Dynamic Study Of Polystyrene-*block*-poly(4-vinylpyridine) Copolymer in Bulk and Confined In Cylindrical Nanopores

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ABSTRACT

AAO template is highly recommended to nanostructure polymers and to study polymer properties under confinement. The dynamic properties of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) under confinement using broadband dielectric spectroscopy are investigated in this work and the results compared to those of the bulk. Anodized aluminum oxide (AAO) membranes, having pore diameters from tens to hundreds of nanometers in size, were used to confine PS-*b*-P4VP. Moreover, the influence of gold nanoparticles (AuNPs) in the copolymer matrix was also studied. The morphology and structure of the bulk copolymer and the copolymer confined in the AAO templates were characterized by transmission electron microscopy, scanning electron microscopy and Small Angle X-Ray Scattering. For PS-*b*-P4VP in bulk, dielectric relaxation techniques allowed studying selectively the P4VP segmental dynamics within the diblock. At high temperature this copolymer presents a dominant peak (MWS relaxation), most likely originated by the relatively high conductivity combined with the presence of interfaces emerging in the nanostructured samples. Moreover, a pronounced β -relaxation is observed for the copolymer compared with that of pure P4VP. This is likely due to a non-negligible contribution from the α -relaxation of the PS component. The γ -relaxation is markedly different in the copolymer, which is evidenced by a distinct temperature dependence of the resulting relaxation times. When the copolymer is embedded in alumina nanopores with small pore diameters (25 and 35 nm) there are significant changes, where the tendency is going to a faster dynamics when the pore diameter decreases more likely related to the relevance of surface effects. The presence of the AuNPs in the system enhances this effect. These results are in agreement with segregated structures found in the block copolymer by TEM and SAXS.

KEYWORDS: dielectric spectroscopy broadband, AAO templates, PS-*b*-P4VP copolymers, confinement effects, small and wide-angle scattering.

Additional Supporting Information may be found in the online version of this article

Introduction

During the last few years there has been a tremendous interest in template-based synthesis of nanomaterials for numerous nanotechnology applications. Anodic or anodized aluminum oxide (AAO) templates, having a hexagonally packed array of nanoscopic pores, where the pore diameter can be controlled by the anodization conditions used, provide a simple platform to generate nanostructured materials and to study the properties of confined polymers.[1-4] The molecular motions in polymer systems can be conveniently investigated by means of relaxation techniques.[5, 6] In this way, in the glassy state rather local motions are detected as weak secondary relaxation processes (named β , γ , in decreasing temperature order). Around and above the glass-transition temperature T_g , the polymer segmental dynamics - responsible of this transition and having a markedly cooperative character - is detected as a prominent relaxation, usually referred to as α -relaxation. Recent Broadband Dielectric Spectroscopy (BDS) studies of polymers confined within AAO templates showed that the dominant influence of confinement was a broadening of the distribution of relaxation times for the α and β processes[7] and the presence of a highly constrained layer at the pore/polymer interface arising from the favorable interactions of one block with the walls of the pores.[8] Neutron spin echo has revealed the single chain dynamic structure factor of entangled polymer chains confined in cylindrical nanopores with chain dimensions either much larger or smaller than the lateral pore sizes. In both situations, a slowing down of the dynamics with respect to the bulk behavior is only observed at intermediate times.[9, 10] Moreover, both Russell et al. and Steinhart et al. have used these templates to confine block copolymers (BCPs) to investigate the influence of cylindrical confinement on the morphology of BCPs where the pore diameter in size is similar to the characteristic period of the BCP microdomain morphology.[11-28] Müller et al. studied the

crystallization behavior in polystyrene-*block*-polyethylene (PS-*b*-PE) within the alumina membrane[29], and Russell et al. studied the capillary flow of a microphase-separated block copolymer into nanoscopic pores, by means of BDS.[30, 31]

The well-defined nanometric geometries of AAO templates in the nanoscale make these platforms interesting systems to investigate the influence of geometrical confinement on dynamics not only of the homopolymers but of block copolymers too. The segmental dynamics of polymeric chains in microphase separated BCPs are expected to be affected by factors like their own spatial confinement and when confined in AAO templates by an additional effect due to the wall restriction.[32-35] Moreover, incorporating metal nanoparticles into a polymer matrix can enhance the relaxation properties.[33, 34]

In this work, we present results on the confinement of polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) in AAO templates having pore diameters from tens to hundreds of nanometers in size. Dynamic properties were investigated by dielectric spectroscopy and results compared to its behavior in bulk. In order to correlate the results to the polymer structures of the BCP, the structural characterization by combining Small Angle X-Ray and electron microscopies is studied. Moreover, in order to enhance the differences, the study of the copolymer with AuNPs has been also investigated.

Experimental Section

Samples.

Anodic Aluminum Oxide Templates. The ordered anodic aluminum oxide (AAO) templates with average pore diameters from 25 to 330 nm were prepared by a two-step anodization process.[36]

Porous alumina films are formed in electrolytes that dissolve alumina sparingly (sulfuric, phosphoric, oxalic acids).[37, 38] The aluminum foil used for the membrane preparation was ultrapure (99.999%) aluminum foil supplied by Sigma-Aldrich (USA). To fabricate the templates,[36] the aluminum foils was cleaned and degreased by sonication with solvents of different polarity, then electropolished at a constant voltage of 20 V (to eliminate the oxide barrier layer formed by the air) in a mixture of HClO₄:EtOH (25:75). After the electropolishing step, two anodization steps were used to generate hexagonal array of cylindrical pores oriented normal to the surface of the template. By selecting the appropriate conditions, the pore diameter in the AAO templates could be varied (Table 1).[39-42]

Table 1. Experimental conditions of the anodizations of aluminum in sulfuric, oxalic and phosphoric acid electrolytes, and corresponding obtained interpore distances and pore diameters.

