Polymer-film Formation on the Surface of a Cathodically Polarized Nickel Electrode in the Presence of 4-Chlorostyrene

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The formation of a polymer film obtained by cathodic polarization of a nickel electrode in the presence of 4-chlorostyrene has been studied for the first time. The different steps of the process were followed through the combined use of electrochemical analytical methods with surface-sensitive spectroscopy (AES and ESCA), ellipsometry, and IR and UV–VIS spectroscopy. The experimental results obtained show the development of two parallel phenomena leading to the formation of a film on the surface of the electrode and to the occurrence of chemical reactions in solution coupled to a charge transfer to the monomer. All the film-formation processes appear to be retarded by the stability of the reaction intermediates (resonances of the carbanion charge due to the aromatic ring). Attempts have been made to correlate these results with preliminary quantum-mechanical calculations carried out on the neutral monomer molecules. The development of parasitical reactions corresponding to the loss of the chlorine atom is also observed. The reactions take place concurrently on the polymer backbone, at the surface and in solution.

The elaboration of polymer films on metals modifies the metal-surface properties and can lead to new materials with potential applications in highly demanding scientific and technological fields (electronics, catalysis, biotechnology, space, *etc.*). As it has already been applied to obtain various polymeric systems, electrochemistry is an obvious methodology for this type of synthesis. In most cases the films were obtained on noble metals anodes,[1–3] while in our laboratory we have developed a technique of formation of polyacrylonitrile (PAN) films on oxidizable metal (Fe, Ni) cathodes,[4] but at the expense of very stringent experimental conditions. These films are homogeneous, adhesive, and chemically pure.[5,6] Studies on the preparation conditions have been reported and reaction mechanisms have also been proposed.[7,8] The monomers considered and results obtained until now are too limited, however, to claim that a definite understanding of the phenomena as well as a real command of the technique have yet been reached.

There are different ways of improving our understanding of the mechanisms of the electrochemical synthesis based on cathodic polarization. For instance, one could choose to experiment further on the preparative conditions imposed in the formation of polyacrylonitrile films. However, this would only enable that particular synthesis to be perfected without providing more general information as to the conditions on the properties (*e.g.* dipole moment, polarizability, volume of substituted functional groups, *etc.*) and the nature of its reactive site (*e.g.* the nature of the reactive function involved in the polymerization) that make a monomer suitable for this type of electrochemical synthesis. Attempts to carry out the electrochemical synthesis with monomers different from acrylonitrile are thus worth pursuing in order to identify with more certainty these essential molecular attributes.

Here we report the results of a preliminary study on the electrochemical polymerization of *p*-chlorostyrene (PCS). Electrochemical data are reported together with the results on (*a*) the characterization of the film by Auger (AES), ellipsometry, X-ray photoelectron (XPS), and infrared (IR) spectroscopy, and (*b*) attempts to identify by IR and UV–VIS measurements the reactive species and the products present in solution. Some of the mechanisms likely to occur during the synthesis are discussed.

The Monomer.—Up to now and to our knowledge, only two monomers, acrylaldehyde $CH_2{=}CH(CHO)$[9] and acrylonitrile $CH_2{=}CH(CN)$,[4–8,10] have been reported to form films on oxidizable metal cathodes. So far, acrylaldehyde has only been the subject of a single study and thus, in the context indicated in the introduction, would naturally deserve further investigation. However, in this work we chose to report an initial attempt to polymerize *p*-chlorostyrene (PCS) using the same procedure that has proved successful for acrylonitrile. This choice of PCS is motivated both by the similarities and differences with the previously considered acrylonitrile and acrylaldehyde monomers.

Among the features considered to be important for a vinylic monomer to undergo ready electrochemical polymerization based on cathodic polarization, is the presence of a polar, electron-attracting group which confers a permanent electric dipole moment. This dipole moment is thought to be responsible for the proper orientation of the monomer as it approaches the cathode. As inferred from the previous cases, *i.e.* acrylonitrile and acrylaldehyde, this polar group should also be conjugated with the C=C double bond (vinylic moiety). Those structural and electronic properties are required for a stable carbanion (negative charge on the α carbon) to form during the electrophilic reaction of the β carbon with the cathode surface.

