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Nucleation and growth of $LiCF_3SO_3$-doped polyalkylthiophenes

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Abstract

The effect of monomer and electrolyte ($LiCF_3SO_3$) concentrations on the nucleation and growth processes of polythiophene, poly(3-methythiophene) and poly(3-hexylthiophene) electrogenerated on a platinum electrode in an acetonitrile media were studied. The current transients were fitted using a mathematical equation that considers up to seven contributions, each of them representing a different classical nucleation and growth mechanism. The results indicate that the electrogeneration of polythiophene and poly(3-methylthiophene) films follow a similar mechanism, two-dimensional processes being detected at short reaction times, the overall processes being governed at longer reaction time by an instantaneous three-dimensional nucleation under charge control mechanism. The electrogeneration of poly(3-hexylthiophene) films, however, takes place without overlapping of nuclei, the process now being governed by an instantaneous nucleation three-dimensional diffusion control mechanism. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polythiophene; Nucleation; Growth

1. Introduction

In recent years, there has been an increasing amount of fundamental and applied research into conducting polymers [1–5]. In particular, polythiophene and its derivatives have been the subject of several studies [6–8] because of their applications in sensors, energy storage devices, electrochromic windows, etc. In spite of detailed studies concerning the physical, chemical, electronic and electrochemical properties of these materials, relatively few studies on the nucleation and growth mechanism during the anodic electropolymerization of these polymers can be found in the literature [9–11]. However, a relationship has to be expected between the nature of the nucleation and growth processes and the properties of the electrogenerated polymers, thus making the knowledge of this relation an important data for a better control of the structure, quality and the properties of the electrogenerated films. A two-dimensional growing nuclei may be expected to lead to a more uniform and compact arrangement of polymer chains while three-dimensional growing nuclei may form a “packed grain” morphology with a substantial amount of empty space, in which boundary the conditions could be crucial in controlling the properties of the whole films [12]. So depending on the type of mechanism, polymers with different micromorphological characteristics, solvation characteristics, etc. may be obtained.

There exist two models described in the literature to explain the nucleation and growth mechanism of electrogenerated conducting polymer films. The first model assumed the adsorption of the monomer onto the electrode surface, followed by a gradual addition of monomer over the adsorbed species [13], while the second model explains the electrodeposition mechanism of conducting polymer films through different stages [14,15]. The first step requires the monomer adsorption on the surface of the supporting electrode, followed by its oxidation, this process being dependent on the chemical nature of the monomer as well as on the surface characteristics of the supporting electrode. In a second step, the oxidized monomer diffuses towards the interface where oligomerization takes place and at the same time, builds on an oligomeric high-density region denominated OHDR. Once this region is established and depending on the supersaturation attained, clusters are deposited on the electrode creating growing nuclei. This process did not take place simultaneously along the entire electrode surface but shows a great dependence on orientation. Once the oligomers are deposited on the electrode surface, the growth can be either due to a homogeneous addition of monomer units at the end of the oligomer chains thus leading to an one-dimensional growth mechanism, characterized by the absence of any increase of the surface, which is in disagreement with the experimentally obtained

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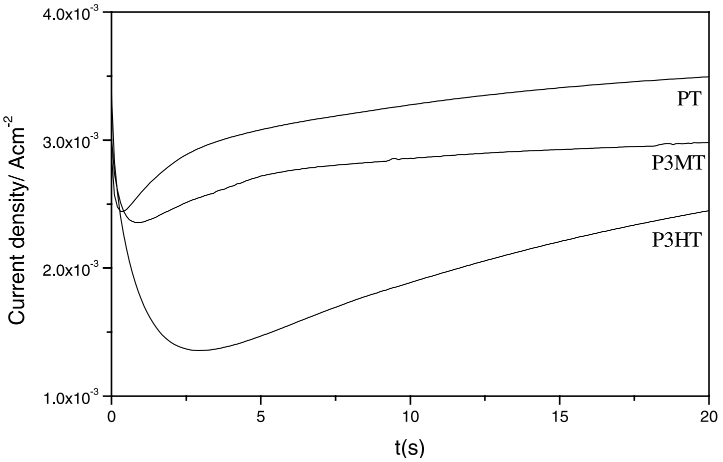

Fig. 1. Chronoamperogramms obtained in the electrogeneration of polythiophene ($V_{ox} = 2.1$ V vs Ag/Ag$^+$), poly(3-methylthiophene) ($V_{ox} = 1.8$ V vs Ag/Ag$^+$) and poly(3-hexylthiophene) ($V_{ox} = 1.8$ V vs Ag/Ag$^+$) on platinum electrodes in an acetonitrile/LiCF$_3$SO$_3$. In all three cases, monomer and electrolyte concentrations are 0.1 M.

I/*t* chronoamperogramms [16], or by a continuous electroprecipitation that further results in growth with nuclei expansion taking place by precipitation of oligomers on top of already formed nuclei [17].

The film growth can take place in three different ways [18]. When the interactions between the surface of the electrode and the deposited material are weak as compared to interactions within the deposited material itself, deposition takes place in the form of three-dimensional nuclei (3D island or Volmer–Weber model), which grow and finally coalesce. When a strong surface–deposit interaction takes place, the deposits tend to form a two-dimensional adlayer; if the formation of the adlayer results in a deformation of the deposit structure, three-dimensional growth centres nucleate on the adlayer and successively growth takes place on these nuclei (3D islands on 2D layer or Stranski–Krastanov model). However, if the deformation is insignificant, the deposit may continue to grow by addition of successive layers upon each other (layer by layer of Frank–van del Merwe model) although three-dimensional growth may originate owing to statistical fluctuations [19].

The deposition electrochemistry of polythiophene was described by Hillman et al. [20], who reported that the formation of the bulk film occurs by the instantaneous nucleation and three-dimensional growth of polymer on top of the monolayer, the rate being constant for growth parallel to the surface of the gold working electrode and the covering polymer layer being very similar. Additionally, growth perpendicular to the surface was observed to be more rapid although it is less dependent on oxidation potential. More recently, Schrebler et al. [10] reported that an instantaneous nucleation under charge transfer control with a three-dimensional growth was the prevailing mechanism while the other contributions are more or less important depending upon electropolymerization conditions.

The oxidation polymerization of substituted polythiophene has also been investigated. Li and Albery [21] studied the nucleation and growth mechanism for thiophene-3-acetic acid, fitting the experimental data to a mechanism involving a progressive nucleation and a two-dimensional layer-by-layer growth. Lang and Clavilier [22] demonstrated that the nucleation and growth of electropolymerized 3-methylthiophene depends strongly on the surface structure of the working electrode. Chao et al. [23], based on chronoamperometric and elipsometric measurements, described several steps in the electrodeposition of poly(3-methylthiophene). Komtturi et al. [24] suggest that in the electrodeposition of poly(thiophene-3-methanol) on platinum electrodes, the first layer of the polymer is formed through adsorption after which the deposition continues by instantaneous nucleation and two-dimensional layer-by-layer growth, etc.