Electrolyte	Concentration	Voltage (V)	Temperature (°C)	1 st anodization time (h)	Pore diameter (nm)	Interpore distance (nm)
H ₂ SO ₄	0.3 M	25	1-2	24	25	65
H ₂ C ₂ O ₄	0.3 M	40	3-5	24	35-60	100
H ₃ PO ₄ (0.02M AlO _x)	2 wt%	195	5	6	330	480

PS-b-P4VP and PS-b-P4VP/Au NP nanocomposites. The PS-*b*-P4VP employed in this work was purchased Polymer Source with $M_n = 51000$ - b -18000 and PDI = 1.15. PS and P4VP homopolymers were purchased from Sigma-Aldrich having M_w of 230000 g/mol and 60000

g/mol, respectively. Synthesis of dodecanethiol covered gold nanoparticles (AuNPs) is described in SI.

Composite films of PS-*b*-P4VP and Au NPs were prepared as follows: 1 mg of dodecanethiol-capped Au NPs was mixed with a 10 wt% solution of PS-*b*-P4VP in 3 mL of chloroform and stirred vigorously for 1 day, then cast onto cleaned microscope slides to obtain a film of around 150 μm of thickness. The solvent was slowly evaporated in air at room temperature. The prepared copolymers films contained 0.1 wt% dodecanethiol-capped Au NPs.

PS-b-P4VP and PS-b-P4VP/Au NPs nanorods. For the preparation of the PS-*b*-P4VP and PS-*b*-P4VP/AuNPs nanorods, the BCP and nanocomposite film were placed directly onto the AAO templates to infiltrate the template under partial wetting regime, at 468 K under nitrogen atmosphere for 2 days, and then cooled to room temperature. The excess material on the surface was scraped off with a razor blade, the samples were re-heated to 468 K, then cooled to room temperature.

Scanning electron microscopy (SEM). A Philips XL-30 ESEM operated at 25 kV was used for the morphology characterization of the AAO templates.

Transmission electron microscopy (TEM). A JEOL 2000FX transmission electron microscope operating at an acceleration voltage of 200kV with LaB₆ filament achieving a resolution of 2.5 Å was used for the morphology/structure characterization of the block copolymer and nanocomposite film. The measurements were carried out at room temperature. Samples were prepared on a copper grid (400 mesh) covered only with carbon (purchased from Electron Microscopy Sciences). A diluted drop of previously prepared solutions was deposited and the solvent was slowly evaporated in air at room temperature.

In order to prepare the nanorods for TEM measurements, the alumina template was dissolved in an aqueous 5 wt% NaOH solution. The NaOH solution containing the released copolymer nanorods was filtered and thoroughly rinsed with deionized water, and deposited onto copper grids coated with carbon films.

Differential Scanning Calorimetry. The DSC measurements were carried out using a Q2000 from TA instruments with a liquid nitrogen cooling system. Measurements were conducted at heating and cooling rates of ± 10 K/min. Two different glass-transition temperatures (T_g 's) associated to both components were observed: $T_g^{\text{PS}} = 375$ K and $T_g^{\text{P4VP}} = 416$ K (see Figure S2).

Small Angle X-Ray Scattering (SAXS). SAXS was used to characterize the center-to-center distance between the pores and the average pore diameter.[43] SAXS was also used to examine the nanostructures formed by the self-assembly of the BCPs and nanocomposite films. The temperature range covered was between 303–473 K. Detailed information of the experiments is reported in SI.

Wide Angle X-Ray Scattering (WAXS). The WAXS measurements of the copolymers were carried out by the same Rigaku PSAXS-L equipment by placing the sample at a distance of 24 cm from the detector. The Q range covered was between 0.1 and 1.7 $\text{\AA}^{-1}$. The same temperature control as for the SAXS measurements was used.

Dielectric Spectroscopy. The complex dielectric permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$, where ε' is the real and ε'' is the imaginary part, was obtained as a function of the frequency ω and temperature T [6] by using a Novocontrol high resolution dielectric analyzer (Alpha-N analyzer). The sample cell was set in a cryostat, and its temperature was controlled via a nitrogen gas jet stream coupled with the Novocontrol Quatro controller. The dielectric measurements were performed at different

temperatures in the range of 143-483 K and at frequencies in the range of 10^{-1} to 10^6 Hz. For homopolymer, copolymer and nanocomposite samples, measurements were carried out in the usual parallel plate geometry with electrodes of 20 mm in diameter. A separation of 100 μ m between both electrodes was maintained by using a cross shaped Teflon[®] spacer of small area. For the samples infiltrated in the AAO templates, the measurements were carried out with a 15 mm electrode placed on top of the template without spacers

Results and discussion.

Morphology. Figure 1 (a-d) shows SEM micrographs of the top side of the AAO templates prepared ranging from 25 nm pore diameter up to 330 nm in diameter. These results evidence the homogeneous size and a real distribution of the pores. Complementary insight into the structure of the AAO templates is provided by SAXS (Figures 1e-h).

Figure 1. SEM micrographs of the surfaces of AAO templates with pores of (a) 25 nm, (b) 35 nm, (c) 60 nm and (d) 330 nm in diameter and the small-angle X-ray scattering obtained respectively from them (e,f,g and h). The solid lines represent the proposed fits.

