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Doping-induced broadening of the hole density-of-states in conducting polymers

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ABSTRACT

The density-of-states distribution in conducting polymers reflects the energy disorder caused by electrostatic and steric interactions resulting from the different environment in which each molecule is placed. In case of *p*-doping (oxidation), the highest occupied molecular orbital (HOMO) manifold spreads in energy following a distribution as a result of long-range electrostatic (dipolar) interactions with the surrounding disordered host. In this paper the repercussion of the dipolar disorder on electrochemical signals of standard polypyrrole films is explored. The analysis is based on the chemical capacitance variation with the applied potential in experiments performed in quasi-equilibrium conditions. In addition to the Gaussian shape of cyclic voltammograms at low-doping levels, the model is able to qualitatively account for the current plateau usually observed at high oxidation potentials. This approach allows to estimating the dipolar moment associated to the polymer/dopant complex.

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1. Introduction

Electronically conducting polymers (CP) are extensively investigated for a variety of applications such as organic light-emitting devices, electrochromics, and organic electronics. Conjugated polymers have the property of changing their conductive state from insulating to semiconducting under electrochemical doping by application of a positive potential. Polymer oxidation changes the occupancy of electronic states creating holes in the conjugated chains suitable for transporting current. Charge carriers resulting upon oxidation undergo self-trapping by local polarization, forming polarons which can move only by carrying along the associated structural deformation. Two polarons in a single polymer chain can react producing a bipolaron because in most cases the energy gained in forming only one deformation may overcome the Coulombic repulsion energy. The density of electronic states (DOS) in conducting polymers and the influence of electrical doping on such DOS are then fundamental pieces of knowledge for understanding charge transport in such compounds.

The DOS distribution reflects the energy disorder caused by electrostatic [1] and steric [2] interactions resulting from the different environment in which each molecule is placed. In case of *p*-doping, the highest occupied molecular orbital (HOMO) manifold spreads in energy as a result of long-range electrostatic (dipolar) interactions with the surrounding disordered host [3]. Such energy disorder gives rise to a DOS which is modeled either by using Gaussian [1] or exponential [4] distributions. When dopants are dispersed in the polymer matrix the intrinsic Gaussian disorder σ_0 is known to be increased by the dipolar interaction caused by the randomly placed charged molecules as $\sigma^2 = \sigma_0^2 + \sigma_p^2$ [5–7]. The dipolar disorder gives rise to a broadening of the DOS which can be approximated as [8,9]

$$\sigma_{\rm p} = k \frac{P}{\gamma^2 E} x^{\alpha} \tag{1}$$

Here *P* represents the dipolar moment of the polymer/dopant complex (P⁺:A⁻), γ is the average distance between polymer units (in Å), *E* stands for the dielectric constant, and *x* indicates the doping level, related to the density of holes. Finally, *k* and α are numerical constants which adopt different values depending on the initial assumptions considered in performing simulations to derive Eq. (1). There have been reported pairs of values *k*=7.04 and α = 1/2 (assuming point dipoles) [8], and *k* = 3.06 and α = 2/3 (for separated point charges) [9], respectively. Eq. (1) is valid as long as reordering of the ensemble of dipoles by effect of their mutual influence is negligible [9].

There exists a variety of methods for measuring DOS in doped polymers and molecular solids. All procedures are based on determining directly the variation of the electronic density (injection of holes) caused by a variation of the Fermi energy [10,11] (or the electrochemical potential). The amount of available states is then monitored by means of a change of the applied potential in conditions close to the thermodynamic equilibrium. Accurate mea-

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surements using an electrochemical transistor set-up, in which polymer films were in contact with the electrolyte, indicated a Gaussian distribution of states with width $\sigma \approx$ 0.1 eV [10]. Other techniques make use of organic thin-film transistor structures to derive the hole DOS using Kelvin probe force microscopy [12]. Finally, electrochemical cyclic voltammetry (CV) of conducting polymer and molecular solids films was also interpreted in terms of the electronic DOS [13]. As it is generally observed, the CV of organic films is characterized by broad non-Nernstian signals what is viewed as an indication of the underlying Gaussian DOS common in disordered organic compounds. This relationship was confirmed in the interpretation of CV peaks of polypyrrole [13], and the hole conductor spiro-OMeTAD (chemical name: 2,2'7,7'-tetrakis(N,Ndi-p-methoxyphenyl-amine)-9,9'-spiro-bifluorene) [14]. Recently CV analysis has been improved by including the formation of both polarons and bipolarons taking into account their respective DOS using a polydicarbazole-based conducting polymer [15].

