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Study of polystyrene microstructures and nanostructures synthesised in particle track-etched membranes used as templates

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Abstract

For the first time, nanostructures of polystyrene (PS) were obtained by chemically synthesising PS within the pores of microporous and nanoporous particle track-etched membranes (PTMs). The emulsion polymerisation of styrene into nanopores with diameters ranging from 50 nm to 2 μm is investigated. The pore size and the polymerisation time have a significant effect on the molecular weights and on the polydispersity index of PS. Thermal analyses were conducted on different PS nanostructures and the glass transition temperature was determined. The morphology of the obtained nanostructures was analysed by field-effect scanning electron microscopy (FE-SEM). Hollow PS tubules were formed because some initiator radicals were adsorbed on the pore walls. By using an initiator and a surfactant, which were both negatively charged, the polymerisation of styrene occurred at two places leading to the formation of PS tubules with PS latex particles that were present inside.

Keywords: Polystyrene nanostructures; Emulsion polymerisation; Particle track-etched membranes

1. Introduction

Nanomaterials constitute an emerging research field because when the material size approaches nanoscopic dimensions, the properties of a material can change between the bulk and the molecular scales. Consequently, there is now a considerable interest in the fundamental understanding of nanomaterial properties and in their potential use for technological applications in varied areas, such as analytical chemistry [1], drug delivery, bioencapsulation [2], and electronic, optical, magnetic, and mechanical devices [3]. Among the different strategies reported in the literature to synthesise nanoscopic materials, template synthesis is an elegant approach [4]. This technique consists of including metallic or organic constituents inside the void spaces of nanoporous host materials. Although there now exists a huge range of hosts, track-etched membranes present a significant advantage because they lead to the production of different kinds of nanotubules and nanowires with monodisperse diameters and lengths.

Until recently, most of the work has been focused on the synthesis of metals, semiconductors and conducting polymers within the pores of commercial particle track-etched membranes (PTMs) [2]. A number of companies (Nucleopore, Poretics and Whatman [7]) are selling microporous polymeric filtration membranes with a wide range of pore diameters (0.1–12 μm) and pore densities (10^5–10^9 pores/cm^2). Concerning the conducting polymers (polypyrrole, polyaniline and polymethylthiophene) nanostructures, which are insoluble and infusible materials, the main studied property is their electrical conductivity [2,3,5].

In order to understand better the effect of the synthesis in a confined medium on the physico-chemical and thermal properties of a polymer, we found it interesting to explore the possibility of synthesising a more classical polymer within the pores of a PTM. We started with the study of polystyrene (PS). PS nanostructures were prepared by styrene emulsion polymerisation inside the pores of commercial polycarbonate (PC) and polyethylene terephthalate (PET) microporous and nanoporous membranes. Due to the cylindrical shape of the pores of the membrane used as a template, a PS nanocylinder should be obtained within each pore of the membrane. Besides the fundamental interest of this study, the obtained PS nanomaterials present some potential applications. In particular, these nanostructures may be useful in the biological field because each nanocylinder may become a bioactive nanocapsule containing enzymes, antibodies, etc. Moreover, these nanocylinders are of great interest because they are high-density ensembles gathered and held by the template membrane which is easy to handle and is mechanically strong.

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Table 1
Characteristics of the template membranes used in this study

Membrane type	Pore diameter (nm)	Pore density (pores/cm^2)	Thickness (μm)
PC	50	2.0×10^9	10
PC	100	6.0×10^8	20
PET	100	6.0×10^8	12
PC	600	4.0×10^7	19
PET	600	4.0×10^7	22
PC	1000	2.2×10^7	19
PC	2000	1.0×10^6	19

In this paper, we report on the study of the morphology and some properties of the obtained PS nanomaterials in terms of some experimental parameters: the monomer and initiator concentrations, the charge of the initiator, the polymerisation time, and the size of the pores of the template membrane. The efficiency of the polymerisation was evaluated by FT-IR. spectroscopy and the molecular weights of PS were determined by size exclusion chromatography (SEC). The glass transition temperature (T_g) was determined by dynamic mechanical thermal analysis (DMTA) and the morphology of the PS nanostructures were analysed using a field-emission scanning electron microscope (FE-SEM).

2. Experimental

2.1. Materials

Microporous and nanoporous PC and PET particle track-etched membranes, supplied by Whatman s.a. (Louvain-la-Neuve, Belgium), were used as template membranes for the synthesis of PS nanostructures. These membranes are available in a variety of pore diameters and densities. The specifications of the membranes used in this study and given by the manufacturer are reported in Table 1.