The general structure revealed by the SAXS profiles is similar in all synthesized AAO templates. The SAXS intensity profile is the product of the cylinder form-factor for the individual pores and a two-dimensional structure factor for the (relatively disordered) array of parallel channels.[43,

44] Clearly, the structure factor dominates the SAXS patterns. The sample with the smallest pore diameter ($D_p = 25$ nm) shows a sharp Bragg reflection, as would be expected. For membranes with a larger pore size and separation distance, the peaks are broader and the Bragg peaks are displaced to lower Q values. A quantitative analysis of the SAXS patterns was carried out by fitting the experimental curves to analytical expressions for the scattering functions. The calculations were done by using software developed by S. Föster and L. Apostol [<http://www.chemie.uni-hamburg.de/pc/polymer/software.html>]. [45, 46] Table 2 compares the values obtained for the structural parameters from the fits of the SAXS data and from the SEM images. Both sets of results are in good agreement.

Table 2. SAXS results analyzed by means of the Scatter software for prepared AAO templates. d is the cross-sectional diameter of the cylinder; σ is the relative standard deviation; a is the unit cell dimension; $\bar{D}$ is the average domain size and l is the length of the cylinder.

Parameter	AAO 25 nm		AAO 35 nm		AAO 60 nm		AAO 330nm	
	SAXS	SEM	SAXS	SEM	SAXS	SEM	SAXS	SEM
d (nm)	24.6	25	31	35	55	60	380	330
σ (R)	0.31	-	0.31	-	0.31	-	0.1	-
a (nm)	61.8	65	100	100	106	100	508	480
$\bar{D}$ (nm)	140	-	135	-	170	-	500	-
l (μm)	123	110	50	47	50	47	100	104

TEM and SAXS techniques were combined to characterize the morphology of the BCP, the composite, and the nanorods formed. In Figure 2, representative micrographs obtained by TEM for PS-*b*-P4VP and PS-*b*-P4VP_0.1% Au copolymers at room temperature are shown. P4VP

domains stained with iodine (I_2) are darker than the background. According to the theoretical phase diagram, from the copolymer volume fractions and the segregation strengths,[47] we would expect hexagonally packed cylindrical microdomains.

Figure 2. TEM micrographs from (a) PS-b-P4VP and (b) PS-b-P4VP_0.1% Au. The dark areas correspond to the P4VP-rich phase. In the panel (b) the dark circles into the P4VP-rich phase correspond to the AuNPs. P4VP domains are selectively stained by iodine (I_2). The red arrows point to the AuNPs.

The observed TEM images suggest such a nanostructure with P4VP cylinders oriented normal to the surface. This morphology is confirmed by the SAXS results (Figure S3). Moreover the TEM images show that the AuNPs are located in the P4VP (see Figure 2b) and also confirmed by SAXS measurements (Figure S3).

In resume, we note that the morphologies of the copolymer and the nanocomposite did not change and the values obtained for the parameters describing the structural features had little temperature dependence.

We attempted to investigate the structure/morphology of the copolymers and nanocomposites within the AAO templates with SAXS, but the overwhelming scattering from the AAO templates prevented any characterization of the infused material. Therefore, the structural characterization was performed by TEM on the bare nanorods obtained by dissolving the alumina layer as explained in the experimental section. Figure 3 shows TEM images of PS-*b*-P4VP 0.1%Au nanorods that had lengths of several micrometers, whereas their diameter of 60 nm corresponded to the diameter of the AAO templates studied.

Figure 3. TEM images of PS-b-P4VP 0.1% Au nanorods with 60 nm in diameter. (a) A view of fabric nanorods without stained sample. The dark spots are the AuNPs into the nanorods. (b), (c) and (d) fabric nanorods with stained samples. The dark spots are the P4VP domains surrounded by the PS domains. P4VP domains are selectively stained by iodine (I_2). Inset in panel (c) shows some dark circles into the P4VP-rich phase correspond to the AuNPs. The red arrows point to the AuNPs.

In Figure 3a nanorods containing AuNPs are shown. The nanorods did not contain a large amount of Au NPs. AuNPs were only visible in non-stained samples. In nanorods stained with

iodine (I_2) (Figures 3b, c and d), the dark area of the P4VP domains masked the Au NPs that appeared in the bulk copolymer (Figure 2b). In the inset of Figure 3c it may be possible to distinguish some AuNPs located in the P4VP microdomains.

As we demonstrated above by TEM and SAXS characterization, the morphology of the copolymer in the bulk consists of cylinders. However, this seems not to be the case in the nanorods. As can be seen in Figure 3, PS-*b*-P4VP nanorods with a diameter value of $D \approx 60$ nm contained regular linear arrays of spherical P4VP domains ~ 34 nm in diameter with a center-to-center distance of ~ 55 nm appearing dark surrounded by a brighter PS matrix. The reduced nanorod diameter value in these nanorods is $D/L_0 \approx 1.3$ ($L_0 \approx 47$ nm: center-to-center distance between the P4VP cylinders in the bulk). In the earlier work of Russell et al. and Steinhart et al., morphologies and morphological transitions of block copolymers under 2-D confinement were studied.[11, 12, 14, 17, 18, 20, 21, 23, 24, 27, 48] In particular, we note the similarities of our system with the PS-*b*-PBD copolymer (PBD: polybutadiene) reported in Ref.21. With PBD being the minor component, this system has cylindrical microdomain morphology in the bulk. However, a layer of PBD is formed at the interface between the PS and the nanopores wall leading to the emergence of spherical microdomains in the nanorods. A similar situation is found in our studies.