Table 1. Relevant bond distances (r_i) and angle (A) of molecules (*a*)–(*f*); equlibrium geometries optimized at the STO-3G level (lengths in Å, angles in degrees). The net atomic charges (q_i), dipole moment p (D), HOMO and LUMO energies (eV) are calculated at the 3-21G level using the STO-3G equilibrium geometries. The angle α measures the orientation of the dipole moment with respect to an axis common to all structures.

Molecules	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)
r_1	1.315	1.312	1.307	—	1.318	1.313
r_2	1.460	1.510	—	—	1.496	1.497
r_3	—	—	—	1.387	1.395	1.396
r_4	—	—	—	1.387	1.396	1.396
r_5	—	—	—	1.387	1.384	1.384
r_6	—	—	—	1.387	1.385	1.385
r_7	—	—	—	1.389	1.386	1.389
r_8	—	—	—	1.389	1.386	1.388
r_9	—	—	1.777	1.784	—	1.783
r_{10}	1.157	—	—	—	—	—
r_{11}	—	1.221	—	—	—	—
A	122.9	122.4	122.7	119.4	124.8	126.8
$q_{\text{C-1}}$	−0.36	−0.38	−0.38	—	−0.42	−0.41
$q_{\text{C-2}}$	−0.21	−0.36	−0.46	—	−0.20	−0.19
$q_{\text{C-3}}$	0.29	0.35	—	−0.24	−0.10	−0.10
$q_{\text{C-4}}$	—	—	—	−0.23	−0.23	−0.22
$q_{\text{C-5}}$	—	—	—	−0.23	−0.22	−0.21
$q_{\text{C-6}}$	—	—	—	−0.19	−0.23	−0.18
$q_{\text{C-7}}$	—	—	—	−0.19	−0.23	−0.18
$q_{\text{C-8}}$	—	—	—	−0.35	−0.24	−0.35
q_{Cl}	—	—	0.05	0.13	—	0.13
q_{N}	−0.51	—	—	—	—	—
q_{O}	—	−0.54	—	—	—	
$\lvert p \rvert$	4.09	3.45	2.32	2.57	0.09	2.64
α	6.9	46	7	0.0	−155	1.5
$\varepsilon_{\text{HOMO}}$	−10.80	−10.88	−10.44	−9.42	−8.21	−8.68
$\varepsilon_{\text{LUMO}}$	2.86	2.61	4.30	3.49	3.05	2.60

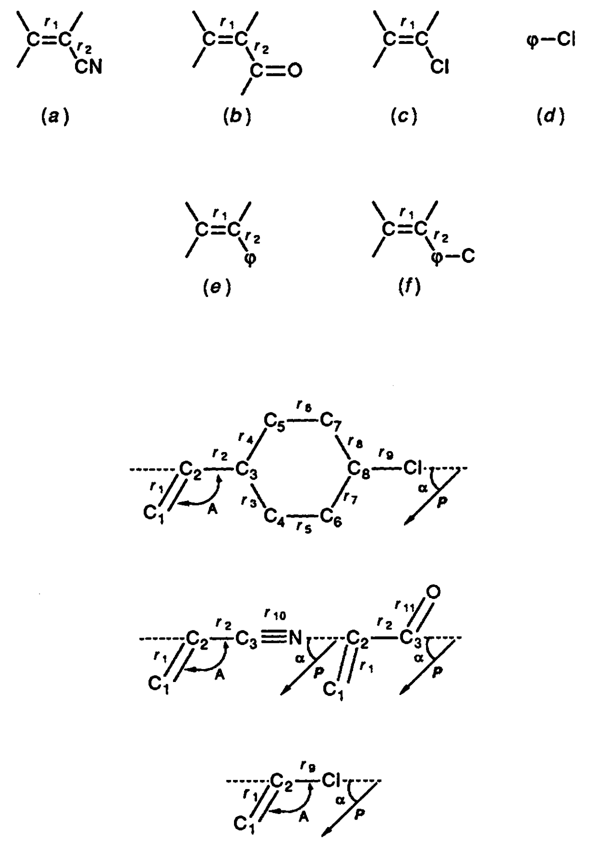

Figure 1. Labelling convention used to identify the parameters given in Table 1 for the molecules considered in this work.

During the polymerization steps, the negative charge sits on the reactive end of the growing chain which is subject to attack from the approaching monomers. All these molecular attributes are present in PCS.

