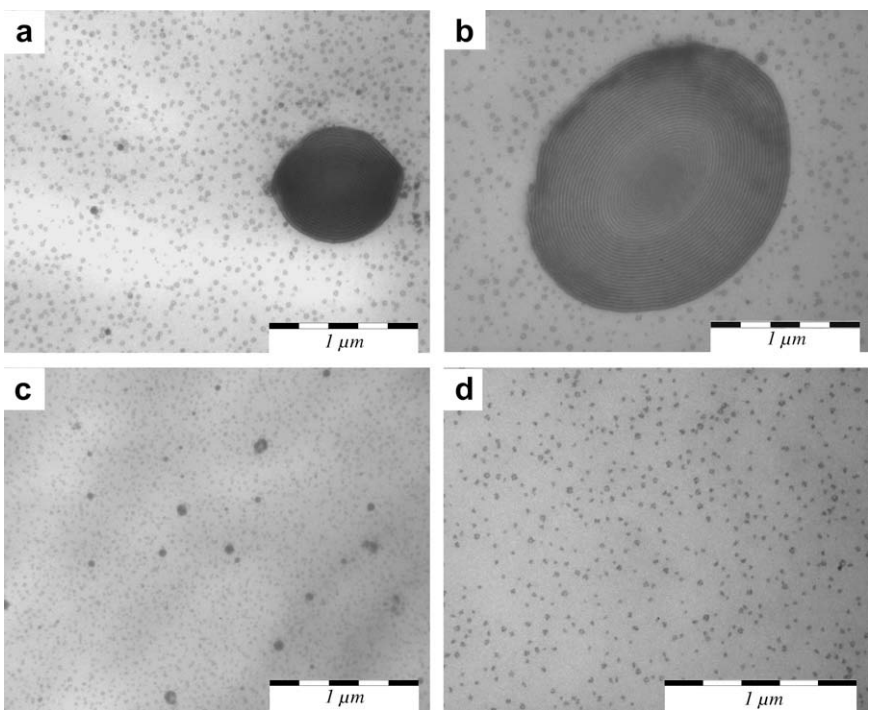


Fig. 8. TEM micrographs of the polymerized blends ([*IPDI*/*BPA-PO3.5*]/5 wt% SBM01); (a) neat SBM, dissolution in *IPDI*; (b) neat SBM, dissolution in *BPA-PO3.5*; (c) purified SBM, dissolution in *IPDI* and (d) purified SBM, dissolution in *BPA-PO3.5*.

BPA-PO1 and 25 °C for that synthesized from pure *BPA-PO3.5*). The reaction with *IPDI* of adequate mixtures of two *BPA-PO*-type oligodiols can lead to any desired value of T_g for the polyurethane matrix. An example was given in this work with the synthesis of a linear polyurethane based on *IPDI* and on a blend between *BPA-PO1* (60 wt%) and *BPA-PO3.5* (40 wt%). This formulation (final T_g = 85 °C) could be modified with 10 wt% SBM01 using a special casting apparatus. The morphology of the resulting material is described in Fig. 9. Two main remarks can be inferred from these pictures:

(1) First, even with 10 wt% neat SBM01 no large particle can be detected in the material, meaning that the used amount of *BPA-PO1* was sufficient to ensure the stabilization of the whole amount of diblock impurities. However there must be a critical amount of *BPA-PO3.5* beyond which these large particles will appear again.
(2) As in this case more SBM-triblock copolymer was incorporated in the polyurethane matrix, a greater number of dispersed particles were formed. These particles display a higher mean diameter (∼45 nm) compared with the material modified with 5 wt% neat SBM01 (∼30 nm, see Figs. 6 and 8). But this double amount of SBM01 is not sufficient to induce a real change of morphology, and the particles still display a (PS core)-(PB shell) structure; this material is also perfectly transparent.

3.2.3. Effect of the chemical nature of the precursors

Since PMMA was shown to be miscible with both *BPA-EO1* and *XDI*, new SBM-modified polyurethanes were prepared by changing the nature of either the diisocyanate or the oligodiol. In these cross-composition matrices (*IPDI*/*BPA-EO1* or *XDI*/*BPA-PO2*), and according to the preliminary experiments with homo-PMMA (see above), the stabilizing block of the SBM-triblock should also remain miscible all along the polymerization reaction. In fact the initial formulations were indeed perfectly clear, however both final materials were opaque. But a more precise investigation using TEM revealed that the reasons for this opaqueness in either case were different (see Fig. 10).