The short-range order of the samples has been characterized by WAXS. The WAXS measurements have allowed determining that the copolymers contain P4VP and PS blocks. These systems show a qualitatively analogous behavior to that of the copolymers. In fact, the structure factor of the copolymers is very similar to that of bulk PS (the majority component). MD-simulations[49] and neutron scattering experiments[50] on PS have qualified the first peak in PS as arising from inter-molecular correlations involving main-chain atoms, while the second

peak is attributed to correlations involving the phenyl rings. Obviously, the similar microstructure of P4VP compared to PS leads to the same kind of pattern and results are reported in Figure S4. The copolymers contain P4PVP and PS blocks show a qualitatively analogous behavior to that of the copolymers. These results support the high degree of segregation of the copolymer at all the temperatures studied (Figures S5 and S6).

To address in more detail the effect of the NPs on the local structure of the copolymer, the effect of temperature has been studied by WAXS (Figure S7). At lower temperatures indistinguishable results are obtained. Thus, the AuNPs hardly influenced the short-range order of the polymer, in particular, of the P4VP phase in whose they are embedded.

Dynamics studies by dielectric spectroscopy.

Homopolymers. Figure 4 shows the temperature and frequency dependences of the imaginary part of the dielectric permittivity, or dielectric loss, ϵ'' , for pure P4VP.

Figure 4. Dielectric loss versus frequency for different temperatures for pure P4VP. The inset displays the dielectric loss versus temperature at a frequency of 1000 Hz for pure P4VP (solid symbols) and for pure PS (open symbols).

The relaxation spectrum of P4VP shows two main relaxation processes identified as the α -relaxation and β -relaxation. A third relaxation process is observed in the isochronal plot shown in the inset. This relaxation, which is identified as γ -relaxation, is weak and detectable only at low temperature. The dramatic increase of the dielectric loss on the low frequency side (more pronounced at higher temperatures) represents the contribution of the conductivity. The dielectric relaxation of PS is well known to be weak (with values of ϵ'' below 0.01). In the inset a direct comparison between the dielectric losses from PS and P4VP is shown. The main relaxation of PS

is identified as the α -relaxation. Signatures of much weaker secondary relaxations[51-53] are also detected, although possible contribution in the copolymer would be negligible.

Copolymer. The dielectric relaxation techniques allowed studying selectively the P4VP segmental dynamics within the PS-*b*-P4VP, since P4VP is the component contributing more to the dielectric relaxation, the PS relaxation strength being very weak. Figure 5 shows the frequency dependences of the imaginary part of the dielectric loss, ϵ'' , for PS-*b*-P4VP copolymer.

Figure 5. Frequency dependence of the imaginary part of the dielectric loss ϵ'' (f) corresponding to different temperatures between 483 K and 303 K for PS-*b*-P4VP copolymer. The inset displays the dielectric loss versus temperature at a frequency of 1000 Hz.

This copolymer shows a prominent relaxation at high temperatures, more prominent than expected for the α -relaxation of P4VP component, which is the minority block of the copolymer. This main peak is combined with a shoulder on the high frequency side, only resolved at the highest temperatures. The position of this shoulder matches well with the α -relaxation of the P4VP homopolymer and the peak intensity is what could be expected according to the P4VP weight fraction in the copolymer. This leads us to associate the main loss peak detected in the copolymers to a Maxwell-Wagner-Sillars (MWS) relaxation most likely originating from the relatively high conductivity in the segregated P4VP phase (it is already evident in the P4VP homopolymer) combined with the presence of sharp interfaces associated with the copolymer nanostructure as evidenced above by SAXS.

The β -relaxation is also shown in Figure 5 and, at first glance, it is consistent with that observed for the homopolymer but more pronounced than expected. Noteworthy, the contribution of the α -dielectric relaxation from PS also occurs in the same range (see inset of Fig. 4) and taking into account the relatively high PS content, the α -relaxation of PS would be also relevant in this loss peak detected in the copolymers. On the other hand, at low temperatures a new, rather intense and relatively narrow relaxation peak is detected. This relaxation does not correspond straightforwardly to the P4VP homopolymer, although taking into account the weak contribution from PS in this temperature range it has to be related with some local reorientation in the P4VP units. Tentatively, as it will be discussed below, one could attribute this γ -relaxation to the mobility of P4VP rings that would occur with sufficient amplitude only in poorly packed regions as expected to arise close to the interface.

Copolymer with AuNPs. The effect of adding gold nanoparticles on the dielectric relaxation of the copolymer is shown in Figure 6.

Figure 6. (a) Frequency dependence of the imaginary part of the dielectric loss ϵ'' (f) corresponding to temperatures between 483 K and 333 K for PS-b-P4VP (black symbols) and PS-b-P4VP 0.1% Au (red symbols) samples. (b) Temperature dependence of the imaginary part

of the dielectric response $\varepsilon''(T)$ at a frequency of 1000 Hz for PS-b-P4VP (black symbols) and PS-b-P4VP 0.1% Au (red symbols) samples.

Figure 6a shows the frequency dependence of the dielectric losses ε'' at selected temperatures: 483 K and 453 K (above the T_g -s), 393 K (intermediate temperature) and 333 K (below T_g -s), for PS-b-P4VP (black symbols) and PS-b-P4VP 0.1% Au (red symbols) samples. Figure 6b shows the temperature dependence of the imaginary part of the dielectric response $\varepsilon''(T)$ at a frequency of 1000 Hz for PS-b-P4VP (black symbols) and PS-b-P4VP 0.1% Au (red symbols) samples. From this comparison it is clear that the presence of AuNPs does not significantly affect the P4VP dynamic behavior; however there are some minor differences. On one hand, the relaxation intensity at low temperatures is significantly reduced. On the other hand, the conductivity contribution at lower frequencies is higher and the MWS relaxation is modified on the low frequency side. This latter effect would suggest that the presence of AuNPs modifies the interfaces without affecting the HCP structure. The minor changes at the interfaces could also be an explanation of the reduction of intensity in the range of the γ -relaxation according to the interpretation proposed above for this process.

