



Microstructure evolution, thermal stability and fractal behavior of water vapor flow assisted *in situ* growth poly(vinylcarbazole)-titania quantum dots nanocomposites



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ABSTRACT

Here, we report a novel strategy for the preparation of TiO₂ quantum dots fillers prepared from alkoxide precursor via *in situ* water vapor flow diffusion into poly(*N*-vinylcarbazole) host. A detailed characterization by means of infrared and Raman spectroscopy, X-ray powder diffraction, small angle X-ray scattering and differential scanning calorimetry is reported. The growth mechanism of both crystallites and particles was mostly governed by the classical coarsening reaction limited growth and the polymer host showed no detectable chemical modifications at the interface or active participation in the growing process. The main relevance of our strategy respect to the typical sol-gel growth in solution is the possibility of the interruption of the reaction by simple stopping the water vapor flow diffusion into the polymer host thus achieving good control in the nanoparticles size. The thermal stability and fractal behavior of our nanocomposites were also studied by differential scanning calorimetry and *in situ* small angle X-ray scattering versus temperature. Strong correlations between modifications in the fractal behavior and glass transition or fusion processes were observed for these nanocomposites.

1. Introduction

One of the most recent technological impacts in the development of novel materials for energy conversion and storage applications are involving the use of hybrid inorganic-organic nanocomposites based in polymers with ceramic nanofillers [1,2]. Moreover, the preparation of donor-acceptor active layers for polymer solar cells is attempting to substitute the typical expensive fullerene derivatives for other acceptors such as ceramic nanoparticles nanofillers [3,4]. In addition, the preparation of low cost and environmentally friendly TiO₂ nanofillers acceptors has been already reported as promising active layers materials for solar cell applications [5–7]. However, the above mentioned preparations involve the simple mixture of TiO₂ with the conjugated polymer and still some microstructural aspects should be solved to lead to better device applications. In particular, the photovoltaic properties of PVK:TiO₂ nanocomposites are mostly limited by the interfacial area and homogeneity between the donor and the acceptor materials [7]. It has been already demonstrated that the preparation of these polymer-ceramic nanocomposites by the *in situ* methodology has shown

many advantages respect to the *ex situ* preparations due to the formation of more macroscopically homogeneous materials [8,9]. The preparation of these nanocomposites by the *in situ* methodology could be interpreted in three general ways; the first one, based in the organic polymerization in the presence of the inorganic material [10,11]; the second one involving the inorganic material growth in the presence of the polymer host [12–15] and the third one, based in both organic polymerization and inorganic material growth carried out simultaneously [16,17]. In the present report, we focused in the second one of the above mentioned by the sol-gel technique using an alkoxide precursor to obtain the *in situ* growth of the inorganic material in the polymer host. Briefly, the alkoxide precursors lead to the formation of metal oxide nanostructures by hydrolysis and condensation reactions at relatively low temperatures [18]. However, the most common route to obtain *in situ* growth of oxide nanoparticles into polymer host are carried out in liquid solution and several precautions should be taken regarding the solubility of both organic and inorganic components. In this report, we showed a novel strategy for obtaining inorganic-organic hybrid nanocomposites in which the *in situ* growth process is triggered via vapor flow diffusion into a

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Table 1Nomenclature of PVK-TiO₂-X(t) with X = 0, 10, 30, 50 and 70 samples.

	0	7 h	9 h	11 h	13 h	16 h
PVK	X	X	X	X	X	*
PVK-TiO ₂ -10(t)	X	X	X	X	X	*
PVK-TiO ₂ -30(t)	X	X	X	X	X	*
PVK-TiO ₂ -50(t)	0	7	9	11	13	16*
PVK-TiO ₂ -70(t)	X	X	X	X	X	*

References: The cross (X) means no specimen synthesized and the asterisk (*) means samples were prepared at t = 16 h and named without (t) extension code.

previously dried organic polymer host mixed with the alkoxide precursor. This strategy favors the *in situ* growth of inorganic nanofillers by the sol-gel method into the polymer host material leading to excellent size control and homogeneity. Specifically, we focused in the preparation of titanium oxide nanoparticles into poly(vinylcarbazole) as promising non fullerene donor-acceptor system for polymer solar cell active layers. A detailed study on the growth and fractal behavior of poly(vinylcarbazole):titanium oxide nanocomposites prepared from alkoxide precursor via *in situ* water vapor flow diffusion into this polymer host is reported.

2. Materials and methods

2.1. PVK-TiO₂-X nanocomposites preparation

PVK-TiO₂-X nanocomposites were synthesized utilizing poly(9-vinylcarbazole) powder with average $M_w \sim 1.100.000$ (PVK) and titanium tetrapropoxide (TTP) 98%, all purchased from Sigma-Aldrich. PVK (0.3 g) was suspended in 50 ml of tetrahydrofuran (THF) and stirred at $T \sim 70^\circ\text{C}$. After the suspension became homogeneously colorless, 1 ml of deionized water was added dropwise and the resulting solution was kept stirred for about 30 min. Different amounts of TTP were aggregated to the PVK suspension under stirring at $T \sim 70^\circ\text{C}$, until dryness forming a yellow powder. The powder was grinded and exposed to deionized water vapor with a flow of ~ 1 ml/min at $T \sim 80^\circ\text{C}$ during 16 h. Finally, all samples were dried for 7 h at $T = 80^\circ\text{C}$ under vacuum. The resulting powder specimens were PVK-TiO₂-X nanocomposites with X = 10, 30, 50 and 70, being X the corresponding weight fraction of TiO₂. In order to

study the growth mechanism, six samples were extracted at different times (t) of water vapor flow exposure with $t = 0, 7, 9, 11, 13$ and 16 h for X = 50, as schematized in Table 1.