First, [*IPDI*/*BPA-EO1*/5 wt% SBM01] displays again very small, core-shell type particles with a diameter ∼30 nm (Fig. 10a), but here these particles underwent flocculation, in contrast with the [*IPDI*/*BPA-PO1*/5 wt% SBM01] blend examined just above (Fig. 6). This confirms the results obtained in the modeling of the behavior of blends of PMMA with a series of *BPA-EO* or *BPA-PO* oligodiols, and with PEO and PPO oligomers [21]: for PMMA/*BPA-PO* blends, the interaction parameter exhibits a very low value, below that of PMMA/*BPA-EO* blends, consistently with a higher miscibility of PMMA with poly(oxypropylene) units than with their poly(oxyethylene) counterpart.

The case of the [*XDI*/*BPA-PO2*/5 wt% SBM01] blend is slightly different (Fig. 10b): first, unlike for the [*IPDI*/*BPA-PO2*/5 wt% SBM01] blend no large, onion-like structure can be detected in these pictures. Although the system seems rather close to flocculation, no large aggregate appears in the micrographs either. Moreover, here larger individual particles are observed. As already mentioned, the aggregation number (number of chains in a single micelle) depends on the polymer/solvent interaction parameters; since both PB and PS are less miscible with *XDI* than with *IPDI*, the average number of chains per micelle is greater in *XDI*, hence larger micelles. All together, these different features can be responsible for the opaqueness of the final SBM01-modified polyurethane.

3.2.4. Effect of increasing amounts of diblock impurities

The high ability of the [*IPDI*/*BPA-PO1*] matrix to be nanostructured even by a neat triblock copolymer was demonstrated above. Therefore this polyurethane was synthesized once again, in the presence of other triblocks containing increasing amounts of diblock impurities. For that purpose, SBM04 (∼17 wt% diblock) and SBM03 (∼52 wt% diblock, see Table 2) were successively used.

As for SBM01, both neat ($S^{16}_{13}B_{15}M_{72}$-SB*17*-S*3*) and purified SBM04 $S^{16}_{13}B_{15}M_{72}$ led to a nanostructured material when 5 wt% triblock copolymer was incorporated in the [*IPDI*/*BPA-PO1*] polyurethane matrix. Therefore in this case both SB diblock and homopolystyrene impurities could be incorporated in the SBM structures. This appears clearly in Fig. 11a and b where the dispersed particles look only slightly larger in the case of the neat copolymer, compared with the results obtained with purified SBM04. As long as

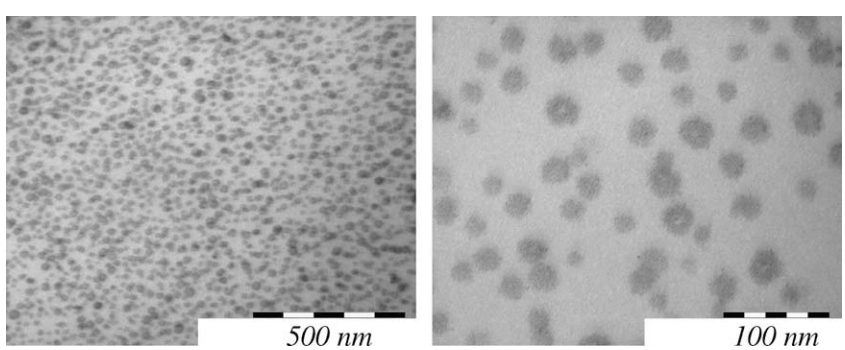


Fig. 9. TEM micrographs of the polymerized blend [*IPDI*/(*BPA-PO1*/*BPA-PO3.5* 60/40 wt%)]/10 wt% neat SBM01, stained with osmium tetroxide.