In PCS, however, there are differences the effects of which on the course of the synthesis cannot be inferred from our present knowledge which require further study in order to be used predictively regarding the nature of potential candidate monomers. The first unknown is the volume effect (steric obstacles to the chain growth) of the chlorophenyl group compared with the somewhat smaller nitrile (–CN) and aldehyde (–CHO) functions. The second question relates to the aromatic character of this group which by its different ability to accommodate an additional electron charge can influence the course of the reaction and the quality of the final material (chemical nature and film structure).

It is thus instructive to compare some of the intrinsic structural and electronic (atomic charges, dipole moment, HOMO and LUMO energies) characteristics of related molecules such as acrylonitrile, acrylaldehyde, chloroethylene, styrene, chlorobenzene, and PCS [Figure 1(*a*)–(*f*)]. Because most of the geometrical data were readily available at the STO-3G level from reference 11 and references therein, we have chosen to compare the structural trends in all molecules (*a*) to (*f*) at this particular level of the theory. The STO-3G results on chlorobenzene are taken from reference 12. As we could not find the corresponding information for styrene and *p*-chlorostyrene, we computed their optimized geometry at the STO-3G level. The absolute values of STO-3G geometrical parameters are known to depart somewhat from experiment, but the structural trends in a series of related molecules are usually accurately predicted.[11] The other quantities of interest (net atomic charges, overlap populations, dipole moment, HOMO and LUMO levels) were computed at the 3-21 G level using the STO-3G

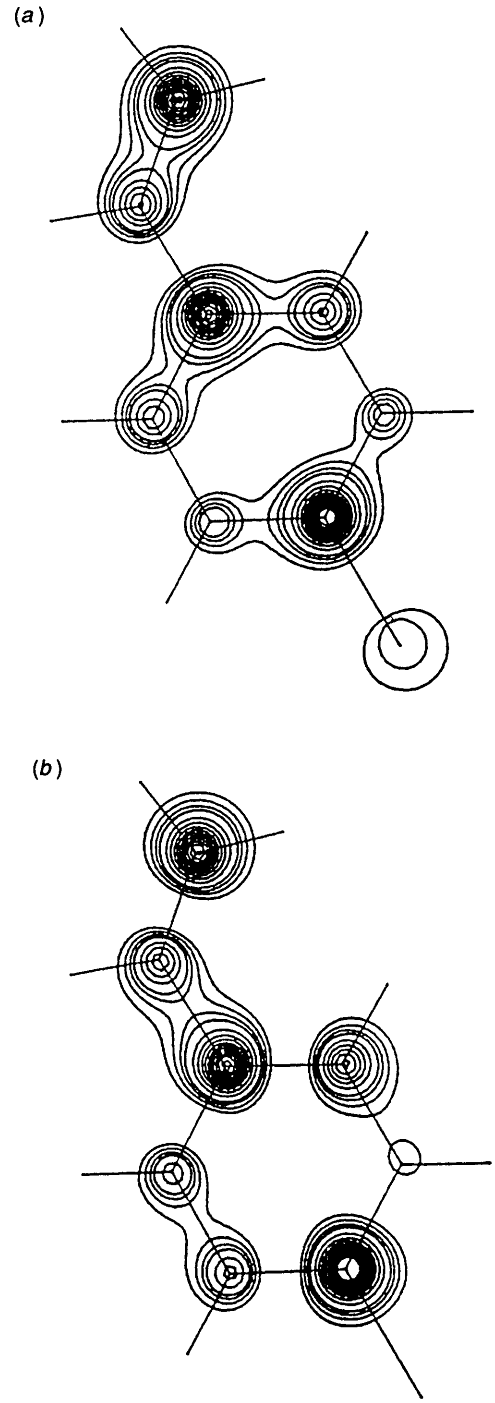

Figure 2. Electronic isodensity contours in a parallel plan of the PCS molecule: (*a*) HOMO; (*b*) LUMO.

equilibrium geometry. The results are listed in Table 1 according to the convention shown in Figure 1.