2.2. PVK-TiO₂-X nanocomposites characterization

PVK-TiO₂-X nanocomposites and the samples for X = 50 at different times were studied by confocal Raman spectroscopy using WITec Alpha 300-RA, using an excitation laser with 532 nm laser wavelength. FT-IR spectra were obtained using a Shimadzu Prestige 21 FT-IR spectrometer using KBr pellets in the range of $400\text{--}4000\text{ cm}^{-1}$ by averaging 30 scans with a 4 cm^{-1} for each spectrum. Small-angle X-ray scattering (SAXS) was performed at SAXS-1 Beamline Station in Laboratório Nacional de Luz Síncrotron (LNLS-CNPEM) working with 8 keV radiation in the range of $q = 0.1\text{--}4.0\text{ nm}^{-1}$. X-ray diffraction (XRD) was performed using a Rigaku Ultima IV diffractometer working in Bragg–Brentano configuration utilizing CuK α radiation in the $2\theta = 5.00\text{--}60.00^\circ$ range using $\Delta 2\theta$ steps of 0.02° with an 8 s integration time per step. The size and morphology for X = 50 at 7 h and 16 h were analyzed by transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) were performed using a JEOL 2100 instrument working under a 200 kV voltage. Differential scanning calorimetry (DSC) was performed using Shimadzu DSC-60 differential scanning calorimeter in static air at the temperature range $T = 25\text{--}250^\circ\text{C}$ with a ramp rate of $5^\circ/\text{min}$.

3. Results and discussion

3.1. *In situ* growth of PVK-TiO₂ nanocomposites

3.1.1. Raman and FT-IR spectroscopy

Raman and FT-IR spectroscopy were used to study the growth process for the PVK nanocomposites with *in situ* growth TiO₂ quantum dots fillers. Raman spectra for PVK-TiO₂-50-t with $t = 0, 7, 9, 11, 13$ and 16 h are shown in Fig. 1a. The peaks located in $\sim 716, 1014, 1121, 1226, 1312, 1444, 1483, 1571$ and 1620 cm^{-1} are ascribed to PVK $\delta(\text{C-C})$ bending, CH_2 rocking, CH_2 twisting, CH_2 wagging, benzene ring $\delta(\text{C-H})$ deformation, tertiary amine ring $\delta(\text{C-H})$ deformation, $\nu(\text{C-N})$, benzene ring $\nu(\text{C=C})$ stretching and tertiary amine ring $\nu(\text{C=C})$ stretching modes, respectively [19,20]. Those peaks showed the major relative intensities

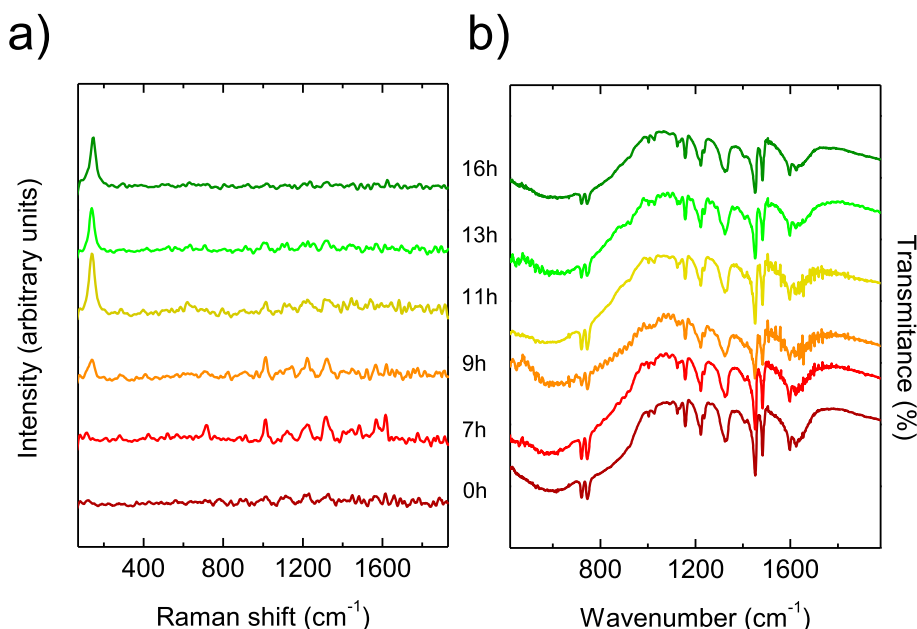


Fig. 1. (a) Raman and (b) FT-IR spectra for PVK-TiO₂-50(t) with $t = 0, 7, 9, 11, 13$ and 16 h showing the *in situ* growth process at different reaction times.

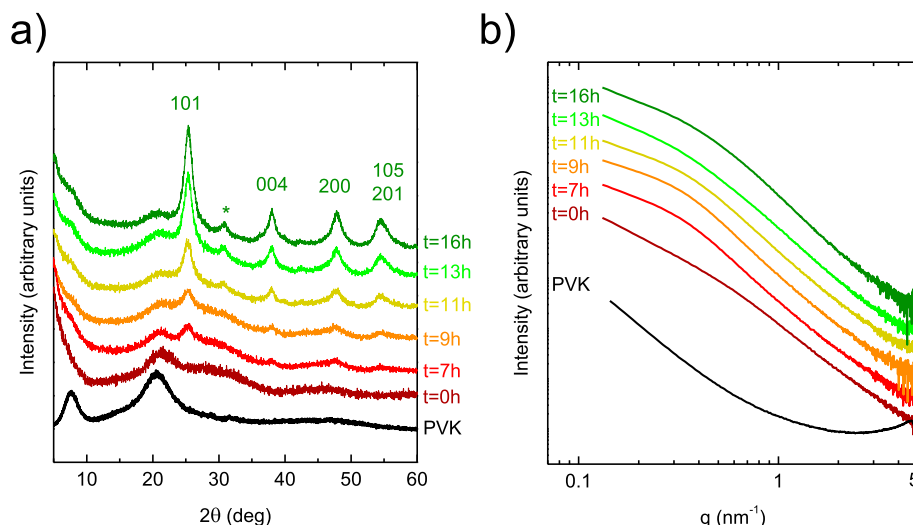


Fig. 2. (a) XRD and (b) SAXS patterns for pure PVK, PVK-TiO₂-50(t) with $t = 0, 7, 9, 11, 13$ and 16 showing the *in situ* growth process at different reaction times. The TiO₂ anatase polymorph Bragg planes are indexed and the asterisk (*) shows presence of small amounts of TiO₂ Brookite polymorph.