Styrene (Acros, 99%) was destabilised and purified by distillation prior to use. Potassium persulphate and 2-2’ azobis (2-methyl-propionamidine) dihydrochloride (Acros, 98%) were used as anionic and cationic initiators, respectively. Dodecyl sulphate sodium salt (Acros, 99%) was chosen as surfactant in the emulsion polymerisation. Water was purified by a Milli-Q water purification system.

2.2. Emulsion polymerisation

As shown in Fig. 1, the membrane was used as a dividing wall in a two-compartment cell. The first compartment was charged with the surfactant (0.02 M). The surfactant concentration was taken higher than the critical micelle concentration (CMC). Styrene was added under stirring and the monomer emulsion was allowed to diffuse through the membrane for 20 min. An aqueous solution of anionic or cationic initiator (0.07 M) was then added in the second compartment. The start of the initiator addition was taken as $t = 0$ min. Polymerisation was allowed to proceed for 2 h with 1 M of styrene. These experimental conditions were taken as standard conditions. In another set of experiments, using template membranes with 100 nm diameter pores, the styrene concentration and the polymerisation time were varied as mentioned in Section 3. The reaction mixture was thermostated at 46°C in the case of the cationic initiator and at 56°C in the case of the anionic initiator. The two-compartment cell was continuously purged with a nitrogen

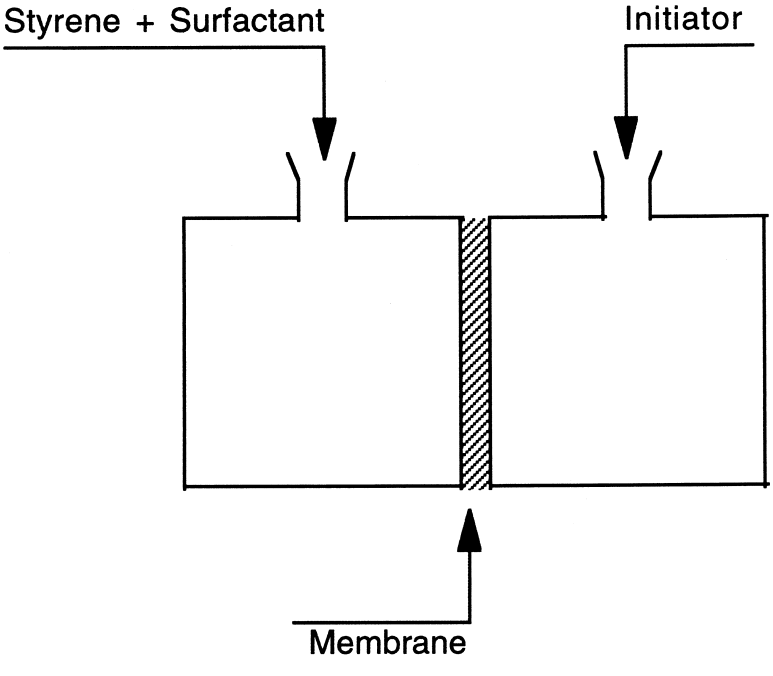

Fig. 1. Schematic representation of the two-compartment cell used to perform the emulsion polymerisation of styrene inside the pores of a template membrane.

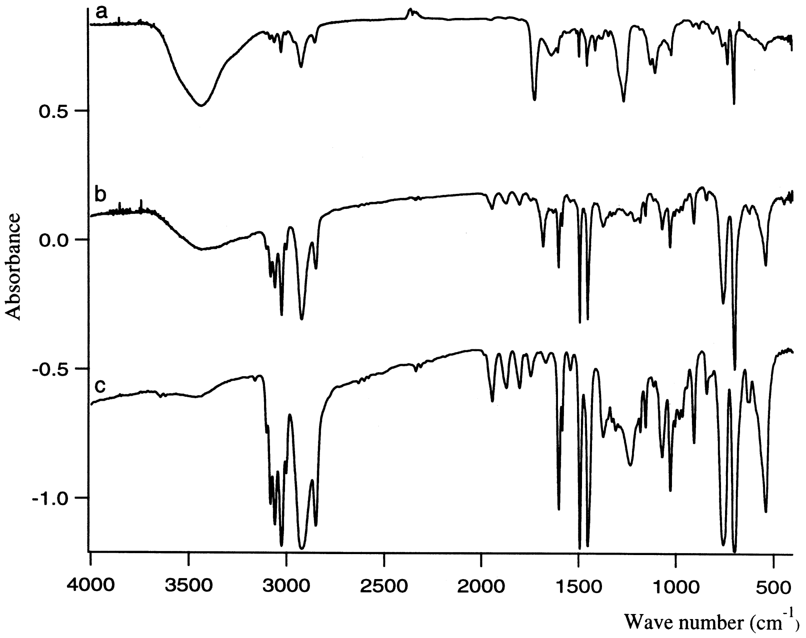

Fig. 2. (a) FT-IR spectrum of PS extracted from the PC membrane pores. (b) FT-IR spectrum recorded on a small amount of solution taken from the first compartment of the chemical synthesis cell after 2 h of polymerisation. (c) FT-IR spectrum of PS prepared by a classical emulsion polymerisation (without membrane in the synthesis medium).