The characteristic dielectric relaxation times of the distinct process have been determined from the maxima of the loss peaks, i.e. $\tau = 1/(2\pi f_{\max})$. Since the various relaxation processes are in general rather superimposed, resolving the peak position in the isothermal curves is subjected to large uncertainties. However, the isochronal representation of the same data, i.e. $\varepsilon''(T)$ at fixed frequency, allows an easier identification of the relaxation peaks and therefore we used this latter

plots to extract the characteristic time scale of the different relaxation processes investigated.

Figure 7 plots the so obtained relaxation times versus the reciprocal temperature.

Figure 7. Dependence of the relaxation time of the α -relaxation, β -relaxation and γ -relaxation from the isochronal plots, with the reciprocal temperature for the P4VP (black square symbols), PS-b-P4VP (red circle symbols) and PS-b-P4VP 0.1% Au (blue triangles symbols) samples. The results on the α -relaxation of pure PS are represented by green stars.

For the α -relaxation associated to the P4VP component segmental dynamics the times obtained on the copolymer (also with gold nanoparticles) coincides rather well with those of the P4VP homopolymer but they are slightly faster. This would be most likely due to a small effect on the P4VP dynamics induced by the faster majority PS component dynamics. The evaluation of time

scale of the β -relaxation of P4VP component has been limited to the low temperature range (in the glassy state) since at higher temperatures it is masked either by the prominent tail of the α -relaxation in the homopolymer or by the significant contribution of PS in the same range in the copolymers. In the explored range the characteristic times of the β -relaxation of P4VP look again not much affected by the nanostructure.

As we explained above, the relaxation that appears at low temperatures (γ -relaxation) is markedly different in the copolymer, which is evidenced by a distinct temperature dependence of the resulting relaxation times. When analyzing the influence of the presence of AuNPs in the copolymer, we can see how the dielectric relaxation times overlap well both in the copolymer and in the copolymer with AuNPs, as it would be anticipated from the strong similarities of the relaxation curves. The dramatic difference in the temperature variation of the γ -relaxation and the above mentioned much larger relaxation strength in the copolymers are the major effects associated to the nanostructure. A way of rationalizing such effects is by considering that the γ -relaxation of P4VP is not originated by a single molecular motion, but it is the result of the superposition of two different local rearrangements in the P4VP polymeric units. This kind of situation is what was found for the dielectric γ -relaxation of polycarbonate[54], where two molecular motions influencing the carbonate dipole fluctuations were identified, each dominating the whole relaxation at low and high temperatures respectively. If a similar situation is assumed for the dielectric γ -relaxation of P4VP, the contribution of the types of molecular motions - the slower ones - contributing to the γ -relaxation is dramatically enhanced in the copolymers, dominating the observed behavior in these systems over the whole temperature range investigated.

To quantify the temperature dependence of the characteristic relaxation times the apparent activation energies of the different processes have been determined by fitting the relaxation time data by an Arrhenius equation

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad \text{Equation 1}$$

where τ is the relaxation time, τ_0 is a pre-exponential factor (or simply the *pre-factor*), E_a is the activation energy, R is universal gas constant and T is the temperature. The obtained values are shown in Table 3.

Table 3. Activation energy E_a and pre-exponential factor of the α , β and γ relaxation for the studied bulk samples.

	E_a^α (kJ/mol) $\pm 10\%$	τ_0^α (s)	E_a^β (kJ/mol) $\pm 10\%$	τ_0^β (s)	E_a^γ (kJ/mol) $\pm 10\%$	τ_0^γ (s)
PS	186	2×10^{-60}	-	-	-	-
P4VP	143	8×10^{-43}	51.3	2×10^{-19}	24.8	2×10^{-17}
PS-b-P4VP	120	2×10^{-36}	51.8	2×10^{-19}	15.6	8×10^{-12}
PS-b-P4VP_Au	119	2×10^{-36}	53.4	4×10^{-20}	16.2	3×10^{-12}

First, it has to be noted that as we used isochronal curves for obtaining the relaxation times the resulting activation energy values have to be considered only as estimates[55] but are still useful for the comparison among the different samples and relaxations despite the remaining uncertainties. These have been estimated to be about 10%. As shown in Figure 7, the given values of the activation energy for the α - and β - relaxations characterize the dynamics in the

range between a few and several hundred milliseconds, whereas it characterizes the whole explored range for the γ -relaxations. As usually the values resulting for the α -relaxations are extremely high as indicative of the cooperative character of the molecular motions in this range. Moreover, the values for PS are even higher than for P4VP evidencing a higher 'fragility' of the former in the Angell's classification.[56] The activation energy values for the β -relaxation of P4VP are still high to be associated to a single molecular motion. This is also a general result usually interpreted as originated by entropic contributions arising from the occurrence of rather complex local molecular reorientations. Concerning the values obtained for the γ -relaxations the situation is different. For the copolymer the activation energy values are rather low and the corresponding pre-factors in the Arrhenius equation are not so far from those corresponding to the reciprocal of typical vibrational frequencies. This suggests that a single molecular motion is dominating the detected dielectric relaxation. Contrary, for the homopolymer the activation energy is much higher and the pre-factor in the Arrhenius equation is much smaller than that expected for single molecular motions, which would be in agreement with the above mentioned possibility that in the homopolymer the γ -relaxation results from the superposition of (at least) two different kinds of motions with relative contribution to the dielectric losses changing with temperature, as it was found for polycarbonate.[54]

AAO confined samples. Figure 8 shows the dielectric loss curves corresponding to the dielectric relaxation from PS-b-P4VP-AAO infiltrated in AAO of 330nm pore diameter.