at $t < 9$ h with a progressive decrease in its relative intensities when the TiO₂ growing process takes place. At $t > 9$ h, Raman spectra showed a sharp peak at ~ 150 cm⁻¹ ascribed to the E_g mode of TiO₂ anatase polymorph [21] revealing the formation of these nanofillers in the PVK matrix. A progressive sharpening of the peak is observed with increasing time, suggesting the growth of TiO₂ nanofillers until $t = 13$ h and no later growth is observed at $t = 16$ h.

FT-IR spectra for PVK-TiO₂-50- t with $t = 0, 7, 9, 11, 13$ and 16 h are shown in Fig. 1b. In all cases, there are no drastic apartment from the typical PVK peaks at ~ 720 and 743 cm⁻¹ ascribed to PVK δ (C-H) bending, ~ 1004 and 1027 cm⁻¹ assigned to CH₂ rocking, ~ 1124 and 1157 cm⁻¹ to CH₂ twisting, ~ 1223 cm⁻¹ ascribed to CH₂ wagging, ~ 1325 cm⁻¹ to benzene ring δ (C-H), ~ 1451 cm⁻¹ assigned to tertiary amine ring δ (C-H) and finally ~ 1483 cm⁻¹ ascribed to ν (C-N) [22]. The absence of any drastic modifications of PVK peaks for all different stages of the growing process is suggesting no chemical modification of PVK due to the presence of TiO₂. In addition, this is also suggesting that the PVK host only serves as a mechanical support and do not suffer chemical modifications in the growth mechanism of TiO₂ nanofillers.

3.1.2. X-ray powder diffraction (XRD)

XRD patterns for PVK-TiO₂-50- t with $t = 0, 7, 9, 11, 13$ and 16 h are shown in Fig. 2a. Pure PVK showed two broad peaks at $2\theta \sim 8^\circ$ and 20° , ascribed to the PVK interchain mean coherence length ($d \sim 1.2$ nm) and to the intrachain mean coherence length ($d \sim 0.4$ nm), respectively [23]. At $t = 0$ h, the peak at $2\theta \sim 8^\circ$ disappeared probably due to the partial loss of interchain coherence due to the formation of primary amorphous nanoparticles formed by early condensation and hydrolysis of the alkoxide precursor. The appearance of a broad peak at $2\theta \sim 30^\circ$ could also be suggesting the presence of highly amorphous primary nanoparticles at $t = 0$ h. The relative long latent period to form crystalline TiO₂ nanoparticles - i.e. $t \sim 7$ h - could be originated because of the difficulty of water vapor to permeate through the polymer host. At $t > 7$ h, typical

peaks of TiO₂ in its anatase polymorph emerge at $2\theta \sim 25.4^\circ, 38.0^\circ, 47.9^\circ$ and 54.6° associated to (101), (004), (200) and (105)/(201) Bragg planes, respectively [24]. These diffraction peaks showed an expected increment in their relative intensities and full width at half maximum reduction with increasing TiO₂ quantum dots growth. The presence of a very low intensity peak at $2\theta \sim 30.8^\circ$ could be ascribed to small amounts of TiO₂ in its brookite polymorph, as typically observed using this preparation method [25,26]. The peak attributed to the PVK interchain mean coherence length practically disappears for the whole stages of the growing process suggesting that the formation of TiO₂ is taking place in between the PVK chains. The mean diameter crystallite size (D_c) of TiO₂ was calculated using the Scherrer equation following:

$$D_c = (0.9\lambda / \beta \cos(\theta))$$

where β is the full width at half maximum, θ is the Bragg angle and λ is the CuK α wavelength [27]. The calculated D_c were 3.7, 4.1, 4.4, 5.1 and 5.4 nm for $t = 7, 9, 11, 13$ and 16 h, respectively, proving the controlled character of the growth, as shown in Table 2. It has been previously reported that the growth kinetics of anatase nanoparticles from alkoxide precursor in solution followed a coarsening and assembly mechanism [28]. However, the typical growth mechanism for titanium oxide nanoparticles from alkoxide precursors can also be explained by the classical coarsening model due to Ostwald ripening mechanism using the following expression:

$$D_c - D_0 = K_c(t - t_0)^{1/n}$$

where D_0 is the size of primary nanocrystallites, t_0 is the onset time for the coarsening stage and k_c is the coarsening growth rate constant [28]. The growth limited parameter (n) is an integer that can be equal to 2 for reaction limited growth, 3 for volume limited growth and 4 for grain boundary diffusion-limited growth [29]. The dependence of the calculated D_c with reaction time for PVK-TiO₂-50- t with $t = 0$ – 16 h are shown

Table 2

D_c , D_p and P for pure PVK, PVK-TiO₂-50(t) with $t = 0, 7, 9, 11, 13$ and 16 h.

X = 50(t)	PVK	$t = 0$ h	$t = 7$ h	$t = 9$ h	$t = 11$ h	$t = 13$ h	$t = 16$ h
D_c (nm)	–	–	3.65	4.08	4.43	5.14	5.45
D_p (nm)	–	–	4.36	6.73	8.60	10.97	10.99
P	3.73	3.07	2.42	2.97	3.20	3.40	3.48

Mean crystallite size (D_c) was estimated from XRD analysis using the Scherrer equation, mean nanoparticle size (D_p) and Porod exponent (P) was estimated from SAXS analysis using the Beaucage unified equation.

in Fig. 3a. The best fit was obtained using the growth limited parameter $n = 2$ suggesting that the crystallite growth mechanism is mostly governed by the reaction limited growth.