stream in order to avoid oxygen which is a strong inhibitor in the styrene polymerisation. The membrane was then removed from the cell and rinsed with pure water. The amount of PS synthesised inside the membranes depends on the pore size, pore density, and thickness of the template membrane. Under our experimental conditions the extracted amount of PS varies between 1 and 100 mg.

Classical emulsion polymerisation of styrene (without a membrane) with both initiators was also carried out in a 200 ml three-neck glass reactor. The obtained PS latexes serve as references against which some properties of the PS nanostructures were evaluated.

2.3. Analytical methods

FT-IR spectra were recorded on a Perkin–Elmer FTIR 1760X spectrophotometer from 4000 to 400 cm^{-1}. The PS synthesised in the membrane pores was dissolved in toluene and precipitated in methanol. The resulting polymer was then mixed with KBr to analyse the pellets by infra-red spectroscopy.

Molecular weights were determined by SEC at 25°C, using Waters equipment consisting of five Ultrastyragel columns (10^6, 10^5, 10^4, 10^3 and 500 Å), a Waters 590 pump and a Waters 484 tuneable absorbance UV detector set at 254 nm. Unstabilised THF was used as eluent at a flow rate of 1.0 cm^3 min^{-1}. PS standards of narrow molecular weight distribution were used for calibration.

DMTA was performed on a Rheometrics RSA II instrument. The PS filled membranes were solicited under shear at 10 Hz between 40 and 200°C to measure the glass transition temperature (T_g) of the synthesised PS inside the pores. This new and very sensitive measurement technique was recently perfected in our lab by Carlier et al. and is reported elsewhere [8].

Scanning electron microscopy (SEM) was performed using a high resolution FEG Digital Scanning Microscope 982 Gemini from Leo, operating at 1 kV. Prior to analysis, the host membrane was removed in two different ways: (1) the host membrane was hydrolysed by NaOH (5 M) in a water/methanol (50/50 v/v) solution at 50°C for 3 h and the PS nanomaterials were collected by filtration on a silver filter; (2) the PS filled membrane was freeze fractured in liquid nitrogen and the fractured area was then analysed by FE-SEM.

3. Results and discussion

3.1. Identification and structural analysis of PS

Nanostructures of PS were chemically synthesised by emulsion polymerisation in the pores of microporous and nanoporous PC or PET membranes used as templates. FT-IR spectroscopy was used to prove the formation of PS inside the pores of the membrane and to evaluate the efficiency of the polymerisation. As shown in Fig. 2(a), the FT-IR spectrum recorded on PS extracted from the template membrane is similar to the spectrum of the PS latex obtained by a classical emulsion polymerisation (Fig. 2(c)). The peak at 3445 cm^{-1}, which is very intense in the spectrum of PS nanostructures, is due to residual methanol

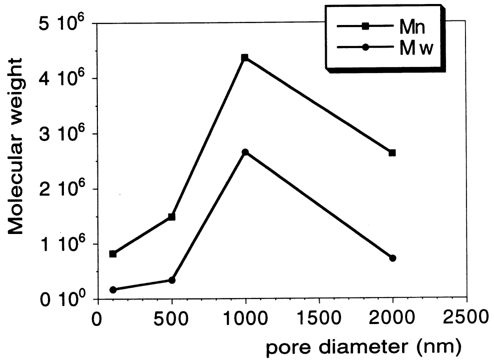

Fig. 3. Plot of PS molecular weights in terms of the pore size. The polymerisation was carried out with the anionic initiator, a monomer concentration of 1 M and a reaction time of 2 h.

used to precipitate and purify the extracted PS. The polymerisation of styrene was found to be successful in all the studied membranes having pore diameters ranging from 50 nm to 2 μm. Nevertheless, in some cases, the conversion was not total as indicated by the presence of a weak absorption band at 1636 cm^{-1}, assigned to the C=C stretching of styrene. The fact that the absorption bands in the spectrum of PS extracted from the membrane (Fig. 2(a)) are less intense than those observed in the spectrum of the PS latex (Fig. 2(c)) is only due to the small amount of extracted PS.