Figure 8. Dielectric results for infiltrated PS-b-P4VP in 330 nm pore diameter: (a) Frequency dependence of the imaginary part of the dielectric loss ϵ'' (f) corresponding to different temperatures between 483 K and 458 K. (b) Dielectric loss versus temperature at different frequencies between 10000 Hz and 1 Hz.

For these samples the dielectric losses have a lower contribution from the copolymers due to the reduction of the volume of the sample capacitor filled by the polymer and an additional background-like signal from the AAO template that is weakly dependent on frequency and temperature. In Figure 8a the isothermal frequency dependence is presented in the temperature range where the P4VP α -relaxation is expected. Actually, a clear peak with a small shoulder in the low frequency flank and an increasing loss contribution from conductivity at even lower frequencies are observed. When considering the highest temperature, it is clear that the main peak corresponds well to that of the α -relaxation of P4VP. Thus, as compared to the bulk copolymer, the MWS relaxation is strongly suppressed after confinement in AAO. The remaining MWS relaxation would likely be the responsible of the shoulder detected in between the main peak and the conductivity related increase at the lowest frequencies. Figure 8b

represents the same dielectric experiments on an isochronal plot. Only in this representation the signature of the copolymer β -relaxation contribution is detectable. However, the intensity of the β -relaxation is extremely weak, preventing a reliable analysis of this signal even in the isochronal representation, and consequently our next discussion will be focused on the α -relaxation results.

Figure 9 shows a direct comparison among the isothermal losses in the copolymer infiltrated in pores of different diameters.

Figure 9. Frequency dependence of the imaginary part of the dielectric loss $\varepsilon''(f)$ corresponding to 473 K for PS-b-P4VP (black symbols), infiltrated PS-b-P4VP with 330 nm in pore diameter (red symbols), infiltrated PS-b-P4VP_Au with 330 nm in pore diameter (blue symbols) and infiltrated PS-b-P4VP with 25 nm in pore diameter (green symbols).

The effect of confinement on the obtained results is clear but the quantitative analysis of such curves is hardly possible. Instead, we again determined the characteristic relaxation times from isochronal representations as that found in Figure 8b. The obtained results for the α -relaxation are shown in Figure 10.

Figure 10. Relaxation times at maximum loss corresponding to the α -process (isochronal plots) of PS-b-P4VP bulk and inside self-ordered AAO with pore diameters ranging from 330 and 25 nm (a) without AuNPs and (b) with AuNPs embedded in the copolymer matrix.

From Figure 10a it is clear that when the copolymer is incorporated in the AAO with the smallest pore diameters (25 and 35 nm) the tendency is an accelerated dynamics with decreasing pore diameter. These effects are typically found in glass-forming systems under confinement situations (see, e. g. [57, 58]). However, for the largest pore what is found is a slowing down of the dielectric relaxation, which could be attributed to the dominant effect of the interaction of the polymer with the pore walls. Moreover, the presence of the AuNPs in the system increased the effect for the smallest pores as shown in Figure 10b. The presence of AuNPs implies a further

reduction of the accessible space for the copolymer. In addition, the AuNP are preferentially located in the segregated P4VP phase where the dielectric relaxation is originated. Thus it is not surprising that the observed effects are amplified by the gold nanoparticles. Interestingly, the non-monotonous effect of the confinement on the α -relaxation might be connected with the change in the segregation geometry of the copolymer detected in the morphological investigation by TEM. In this interpretation, the interaction of the copolymer with the pore walls slows-down the relaxation but the segregation of P4VP inside nano-spheres would avoid the direct interaction of P4VP units with the pore wall allowing a faster relaxation likely promoted by the relatively fast surrounding PS environment. The rather small size of the spherical P4VP regions (necessarily smaller than the pore diameter), implies a large surface to volume ratio and therefore would enhance the influence of PS motions on the P4VP dielectric relaxation.

The effect of confinement on the α -relaxation times of P4VP has been quantitatively analyzed by evaluating the apparent activation energy as it was made above (see lines in Fig. 10). The resulting values are presented in Table 4.

Table 4. Activation energy E_a and pre-exponential factor of the α relaxation for the studied AAO confined samples.

	E_a^a (kJ/mol) $\pm 10\%$	τ_0^a (s)		E_a^a (kJ/mol) $\pm 10\%$	τ_0^a (s)
PS-b-P4VP 330nm	138	6×10^{-41}	PS-b-P4VP_Au 330nm	186	1×10^{-53}
PS-b-P4VP 60nm	120	6×10^{-36}	PS-b-P4VP_Au 60nm	124	1×10^{-21}
PS-b-P4VP 35nm	96.2	5×10^{-30}	PS-b-P4VP_Au 35nm	96.0	7×10^{-30}
PS-b-P4VP 25nm	77.5	2×10^{-25}	PS-b-P4VP_Au 25nm	77.0	1×10^{-25}

The activation energy values in the more confined copolymers are significantly lower and approach that observed for the β -relaxation of P4VP, being however detected at significantly higher temperatures. Nevertheless, as already commented the variation is non monotonic with a first increase for the largest pore (330 nm), being the activation energy values quite independent on the presence of AuNPs. The decrease of the apparent activation energy values - as observed for the copolymers infiltrated in the pores of smallest diameter- is usually considered as indicative of an associated reduction in the cooperative character of the α -relaxation. This could be indicative that in these samples size effects start to have a major effect on the α -relaxation,[59] most likely in combination with significant interface induce phenomena.

Conclusions

We have studied the dynamics and structure of PS-*b*-P4VP copolymer in bulk and confined in AAO templates having pore diameters from tens to hundreds of nanometers in size by using broadband dielectric spectroscopy and SEM, TEM, SAX and WAXS techniques. The effect of adding gold nanoparticles has been also studied.