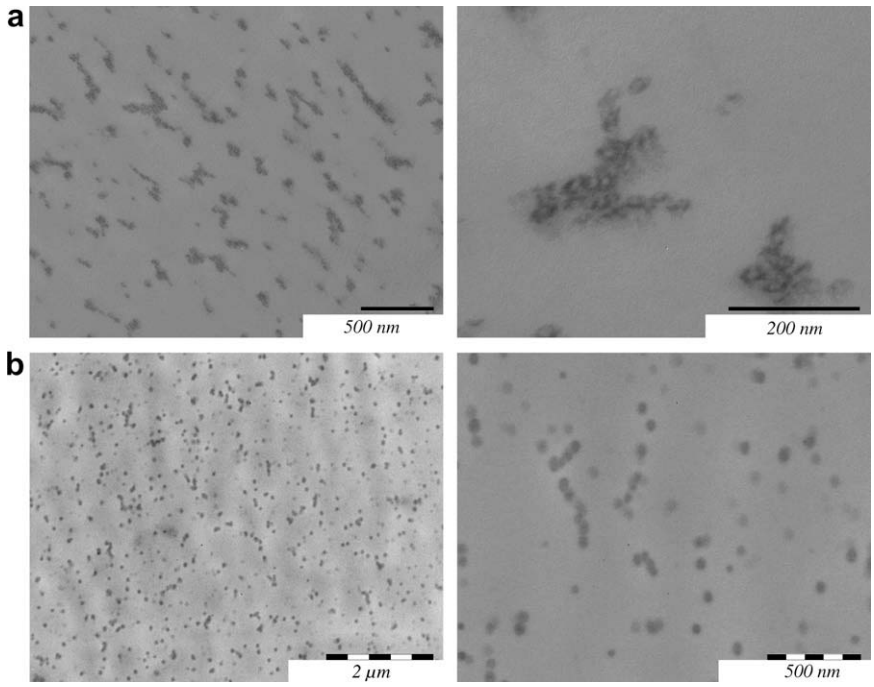


Fig. 10. TEM micrographs of the polymerized blends (a) ([*IPDI*/*BPA-EO1*]/5 wt% neat SBM01) and (b) ([*XDI*/*BPA-PO2*]/5 wt% neat SBM01), stained with osmium tetroxide.

the highest amount of incorporable diblock copolymer has not been reached, the mean diameter of the dispersed particles should keep on increasing. The advantage is that using this formulation, the purification of the neat triblock copolymer, even added up to ~20 wt% amounts, is not necessary to obtain nanostructured polyurethanes.

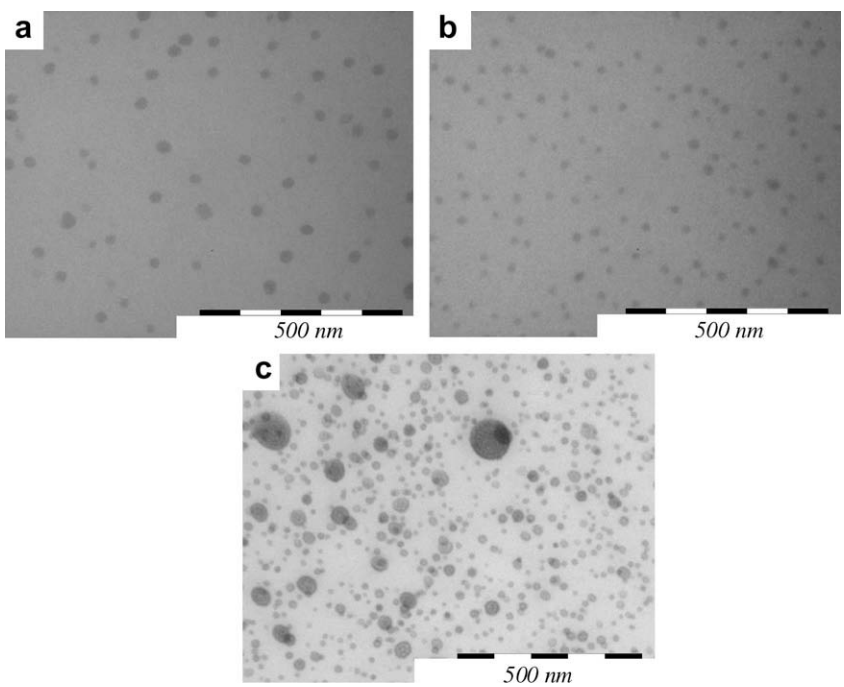


Fig. 11. TEM micrographs for the polymerized blends ([*IPDI*/*BPA-PO1*]/5 wt% SBM) using (a) neat SBM04 ($S^{16}_{13}B_{15}M_{72}$-SB17-S3); (b) purified SBM04 ($S^{16}_{13}B_{15}M_{72}$); (c) neat SBM03 ($S^{6.8}_{18}B_{28}M_{54}$-SB52); the samples were stained with osmium tetroxide.

However a limit still exists, even with *IPDI*/*BPA-PO1*. Fig. 11c shows the morphology of the same polyurethane modified with 5 wt% neat SBM03 ($S_{18}^{6.8}B_{28}M_{54}$-SB*52*). In this case the average size of the dispersed particles is rather high, and some very large particles can also be observed: the amount of SB diblock impurities is so high (52%) that the incorporation threshold has been reached and that the excess diblock copolymer cannot be stabilized and macroseparates from the matrix. Therefore for this block copolymer, the maximal amount of incorporable diblock in the neat SBM should lie between 20 and 50 wt%, for 5 wt% of added SBM (i.e. between 1 and 2.5 wt% SBM with respect to the overall formulation). But in contrast the use of purified triblocks would allow both the use of higher amounts of modifier, or that of other polyurethane formulations, particularly those based on *BPA-PO2* or *PO3.5*.