A small amount of solution was taken from the first compartment (containing initially the monomer emulsion) at the end of the polymerisation. The FT-IR spectrum of this product was recorded and was found to be characteristic of PS. This proves that the initiator had diffused well through the pores of the membrane and had reacted with the monomer in the first compartment to yield PS.

Molecular weights of the PS synthesised in membranes with different pore sizes under the standard polymerisation conditions (see Section 2) were determined by SEC. Prior to analysis, the extracted PS was first purified by precipitation in methanol and then dissolved in THF. In Fig. 3, we plotted the values of the number average molecular weight (M_n) and the weight average molecular weight (M_w) of the extracted PS in terms of the pore diameter. We noticed that although the success of styrene polymerisation in the pores of 50 nm diameter was proved by FT-IR spectroscopy and by electronic microscopy (see the next section), the amount of extracted PS from these small pores was insufficient to be detected by the SEC analysis.

The plot in Fig. 3 clearly shows the existence of an optimum diameter of the pores: 1 μm for which the molecular weights of the PS extracted from the pores are the highest and the molecular distribution the narrowest. Moreover, under the used polymerisation conditions, the total monomer conversion was only reached when carrying out the PS synthesis in the 1 μm diameter pores. This is illustrated in Fig. 4 in which typical chromatograms of the PS synthesised in 0.1 and 1 μm diameter pores are reported. Indeed traces of styrene were found in all the chromatograms of PS extracted from the membranes except in the chromatogram of PS extracted from the membrane with 1 μm diameter pores.

In pores with a diameter lower than 1 μm, reagent diffusion, in particular the monomer diffusion, is limited. This limited diffusion, which is more significant for smaller pores than for larger ones, results in a lack of monomer at the reaction site. This leads to a slow rate of polymerisation and thus to low molecular weight PS when the polymerisation is stopped after 2 h.

The polymerisation of styrene in 2 μm diameter pores leads to the formation of PS with molecular weights similar to those obtained for PS synthesised under the same conditions but with no membrane in the medium (Table 2). This result indicates that in pores with diameters higher than 1 μm the effect of the confined medium is lost. In a pore, it is possible that the initiator radicals are adsorbed on the

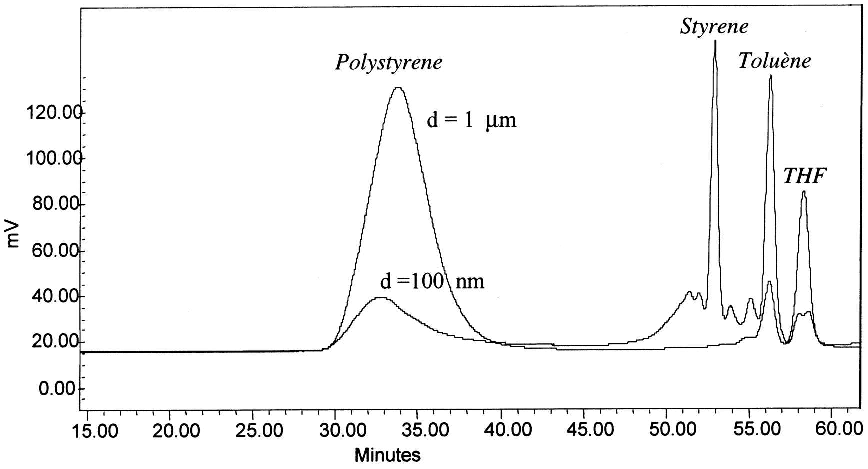

Fig. 4. Chromatograms of PS extracted from pores of 100 nm and 1 μm. The polymerisation was carried out with the anionic initiator, a monomer concentration of 1 M and a reaction time of 2 h.

Table 2
Molecular weights and molecular weight distribution of PS synthesised by a classical emulsion polymerisation using two different initiators (anionic and cationic)

Initiator	M_n	M_w	PDI	Residual styrene
Anionic	1 017 700	2 874 500	2.8	No
Cationic	52 130	244 250	4.7	Yes

curved pore walls where the polymerisation also takes place. In a 2 μm pore, the curvature of the walls is rather low and it is thus more difficult to capture radicals on that locally more planar surface. Consequently, in this case, one may consider that the polymerisation proceeds only by the classical emulsion process in the micelles.

Therefore, a tentative explanation for the existence of the 1 μm optimum diameter could be that, on the one hand, the pore size is large enough to allow the reagents to diffuse rather easily and react at a relatively high rate. On the other hand, the pore size is small enough to be considered as a confined medium in which polymerisation can occur at two different places. Firstly, polymerisation can take place along the pore walls where some initiators radicals are adsorbed. There, the growing polymer chains are forced to align along the pore walls leading to the production of high molecular weight PS. Secondly, polymerisation can occur in the micelles present in the pores in which, due to the limited mass transport, the life time of the radical propagation centre is long. This phenomenon is also in favour of the formation of high molecular weight PS.