It is known that upon oxidation the total density of holes *x* will be determined by the position of the electrochemical potential (Fermi level) μ . In quasi-equilibrium conditions in an electrochemical set-up, variations of the Fermi level corresponds to changes of the applied potential *U* as $d\mu = -edU$ (here *e* stands for the positive elementary charge) [16]. Therefore the chemical capacitance per unit volume is defined as (for a single-charged carrier) [13]

$$C_{\mu} = e^2 \frac{\mathrm{d}x}{\mathrm{d}\mu} \tag{2}$$

The cyclic voltammetry technique usually monitors the current j(U) as the potential U varies at a constant scan rate, s = dU/dt. At slow enough scan rates and thin films, kinetic processes can be neglected so that the doping of the film practically occurs in quasi-equilibrium conditions. Therefore the current involved is proportional to the chemical capacitance C_{μ} ,

$$j = sLC_{\mu} \tag{3}$$

with *L* being the thickness of the polymer film. Note here that the chemical capacitance in Eq. (2) marks the low-frequency limit of the capacitance extracted from electrochemical impedance measurements (EIS) [17]. This is because EIS technique applies a small perturbation to certain steady state, and conversely CV analysis at slow enough scan rate allows for the polymer charging in quasi-equilibrium conditions. Both techniques are then complementaries. Additionally, the kinetics of doping is extracted from the analysis of EIS and other modulated techniques as well-established by Gabrielli et al. [18–20].

The aim of this work is to examine to what extent the dopinginduced variations of the polaron statistics could explain the observed behavior of the oxidation peak. Namely, it is usually observed by electrochemical analysis of conducting polymer films a CV plateau at potentials higher than that of the oxidation peak. Such CV plateau appears in addition to the broadening of the anodic part of the oxidation peak commented previously. First we analyze general consequences of the doping-induced disordering. In particular, we are going to explore the repercussion of the dipolar disorder model of Eq. (1) on CV signals of standard polypyrrole films. Our intention is to ascertain possible relations between the DOS width broadening caused by the dipolar disorder and the whole shape of the CV oxidation peaks, including the current plateau at high oxidation potentials.

2. Hole density-of-states and chemical capacitance

A brief outline of the model of Ref. [13] for the analysis of CV peaks is in order here, which allows us to interpret the experimental results shown below. The polymer is considered as a collection of conjugated chain segments per unit volume, each containing *m*

monomers. The total density of hole states N_s corresponds to the limit of full oxidation (complete doping). Taking the energy reference at the center of the gap of width 2ε , the energy for extracting an electron is $\varepsilon_v = -\varepsilon$. If a hole is injected, the relaxation of the surrounding environment occurs extremely rapidly. The energy of polaron $-\varepsilon_p$ is lower than the unrelaxed hole ε_v . When the energy of a bipolaron formation $-\varepsilon_b$ is lower than that necessary to create two polarons ($2\varepsilon_p > \varepsilon_b$), i.e. the bipolarons are energetically favored, polymer oxidation and consequently CV analysis are simply determined by the bipolaron statistics. In which case CV exhibits a unique peak. The opposite case $2\varepsilon_p < \varepsilon_b$, the formation of energetically favored polarons gives rise to pairs of CV peaks determined by polarons, respectively [15].