We first compare the structure of the vinylic moiety in molecules that incorporate it. Except for chloroethylene (*c*) in which the positive net atomic charge on chlorine ($q_{Cl} = 0.05$) indicates a net electron transfer towards the vinyl group, the C=C bond is generally longer than the corresponding double bond in ethylene (1.306 Å at the STO-3G level[11]). This can be interpreted as an overall movement of electrons from the C=C bond towards the electron-attracting substituents $-C{\equiv}N$ and $-HC{=}O$. This also holds in the case of styrene (1.318 Å) and *p*-chlorostyrene (1.313 Å). The shorter C=C distance of the vinylic moiety in *p*-chlorostyrene probably results from the competing electron donation between the vinyl and the chlorine substituents on the phenyl ring. The overall electron transfer from the vinyl group to the phenyl ring is thus less effective in *p*-chlorostyrene than in styrene. The electron-donating character of chlorine is reflected by a positive net atomic charge on Cl, (*ca.* 0.13) and a shorter C–Cl distance [1.784 and 1.783 Å in (*d*) and (*f*), respectively] in these conjugated structures as compared with a net negative charge (*ca.* −0.04) and a longer C–Cl distance (1.802 Å at the STO-3G level[10]) in the saturated chloromethane, $H_3C{-}Cl$.

In spite of its more elongated shape compared with acrylonitrile, *p*-chlorostyrene exhibits a smaller dipole moment (2.64 *vs.* 4.09 D* at the 3-21G/STO-3G level); this is partly due to opposing charge-transfer effects which prevent the separation of opposite charges across the whole nuclear framework. The calculated charge pattern is thus consistent with this somewhat low dipole moment. In the absence of an electric field (*e.g.* the electric field double layer and the reacting fields close to the cathode surface) the negative charge (−0.41) on the terminal carbon C-1 is larger than on C-2 (−0.19) as already noted in the case of acrylonitrile .[13] Thus unfavourable polarity does not preclude the possibility of the CH_2 vinylic end acting as the reacting site of the monomer with the cathode. Indeed, calculations on acrylonitrile[13,14] have shown an enhancement of the electrophilic character of the terminal CH_2 group with increasing electric field. Electric-field calculations are planned for PCS to verify this hypothesis, but it is almost certain that the same behaviour as observed for acrylonitrile will be obtained. The tilt angle α between the dipole-moment direction and an axis common to all molecules shown in Figure 1 is larger in acrylonitrile than in *p*-chlorostyrene (6.9 and 1.5°, respectively). This is partly attributable to geometrical factors, the angle *A* being larger (126.8°) in *p*-chlorostyrene than in acrylonitrile (122.9°). Finally, note the reversed direction of the dipole moment in styrene which is also consistent with the above discussion.

The 3-21G/STO-3G electron charge distributions of the HOMO [Figure 2(*a*)] and LUMO [Figure 2(*b*)] reveal patterns of substantial delocalization required to stabilize the electron charge transferred during the heterolytic bond breakage of the HOMO involved in the polymerization process. At this point this is only conjecture based on the features of the neutral reactant; more refined calculations on model anionic species are needed to elucidate the possible reorganizations in both the electron-charge distributions and molecular structures. Also of interest, the PCS HOMO is significantly shifted towards higher energy values (−8.68 instead of −10.80 eV† for acrylonitrile) and its LUMO energy is comparable to that of acrylonitrile.

This preliminary theoretical analysis of monomer molecules highlights the fact that, in spite of having electronic characteristics similar to acrylonitrile (a vinylic group conjugated to a polar group), PCS exhibits essential differences that are likely to affect the course of the synthesis of the polymer and the resultant material, namely, larger monomer size, smaller dipole moment, higher HOMO energy, and electron-donating character of the chlorine atom attached to the phenyl ring.

Experimental

The synthesis was carried out according to our previous methodology for the polymerization of AN. To avoid proton

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* 1 D = 3.335 64 × 10^{-50} C m.

† 1 eV = 1.602 18 × 10^{-19} J.