The influence of the monomer concentration and of the polymerisation time on PS molecular weights was investigated for the emulsion polymerisation of styrene using a template membrane with 100 nm diameter pores. As reported in Table 3, an increase in styrene concentration leads to the formation of higher molecular weight PS but with a broader molecular weight distribution. Lengthening the polymerisation time also leads to an increase in the molecular weights, but this time with very little effect on the molecular weight distribution (Table 4, entries 1–3). The PS extracted from 100 nm diameter pores after 16 h of polymerisation (Table 4, entry 3) has molecular weights comparable to those obtained for PS extracted from 1 μm pores after only 2 h of polymerisation (Table 4, entry 5). This result is consistent with the fact that in emulsion polymerisation the degree of polymerisation is directly proportional to the rate of polymerisation and that chain propagation is controlled by the monomer diffusion. The observed increase in the PS molecular weight with the time of the reaction can be rationalised by considering that lengthening the polymerisation time does not lead to the formation of new polymer chains but to an increase in the degree of polymerisation of the already existing polymer chains supposing that the radicular reaction site on the growing polymer chains remains active. In order to check this assumption, after polymerisation of 2 h, the initiator solution was removed from the second compartment of the chemical cell and replaced by milli-Q water. The polymerisation was then carried on for an additional 16 h. As presented in Table 4 (entry 4) under these conditions, PS of very high molecular weights ($M_w = 6\ 277\ 690$) and very low polydispersity (PDI = 1.4) is obtained. This result confirms the remaining reactivity of the growing polymer chains. As during the 16 additional hours of polymerisation, no new initiator radicals were created, there is a lack of formation of new polymer chains. Consequently, the monomer units diffusing inside the pores add up to the existing chains, resulting in a higher molecular weight product.

Table 3
Evolution of the molecular weights of PS extracted from 100 nm diameter pores in terms of the monomer concentration ([styrene]) ($t_{polymerisation} = 2$ h; PDI = polydispersity index)

Entry	Φ_{pore} (nm)	[Styrene] (mol/l)	M_n	M_w	PDI
1	100	0.1	306 140	945 630	3.1
2	100	1	174 580	823 770	4.7
3	100	2	262 340	2 139 740	8.2
4[a]	1000	1	2 656 880	4 366 470	1.6

[a] These values are reported in the table for comparison.

In another set of experiments, a cationic initiator was used to start the emulsion polymerisation. In this case, the charge of the initiator is opposite to that of the anionic surfactant employed. A similar evolution of the molecular weights in terms of the pore size was observed for the PS synthesised with the cationic initiator. However, using the anionic initiator ($K_2S_2O_8$ at 56°C) produces PS of a considerably higher molecular weight than the PS obtained with the cationic initiator at 46°C (Table 2). Indeed, M_w of 2.9×10^6 was reached for PS synthesised with the anionic initiator, whereas M_w of only 2.5×10^5 was obtained for the PS synthesised with the cationic initiator. These values are in perfect agreement with those reported in the literature [9,10]. Another difference between the anionic and cationic systems is that the polymerisation started with the cationic initiator in 1 μm diameter pores is not complete (residual monomer was detected by SEC). Under similar conditions, this was not the case for the polymerisation started with the anionic initiator. This difference in reactivity can be explained by the different decomposition rates of the two initiators. The decomposition rate of $K_2S_2O_8$ is slower [11] than that of the cationic initiator and for a given particle diameter when the rate of initiating radical generation decreases, the degree of polymerisation increases [12].

In order to get an additional proof of the presence of PS inside the pores, the glass transition temperature (T_g) of the polymer synthesised inside the pores of the PET template membranes was determined. A new and very sensitive method developed in the laboratory by Carlier et al. [8] allowed us to make dynamic mechanical thermal analysis (DMTA) measurements on the filled PET membranes. The results of the DMTA analysis carried out on a virgin PET

Table 4
Evolution of the molecular weights of PS extracted from 100 nm diameter pores in terms of the polymerisation time ($t_{\mathrm{polymerisation}}$) ([styrene] = 1 M; PDI = polydispersity index)

Entry	Φ_{pore} (nm)	$t_{\mathrm{polymerisation}}$ (h)	M_n	M_w	PDI
1	100	2	174 580	823 770	4.7
2	100	6	383 670	1 868 400	4.9
3	100	16	1 072 360	4 079 030	3.8
4[a]	100	18*	4 467 260	6 277 690	1.4
5[b]	1000	2	2 656 880	4 366 470	1.6

[a] The polymerisation was carried out during 2 h under the standard conditions. Then the initiator solution was removed from the second compartment cell and replaced by milli-Q water. The reaction was then carried on for 16 additional hours.