Assuming single occupancy of the hole states, all with a unique energy ε_0 the carrier density (doping level) is given by

$$x(\mu) = N_{\rm s} f(\mu, \varepsilon_0) \tag{4}$$

Here *f* is the Fermi-Dirac function

$$f(\mu, \varepsilon_0) = \frac{1}{1 + \exp((\varepsilon_0 - \mu)/k_{\rm B}T)}$$
(5)

where $k_{\rm B}T$ corresponds to the thermal energy. The energy disorder common for organic conductors is usually modeled by means of Gaussian DOS with mean energy ε_0 and width σ ,

$$g(\varepsilon) = \frac{N_{\rm s}}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(\varepsilon - \varepsilon_0)^2}{2\sigma^2}\right]$$
(6)

The carrier density results as

$$x(\mu) = \int_{-\infty}^{+\infty} g(\varepsilon) f(\mu, \varepsilon) d\varepsilon$$
(7)

and the chemical capacitance in Eq. (2) results for single-charged carriers in

$$C_{\mu} = e^{2} \int_{-\infty}^{+\infty} g(\varepsilon) \frac{\mathrm{d}f(\mu,\varepsilon)}{\mathrm{d}\mu} \mathrm{d}\varepsilon$$
$$= \frac{e^{2}}{k_{\mathrm{B}}T} \int_{-\infty}^{+\infty} g(\varepsilon) f(\mu,\varepsilon) [1 - f(\mu,\varepsilon)] \,\mathrm{d}\varepsilon$$
(8)

Assuming that the holes follow the zero-temperature Fermi distribution the overall result is that the chemical capacitance monitored by cyclic voltammetry is proportional to the density-of-states, and then it reflects the Gaussian shape of the DOS [13]

$$C_{\mu} = e^2 g(-\mu) \tag{9}$$

This last approximation strictly holds in case of high (x > 0.1) doping level [15], while for $x < 10^{-2}$ the chemical capacitance diverges from the DOS shape because the mean energy of the holes turns out to be independent of the Fermi level. In this low-doping limit the holes thermalize in the Gaussian tail with an average energy $\sigma^2/k_{\rm B}T$ above the mean.

3. Hole density-of-states broadening

As shown in the previous section, Eq. (9) links the capacitance and the DOS distribution function. For the Gaussian DOS function [Eq. (6)] one would expect to observe the capacitance curve symmetrical with respect to the oxidation peak. However in reality the peak is followed by a rather broad plateau. Based on Eq. (9) it would seem reasonable to assume that the DOS function is not Gaussian. On the other hand, experimental analysis reveals significant modifications of the film morphology in the course of doping [21]. This suggests that the DOS could depend either on μ or on the doping level $x(\mu)$. In this case one has to deal with a conditional probability

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Fig. 1. Capacitance C_{μ} (from Eqs. (13) and (14)) as a function of the electrochemical potential μ at different degrees of disorder: Gaussian with $\varepsilon_0 = 0$, $\sigma_0 = 0.2$, smooth disorder $\varepsilon_0 = -0.22$, $\sigma_0 = 0.2$, $\Delta = 0.5$, $\delta = 0.5$, sharp disorder $\varepsilon_0 = -0.22$, $\sigma_0 = 0.3$, $\Delta = 0.5$, $\delta = 0.2$. All quantities are dimensionless.

distribution $g(\varepsilon|\mu)$ (or $g[\varepsilon|x(\mu)]$). The carrier density of Eq. (7) then becomes

$$x(\mu) = \int_{-\infty}^{+\infty} g(\varepsilon | \mu) f(\mu, \varepsilon) \,\mathrm{d}\varepsilon \tag{10}$$

Differentiating we obtain for the capacitance

$$C_{\mu} = e^{2} \int_{-\infty}^{+\infty} g(\varepsilon|\mu) \frac{\partial f(\mu|\varepsilon)}{\partial \mu} d\varepsilon + e^{2} \int_{-\infty}^{+\infty} \frac{\partial g(\varepsilon|\mu)}{\partial \mu} f(\mu|\varepsilon) d\varepsilon \quad (11)$$

In comparison to the previous section [Eq. (8)] we have an additional term that reflects the doping-induced modification of the random film environment. Taking again the zero-temperature approximation for $f(\mu|\varepsilon)$ we obtain an analog of Eq. (9)

$$C_{\mu} = e^{2}g(-\mu|\mu) + e^{2}\int_{-\mu}^{\infty} \frac{\partial g(\varepsilon|\mu)}{\partial \mu} d\varepsilon$$
(12)