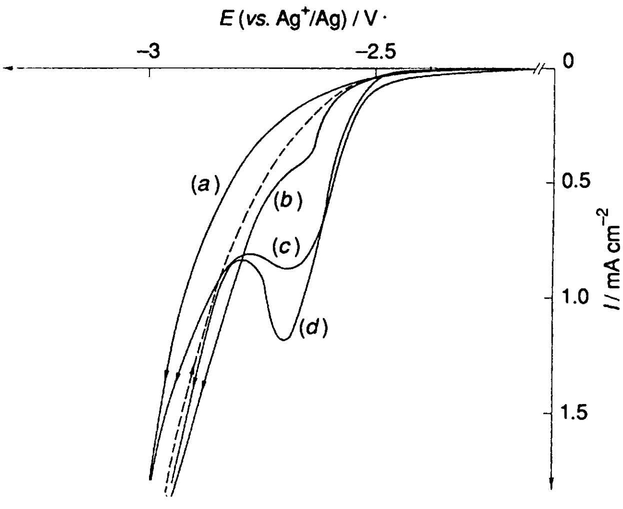


Figure 3. Voltage–intensity curves (cathodic curve) recorded for low PCS concentrations (10^{-3} to 10^{-2} mol dm^{-3}): (*a*) reference curve without monomer; (*b*) forward and return curves [PCS] = 1×10^{-3} mol dm^{-3}; (*c*) forward curve [PCS] = 5×10^{-3} mol dm^{-3}; (*d*) forward curve [PCS] = 1×10^{-2} mol dm^{-3}. Sweep velocity 5 mV s^{-1}.

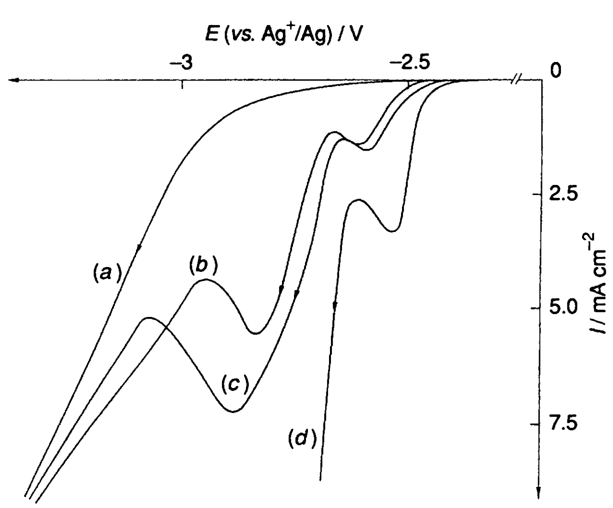


Figure 4. Voltage intensity curves (cathodic curve) recorded for high PCS concentrations (5×10^{-2} to 0.5 mol dm^{-3}): (*a*) reference curve without monomer; (*b*) [PCS] = 5×10^{-2} mol dm^{-3}; (*c*) [PCS] = 1×10^{-1} mol dm^{-3}; (*d*) [PCS] = 0.5 mol^{-1} dm^{-3}. Sweep velocity 5 mV s^{-1}.

reduction, which could inhibit the process, the reaction medium was rigorously dried prior to the polymerization. An aprotic solvent (acetonitrile) was used, the cation of the supporting electrolyte (tetraethylammonium perchlorate) being characterized by a low degree of solvation by the residual water. In order to increase the probability of reacting events at the cathode surface, we used a high concentration of monomer in the electrolytic solution.

Preparation of the Reaction Medium.—This is carried out by dissolution of the monomer (concentrations ranging from 10^{-3} to 2.5 mol dm^{-3}) in an electrolytic solution consisting of the aprotic solvent, acetonitrile, and the supporting electrolyte, tetraethylammonium perchlorate (5.10^{-2} mol dm^{-3}). PCS (Aldrich 99%) and acetonitrile (UCB 99.5%) were purified by being stored over molecular sieves (4 Å) (which were renewed) then fractionally distilled under argon at reduced pressure. The amount of water in the distillate was determined by the Karl Fisher method and only the fractions in which the water concentration was less than 5×10^{-4} mol dm^{-3} were retained. The supporting electrolyte (Fluka 99%) was dried by permanent storage at 110 °C under reduced pressure.

Preparation of the Electrode Surface.—Two types of electrode supports were used depending on the tests to be carried out. (*a*) Solid nickel 8 mm diameter disks polished to a particle-size distribution of 1 µm (dynamic potential tests of the PCS behaviour). (*b*) Pyrex glass plates, 2.5 × 2 cm^2 (spectroscopic studies of the electrode surfaces modified by a static potential process).

In both cases, the work surface was obtained by cathodic sputtering of a 1 µm thick surface layer of Marz nickel (99.99%).

Electrolysis Cell.—A standard three-electrode arrangement was used; the auxiliary electrode consisted of a platinum grid and the reference electrode was made using the electrochemical Ag/Ag$^+$ couple. The cell compartments were separated by a fritted glass plate. The electrolytic polarization of the working electrode was carried out by means of a dynamic or a static potential method employing a Tacussel type PRT 30.01 potentiostat controlled by a type UAP4 pulse unit.