[b] These values are reported in the table for comparison.

membrane and on a filled PET membrane are presented in Fig. 5.

In Fig. 5(a), which shows the DMTA curve recorded on the virgin membrane, only a very low decrease in the shear modulus is observed due to the high crystallinity of the PET bioriented film. Consequently, the well marked decrease in the shear modulus and the presence of the tan δ peak observed on the DMTA curve of the filled PET membrane (Fig. 5(b)), can be attributed to the PS synthesised in the pores of the template membrane. Glass transition temperatures (T_g) measured on different samples are reported in Table 5. The T_g values around 110°C are characteristic of PS. Moreover, as expected, the T_g increases with the molecular weight of PS.

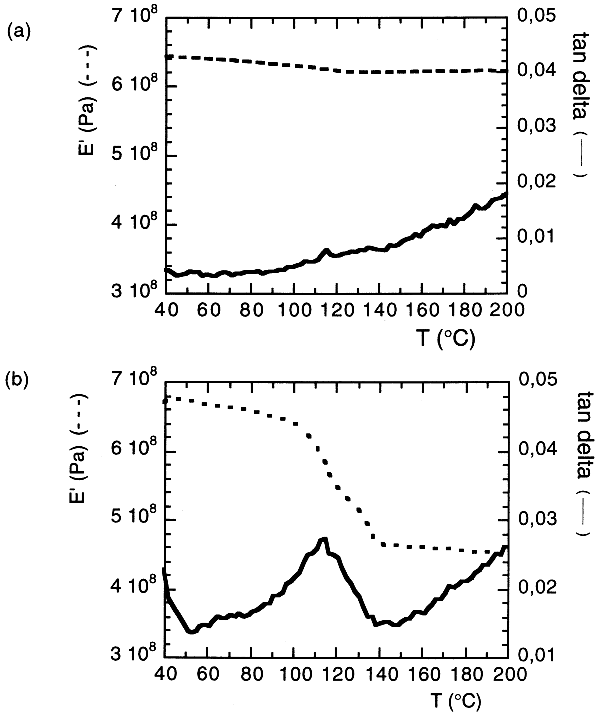

Fig. 5. Evolution of the viscoelastic properties (shear modulus and tan δ transition) of: (a) a virgin PET membrane; and (b) a PET membrane with 600 nm pores filled with PS.

Table 5
Glass transition temperature (T_g) of PS synthesised in a medium without any membrane and within membranes with pores of 100 and 600 nm diameter. The polymerisation of styrene was carried out with the cationic initiator

Reference	T_g (°C)	M_w
PS latex	117	244 250
PET membrane filled with PS inside 600 nm pores	112	112 250
PET membrane filled with PS inside 100 nm pores	109	79 940

3.2. Morphology of the PS nanostructures

In order to observe the morphology of PS nanostructures established in the pores, the host membrane has to be removed. As it was not possible to find a solvent for the membrane (PC or PET), which was a non-solvent for PS, two other sample preparation methods were developed: (1)