Now the shape of the capacitance curve depends not only on the functional form of the energy distribution but also on its dependence on the electrochemical potential μ . Therefore, we may expect a non-Gaussian behavior of $C(\mu)$ even if $g(\varepsilon|\mu)$ is Gaussian (as a function of ε). Let the distribution be of the Gaussian form [Eq. (6)] with a width depending on μ as $\sigma = \sigma(\mu)$. Then from Eq. (12) we arrive at

$$C_{\mu} = e^{2}g(-\mu|\mu) \left[1 - \frac{\mu}{\sigma(\mu)} \frac{\partial \sigma(\mu)}{\partial \mu} \right]$$
(13)

In order to deal with this equation we have to define a $\sigma(\mu)$ dependence. There could be various mechanisms of the broadening (the film morphology or/and polymer conformation variations, formation of traps and disordered dipolar type arrays, etc.). For the moment, without resorting to a concrete model one can easily imagine that the width varies smoothly from some initial value σ_0 at low-doping level ($\mu \rightarrow -\infty$) to some final value $\sigma_0 + \Delta$ corresponding to a saturation ($\mu \rightarrow +\infty$). This can be modeled as

$$\sigma(\mu) = \sigma_0 + \frac{\Delta}{2} \left(1 + \operatorname{erf}\left[\frac{\sqrt{2}}{2\delta}(\mu + \mu_0)\right] \right)$$
(14)

where Δ controls the magnitude of the width variation, δ determines the smoothness and the point of inflection is given by μ_0 . It should be noted that the results are not sensitive to the specific functional form chosen for $\sigma(\mu)$, provided that the essential details of this "sigmoidal" shape (asymptotics and inflection points) are reproduced in a qualitatively similar way.

In Fig. 1 one can observe some of the possible expected behaviors of C_{μ} depending on the functional parameters. Namely the broadening is reproduced as a superposition of two processes. One is governed by the low-doping distribution of states (nearly Gaussian) around the mean energy level ε_0 , the other involves the dopinginduced fluctuations (due to increasing $\sigma(\mu)$) displaced at $\mu = \mu_0$. Increasing the sharpness of the $\sigma(\mu)$ variation (decreasing δ) transforms the plateau into a second peak. It should be noted that the second peak has not been observed in experiments on polymer films in which only one electronic species is involved. This suggests that either the two processes are weakly separated ($\varepsilon_0 \approx \mu_0$) or the width $\sigma(\mu)$ varies rather smoothly, probably even without a clear inflection, as in the dipolar disorder models considered below and introduced in Eq. (1).

A more complicated situation arises if the DOS function depends on the doping level, i.e. $g[\varepsilon|x(\mu)]$. In that case we have to solve for the doping level

$$\mathbf{x}(\mu) = \int_{-\infty}^{+\infty} g[\varepsilon | \mathbf{x}(\mu)] f(\mu | \varepsilon) \,\mathrm{d}\varepsilon$$
(15)

Note that we deal here with a feed-back effect [22]. Namely, the doping level depends on the energetic disorder and vice versa. Some interesting consequences of such a host-guest coupling have recently been analyzed [22,23]. In particular, it has been demonstrated that negative average compressibility states can be stabilized. In our case the capacitance has the following form

$$C_{\mu} = e^{2} \frac{\int_{-\infty}^{+\infty} g[\varepsilon|\mathbf{x}(\mu)] (\partial f(\mu|\varepsilon)/\partial \mu) d\varepsilon}{1 - \int_{-\infty}^{+\infty} (\partial g[\varepsilon|\mathbf{x}(\mu)]/\partial \mathbf{x}(\mu)) f(\mu|\varepsilon) d\varepsilon}$$
(16)

The numerator is the average conditional capacitance and therefore is strictly positive from the thermodynamic stability conditions. All possible traces of the phase transitions, for instance polaron–polaron attractive interactions, resulting from Eq. (16) are related to its numerator representing the average density fluctuation. In what follows $f(\mu|\varepsilon)$ is taken to be the Fermi distribution (non-interacting fermions) that does not take into account possible interactions among the charge carriers. In contrast, nothing prevents the denominator from being zero or even negative. This is not related to phase transitions or system instability. This is a consequence of the feed-back effect that vanishes when the disorder distribution becomes independent of the doping level. A detailed analysis of the electrochemical phenomena, in particular the class of functional dependences $x(\mu)$ of consistent physical meaning, which could result from such a coupling is left for a future study.