WAXS, TEM and SAXS results support the high degree of segregation of the copolymer sample: the diffracted intensity at local scales results from the superposition of the structure factors corresponding to the polymers in their respective bulk phases in agreement with the results of the literature. We note that the morphologies and the values obtained for the parameters describing the structural characteristics of the copolymer and the nanocomposite did not change with temperature over the whole range investigated. Moreover, PS-*b*-P4VP nanorods with a diameter value of $D \approx 60$ nm contain regular strings of spherical P4VP domains about 34 nm in diameter with a center-to-center distance of about 55 nm appearing dark surrounded by a brighter PS matrix.

Regarding the dynamical aspects, dielectric relaxation techniques allowed studying selectively the segmental dynamics of the nano-segregated minority component P4VP of the diblock PS-*b*-P4VP. At high temperature this copolymer presents a dominant peak (MWS relaxation), most likely originated by the relatively high conductivity of the P4VP phase combined with the interfaces present in the nanostructured samples. A β -relaxation is also observed for the copolymer with properties similar to those in pure P4VP. The γ -relaxation is markedly different in the copolymer, which is evidenced by a distinct temperature dependence of the resulting relaxation times. When the copolymer is embedded in alumina nanopores with large pore diameters there is a measurable slowing down of the P4VP segmental dynamics attributable to

the interactions with the pore walls. However, for the smallest pore diameters (25 and 35 nm) there is a marked tendency to a faster dynamics as the pore diameter decreases. The presence of the AuNPs in the system enhances this effect.

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REFERENCES

- [1] Martín J, Maiz J, Sacristan J, and Mijangos C. *Polymer* 2012;53(6):1149-1166.
- [2] Maiz J, Schäfer H, Trichy Rengarajan G, Hartmann-Azanza B, Eickmeier H, Haase M, Mijangos C, and Steinhart M. *Macromolecules* 2013;46(2):403-412.
- [3] Maiz J, Martin J, and Mijangos C. *Langmuir* 2012;28:12296-12303.
- [4] Maiz J, Sacristan J, and Mijangos C. *Chemical Physics Letters* 2010;484(4-6):290-294.
- [5] Hoffman JD. *Journal of Polymer Science Part A-2: Polymer Physics* 1969;7(4):750-750.
- [6] Kremer F and Schönhals A. Springer 2003.
- [7] Suzuki Y, Duran H, Steinhart M, Butt H-J, and Floudas G. *Soft Matter* 2013.
- [8] Martín J, Mijangos C, Sanz A, Ezquerra TA, and Nogales A. *Macromolecules* 2009;42(14):5395-5401.
- [9] Martín J, Krutyeva M, Monkenbusch M, Arbe A, Allgaier J, Radulescu A, Falus P, Maiz J, Mijangos C, Colmenero J, and Richter D. *Physical Review Letters* 2010;104(19):197801.
- [10] Krutyeva M, Wischniewski A, Monkenbusch M, Willner L, Maiz J, Mijangos C, Arbe A, Colmenero J, Radulescu A, Holderer O, Ohl M, and Richter D. *Physical Review Letters* 2013;110(10):108303.
- [11] Shin K, Xiang H, Moon SI, Kim T, McCarthy TJ, and Russell TP. *Science* 2004;306(5693):76.
- [12] Xiang H, Shin K, Kim T, Moon SI, McCarthy TJ, and Russell TP. *Macromolecules* 2004;37(15):5660-5664.
- [13] Sun Y, Steinhart M, Zschech D, Adhikari R, Michler GH, and Gösele U. *Macromolecular Rapid Communications* 2005;26(5):369-375.
- [14] Xiang H, Shin K, Kim T, Moon SI, McCarthy TJ, and Russell TP. *Macromolecules* 2005;38(4):1055-1056.
- [15] Chen JT, Zhang M, Yang L, Collins M, Parks J, Avallone A, and Russell TP. *Journal of Polymer Science, Part B: Polymer Physics* 2007;45(20):2912-2917.
- [16] Darling SB. *Progress in Polymer Science (Oxford)* 2007;32(10):1152-1204.
- [17] Wang Y, Gösele U, and Martin S. *Nano Letters* 2008;8(10):3548-3553.