3.3. Nanostructured crosslinked polyurethanes modified with low amounts of SBM-triblock copolymer (<10 wt%)

If needed, the chemical nature of the matrix can also be varied through the use of adjustable amounts of multifunctional precursors that will lead to polyurethane networks. Starting from the well-known system *IPDI*/*BPA-PO1*, several attempts were made to modify the formulation in order to obtain clear, nanostructured thermosetting PU matrices. For this purpose, both *PCL*^{t}*OH* and ^{t}*HDI* were successively incorporated in various amounts in the reactive blend, still modified with 5 wt% neat SBM01. Whereas both PB and PS are totally immiscible with these two monomers, blends of PMMA with *PCL*^{t}*OH* display a UCST-type behavior described in Fig. 12; precipitation occurs below ~80 °C for a rather broad range of concentration. Finally PMMA was also found totally immiscible with ^{t}*HDI*.

The morphologies of several SBM-modified polyurethane networks are shown in Fig. 13. The materials obtained by replacing only a small part (20 wt%) of the diisocyanate or oligodiol by a trifunctional monomer are still nanostructured and transparent (Fig. 13a and c). In contrast, increasing the proportion of crosslinking agent to 50 wt% led to a flocculation of the SBM particles and to hazy materials (Fig. 13b and d), although the initial reactive mixtures were also transparent. This illustrates the necessity of stabilizing the micelles throughout the reaction with the help of the PMMA block. As both crosslinking agents, but especially ^{t}*HDI*, are unfavorable to PMMA miscibility, a threshold amount of these monomers exists, beyond which the SBM-triblock micelles can no longer be stabilized until the end of the process. More generally, the conclusion is that the best way of obtaining nanostructured polyurethane materials is to be able to define a formulation where one of the end blocks of the modifier (the "nanostructuring" or "stabilizing" block) will definitely remain miscible throughout the polyaddition reaction.

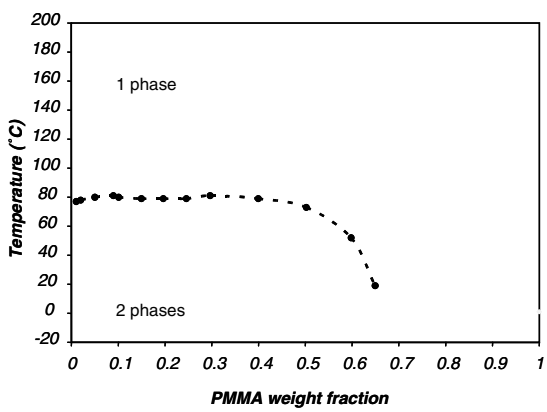


Fig. 12. Cloud point curve measured for partially miscible *PCL*^{t}*OH*/PMMA blends.

3.4. Nanostructured linear polyurethanes and polyurethane-urea modified with high amounts of SBM02-triblock copolymer (>50 wt%)

3.4.1. SBM/monomer preliminary blends

According to the rheological measurements, the blends of the various precursors (*IPDI*/*BPA-PO3.5*) with high amounts of SBM are physical gels up to quite high temperatures. Therefore these materials were processed with the help of a twin-screw microcompounder. For an optimal precision in the adjustment of the respective amounts of diisocyanate and oligodiols, blends of SBM02 with both precursors (*IPDI* and *BPA-PO3.5*) were prepared separately. The resulting rods were then granulated, and in a second stage mixed in stoichiometric proportions in the microcompounder.

For both initial solutions, three different compositions were prepared (SBM02/monomer = 70/30, 60/40 or 50/50 wt%). For each reactive solvent (*IPDI* or *BPA-PO3.5*) the first two blends, i.e. the most concentrated SBM02 solutions, were obtained by adding more SBM02 to the previously prepared 50/50 masterbatches. For each masterbatch, the monomer (*IPDI* or oligodiol) was first injected in the microcompounder. The SBM02 powder was then progressively added, and the blend was allowed to recirculate for about 30 min (10 rpm) until a homogeneous rod was obtained and finally recovered. During this mixing step, the torque progressively increased until a stable value was achieved.

The *IPDI*/SBM02 blends could be processed easily at 80 °C, whereas a much higher temperature was necessary for *BPA-PO3.5*/SBM02 blends (at least 140 °C). This is the result of the different miscibility behaviors observed for the three blocks in these two solvents. In *IPDI*, all three blocks can be swollen even at moderate temperature (above 65 °C for PB in the most unfavorable case, see Fig. 2). In contrast, both PB and PS are entirely immiscible with *BPA-PO3.5*, and even though PMMA is miscible with this oligodiol [21] it is necessary to heat the *BPA-PO3.5*/SBM02 blends up to high enough temperatures in order to be able to swell the PMMA block (typically above its T_g) and to obtain a thermodynamically stable morphology.