For technical purposes we take again the zero-temperature approximation for the Fermi distribution $f(\mu|\varepsilon)$ obtaining from Eqs. (15) and (16) the following

$$\mathbf{x}(\mu) = \int_{-\mu}^{\infty} g[\varepsilon | \mathbf{x}(\mu)] \,\mathrm{d}\varepsilon \tag{17}$$

$$C_{\mu} = e^{2} \frac{g[-\mu|x(\mu)]}{1 - \int_{-\mu}^{\infty} (\partial g[\varepsilon|x(\mu)] / \partial x(\mu)) d\varepsilon}$$
(18)

Let the distribution be again of the Gaussian form [Eq. (6)] with a doping dependent width $\sigma[x(\mu)]$. Then Eq. (17) becomes

$$x(\mu) = \frac{1}{2} \left[1 + \operatorname{erf} \left[\frac{\sqrt{2}(\mu + \varepsilon_0)}{2\sigma[x(\mu)]} \right] \right]$$
(19)

In order to calculate the capacitance curves we have to specify how the width $\sigma[x(\mu)]$ depends on the doping level $x(\mu)$. As discussed in Section 1, in this work we consider dipolar disorder models with the Gaussian width

$$\sigma[x(\mu)] = \sigma_0 \sqrt{1 + a[x(\mu)]^{\beta}}$$
⁽²⁰⁾

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which corresponds to the notation of Eq. (1) as $a = (kP/E\sigma_0\gamma^2)^2$ and $\beta = 2\alpha$. In the next section the theoretical predictions coming from Eqs. (18) and (20) are tested against the experimental data for polypyrrole films.

4. Experimental

Experiments consisted in the electrochemical doping of polypyrrole films which were synthesized galvanostatically onto a Pt sheet ($\sim 1 \text{ cm}^2$ of active area in both cases) using acetonitrile (Baker, high purity grade), with 2% of water content, as solvent, 0.1 M LiClO₄ (Aldrich, >95% content) as electrolyte, and 0.1 M pyrrole (Merck) previously distilled as monomer. Constant current densities of $0.4 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ were employed yielding after a sharp maximum a constant voltage near 0.75 V vs. Ag/AgCl reference electrode at room temperature. Polypyrolle films were prepared in the oxidized state by using polymerization charges within the range of 60-120 mC cm⁻² yielded estimated film thickness of \sim 120–240 nm. Then films were removed from the solution and washed in distilled water, dried in air and transferred to a solution of 0.1 M LiClO₄ in propylene carbonate (Merck, >99% content) in which electrochemical CV experiments were performed. Acetonitrile, lithium perchlorate and propylene carbonate were used as received.

The polymer films deposited onto Pt substrates made up the working electrodes, Pt sheet was used as counter electrode, and Ag/AgCl electrode as reference. For the electrochemical experiments, the solutions were deoxygenated by dry nitrogen flow through the solution maintained 30 min prior and over the experiments. All the experiments were performed at room temperature. Cyclic voltammetry was performed using a potentiostat–galvanostat AutoLab PGSTAT30 equipment with a slow enough scan rate to avoid kinetic limitations [17].

As observed in Fig. 2 the oxidation peak exhibits the typical shape: the current density as a function of the electrode potential shows a broadened peak which tends to form a plateau at higher oxidation potentials >0.3 V. It should be noted here the potential shift between oxidation and reduction peaks which is attributed to the so-called redox hysteresis. Several explanations have been proposed for polymer redox hysteresis: effects of local rearrangements of polymer chains [24], electron–ion interaction contribution to the statistics of species involved in the charging–discharging process [25], and influence of the low conductivity of the film at the beginning of the anodic process [26]. Conventional rate–limiting mechanisms such as diffusion or slow

interfacial transfer kinetics may produce the mentioned potential difference between oxidation and reduction peaks, but under slow enough potential sweeping their effect can be safely discarded. Disorder induced during the film preparation has great influence on the actual potential shift observed by CV. For instance, galvanostatically electrodeposited polypyrrole films using low current densities ($\sim 80 \ \mu A \ cm^{-2}$) did not exhibit redox hysteresis [27]. However, for the films prepared in this study electropolymerization current was high enough (0.4 mA cm⁻²) to induced great disordered layers and promoting strong coupling between charge carriers and the disordered polymer host.