- [18] Wang Y, Gösele U, and Steinhart M. *Chemistry of Materials* 2008;20(2):379-381.
- [19] Chen D, Chen JT, Glogowski E, Emrick T, and Russell TP. *Macromolecular Rapid Communications* 2009;30(4-5):377-383.
- [20] Mendoza C, Pietsch T, Gutmann JS, Jehnichen D, Gindy N, and Fahmi A. *Macromolecules* 2009;42(4):1203-1211.
- [21] Dobriyal P, Xiang H, Kazuyuki M, Chen JT, Jinnai H, and Russell TP. *Macromolecules* 2009;42(22):9082-9088.
- [22] Ryu DY, Ham S, Kim E, Jeong U, Hawker CJ, and Russell TP. *Macromolecules* 2009;42(13):4902-4906.
- [23] Wang Y, Qin Y, Berger A, Yau E, He C, Zhang L, Gösele U, Knez M, and Steinhart M. *Advanced Materials* 2009;21(27):2763-2766.
- [24] Bohley C, Yau MYE, Erk C, Wang Y, Wehrspohn RB, Schlecht S, and Steinhart M. *Physica Status Solidi (B) Basic Research* 2010;247(10):2470-2475.
- [25] Li L, Matsunaga K, Zhu J, Higuchi T, Yabu H, Shimomura M, Jinnai H, Hayward RC, and Russell TP. *Macromolecules* 2010;43(18):7807-7812.
- [26] Pulamagatta B, Yau MYE, Gunkel I, Thurn-Albrecht T, Schröter K, Pfefferkorn D, Kressler J, Steinhart M, and Binder WH. *Advanced Materials* 2011;23(6):781-786.
- [27] Wang Y, Tong L, and Steinhart M. *ACS Nano* 2011;5:1928-1938.
- [28] Mei S, Feng X, and Jin Z. *Soft Matter* 2013;9(3):945-951.
- [29] Michell RM, Lorenzo AT, Müller AJ, Lin MC, Chen HL, Blaszczyk-Lezak I, Martín J, and Mijangos C. *Macromolecules* 2012;45(3):1517-1528.
- [30] Serghei A, Zhao W, Wei X, Chen D, and Russell TP. *European Physical Journal: Special Topics* 2010;189(1):95-101.
- [31] Serghei A, Chen D, Lee DH, and Russell TP. *Soft Matter* 2010;6(6):1111-1113.
- [32] Sanz A, Nogales A, and Ezquerro TA. *Soft Matter* 2011;7(14):6477-6483.
- [33] del Valle-Carrandi L, Alegría A, and Colmenero J. *European Physical Journal: Special Topics* 2010;189(1):257-261.
- [34] Del Valle-Carrandi L, Alegría A, Arbe A, and Colmenero J. *Macromolecules* 2012;45(1):491-502.
- [35] Floudas G, Meramveliotaki K, and Hadjichristidis N. *Macromolecules* 1999;32(22):7496-7503.

- [36] Masuda H and Fukuda K. *Science* 1995;268(5216):1466-1468.
- [37] Diggle JW, Downie TC, and Goulding CW. *Chemical Reviews* 1969;69(3):365-405.
- [38] Patermarakis G and Pavlidou C. *Journal of Catalysis* 1994;147(1):140-155.
- [39] Li AP, Muller F, Birner A, Nielsch K, and Gosele U. *Journal of Applied Physics* 1998;84(11):6023-6026.
- [40] Li Y, Zheng M, Ma L, and Shen W. *Nanotechnology* 2006;17(20):5101-5105.
- [41] Sun C, Luo J, Wu L, and Zhang J. *ACS Applied Materials and Interfaces* 2010;2(5):1299-1302.
- [42] Martín J, Manzano CV, and Martín-González M. *Microporous and Mesoporous Materials* 2012;151(0):311-316.
- [43] Dore JC, Benfield RE, Grandjean D, Schmid G, Kröll M, and Le Bolloc'h D. *Studies in surface Science and catalysis* 2002;144:163-170.
- [44] Waheed A, Mehmood M, Benfield R, Ahmad J, Amenitsch H, Aslam M, Rauf A, and Hassan M. *Materials Chemistry and Physics* 2011;131(1-2):362-369.
- [45] Förster S, Timmann A, Konrad M, Schellbach C, Meyer A, Funari SS, Mulvaney P, and Knott R. *Journal of Physical Chemistry B* 2005;109(4):1347-1360.
- [46] Förster S and Burger C. *Macromolecules* 1998;31(3):879-891.
- [47] Bates FS and Fredrickson GH. *Physics Today* 1999;52(2):32-38.
- [48] Kriha O, Zhao L, Pippel E, Gösele U, Wehrspohn RB, Wendorff JH, Steinhart M, and Greiner A. *Advanced Functional Materials* 2007;17(8):1327-1332.
- [49] Ayyagari C, Bedrov D, and Smith GD. *Macromolecules* 2000;33(16):6194-6199.
- [50] Iradi I, Alvarez F, Colmenero J, and Arbe A. *Physica B: Condensed Matter* 2004;350(1–3, Supplement):E881-E884.
- [51] Lupaşcu V, Picken SJ, and Wübberhorst M. *Macromolecules* 2006;39(15):5152-5158.
- [52] Priestley RD, Broadbelt LJ, Torkelson JM, and Fukao K. *Physical Review E - Statistical, Nonlinear, and Soft Matter Physics* 2007;75(6).
- [53] Boucher VM, Cangialosi D, Alegría A, Colmenero J, Pastoriza-Santos I, and Liz-Marzan LM. *Soft Matter* 2011;7(7):3607-3620.
- [54] Alegría A, Mitxelena O, and Colmenero J. *Macromolecules* 2006;39(7):2691-2699.

- [55] Puértolas JA, Castro M, Tellería I, and Alegría A. *Journal of Polymer Science, Part B: Polymer Physics* 1999;37(12):1337-1349.
- [56] Angell CA. *Journal of Non-Crystalline Solids* 1991;131-133(PART 1):13-31.
- [57] Zorn R, van Eijck L, Koza MM, and Frick B. *European Physical Journal-Special Topics* 2010;189(1):1-2.
- [58] Blaszczyk-Lezak I, Hernández M, and Mijangos C. *Macromolecules* 2013;46(12):4995-5002.
- [59] Solar M, Mapesa EU, Kremer F, Binder K, and Paul W. *EPL (Europhysics Letters)* 2013;104(6):66004.

Graphical Abstract

Dynamic Study Of Polystyrene-*block*-poly(4-vinylpyridine) Copolymer in Bulk and Confined In Cylindrical Nanopores

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TEM micrographs from bulk PS-*b*-P4VP_0.1% Au and confined PS-*b*-P4VP_0.1% Au. Relaxation times at maximum loss corresponding to the α -process (isochronal plots) of PS-*b*-P4VP bulk and inside self-ordered AAO with pore diameters ranging from 330 and 25 nm with AuNPs embedded in the copolymer matrix.