Although these blends were only physical gels, attempts were made to analyze the rods by Transmission Electron Microscopy; typical morphologies are shown in Fig. 14. These rods were slightly hazy. As the materials were soft, their ultramicrotomy was rather delicate and the phases do not look as well defined as for cured materi-

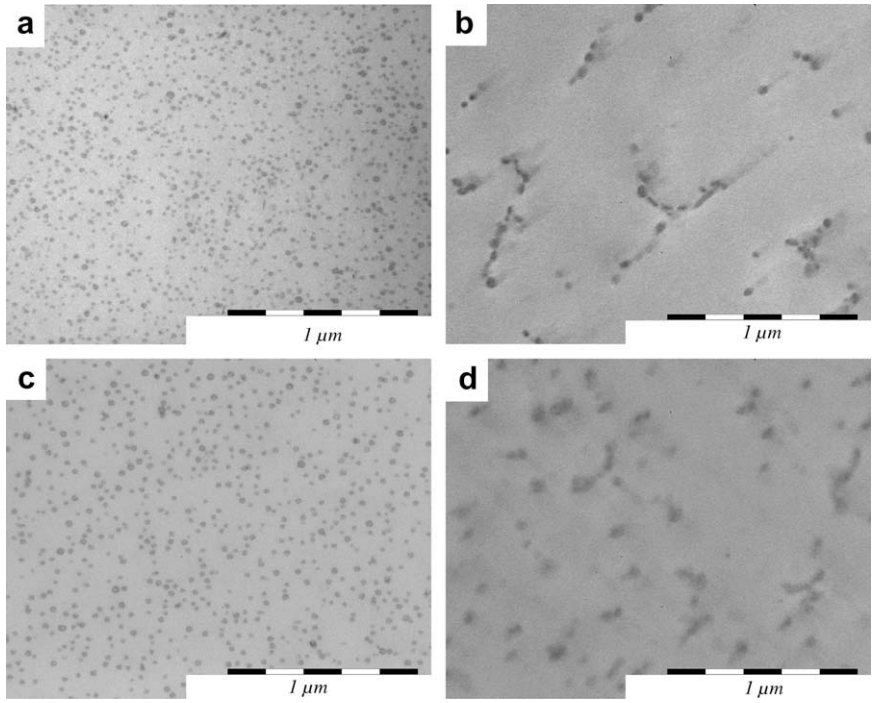


Fig. 13. TEM micrographs of the polymerized blend [*IPDI*/*BPA-PO1*/5% neat SBM01] modified with various amounts of crosslinking agents: (a) *IPDI*/^{t}*HDI* = 80/20 wt%; (b) *IPDI*/^{t}*HDI* = 50/50 wt%; (c) *BPA-PO1*/*PCL*^{t}*OH* = 80/20 wt%; (d) *BPA-PO1*/*PCL*^{t}*OH* = 50/50 wt%.

als. However, "cylinder in cylinder"-type structures are nevertheless visible and can be associated with a cylindrical (PS core)-(PB shell) morphology in a PMMA matrix swollen by the used solvent. At such a high concentration (70 wt% SBM02), the morphology should indeed logically be close to that of the neat triblock copolymer that is lamellar, as shown in Fig. 15. Moreover, the substructures look slightly larger in the *IPDI*-based blend, maybe reflecting a partial swelling of the PS and maybe PB phases with the diisocyanate. With decreasing amounts of SBM-triblock, this phenomenon should eventually lead to different morphologies for the blends of SBM02 with *IPDI* or *BPA-PO3.5*, and might therefore be crucial with respect to the final morphologies of the modified polyurethanes, depending on the process used to prepare them.