3.1.3. Small angle X-ray scattering (SAXS)

The scattering intensity $I(q)$ of SAXS curves can be expressed as a function of the form factor $P(q)$, structure factor $S(q)$, number density of nanoparticles (N) and the contrast in electron density between those nanoparticles and the medium ($\Delta\rho$) by the following equation:

$$I(q) = N \cdot (\Delta\rho)^2 \cdot P(q) \cdot S(q)$$

In our modeling of SAXS curves, for sake of simplicity, we assume a spherical morphology to describe the form factor $P(q)$ and also that the structure factor $S(q) \sim 1$, which is strictly valid for poor interacting nanoparticles. SAXS curves for PVK-TiO₂-50- t with $t = 0, 7, 9, 11, 13$ and 16 h are shown in Fig. 2b. PVK-TiO₂-50- t (with $t = 0, 7, 9, 11, 13$ and 16 h) were fitted using the Beaucage unified equation for spherical particles [30]. Briefly, the Beaucage unified equation is based in the combination of Guinier and Porod laws at low- q and high- q regions, respectively. At low- q region, the Guinier law can be expressed using the following equation:

$$I(q) \sim \exp\left(-R_g^2 q^2 / 3\right)$$

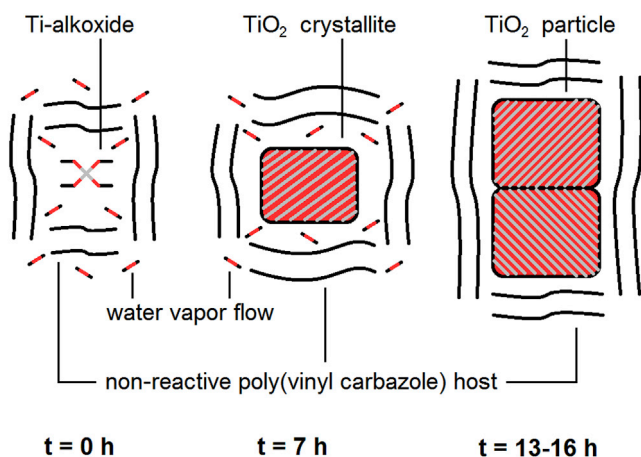
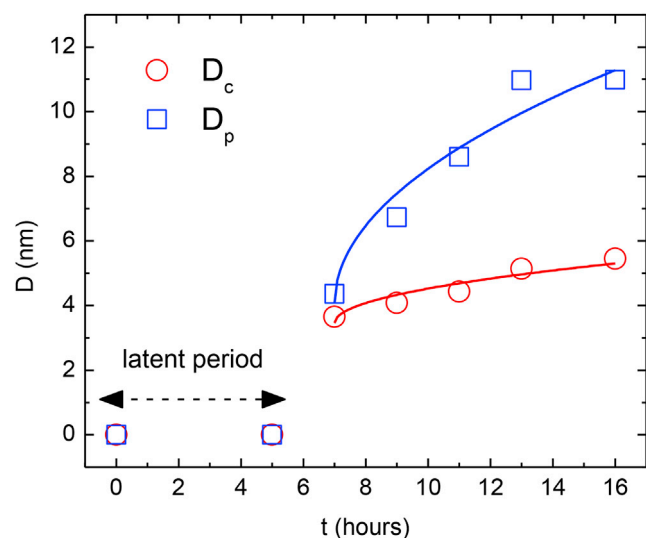


Fig. 3. Crystallite (D_c), nanoparticle (D_p) size and scheme of the TiO₂ quantum dots growth process for PVK-TiO₂-50(t) with $t = 0, 5, 7, 9, 11, 13$ and 16 h as an example of the *in situ* growth process at fixed temperature $T = 100$ °C and different reaction times (t).

where R_g represents the gyration radius of the scatterers diluted in the polymer host. At high- q region, the Porod law can be expressed using the following equation:

$$I(q) \sim q^{-P}$$

where P is the Porod exponent, which is related to the fractal dimension of the hybrid nanocomposites. High negative Porod exponent i.e. $P = 4$ represents no deviations from Porod law and is usually ascribed to the fractal smoothness of surfaces. Pure PVK showed a Porod exponent of $P \sim 3.7$ and a characteristic peak at $q_{\max} \sim 4.8 \text{ nm}^{-1}$ with associated $d \sim 2\pi/q_{\max} = 1.3 \text{ nm}$ that could be ascribed to PVK mean correlation distance between the polymer backbone. At $t = 0$, the PVK peak at $q_{\max} \sim 4.8 \text{ nm}^{-1}$ disappeared and the Porod exponent showed a decrease to $P \sim 3$, significantly lower than that observed for pure PVK. This is suggesting that early hydrolysis and condensation of the alkoxide precursor is probably leading to the loss of PVK interchain mean correlation length added to the appearance of fractal roughness. Only a slight change in the Porod exponent was observed at $q \sim 0.7\text{--}1.2 \text{ nm}^{-1}$ that could be speculatively associated to the presence of very small, i.e. $\sim 4 \text{ nm}$ amorphous scatterers. At $t = 7$, the Porod exponent reduces even more to $P \sim 2.4$ suggesting the increase of the fractal roughness of the samples, probably associated to the formation of small nanoparticles embedded in the polymer host with a well-defined TiO₂ anatase crystalline structure according to X-ray diffraction analysis discussed above. At high- q region, PVK-TiO₂-50- t with $t = 7, 9, 11, 13$ and 16 h showed a trend marked by the increase in the Porod exponent from $P \sim 2.4$ to ~ 3.5 with increasing time. This is associated to a transition from a fractally rough to a smooth non-fractal behavior probably linked to increase in the overall crystallinity due to the titanium oxide quantum dots growth. At lower q region, the presence of two bumps are associated with two populations at $q < 0.4 \text{ nm}^{-1}$ and $q \sim 0.8 \text{ nm}^{-1}$, where the first one could be probably associated to the presence of nanofillers clusters and the second one related to the smaller nanoparticle scatterers. The estimated mean diameter size (D_p) was calculated assuming a spherical morphology using the following expression:

$$D_p = 2R_g \sqrt{\frac{5}{3}}$$

where R_g is the Guinier radius extracted from the Beaucage unified equation fitting [30]. In agreement with the observed trend for D_c extracted from XRD analysis, D_p increases from ~ 4.4 to $\sim 11.0 \text{ nm}$ when the time of water exposure increases (Table 2), as typically observed for sol-gel growth of alkoxide derived oxide nanoparticles [31]. The values of D_c and D_p as a function of time and a scheme of the TiO₂ quantum dots growth process for PVK-TiO₂-50- t are represented in Fig. 3a. It is observed that nanoparticles size (D_p) values are very similar in comparison with calculated crystallite size (D_c) at $t = 7$ h and almost twice higher for $t \sim 13\text{--}16$ h. This could be associated with a two stage growth mechanism suggesting that at $t > 9$ h the coalescence process lead to the formation of nanoparticles with approximately two crystallite domains per nanoparticle. The nanoparticle growth also showed best fit with the classical coarsening mechanism using the growth limited growth parameter $n = 2$, as shown in Fig. 3a. A representative scheme is shown in Fig. 3b to show the difference between the crystallite and nanoparticle growth for PVK-TiO₂-50- t with $t = 0\text{--}16$ h. Our preliminary conclusions from this section is that the presence of the non-reactive PVK polymer host does not alter significantly the growth mechanism in comparison to the solely alkoxide synthesis of titanium oxide nanoparticles in solution. Moreover, the water vapor flow diffusion into the non-reactive PVK polymer host seems to be responsible of the reaction limited growth mechanism. However, the use of water vapor flow diffusion into the polymer host allows the interruption of the growing process at any time in comparison with the typical methodology where the water source is available in solution during the reaction.

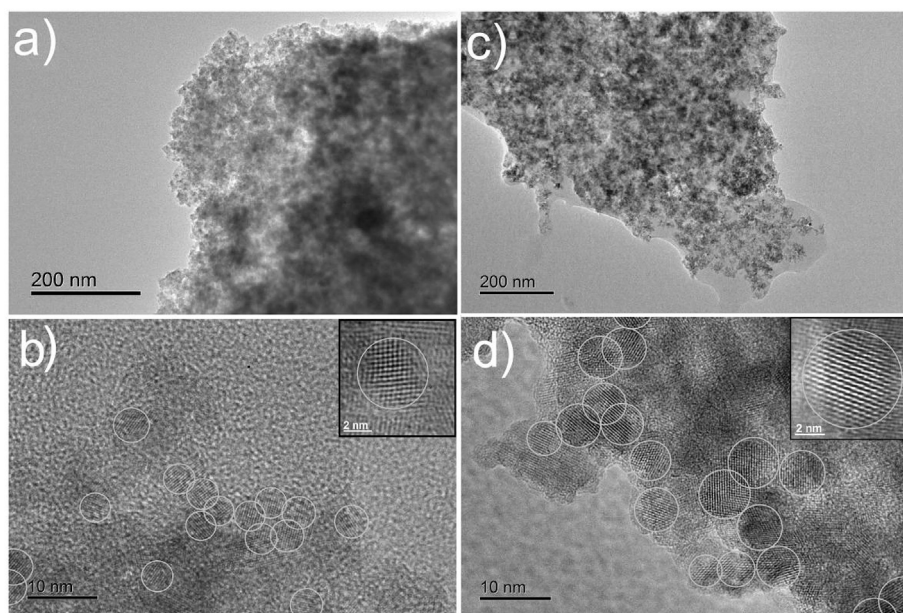


Fig. 4. TEM images for PVK-TiO₂-50(t) with (a,b) $t = 7$ and (c,d) 16 h. The grey circumferences represent a simplification of the grain boundary edges for crystallites. Fig. 4b,d-inset showed a close up in higher magnification for a single TiO₂ quantum dot crystallite embedded in PVK host.

3.1.4. Transmission electron microscopy

Transmission electron microscopy (TEM) images for PVK-50(t) with $t = 7$ and 16 h is shown in Fig. 4. TEM images for PVK-50(t) with $t = 7$ h showed the presence of specimens with a good homogeneity (Fig. 4a) and small TiO₂ rounded-shape crystallites with ~ 4 –5 nm size embedded in the polymer host (Fig. 4b). These nanocrystallite sizes are in excellent agreement with those estimated using X-ray diffraction and small angle X-ray scattering as discussed above. TEM images for PVK-50(t) with $t = 16$ h showed the presence of TiO₂ nanoparticles embedded in the PVK host polymer with a good homogeneity (Fig. 4c). TEM image for PVK-50(t) with $t = 16$ h with higher magnification (Fig. 4d) showed the presence of nanocrystallites and nanoparticles with sizes ~ 5 –8 nm and 10–15 nm, respectively. This is in excellent agreement with the estimation of mean crystallite and nanoparticle size obtained by X-ray diffraction and small angle X-ray scattering, respectively. Both nanocrystallites and nanoparticles showed quasi-spherical shape with mostly smooth grain boundaries and the polymer host showed an amorphous structure. In all cases, energy dispersive spectroscopy (EDS) analysis confirmed the presence of titanium and oxide associated to TiO₂ nanoparticles and carbon plus nitrogen ascribed to PVK polymer.