In this paper, we report on the effect of variables such as monomer and electrolyte concentrations on the nucleation and growth mechanism of polythiophene (PT), poly(3-methylthiophene) (P3MT) and poly(3-hexylthiophene) (P3HT) films electrogenerated potentiostatically on platinum electrodes in an acetonitrile media using lithium trifluoromethanesulfonate (LiCF$_3$SO$_3$) as the electrolyte.

2. Experimental

Acetonitrile solvent (Panreac) was purified by refluxing over P$_2$O$_5$ for 48 h, then distilled and stored over a 4 Å molecular sieve. The electrolyte, LiCF$_3$SO$_3$ was an Aldrich product and was dried under vacuum at 120°C for 24 h. Polythiophene, poly(3-methylthiophene) and poly(3-hexylthiophene) monomers were purchased from Aldrich and used as-received.

Experiments were performed at room temperature in a dry nitrogen atmosphere in a one compartment, three-electrode glass cell. The counter electrode was a stainless steel plate (4.1 cm^2 on each side). An Ag/Ag^+ electrode filled with a LiCl-saturated EtOH solution was used as the reference. Platinum working electrodes (0.5 cm^2 surface on each side) were cleaned on a reducing flame before each experiment. Due to the high oxidation potentials required for polythiophene, poly(3-methylthiophene) and poly(3-hexylthiophene) electrogeneration, all handling operations were made inside an argon-filled dry-box with a humidity level lower than 1 ppm to avoid any interference of water in the results.

A PGSTAT 30 Potentiostat/Galvanostat provided with adequate software for data acquisition and analysis was employed for the electrogeneration of films. Electropolymerization takes place on both sides of the working electrodes in all the experiments, the distance of working to counter electrode being fixed at 1.2 cm by using a specially designed homemade holder. PT films were electrogenerated potentiostatically by applying a constant potential of 2.1 V against Ag/Ag^+ during different periods of time, P3MT and P3HT films being synthesized at $E = 1.8$ V against Ag/Ag^+. Each measurement was repeated five times and the results are given as mean values. The repeatability and the reproducibility of experiments are established such that the variation on energy density between the chronoamperogramms was lower than 10%.

The nucleation and growth data were fitted to the proposed mathematical equation by using the non-linear least-square Marquardt–Levenberg algorithm as available in the ORIGIN software (Microcal, Northampton, MA). A minimum of 50 iterations was performed until the fractional change in the x^2 value was within the tolerance limit, which was set to 0.0005.

3. Results and discussion

Fig. 1 shows the chronoamperogramms corresponding to the electrogeneration of polythiophene (PT), poly(3-methylthiophene) (P3MT) and poly(3-hexylthiophene) films. Oxidation potentials are 2.1 V vs Ag/Ag^+ for polythiophene and 1.8 V vs Ag/Ag^+ for poly(3-methylthiophene) and poly(3-hexylthiophene). These values of the oxidation potential were determined in a previous work [25–27] from charge storage efficiency and current productivity results data. The description of the different stages appearing on the amperogramms was reported in the literature [28,29]. The first step is associated to the charge of the double layer of the electrode surface (not observed in the chronoamperograms due to the relatively high oxidation potential employed); after this point, the current falls to a minimum up to $t = t_0$ (induction time), following a I vs $t^{-1/2}$ relationship that corresponds to diffusion-controlled process. This process has been assigned in the literature [12,30,31] to the oxidation of the monomers diffusing from the solution to the electrode surface and once they are oxidized return to the solution, where the oligomerization process occurs and the OHDR is established. After this region reaches a determined supersaturation, the nucleation and growth begins to take place, which is traduced in the chronoamperogramms as an increase in the intensity until it reaches a current plateau. The increase in the intensity reflects the surface increase during the nucleation stage up to a point where the larger number and size of nuclei lead to overlapping processes with the subsequent decrease of the active area. This situation leads to decrease on the slope in the chronoamperogramms and is commonly associated to the existence of monolayers, the electrogeneration process then being governed by growth processes.

Looking at the graph, it is clear that the induction time t_1 increases from polythiophene ($t_0 = 0.5$ s), to poly(3-methylthiophene) ($t_0 = 1.25$ s) and poly(3-hexylthiophene) ($t_0 = 2.9$ s). It can be observed that t_0 increases as the alkyl chain length increases, which could be explained in terms of increasing solubility and steric hindrance effects [32,33]. The introduction of an alkyl chain on the β-position of the thiophene ring leads to an increase in the solubility and so the time required to reach the critical solubility point is higher. In a similar manner, the steric hindrance effect exerted by the alkyl chain leads to a decrease in the oligomerization rate favouring the existence of well-packed shorter chains.

The theory of nucleation developed for electrocrystallization of metals could be applied to the electropolymerization of conducting polymers taking note of the difference among metals and polymer deposits. In order to define the nucleation and growth mechanism of electropolymerization, different equations were considered in the literature [34,35]. One of the proposed equations was the following:

$$I = at + bt^3 + ct^{0.5} + dt[\exp(-et^2)] + f[(1 - \exp(-gt^2)] + ht^{-0.5}[1 - \exp(-it)] + jt^{-0.5}[1 - \exp(-kt^2)] \qquad (1)$$

where the first term in Eq. (1) represents a two-dimensional nucleation process with charge transfer as the limiting step (IN2DWOTC) (Instantaneous Nucleation Two Dimension Without Overlap Transfer Control); the second term corresponds to progressive three-dimensional nucleation, again with charge transfer as the limiting step (PN3DWOTC) (Progressive Nucleation Three Dimension Without Overlap Transfer Control); the third term is associated to an instantaneous three-dimensional nucleation and growth process, but in this case diffusion being the limiting factor (IN3DWODC) (Instantaneous Nucleation Three Dimension Without Overlap Diffusion Control); the fourth term of the equation corresponds to an instantaneous nucleation mechanism under charge transfer control with a two-dimensional growth but with overlapping of nuclei (IN2DTC) (Instantaneous Nucleation Two Dimensions Transfer Control). The last three terms correspond to three-dimensional nucleation models involving overlapping of nuclei;