3.4.2. Nanostructured linear polyurethanes

As said above, the modified polyurethanes were obtained by granulating the solvent/SBM02 blend rods, and in a second stage mixing them in stoichiometric proportions ([NCO]/[OH] = 1) in the microcompounder. The reactive blends were processed at 130 °C, and the final reactive rods were compression-molded and cured at 150 °C for 14 h (as the reactive functions were highly dilute, rather long reaction times were required). A comparison was made between neat and purified SBM02. These modifiers led to different final morphologies: the materials based on neat SBM02 were opaque, whereas those based on the purified triblock copolymer were transparent. Fig. 16 shows more precisely the morphologies observed by TEM on the cured ([*IPDI*/*BPA-PO3.5*]/50 wt% SBM02 (neat or

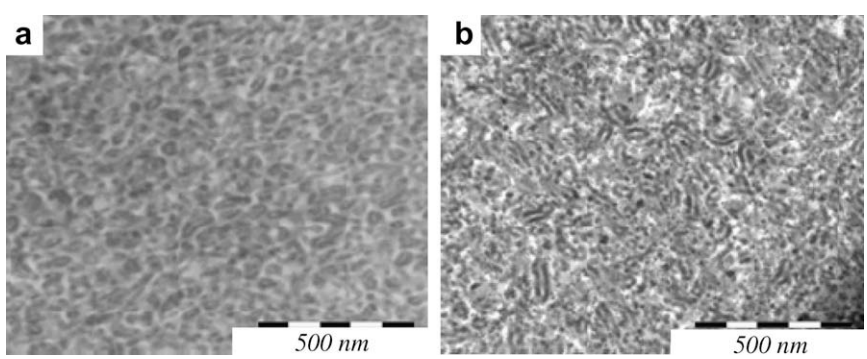


Fig. 14. TEM micrographs of the non-polymerized blends: (a) *IPDI*/SBM02 (30/70 wt%) and (b) *BPA-PO3.5*/SBM02 (30/70 wt%), stained with osmium tetroxide.

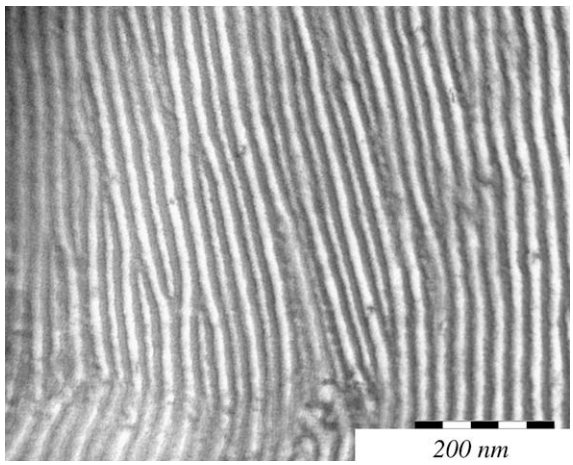


Fig. 15. TEM micrograph of a neat SBM02 film obtained by solvent evaporation, stained with osmium tetroxide.

purified)) blends, as well as that of the associated uncured blend based on neat SBM02.

Initially, PS cylinders covered by PB cylinders are observed, and no large, micron-size structure can be detected in the uncured blend, although the oligodiol was *BPA-PO3.5* and the additive contained 20 wt% diblock impurities. The overall structure looks rather ordered, as observed in a previous work by Ritzenthaler on diepoxide-diamine based uncured systems [20]. Moreover this publication showed that such morphologies did not depend on the way of preparing the blends (mechanically in bulk, or by solvent evaporation); this should also apply here, where 50 wt% fluid solvent should be sufficient to avoid diffusion and viscosity effects. Although the picture in Fig. 16a only reflects the morphology at room temperature and not at the reaction temperature (150 °C), the facts that both PB and PS are totally immiscible with the formulation at any temperature and that the rod displays an elastic behavior at its processing temperature (130 °C) strongly suggest that the order-disorder transition temperature, T_{ODT}, should without doubt lie above these working temperatures.

The morphology was somewhat modified by the reaction (Fig. 16b). The cured material displays large cylindrical or lamellar structures, sometimes with multiple layers. A possible macrophase separation of the SB diblock impuri-