3.2. Thermal stability and fractal behavior of PVK-TiO₂ nanocomposites

3.2.1. X-ray powder diffraction at room temperature

XRD patterns for PVK and PVK-TiO₂-X nanocomposites with $X = 10, 30, 50$ and 70 are shown in Fig. 5. All samples showed two broad peaks at $2\theta \sim 8^\circ$ and 20° , ascribed to the PVK interchain mean coherence length ($d \sim 1.2$ nm) and to the intrachain mean coherence length ($d \sim 0.4$ nm), respectively, as discussed above. The addition of low amounts of TiO₂ quantum dots ($X = 10$) only lead to a small decrease in the relative intensity of the peak at $2\theta \sim 8^\circ$ suggesting the partial loss of PVK mean interchain coherence. At higher TiO₂ additions ($X > 30$), an expected decrease in relative intensity of both PVK peaks at $2\theta \sim 8^\circ$ and 20° is mostly due to the decrease of the PVK fraction in the nanocomposites. Moreover, $X = 30, 50$ and 70 samples showed typical XRD profiles for TiO₂ in its anatase polymorph with peaks in $2\theta \sim 25.4^\circ, 38.0^\circ, 47.9^\circ, 54.6^\circ$, with an increment in the relative intensity related to TiO₂ quantum dots concentration. PVK-TiO₂-X with $X = 30, 50$ and 70 showed $D_C \sim 4.0, 5.4, 6.0$ nm, respectively. There is an increment in crystallite size with the TiO₂ concentration probably due to the increase of the statistical

probability of coarsening process. It is important to remark that for $X = 10$ it was not possible to calculate D_C due to the absence of any peaks ascribed to TiO₂ in the XRD pattern, probably due to a very small crystallite size added to its high dilution in the polymer matrix.

3.2.2. In situ small angle X-ray scattering versus temperature

The temperature influence in the range of $T = 25$ – 250°C was

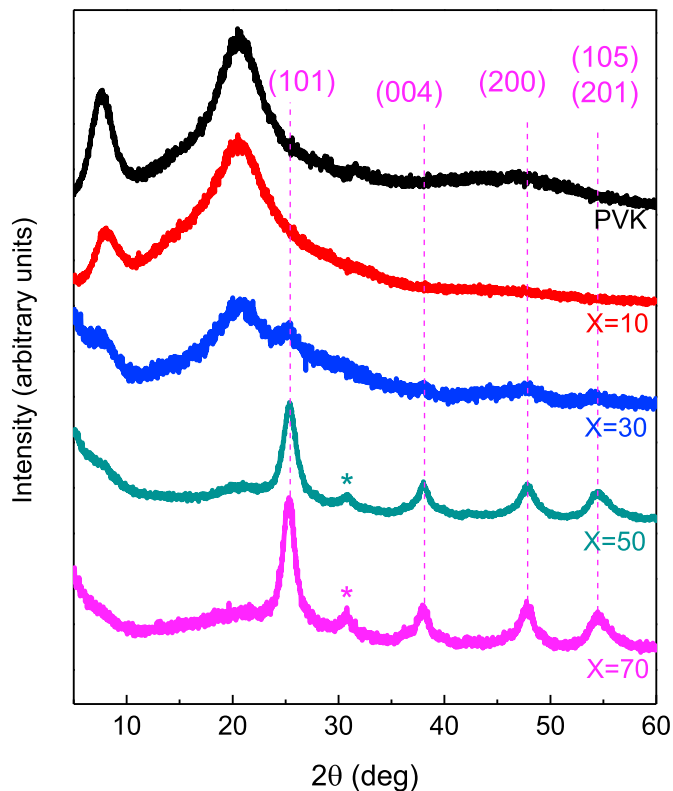


Fig. 5. XRD patterns for PVK-TiO₂-X with $X = 0, 10, 30, 50$ and 70 measured at room temperature. The TiO₂ anatase polymorph Bragg planes are indexed and the asterisk (*) shows presence of small amounts of TiO₂ Brookite polymorph.

studied by means of SAXS technique for pure PVK and PVK-TiO₂-X nanocomposites with X = 10, 30, 50 and 70, as shown in Fig. 6. The Porod exponent (P) and mean nanoparticle size (D_p) were estimated using the Beaucage unified equation. At room temperature, the mean nanoparticle size (D_p) showed a slight increase with increasing TiO₂ concentration with D_p ~ 8–12 nm and no drastic modifications were observed in the whole T = 25–250 °C temperature regime. The increasing concentration of TiO₂ could be favoring the coalescence process explaining the slight increase of D_p for the concentrated regime, as also observed for crystallites in XRD analysis. However, once the TiO₂ nanoparticles growth is completed, no further coalescence is observed with increasing temperature probably due to the blocking impediment due to the presence of the polymer. It has been recently reported using *in situ* SAXS analyses that, in the absence of a polymer host, the mean nanoparticle size increases during the aging process, even below 50 °C [31]. At room temperature, the negative Porod exponent showed a drastic decrease from P ~ 3.6 to P ~ 2.5 for X = 10 respect to pure PVK, while an increase to P ~ 3.5 was observed for higher TiO₂ additions (X > 30), as shown in Fig. 7-inset and schematized in Table 3. High negative Porod exponent i.e. P = 4 represents no deviations from Porod law and is usually ascribed to a fractal smoothness with negligible roughness. The drastic decrease of the negative Porod exponent for X = 10 is suggesting that this low concentration of TiO₂ nanofillers increase the fractal roughness probably due to a decrease in the degree of order of PVK chains, as already observed for other polymer nanocomposites with low amount of silica nanofillers additions [32]. On the other hand, the presence of higher concentration of TiO₂ nanofillers (X > 30) with higher Porod exponents is probably due to the increase in the concentration of the ceramic phase and also to an increase in the degree of order of PVK chains.