Experimental Set-up.—All of the reactant purification and the electrochemical processes were carried out in an assembly of glove boxes in an argon atmosphere. The amounts of residual water vapour and oxygen in the recycled argon were continuously measured and kept at levels of 1 and 5 ppm, respectively, by passage through various purifiers.[15]

Characterization of the Electrode Surfaces.—After the electrochemical treatment, the cathodic surfaces were studied *ex situ* by Auger spectroscopy (JEOL-type ESSM spectrometer), XPS spectroscopy (Vg Escalab MK II spectrometer), and reflection–absorption infrared spectroscopy (Bruker type IFS 66 spectrometer). The thickness of the films were determined by spectroscopic ellipsometry (SOPRA type ES2G ellipsometer). The study of the solutions was carried out by UV–VIS spectroscopy (Varian type Cary 2300 spectrometer) and by infrared transmission spectroscopy.

Results

Electrochemical Behaviour of the Reaction Medium.—The electrochemical behaviour of the PCS was studied by recording the cathodic part of the current–potential curves. The complexity of the phenomena made it necessary to carry out two series of readings as a function of the PCS concentration.

At low PCS concentrations (Figure 3) the curves obtained showed an inhibition peak under cathodic conditions (centred at −2.7 V Ag/Ag$^+$). The examination of the electrochemical parameters: E_p (peak potential), I/C (intensity/concentration ratio of electroactive species), $I/\sqrt{v}$ (intensity/square root of the sweep velocity ratio), shows that E_p does not change with the concentration, that the ratio I/C is constant at a given sweep velocity and that the ratio $I/\sqrt{v}$ is also constant at a given concentration. This behaviour is characteristic of a diffusion-controlled reduction. In addition, the values of the measured potentials correspond to those already observed in the reduction of various vinyl monomers.[16] This observation clearly supports the conclusion of the reduction of the vinylic double bond.

At higher concentrations (Figure 4) two inhibition peaks are observed under reducing conditions. (*a*) The first peak centred at −2.6 V *vs.* Ag/Ag$^+$, previously identified as a diffusion-controlled reduction at low concentrations, became anomalous. Indeed, a careful analysis of the electrochemical parameters, in

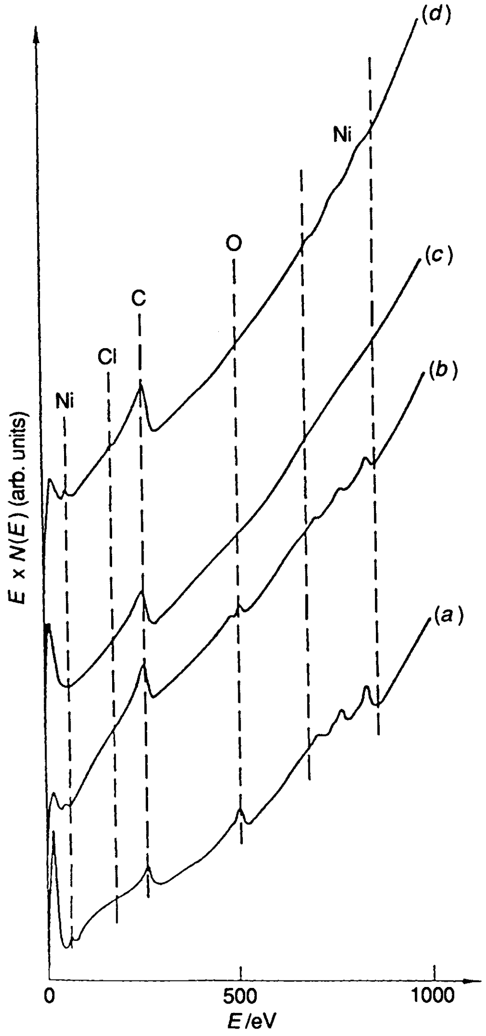


Figure 5. Auger spectra. $E_p = 2.5$ kV; $I_a = 5 \times 10^{-9}$ A. (*a*) initial nickel surface; (*b*) electrochemical process: [PCS] = 0.5 mol^{-1} dm^{-3}, $E = -2.5$ V *vs.* Ag/Ag$^+$, polarization time $t = 1$ min; (*c*) electrochemical process: [PCS] = 0.5 mol dm^{-3}, $E = -2.9$ V *vs.* Ag/Ag$^+$, $t = 1$ min; (*d*) surface (*c*) after controlled ionic abrasion with Ar$^+$, $E = 4$ kV, $I = 9$ μA.