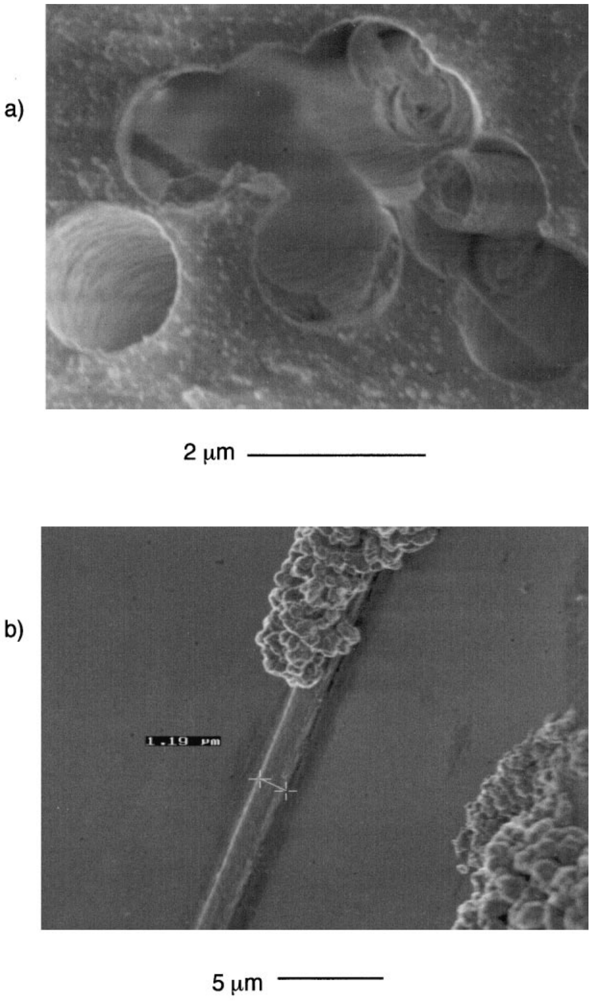

Fig. 6. FE-SEM micrographs of PS nanostructures synthesised in 1 μm diameter pores: (a) after a partial hydrolysis of the PC membrane; and (b) after the complete hydrolysis of the PC membrane.

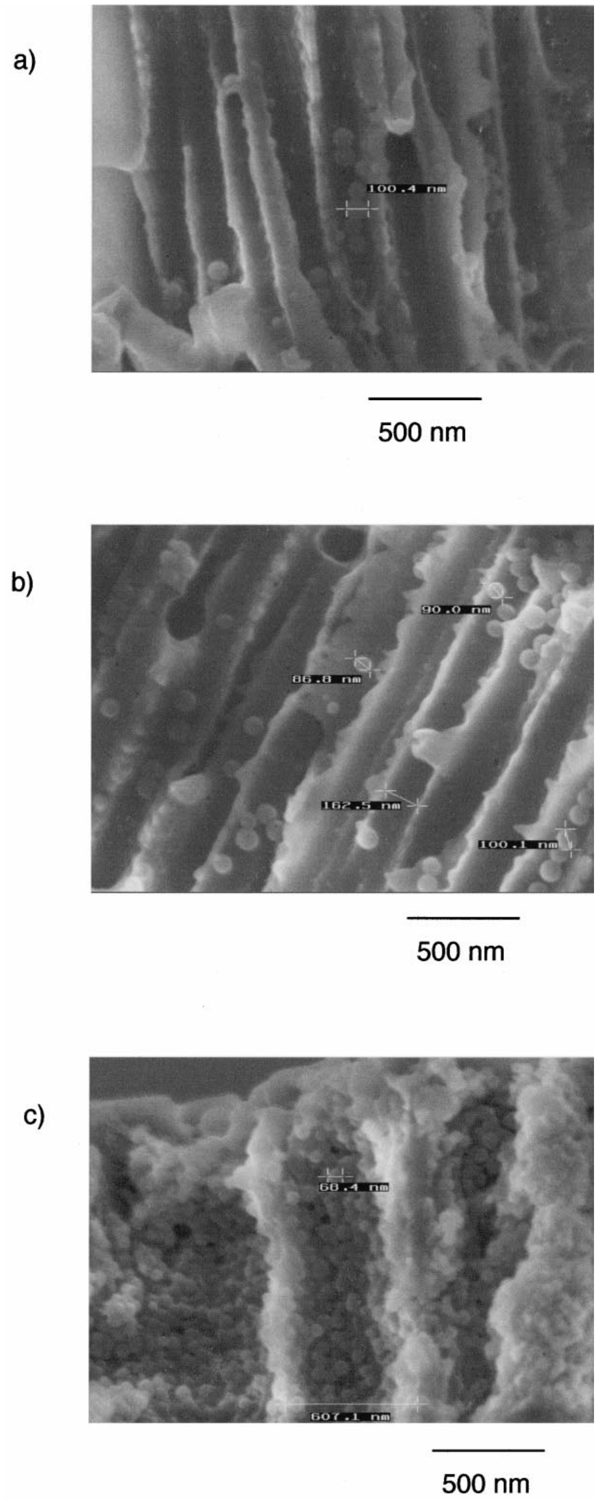

Fig. 7. FE-SEM micrographs of PS nanostructures after fracture of the membrane in liquid nitrogen: (a) PC membrane with 50 nm pores; (b) PC membrane with 100 nm pores; and (c) PET membrane with 600 nm pores.

the host membrane was hydrolysed by NaOH (5 M) in a water/methanol solution and the PS nanomaterials were collected by filtration on a silver filter; (2) the PS filled membrane was freeze fractured in liquid nitrogen and the fractured area was then analysed by FE-SEM. Firstly, we reported on the morphology study of the PS nanostructures obtained by emulsion polymerisation of styrene with the anionic initiator. Images of PS nanostructures synthesised inside 1 μm diameter pores after hydrolysis of the PC template membrane are presented in Fig. 6. Fig. 6(a) clearly shows that PS tubules are formed when styrene is polymerised within the pores of the membrane.