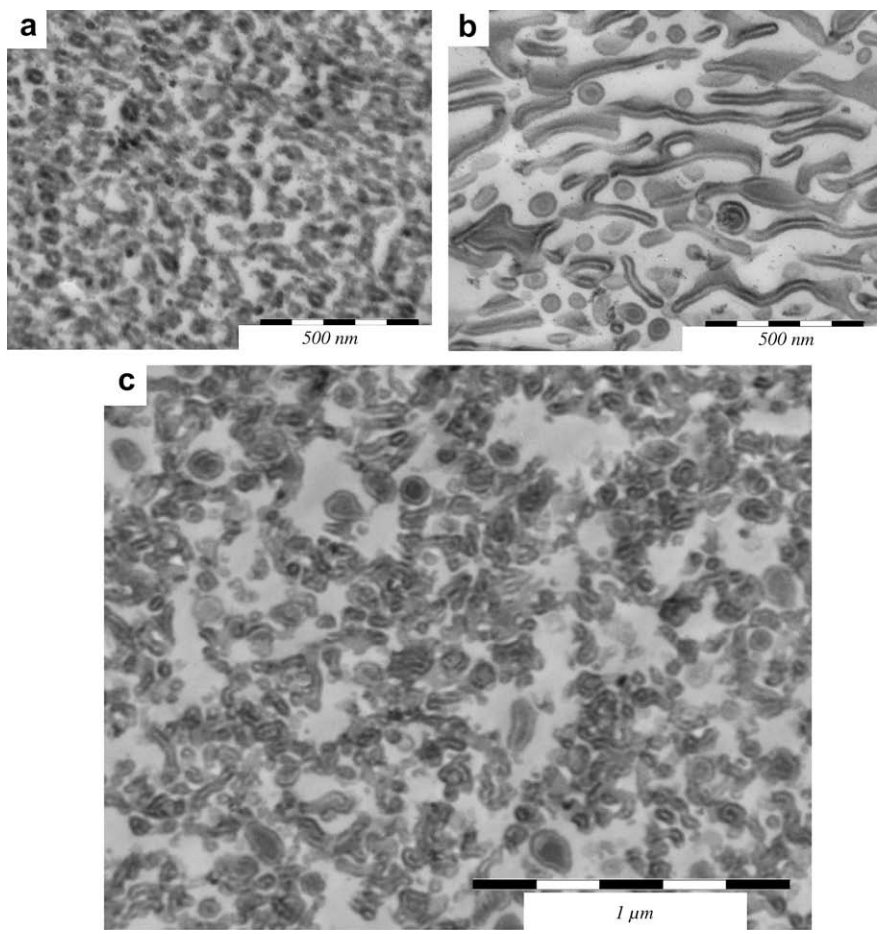


Fig. 16. TEM micrographs of the blends: (a) [*IPDI*/*BPA-PO3.5*]/50% neat SBM02 ($S^{9.2}_{23}B_{26}$M51-SB20) before reaction, (b) after reaction and (c) [*IPDI*/*BPA-PO3.5*]/50% purified SBM02 ($S^{9.2}_{23}B_{26}M_{51}$) after reaction.

ties as the reaction proceeds could account for the formation of these large objects. A decrease in the affinity between the stabilizing block and the growing matrix could also explain the formation of rather large, clear areas where the triblock seems missing.

When the same experiment was run using purified SBM02, the same kind of structures were observed in the cured material except for the largest objects that were now missing (Fig. 16c). Therefore this material was transparent whereas that based on neat SBM02 (Fig. 16b) was opaque.

3.4.3. Nanostructured segmented polyurethane-ureas

Previous works on polyepoxide networks demonstrated the high miscibility of SBM-triblock copolymers with 4,4′-methylene bis(3-chloro-2,6-diethylaniline), MCDEA [20,24]. In such networks, the use of this particular diamine was shown to ensure the solubility of the PMMA block throughout the reaction [33], and it can therefore be assumed that its incorporation in PU formulations should not jeopardize, and might even enhance their ability to remain nanostructured throughout polyaddition. More precisely, the idea was here to use this diamine as an additional chain extender in the former SBM02-modified polyurethane formulation, and to try to obtain a real nanostructured segmented polyurethane-urea. This new reactive blend was therefore based on *BPA-PO3.5*/*IPDI*/MCDEA (OH/NCO/NH_2 = 1/2/1) and was once again modified with 50 wt% SBM02.

As the reaction between aromatic amines and isocyanate functions is quite fast at high temperature, the processing of these blends was non-trivial. In a first attempt, 3 preliminary blends of the different monomers with neat SBM02 were prepared (*BPA-PO3.5*/SBM02 [140 °C], MCDEA/SBM02 [110 °C] and *IPDI*/SBM02 [110 °C], 50/50 wt%) using the microcompounder. The first two rods were then granulated and re-blended at 110 °C; finally the (*IPDI*/SBM02) blend was added in stoichiometric amount ([NCO]/([OH]+[NH_2]) = 1) and all the components were mixed together at 110 °C for 30 min. After this time, and although the torque was not really stable, the final rod was recovered and press-cured for 15 h at 130 °C. The morphology of the opaque resulting material was examined by TEM and the results are shown in Fig. 17a and b. Nanoscopic structures can be detected, but they are surrounded by huge white particles. The process used is equivalent to a one-stage synthesis for the polyurethane-urea, and the reaction between *IPDI* and MCDEA must be much faster than that with the oligodiol that bears secondary hydroxyl groups, resulting in isolated polyurea hard segments that rapidly phase-separate. After this point the stoichiometry is no longer balanced and the oligodiol is unable to react [34]. These separated hard segments can presumably be related with the clear areas in the TEM micrographs.