particular the decrease of E_p with *C*, led us to assign this peak to a passivation of the reduction conditions resulting from the modification of the electrode surface due to the formation of a film. (*b*) The second peak, centred at -2.9 V *vs.* Ag/Ag$^+$ corresponds to the diffusion limit for the electroactive species on the modified electrode surface. In all cases, the monotonic decrease of the current density on the return sweep implies the existence of irreversible phenomena.

Characterization of Electrode Surfaces after Cathodic Polarization.—The usual spectroscopic methods for surface analysis (AES, ESCA) were used to carry out the *ex situ* characterization of the films formed on the cathode surfaces. The thickness of these films has been determined by ellipsometry and their molecular structures by infrared reflection–absorption spectroscopy.

Elementary chemical analysis of the films (AES). Taking into account the small values of the mean free path of the Auger electrons (5 Å < λ < 20 Å), this spectroscopic method is appropriate to conduct an elementary qualitative analysis of the outer atomic layers of the sample. In particular, the disappearance of the Auger lines characteristic of the metallic substrate indicates the presence of a surface film. The Auger spectra recorded at different stages of the electrochemical process are shown in Figure 5.

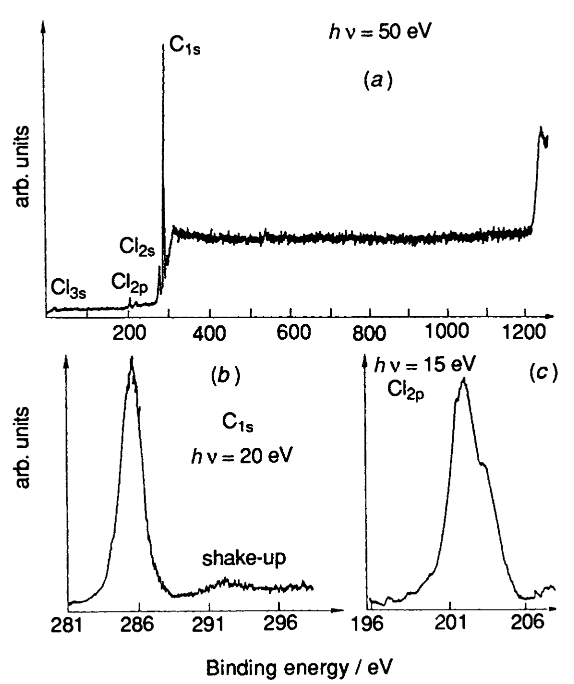


Figure 6. X-Ray photoelectron spectroscopy—electrode surface after electrochemical process. ([PCS] = 0.5 mol dm^{-3}; E(Ag/Ag$^+$) = -2.9 V; $t = 5$ min). (*a*) total spectrum; (*b*) C 1s level; (*c*) Cl 2p level.

In Figure 5(*a*), the spectrum contains, along with the nickel Auger lines, those of carbon and oxygen. They reveal the existence of surface oxides probably contaminated by carbon traces (due to exposure of the electrodes to the laboratory atmosphere before the electrochemical process). The spectrum in Figure 5(*b*) has an appearance similar to that in Figure 5(*a*) thus showing that the surface to be incompletely covered. In the spectrum of Figure 5(*c*) only the carbon Auger line is visible. It has a much higher intensity than the corresponding lines in Figures 5(*a*) and 5(*b*) indicating that the surface is covered by a film. Finally, in Figure 5(*d*), the spectrum was recorded after controlled ionic etching of the surface; it provides the chemical composition of the metal–film interface. The nickel Auger lines are observed again together with those of carbon and chlorine (though with very low intensity in the case of chlorine). The lines of oxygen are absent which means that their corresponding intensities are below the instrument detection threshold. The absence of oxygen in the interface region suggests that an electrochemical reduction of the surface oxide occurred prior to the chemisorption of the monomer molecules and the growth of the film.