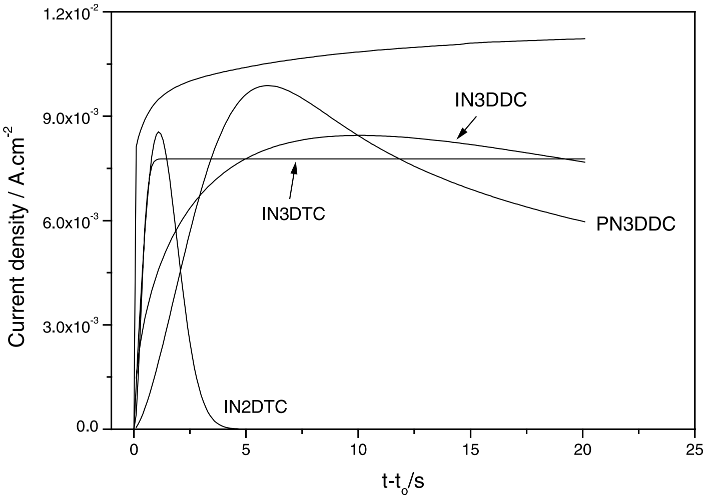

Fig. 2. Current–time transients fitted by means of Eq. (1) of polythiophene films electrogenerated on a platinum electrode at $V_{ox} = 2.1$ V vs Ag/Ag$^+$. [Thiophene] = [LiCF$_3$SO$_3$] = 0.1 M. The contributions from the different mechanisms to the overall process were calculated from the respective terms of the same equation.

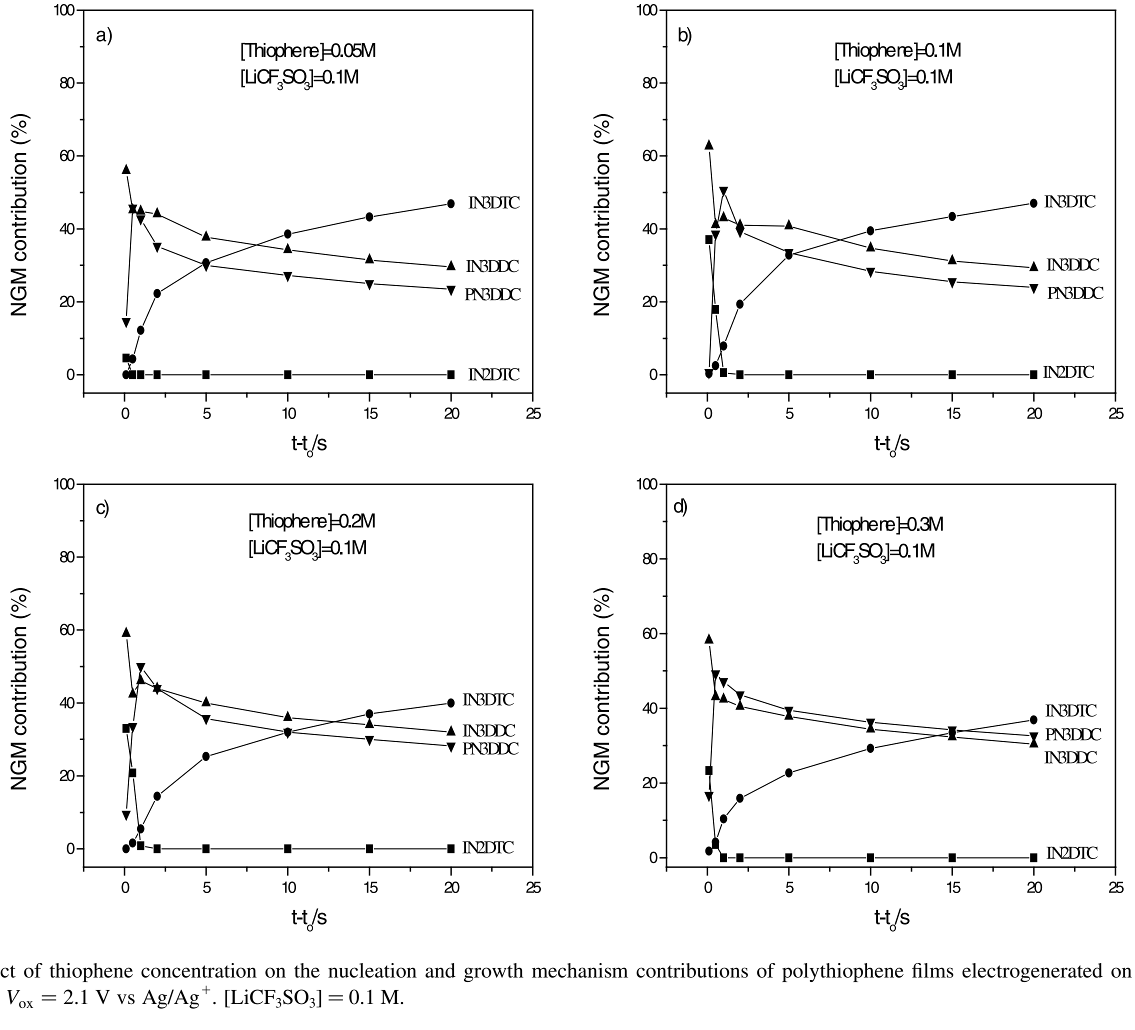

Fig. 3. Effect of thiophene concentration on the nucleation and growth mechanism contributions of polythiophene films electrogenerated on a platinum electrode at $V_{ox} = 2.1$ V vs Ag/Ag$^+$. [LiCF$_3$SO$_3$] = 0.1 M.