The formation of these tubules can be explained by the fact that the initiator radicals are easily adsorbed on the curved surfaces of the pores. Therefore, styrene polymerisation can be initiated there and polymer chains can grow along the pore walls, resulting in the formation of a PS film.

As revealed by the FE-SEM photographs, spherical latex particles are also formed. These cover the membrane surface (Fig. 6(a)) as well as the PS tubules (Fig. 6(b)). The analysis of the fractured PS/PC membrane in liquid nitrogen allowed us to observe that latex particles are also formed inside the PS tubules. Indeed, whatever be the pore size (from 50 nm to 1 μm), small monodisperse particles of a diameter lower than 100 nm are present (Fig. 7(a)–(c)). It is worth mentioning that when the pore size increases, the number of particles also increases, but they are of a smaller size. The morphological analysis by FE-SEM confirms our hypothesis that when carried out in pores of a PTM, the polymerisation of styrene occurs at two different places. This is due to the fact that initiator radicals do not only penetrate inside the micelles but are also adsorbed on the curved walls of the membrane pores to initiate the polymerisation. As a result, in addition to the classical formation of latex particles during emulsion polymerisation, a PS film covering the pore walls is formed.

Fig. 8 shows a scanning electron micrograph of PS nanomaterials synthesised with the cationic initiator. This figure reveals the formation of a PS film covering the pore walls of the membrane but with no latex particles inside the tubules. This kind of morphology was observed for all the studied pore diameters. An identical morphology was also obtained when the synthesis was carried out without a surfactant. Therefore, although Cochin et al. [9] found that the use of initiators of opposite charge did not affect the conventional surfactants, the lack of latex particles is due to the fact that particle stabilisation by the surfactant is not sufficient due to the opposite charge between the cationic initiator and the anionic surfactant. Consequently, flocculation occurs.

4. Conclusions

PS nanostructures were successfully prepared by emulsion polymerisation of styrene in nanopores of PC and PET template membranes. The advantage of the synthesis of a classical polymer, such as PS, in the nanopores of a membrane compared to that of insoluble and infusible conducting polymers reported previously [2,3,5,6] is that the physico-chemical and thermal properties of the created

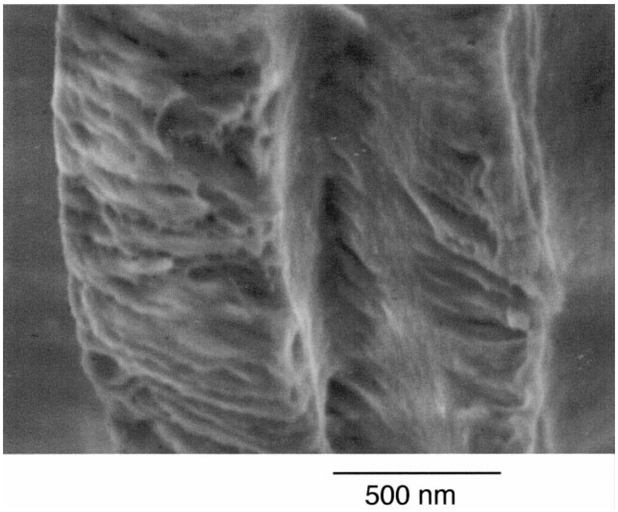

Fig. 8. FE-SEM micrograph of PS nanostructures synthesised with a cationic initiator within 1 μm diameter pores, after fracture of the PS/PET membrane in liquid nitrogen.

nanomaterials can be investigated. FT-IR spectroscopy allowed us to prove that styrene emulsion polymerisation, inside the pores of the membrane, can be carried out successfully. DMTA confirms the presence of PS inside the membrane by measurement of T_g. SEC analyses revealed that under our reference experimental conditions, the PS synthesised in 1 μm pores had the highest molecular weight and the narrowest polydispersity index. One micron is an optimum pore size because it is large enough to allow the diffusion of each reagent through the pores of the membrane but is also small enough to be considered as a confined medium and keep the properties linked to this effect. In this confined medium, the initiator radicals can adsorb on the curved walls of the pores and the polymer chains can propagate from and along the pore walls. Our study also reveals that the radicular reaction site on the growing polymer chains remains active inside the pores. Indeed, by lengthening the polymerisation time, the new monomer units diffusing inside the pores add up to the existing growing chains resulting in a higher molecular weight polymer with a much narrower molecular weight distribution. Studies carried out by FE-SEM revealed that the morphology of the created PS nanostructures is different when using an anionic initiator than when using a cationic one. Although, in both cases, formation of PS tubules was observed confirming that styrene polymerisation occurs along the pore walls, latex particles were only present inside the PS tubules when using the anionic initiator.

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