The temperature dependence of the Porod exponent for all samples is

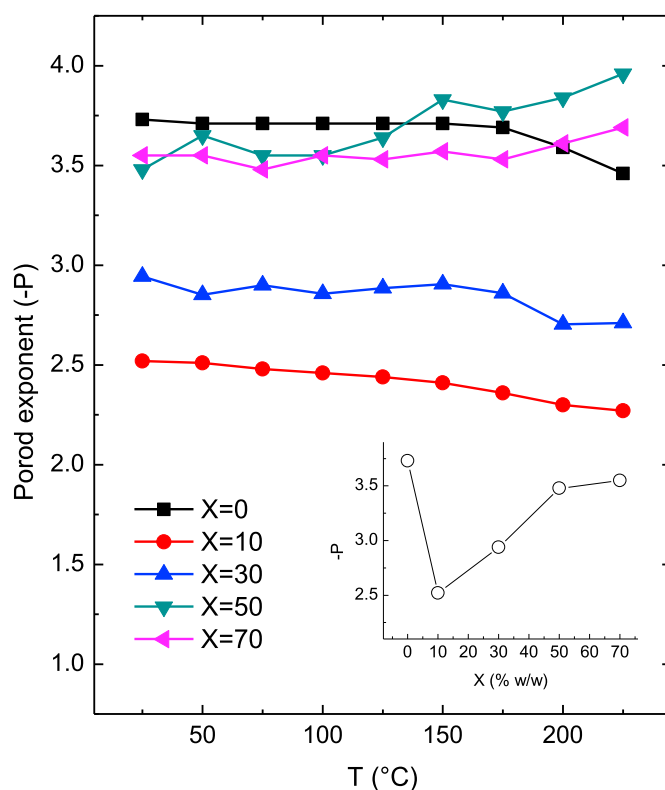


Fig. 7. Porod exponent (-P) for PVK-TiO₂-X with X = 0, 10, 30, 50 and 70 at different heating temperatures in the T = 25–225 °C range. The inset shows the Porod exponent (-P) dependence with TiO₂ concentration (X) at room temperature.

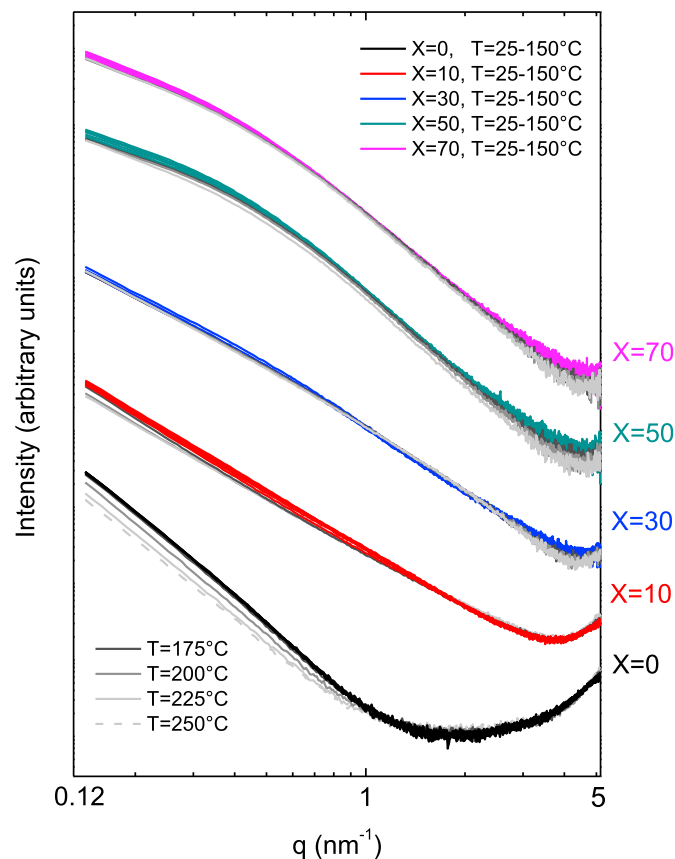


Fig. 6. *In situ* SAXS curves versus temperature for PVK-TiO₂-X with X = 0, 10, 30, 50 and 70 measured at heating temperatures in the T = 25–250 °C range.

shown in Fig. 7. In all cases, no drastic change of D_p was evidenced for all compositions in the whole measured T = 25–250 °C temperature range. At T > 175 °C, a slight decrease of the negative Porod exponent was observed for pure PVK and X < 30, while at T > 150 °C, a slight increase was observed for X > 30. The slight decrease of the negative Porod exponent at T > 175 °C observed for X < 30 could be suggesting an increase in the PVK chains disorder due to the transition to a less ordered microstructure in agreement with a glass transition process, typically observed at ~190–220 °C temperatures for pure PVK [33]. On the other hand, the slight increase of the negative Porod exponent at T > 150 °C observed for X > 30 could be explained by the thermal activated diffusion of highly concentrated TiO₂ nanofillers leading to the formation of highly homogeneous and dense nanocomposites.

3.2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was performed to study the thermal processes involved in PVK nanocomposites with TiO₂ nanofillers. DSC thermal profiles for PVK-TiO₂-X with X = 0, 10, 30, 50 and

Table 3
Porod exponent (P) for X = 0, 10, 30, 50 (16 h) and 70 in the range of T = 25–250 °C.

T (°C)	P _{X=0}	P _{X=10}	P _{X=30}	P _{X=50}	P _{X=70}
25	3.73	2.52	2.944	3.48	3.55
50	3.71	2.51	2.851	3.65	3.55
75	3.71	2.48	2.900	3.55	3.48
100	3.71	2.46	2.857	3.55	3.55
125	3.71	2.44	2.885	3.64	3.53
150	3.71	2.41	2.905	3.83	3.57
175	3.69	2.36	2.860	3.77	3.53
200	3.59	2.30	2.704	3.84	3.61
225	3.46	2.27	2.710	3.96	3.69
250	3.36	–	–	–	–

Porod exponent (P) was estimated from SAXS analysis using the Beaucage unified equation.