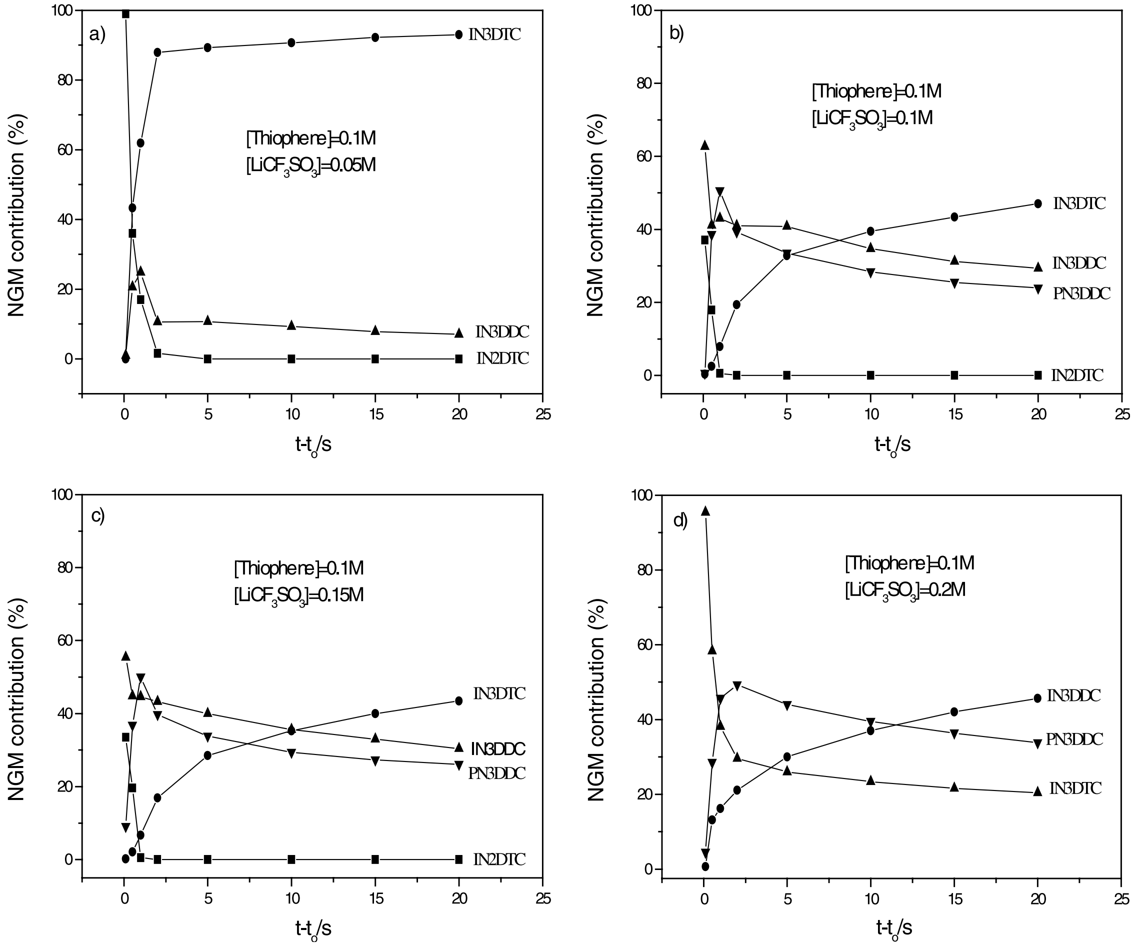

Fig. 4. Effect of $LiCF_3SO_3$ concentration on the nucleation and growth mechanism contributions of polythiophene films electrogenerated on a platinum electrode at $V_{ox} = 2.1$ V vs Ag/Ag^+. [Thiophene] = 0.1 M.

the fifth term is associated to an instantaneous three-dimensional mechanism with charge transfer as the limiting factor (IN3DTC) (Instantaneous Nucleation Three Dimensions Transfer Control), the sixth term corresponds to an instantaneous nucleation, three-dimensional diffusion-controlled mechanism (IN3DDC) (Instantaneous Nucleation Three Dimensions Diffusion Control) and finally the last term is associated to a progressive three-dimensional nucleation under diffusion-controlled process (PN3DDC) (Progressive Nucleation Three Dimension Diffusion Control).

The constants a, b, c, d, e, f, g, h, i, j and k are described through the equations:

$$a = \frac{2N_{2D}\pi n\mathrm{F}k_2^2hM}{\rho} \qquad b = \frac{2\pi n\mathrm{F}M^2N_{3D}k_3^3}{3\rho^2}$$

$$c = \frac{\pi n\mathrm{F}N_{3D}(2D_c^0)^{3/2}M^{1/2}}{3\rho^{1/2}}$$

$$d = \frac{2\pi nMh\mathrm{F}N_{2D}k_2^2}{\rho} \qquad e = \frac{\pi N_{2D}M^2k_2^2}{\rho^2}$$

$$f = N\mathrm{F}Dk_3 \qquad g = \frac{\pi M^2k_3^2N_{3D}}{\rho^2}$$

$$h = \frac{\pi \mathrm{F}D^{1/2}C_\infty}{\pi^{1/2}} \qquad i = N_{3D}\pi kD$$

$$j = \frac{\pi \mathrm{F}D^{1/2}C_\infty}{\pi^{1/2}} \qquad k = \frac{A''k'\pi D}{2}$$

where n, F, M and ρ are the number of electrons, the Faraday constant, the molar mass and the density, respectively; h and k_2 are the height and the growth rate constant of the 2D nucleus, respectively; N_{2D} and N_{3D} are the number of instantaneous nuclei formed at $t = 0$ in 2D and 3D forms; k_3 and k_3' are the rate constants of the 3D nucleus for the growth parallel and perpendicular to the surface; D and C_4 are the diffusion coefficient and the bulk concentration of the monomer. Finally A', k and k' are described by the following mathematical expressions:

$$A' = AN_{\mathrm{DIF}}$$

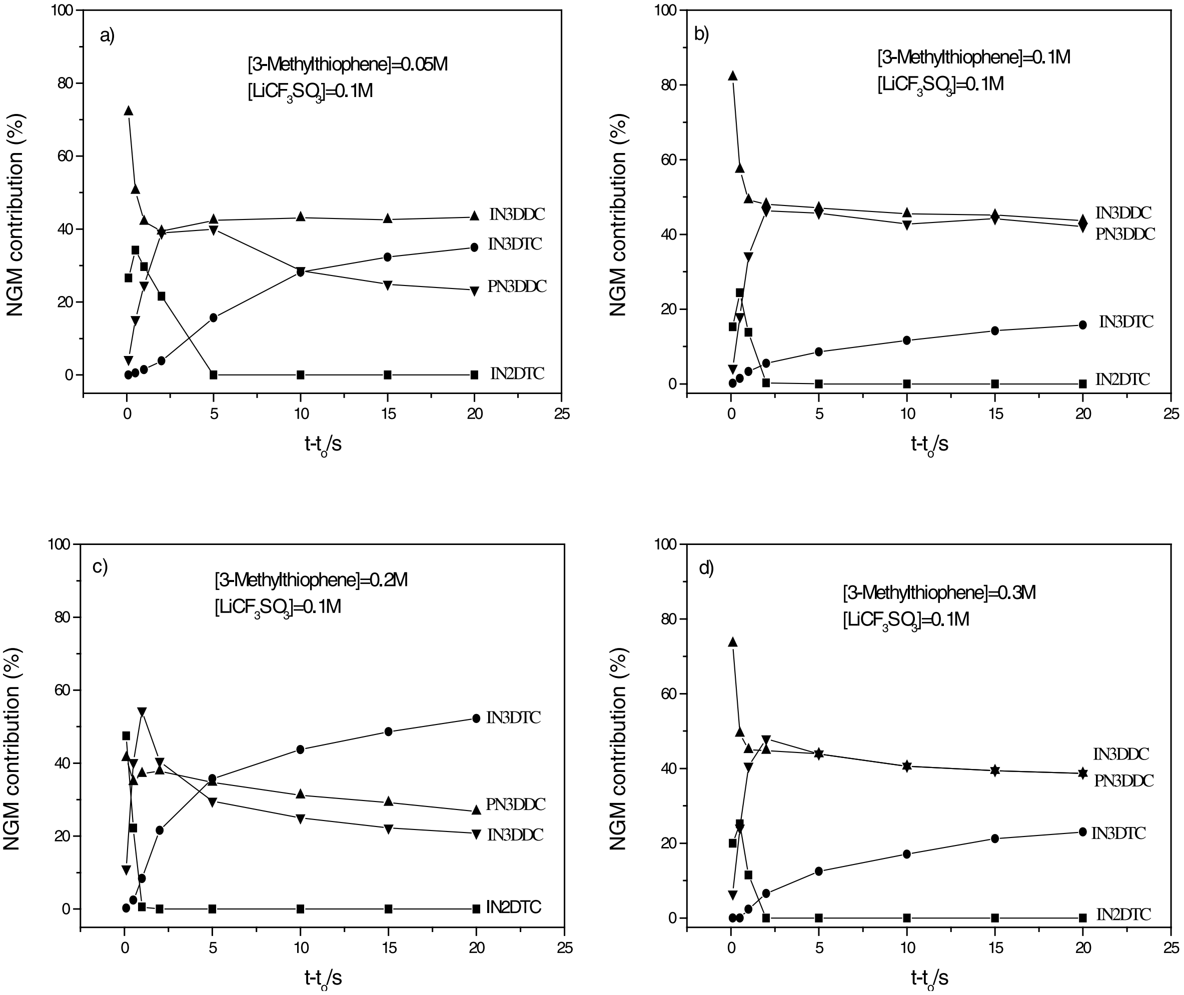

Fig. 5. Effect of 3-methylthiophene concentration on the nucleation and growth mechanism contributions of poly(3-methylthiophene) films electrogenerated on a platinum electrode at $V_{ox} = 1.8$ V vs Ag/Ag$^+$. [LiCF$_3$SO$_3$] = 0.1 M.

$$k = \left(\frac{8\pi C_\infty M}{\rho}\right)^{1/2} \qquad k' = \frac{4}{3}\left(\frac{8\pi C_\infty M}{\rho}\right)^{1/2}$$

where A is the rate constant of nucleus formation and N_{DIF} the number of nuclei formed at $t = 0$ under diffusion control.

In order to get a deeper insight into the knowledge of the effect produced by varying monomer and electrolyte concentrations on the nucleation and growth mechanism in the electrogeneration of LiCF$_3$SO$_3$-doped polythiophene, poly(3-methyl thiophene) and poly(3-hexyl thiophene), we applied Eq. (1) to the obtained I vs $t - t_0$ chronoamperogramms. Fig. 2 shows, as an example, the application of Eq. (1) to the chronoamperogramm, obtained in the electrogeneration of a polythiophene film with [Thiophene] = [LiCF$_3$SO$_3$] = 0.1 M. The mathematical fit results obtained reveal the contribution of four mechanisms to the nucleation and growth processes, the sum of them reproducing the experimentally obtained curve.

Fig. 3 shows the effect of thiophene concentration keeping the electrolyte concentration fixed at 0.1 M on the contributions of the different nucleation and growth model mechanisms to the overall electrogeneration process. It can be observed that the model mechanisms involved are the same independent of the monomer concentration while differences were observed in the numerical value of the contribution of each mechanism to the global processes. Looking at the results, it has to be remarked that the four contributions detected are characterized by the overlapping of the generated nuclei, i.e. out of the last four contributions in Eq. (1), two contributions being characterized by charge transfer as the limiting factor, two dimensional (IN2DTC) and three-dimensional (IN3DTC), while the other two contributions detected were three-dimensional mechanism with diffusion as the limiting stage, but the nucleation is progressive in one case (PN3DDC) and instantaneous in the other (IN3DDC).

The data obtained indicate that the contribution of two-dimensional mechanism (IN2DTC) is only significant at short times. Numerical contribution values are between 20 and 30% at $t - t_0 = 0.1$ s) but the contribution decreases, being practically neglected at $t - t_0 = 1$ s. It is also remarkable that this contribution of this mechanism increases as thiophene concentration goes up. At the lower thiophene concentration employed ([Thiophene] = 0.05 M), the process is governed by a combination of IN3DTC, IN3DDC and PN3DDC mechanisms, but while the IN3DTC contribution to the overall process increases with time, the main contribution being at $t - t_0 > 8$ s. The contributions from the other two mechanisms decrease as electrogeneration time increases. Based on these data, it can be inferred that at short electrogeneration times, the number of oligomers electrodeposited is low and the process is governed by the diffusion of the monomer from the solution to the electrode. As electrogeneration proceeds, the formation of oligomers is higher, the process then becomes governed by charge transfer processes. Similar results were obtained for thiophene concentration of 0.1 M. At thiophene concentrations of 0.2 and 0.3 M, the profile is quite similar to that obtained at [Thiophene] = 0.1 M (Fig. 3c and d), with only differences in the relative contributions of each mechanism to the overall process being observed. The IN3DTC is again the prevailing mechanism at high reaction times, but the time required increases as well as the numerical value of the contribution of this mechanism is observed to decrease at high thiophene concentrations, while the contribution from the two diffusion-controlled mechanisms (IN3DDC and PN3DDC) increases slightly.

Fig. 4 shows the contributions to the nucleation and growth processes in the electrogeneration of polythiophene keeping monomer concentration fixed at 0.1 M and varying the electrolyte concentration between 0.05 and 0.2 M. First of all, it has to be pointed out that electrolyte concentration has great influence on the nucleation and growth mechanism. Again, the contribution of two-dimensional mechanism is important at very short times, e.g. 99% at $t - t_0 = 0.1$ s when $[\mathrm{LiCF_3SO_3}] = 0.05$ M (Fig. 4a). This contribution is neglected as electropolymerization proceeds. It also has to be pointed out that this contribution was not detected at the higher electrolyte concentration employed ($[\mathrm{LiCF_3SO_3}] = 0.2$ M). At the lower electrolyte concentration (Fig. 4a), the IN3DTC contribution, which is negligible in the electrogeneration process, increase very fast, reaching values close to 90% at $t - t_0 = 2.5$ s. It is also remarkable that in the absence of the progression nucleation, the IN2DDC mechanism is much less important if we compared with the results reported in Fig. 3, the process being practically governed by the IN3DTC mechanism.