5. Results and discussion

The broadening effect of the left part of the oxidation peak was previously accounted for in terms of the Gaussian DOS (independent of the doping level) [13]. Here we are concerned with an explanation of the whole CV response which considers the effect of the dipolar broadening of the DOS in the course of doping.

The experimental data are fitted using Eqs. (18)–(20) for the separated point charges model (β = 4/3) and the point dipoles model (β = 1). As expected from our general theoretical analysis, both models predict the oxidation peak broadening at positive potentials as a result of the disordering (increasing $\sigma[x(\mu)]$) in the polaron energy distribution (Fig. 3). In the low-doping domain (negative potentials) the behavior is almost purely Gaussian, as analyzed in previous works [13]. It is seen that both models are only in a qualitative agreement with the experiment. This last observation might suggest that a sharp dependence of $\sigma(\mu)$ instead of the smooth variation in Eq. (20) has take place. Instead we are inclined to think that a variety of effects act simultaneously which gives a complex scenario of the conducting polymer oxidation at high level doping. Particularly influencing are structural changes that conducting polymer matrices undergo during doping.

Nevertheless it could be illustrative to explore the validity of the parameters of disorder models appearing in Eq. (1) extracted from the fittings in Fig. 3. The values of the fitted parameters for the point dipoles model (β =1) are ε_0 =-0.10V vs. Ag/AgCl, σ_0 =0.22 eV, and *a*=2.5. For the point charges model (β =4/3) we obtain ε_0 =-0.15V vs. Ag/AgCl, σ_0 =0.25 eV, and *a*=4. The total density-of-states results in both cases equal to N_s =2 × 10²² cm⁻³ which gives an average distance between sites γ =3.7 Å. Tacking into account that this value is of the order of the size of the pyrrole ring, it is derived that N_s effectively corresponds to the total



Fig.2. Stable cyclic voltammograms of polypyrrole films in a solution of 0.1 M LiClO₄ in propylene carbonate onto Pt substrate and 120 mC cm⁻² of polymerization charge. Scan rate was 50 mV s⁻¹.



Fig. 3. Comparison between experimental and model predictions in case of Gaussian, point dipoles model (β =1, ε_0 =-0.10 V vs. Ag/AgCl, σ_0 =0.22 eV, and a=2.5); and point charges model (β =4/3, ε_0 =-0.15 V vs. Ag/AgCl, σ_0 =0.25 eV, and a=4). The total density-of-states results in both cases equal to N_s =2 × 10²² cm⁻³.

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hole density. Assuming that the polypyrrole dielectric constant is $E \approx 3$, one can readily calculate the dipolar moment of the polymer/dopant complex (P⁺:A⁻) *P* in Eq. (1) which results in *P*=2.0 D (for β = 1) and *P*=6.7 D (for β = 4/3). Both models predict a low dipolar moment value which implies distances between Ppy⁺ and the ClO₄⁻ counterions of 0.4 Å and 1.4 Å, respectively. These last distances clearly indicate that the doping ions are in fact tightly packed to the polypyrrole segments, as expected for small size counterions like ClO₄⁻.

6. Conclusions

We have studied the role of the doping-induced modifications in the polaron statistics from the shape of voltammograms observed in films of conducting polymers. It is shown that the broadening of the oxidation peaks, commonly detected in such systems, can be explained as a result of the doping-induced disordering of the polaron energy distribution. This is coherent with the experimental observations of the changes in the films morphology upon the doping [21]. Theoretical predictions, based on the separated point charges and the point dipoles models, have been tested against the experimental results on polypyrrole films on Pt substrates. Theoretical predictions are in qualitative agreement with the experimental data. Interestingly both models give quite similar results concerning the dipole moment associated to polymer/dopant complex.

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