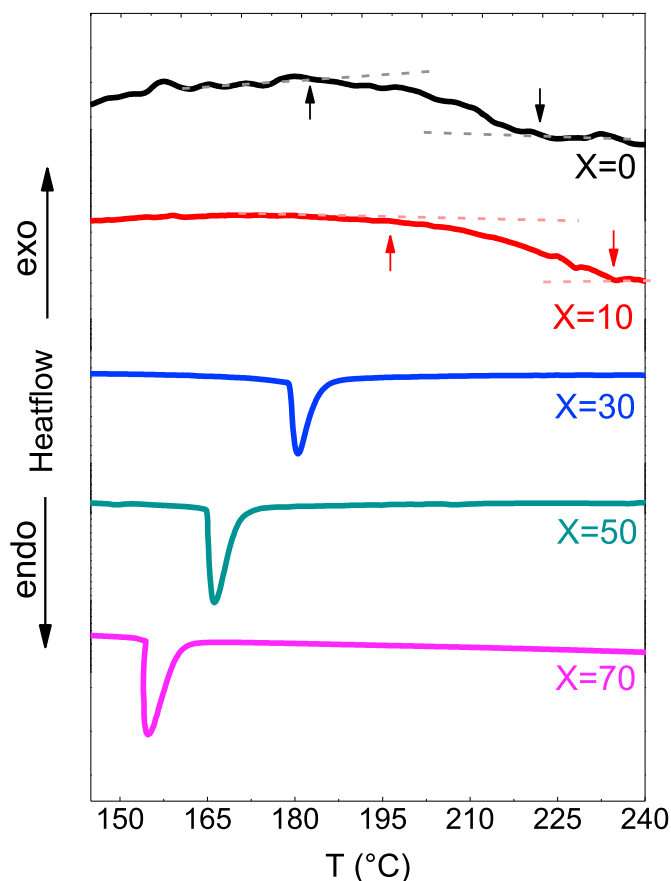


Fig. 8. DSC thermal profiles for PVK-TiO₂-X with X = 0, 10, 30, 50 and 70. The arrows indicate the on set and end set temperatures for the glass transition process.

70 in the temperature range $T = 25\text{--}250\text{ }^{\circ}\text{C}$ are shown in Fig. 8. Pure PVK showed a typical glass transition with onset and endset temperatures at $T_g \sim 177\text{ }^{\circ}\text{C}$ and $\sim 215\text{ }^{\circ}\text{C}$, respectively [33]. The temperature of the glass transition is in good agreement with the temperature for which the Porod exponent showed a slight decrease in our SAXS analysis discussed above. Moreover, $X = 10$ showed an increase in the temperature range where the glass transition takes place with onset and endset temperatures at $T_g \sim 195\text{ }^{\circ}\text{C}$ and $232\text{ }^{\circ}\text{C}$, respectively. It has been already reported that the addition of small amounts of nanofillers could lead to an increase of the glass transition temperature for similar polymer nanocomposites [34]. The increase in T_g observed for low nanofiller loadings ($\sim 10\%$) could be associated to the slower relaxation of segments located farther away from the interface overcompensating the higher mobility of segments [34]. On the other hand, it has been also observed that the increasing ceramic nanofiller loadings could create non-uniform forces at the weak interface leading to quicken relaxation thus reducing the glass transition temperature [35]. However, $X = 30, 50$ and 70 showed no detectable glass transition but a well-defined endothermic peak at $T \sim 181, 166$ and $154\text{ }^{\circ}\text{C}$, respectively, which could be ascribed to a fusion process. This is suggesting that the presence of higher amounts of TiO₂ nanofillers ($>30\%$) could be favoring a higher degree of order of PVK chains, as already reported for similar nanocomposites [36]. It has been already demonstrated that the presence of TiO₂ nanoparticle fillers acts as a nucleating agent and improves the degree of crystallinity of the polymer matrix [36]. These results showed excellent agreement with the increase of the negative Porod exponent observed for $X > 30$ in the whole temperature regime, as discussed above in our SAXS analysis. At higher temperatures ($T > 150\text{ }^{\circ}\text{C}$) a slight increase was observed for $X > 30$ in the negative

Porod exponent was observed, probably due to the formation of highly homogeneous and dense PVK-TiO₂ nanocomposites with the lower amounts of PVK acting as binder due to the well-defined fusion process. Our preliminary conclusions of this section showed that small angle X-ray scattering technique showed precise estimation and prediction about the fractal nature of both crystalline and amorphous polymeric structures in excellent agreement with differential calorimetry analysis.

4. Conclusions

In summary, we showed a novel strategy for obtaining inorganic-organic hybrid nanocomposites in which the TiO₂ nanofillers *in situ* growth process is triggered via vapor flow diffusion into poly(*N*-vinyl-carbazole) host. The presence of the non-reactive PVK polymer host does not alter significantly the growth mechanism in comparison to the solely alkoxide synthesis of titanium oxide nanoparticles in solution. Moreover, the water vapor flow diffusion into the non-reactive PVK polymer host seems to be responsible of the reaction limited growth mechanism. However, the main relevance of our strategy respect to the typical sol-gel growth in solution is the possibility of the interruption of the reaction by the simple interruption of the water vapor flow diffusion into the polymer host thus achieving good control in the nanoparticles size. The presence of low concentration of TiO₂ nanofillers increases the fractal roughness probably due to a decrease in the degree of order of PVK chains while the presence of higher concentration of TiO₂ nanofillers are probably increasing the degree of order of PVK chains. *In situ* small angle X-ray scattering showed good estimation on the fractal behavior dependence with temperature in strong correlation with phase transitions between crystalline and amorphous structures in these polymeric nanocomposites.

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