Another procedure was finally tested in order to ensure the reaction between *IPDI* and *BPA-PO3.5*. This time the (*BPA-PO3.5*/SBM02) and (*IPDI*/SBM02) rods were granulated and re-blended at first (NCO/OH = 2), in order to synthesize a diisocyanato-terminated polyurethane prepolymer. The resulting pellets were allowed to react for one week at 130 °C under a vacuum; then they were mixed with the (MCDEA/SBM02) blend for 20 min at 110 °C (NCO/NH_2 = 1), and finally press-cured at 150 °C

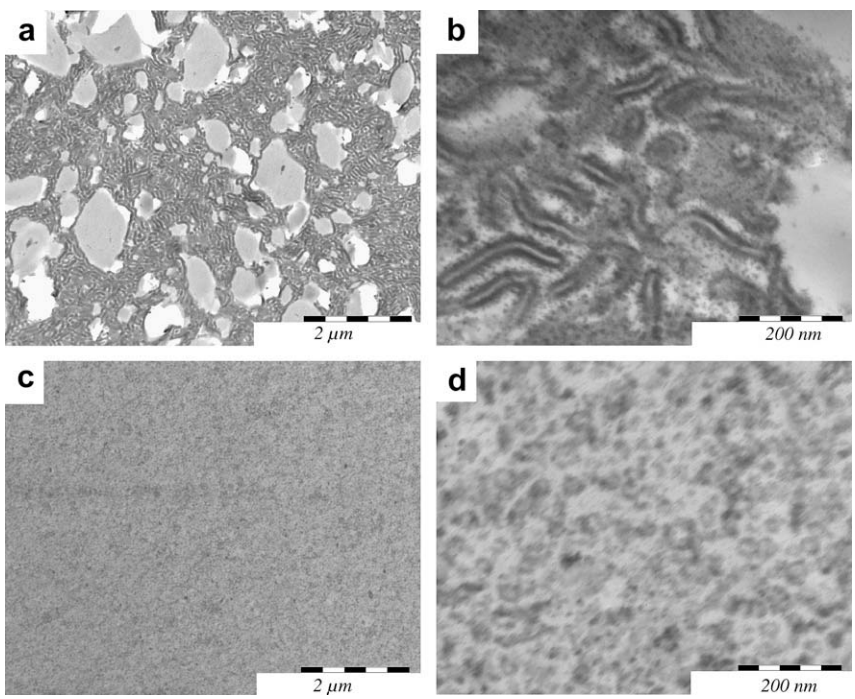


Fig. 17. TEM micrographs of the SBM-modified polyurethane-urea (*BPA-PO3.5*/*IPDI*/MCDEA [OH/NCO/NH_2 1/2/1]/SBM02, 50/50 wt%); (a) and (b): first process (one-stage reaction); (c) and (d): second process (prepolymer process).

for 12 h. In this case the final material was transparent. The TEM analysis revealed no large particle (Fig. 17c and d) but a nanostructured morphology. The comparison between these 2 experiments highlights the fundamental importance of the order of addition of the various reactants in such reactive systems.

4. Conclusion

The possibility of obtaining transparent, nanostructured polyurethane and polyurethane-urea materials from the polyaddition of reactive solutions of SBM-triblock copolymers was demonstrated on numerous systems. Many precursors, di- or multi-functional, could be used for that purpose, pure or in blends, as well as several neat triblocks containing increasing amounts of homopolymer and diblock impurities. This allowed the synthesis of modified linear PUs and/or PU networks with adjustable T_g's, and from low to very high amounts of triblock copolymers could be incorporated in the materials. The main condition for that was the choice of a reactive blend where the "nanostructuring" PMMA end block in SBM remained soluble throughout the polyaddition reaction. Moreover, the precursors must also be sufficiently good solvents for the non-structuring blocks (PS and PB) under the used conditions to allow the stabilizing of all the homopolymer and diblock impurities, or the latter must be present in sufficiently low amounts not to be expelled from the triblock micelles during the reaction: for every reactive system, a threshold diblock concentration can be defined beyond which macroseparation of large particles will occur.

Finally, the rheological behavior of the SBM solutions in the various precursors is strongly dependent on their chemical nature and on the concentrations used. Since fluid solutions were usually obtained with concentrations below 10 wt% SBM, PUs modified with low amounts of triblock copolymer could be prepared by traditional casting procedures. In contrast, above this value SBM solutions in the precursors were often ordered micelle dispersions that displayed a gel-like behavior over a sometimes large temperature range, and in this case modified PUs or PUUs could only be processed by reactive extrusion.

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