A different pattern was observed in Fig. 4b ($[\mathrm{LiCF_3SO_3}] = 0.1$ M), where four mechanisms were observed to describe the nucleation and growth processes. It can be observed that, at the same time when electropolymerization time increases, the mechanisms associated to diffusion as the limiting stage decrease their importance, while the contribution from the charge transfer controlled IN3DTC mechanism increases its contribution with time. Similar behaviour was observed at $[\mathrm{LiCF_3SO_3}] = 0.15$ M (Fig. 4c). At the higher electrolyte concentration (Fig. 4d), it can be observed that no contribution from a two-dimensional mechanism was detected together with the fact that while the global contribution from the diffusion-limiting mechanisms IN3DDC and PN3DDC is similar to that obtained previously. A higher contribution was calculated from the IN3DDC mechanism, instead of the PN3DDC, i.e. progressive nucleation is predominant over the instantaneous nucleation in the case of diffusion-controlled mechanisms. Finally, it has to be pointed out that at very short reaction times ($t - t_0 = 0.1$ s), the contribution from the IN3DTC mechanism reaches 99% of the overall process.

Fig. 5 shows the results obtained by applying Eq. (1) to the electrogeneration of poly(3-methylthiophene) films when monomer concentration changes from 0.05 to 0.3 M keeping the electrolyte concentration (0.1 M) constant. The results indicate that the electrogeneration of poly(3-methilthiophene) films take place in a similar way to that previously described for polythiophene, even though differences were observed as monomer concentration is increased.

At low monomer concentration and short reaction times (Fig. 5a), the IN3DDC is the prevailing mechanism but its contribution decreases rapidly, reaching a 40% contribution value at $t - t_0 = 1$ s, a value which is then practically maintained constant over time. It has to be pointed out that the contribution of 2D mechanism decreases with reaction time, being practically neglected at $t - t_0 \geq 5$ s. If we compare this results with those obtained previously in the electropolymerization of polythiophene at the same monomer concentration, it can be observed that there is a larger contribution to the electrogeneration process from diffusion-controlled mechanisms. The instantaneous nucleation IN3DTC mechanism contribution increases with time reaching a maximum value of 35% at $t - t_0 = 20$ s, while the diffusion-controlled nucleation PN3DDC contribution reaches a maximum at $t - t_0$ between 3 and 5 s, then decreasing to a 23% value at $t - t_0 = 20$ s. When 3-methylthiophene concentration increases to 0.1 M (Fig. 5b), the nucleation and growth process is mainly governed by diffusion-controlled mechanisms IN3DDC and PN3DDC and even the value of these contributions show great difference up to $t - t_0 = 2$ s. Before this time, the contribution of instantaneous nucleation mechanism decreases with time while an inverse behaviour was detected in the PN3DDC mechanism. After this time ($t - t_0 = 2$ s), both contributions are practically identical in value, the numerical contribution values being constant with time. Again the two-dimensional IN2DTC contribution disappears at $t - t_0 \geq$ 2 s. Another important factor is that the three-dimensional IN3DTC is not the major contributor at any time.

Fig. 5c shows the results obtained at [3-methylthiophene] = 0.2 M. At very short reaction times, the two-dimensional IN2DTC mechanism mainly governs the nucleation and growth process, but this contribution is neglected at $t - t_0 \leq 1$ s. Another important factor is that at $t - t_0 \leq 5$ s the process is governed by the diffusion-controlled PN3DDC and IN3DDC mechanisms while at

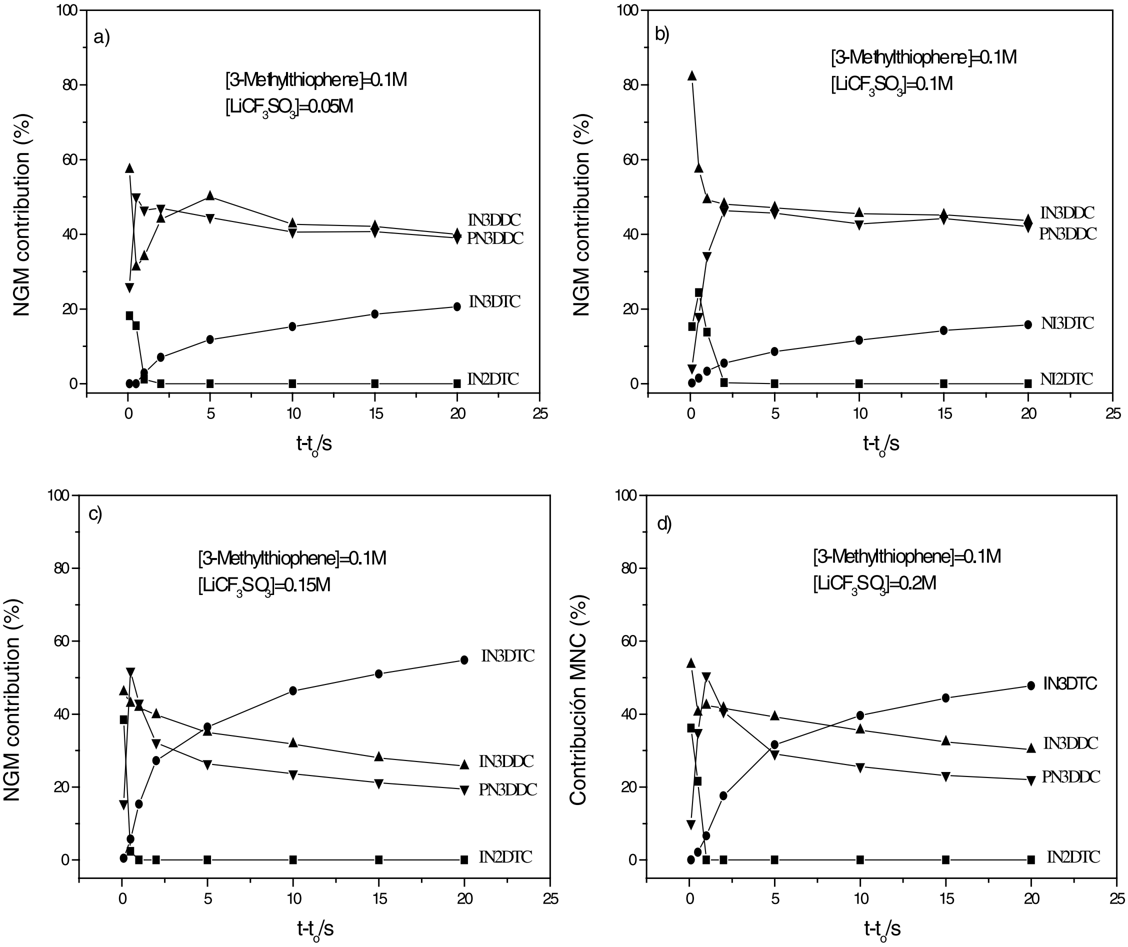

Fig. 6. Effect of $LiCF_3SO_3$ concentration on the nucleation and growth mechanism contributions of poly(3-methylthiophene) films electrogenerated on a platinum electrode at $V_{ox} = 1.8$ V vs Ag/Ag$^+$. [3-Methylthiophene] = 0.1 M.

higher electrogeneration times, the main contribution to the overall nucleation and growth mechanism is from the charge transfer controlled IN3DTC mechanism. Finally, when 3-methylthiophene concentration is 0.3 M (Fig. 5d), the profile obtained is very similar to that obtained previously at [3-methilthiophene] = 0.1 M.

The results obtained by applying Eq. (1) to chronoamperogramms resulting from the electrogeneration of poly(3-methylthiophene) films, keeping the monomer concentration constant and varying the $LiCF_3SO_3$ concentration between 0.05 and 0.2 M, are compiled in Fig. 6.

First of all, differences observed between Fig. 6a and b with Fig. 6c and d have to be pointed out. At an electrolyte concentration of 0.05 M (Fig. 6a), it can be observed that the main contribution at $t - t_0 = 0.1$ s corresponds to the IN3DDC mechanism with a value close to 57% of the overall process. At this reaction time, the contribution for the IN3DTC is negligible, while the contribution from the progressive nucleation PN3DDC and the instantaneous nucleation IN2DTC mechanisms reach values of 26 and 15%, respectively. At $t - t_0 = 2$ s, there is no significant contribution from the IN2DTC mechanism, the main contribution (∼90%) resulting from the diffusion-controlled IN3DDC and PN3DDC mechanisms. At higher electrogeneration times, there is a continuous decrease on the contributions from these two diffusion-controlled mechanisms. However the contribution from charge transfer control mechanism was always lower than 20% of the global electrogeneration process.

Similar results where obtained at $[LiCF_3SO_3] = 0.1$ M. The profile is almost identical to that obtained previously. Little differences on the numerical values of the contribution of each mechanism to the electrogeneration process obtained were compared with that obtained when $[LiCF_3SO_3] = 0.05$ M, especially at low reaction times.

A different behaviour was observed at $LiCF_3SO_3$ concentration equal to 0.15 M (Fig. 6c). First of all, it has to be noticed that even the contribution from the two-dimensional IN2DTC mechanism at $t - t_0 = 0.1$ s was higher than that obtained previously. This contribution disappears at lower reaction times than that previously calculated for electrolyte concentrations of 0.05 and 0.1 M. The contribution from the IN3DDC mechanism at this time was of the order of 46% lower than that shown in Fig. 2b; the contribution from the

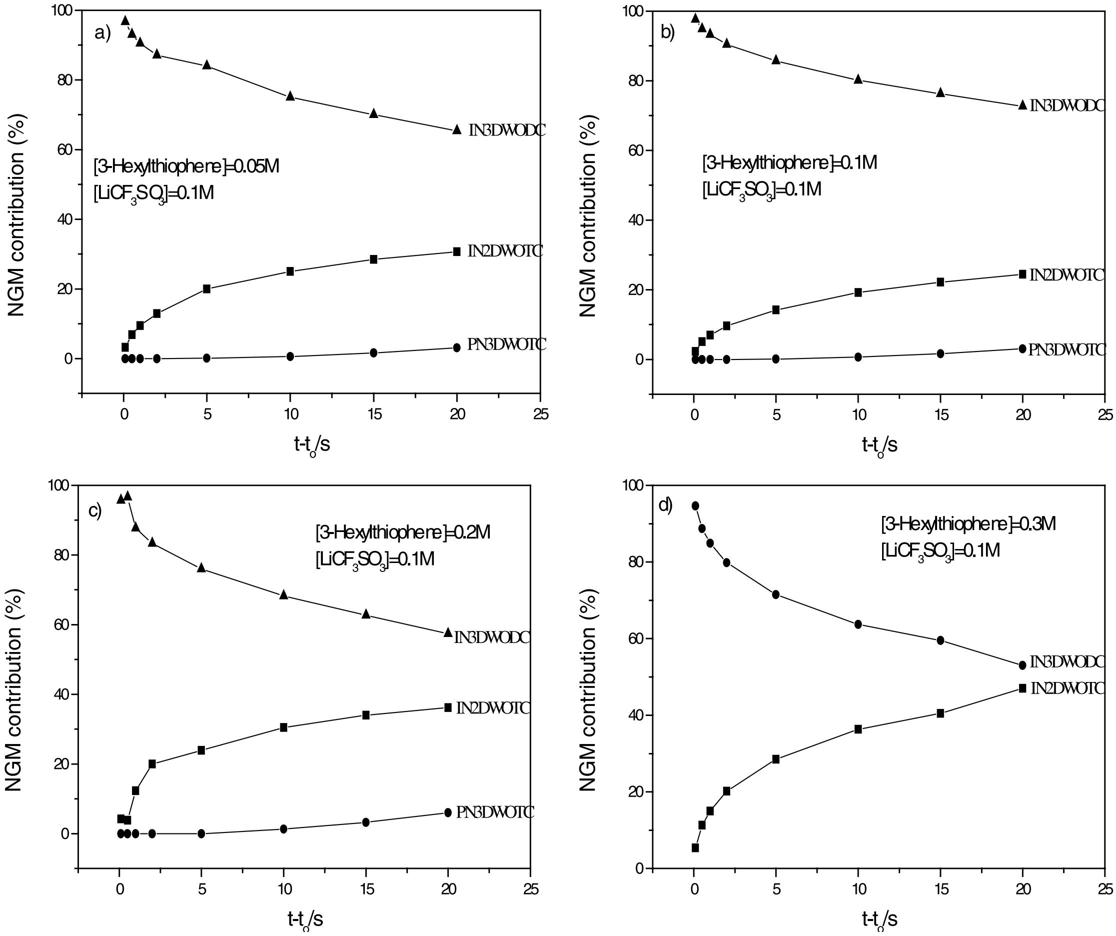

Fig. 7. Effect of 3-hexylthiophene concentration on the nucleation and growth mechanism contributions of poly(3-hexylthiophene) films electrogenerated on a platinum electrode at $V_{ox} = 1.8$ V vs Ag/Ag$^+$. [$LiCF_3SO_3$] = 0.1 M.

PN3DD diffusion-controlled mechanism not being significant at this time. As electrogeneration proceeds, the PN3DD contribution increases its maximum close to a value up to 50% of the overall process, then decreases continuously up to a value of 19% at $t - t_0 = 20$ s. A similar behaviour was observed for the IN3DDC contribution and the contribution to the nucleation from the IN3DTC mechanism increasing with time up to values higher than 50% at $t - t_0 = 20$ s.

A previously identical profile was obtained at [$LiCF_3SO_3$] = 0.2 M. The results obtained seem to indicate that when $LiCF_3SO_3$ concentration is increased, the mechanisms characterized by the charge transfer as the limiting stage increase their contribution to the electrogeneration process. This behaviour can be explained if we consider that an increase on the electrolyte concentration will be transduced in an increase of the conductivity of the medium with the consequent enhancement of the oligomerization process.

Fig. 7 compiles the results obtained from the mathematical fit to Eq. (1) of the chronoamperograms obtained in the electrogeneration of poly(3-hexylthiophene) films at different monomer concentrations. The first point to be remarked is the appearance of mechanisms that take place without overlapping of nuclei. The results indicate that at all monomer concentrations tested, the main contribution to the overall nucleation and growth processes is from a IN3DWODC mechanism, numerical values of the order of 96% being obtained at short times. For electrogeneration process, this contribution decreases continuously decreasing with time, the numerical value being a function of the monomer concentration (61% at 0.05 M, 73% at 0.1 M, 58% at 0.2 M and 54% at 0.3 M). A small contribution from a progressive nucleation PN3DWOTC was detected up to monomer concentration equal to 0.2 M and even this contribution to the overall process is not very significant independent of the electrogeneration time. Finally, the contribution from the two-dimensional IN2DWOTC mechanism increases with time reaching values close to 47% at monomer concentrations of 0.3 M.

Fig. 8 shows the results obtained from the mathematical fit from the electrogeneration of poly(3-hexylthiophene) films at monomer concentration fixed at 0.1 M, while electrolyte concentration is changed between 0.05 and 0.2 M. At electrolyte concentration of 0.05 M, the process is practically governed by an IN3DWODC mechanism, with only a small contribution from a two-dimensional IN2DWOTC

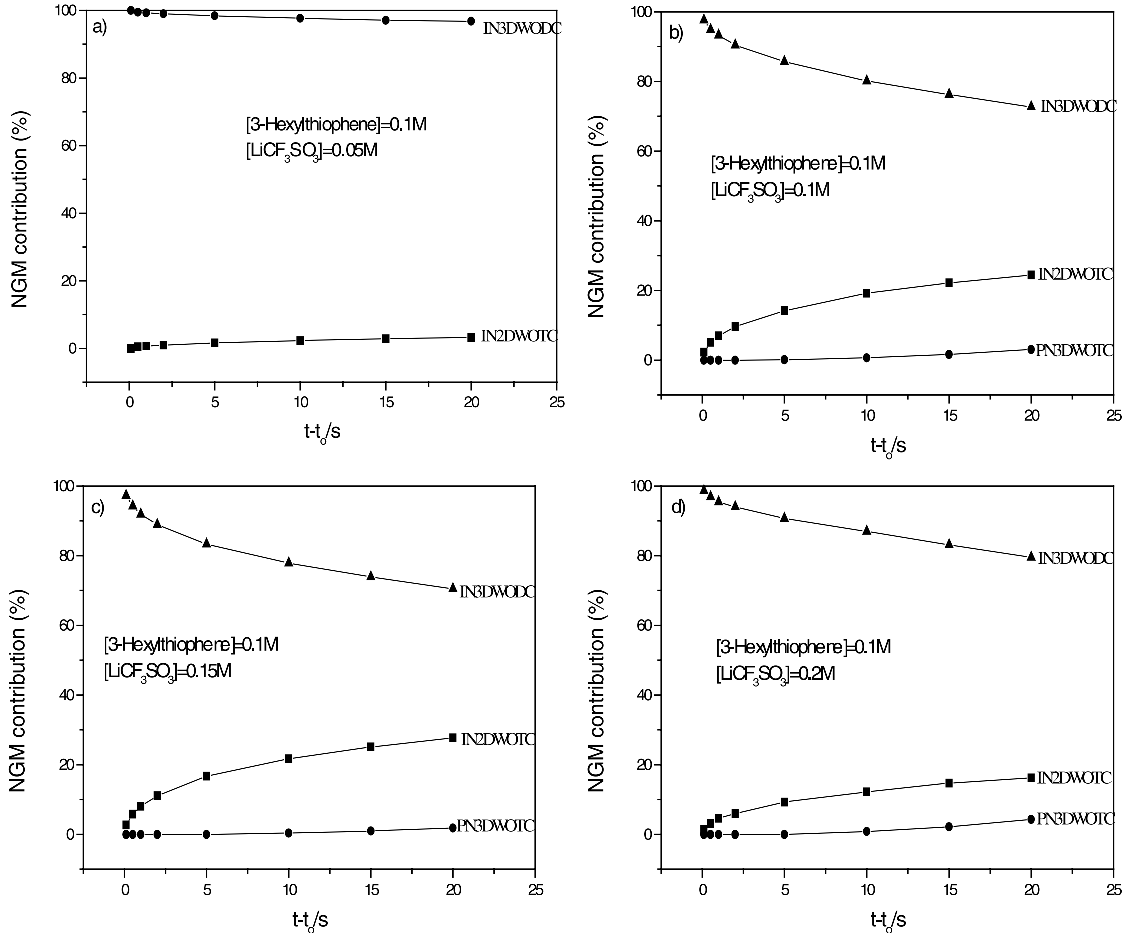

Fig. 8. Effect of $LiCF_3SO_3$ concentration in the nucleation and growth mechanism contributions of poly(3-hexylthiophene) films electrogenerated on a platinum electrode at $V_{ox} = 1.8$ V vs Ag/Ag^+. [3-Hexylthiophene] = 0.1 M.

mechanism being detected, both contributions being practically constant independent of time.

4. Conclusions

The effect of monomer and electrolyte concentrations on the nucleation and growth mechanism of electrogeneration of $LiCF_3SO_3$-doped polythiophene, poly(3-methylthiophene) and poly(3-hexylthiophene) have been investigated. The results obtained indicate that the nucleation and growth mechanism of electrogenerated $LiCF_3SO_3$-doped polythiophene and poly(3-methylthiophene) films are similar. The nucleation and growth processes take place with overlapping of nuclei, two-dimensional mechanism being only detected at low reaction times and as reaction times increases the process is governed by an instantaneous three-dimensional nucleation under charge transfer control mechanism. However, results indicate that the electrogeneration of poly(3-hexylthiophene) films followed a different mechanism; the nucleation and growth processes take place without overlapping of nuclei suggesting that both the formation of oligomers and the subsequent electrodeposition take place at a slow rate compared to that observed for polythiophene and poly(3-methylthiophene) films. The process is now governed by an instantaneous three-dimensional nucleation without overlapping diffusion-controlled mechanism. Only small differences in the contributions of the different mechanisms to the global process is observed when monomer or electrolyte concentrations are changed.

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