Determination of film thickness: spectroscopic ellipsometry. With this method it is possible to monitor any modification (adsorption or growth of an organic film) occurring on the surface of a reference sample (coating of a polymicrocrystalline nickel obtained by cathodic sputtering). The changes in film thickness as a function of the different parameters of the electrochemical process are given in Table 2. It can be seen that the thickness of the films decreases both at high potentials and high concentrations. In all cases, it reaches a limiting value (*ca.* 100 nm) as a function of time. Compared with the results obtained for an acrylonitrile,[15] this constitutes a low growth rate.

Chemical nature of the film (ESCA). The core lines (Figure 6) of ESCA of X-ray photoelectron spectra are a valuable source of information on the environment of the chemically bonded atoms. The full ESCA spectrum [Figure 6(*a*)] of the surface

Table 2. Dependence of the thickness of the films[a] on the electrochemical parameters.

Influence of	Potential E(Ag/Ag$^+$)/V	Electrolysis time/min	Initial conc./ mol dm^{-3}	Charge/C	Film thickness/nm
Potential	−2.6	3	1	3.6	22
	−2.8	3	1	4.5	46
	−2.9	3	1	4.5	54
	−3.0	3	1	4.5	56
	−3.2	3	1	4.5	23
Time	−2.8	1	0.5	1.4	10
	−2.8	2	0.5	2.8	28
	−2.8	3	0.5	4.5	60
	−2.8	4	0.5	5.8	100
	−2.8	6	0.5	8.6	90
Conc.	−2.8	3	0.5	4.5	60
	−2.8	3	1	3.8	46
	−2.8	3	2.5	2.8	41

[a] Measured by reflection on the surface of the modified electrode. Angle of incidence 70°.

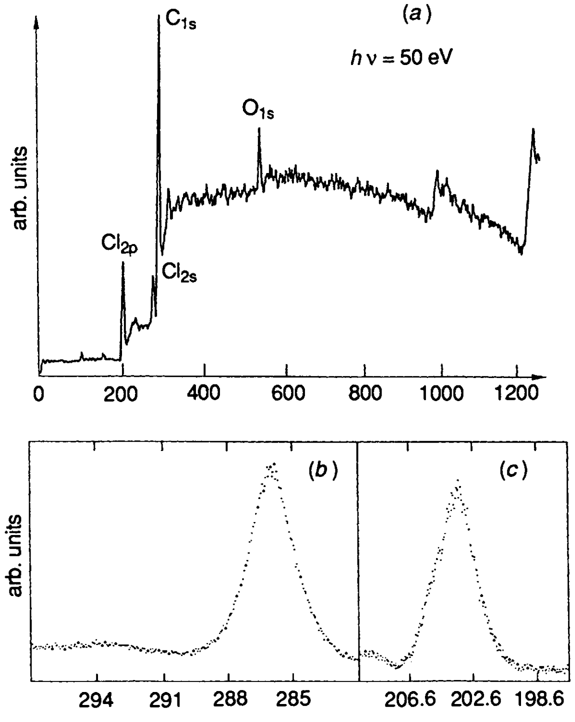


Figure 7. X-Ray photoelectron spectroscopy—poly(4-chlorostyrene) produced by radical reactions: (*a*) total spectrum; (*b*) C 1s level; (*c*) Cl 2p level (the O 1s peak in the total spectrum is due to the type of polymerization of this sample).

Table 3. Dependence of the intensity ratios C 1s/Cl 2p on the conditions of film formation.

	Reference polymer	(PCS) = 2.5 mol dm^{-3}, $E = -2.4$ V, $t = 20$ min, 115 Å, $Q = 2.4$ C	(PCS) = 1.0 mol dm^{-3}, $E = -3.2$ V, $t = 3$ min, 230 Å, $Q = 4.5$ C
C 1s/Cl 2p	3.91	11.47	42.57
Effective ratio[a]	8/1	24/1	88/1
Calculated ratio[b]	8.9/1	26/1	97/1

[a] Calculated from the areas of the photo-peaks. [b] Calculated using the formula:[19]

$$n_a/n_b = \sigma_b/\sigma_a{}^*I_a/I_b$$

where n_a/n_b is the ratio of relative concentrations of elements a and b, I_a/I_b is the ratio of the areas of photo-peaks a and b, and σ_a/σ_b is the ratio of effective cross sections of photo-peaks a and b.

electrode after the electrochemical process shows the presence of lines characteristic of chlorine (Cl 2p, Cl 2s) and of carbon (C 1s). The chemical purity of the sample over a thickness of approximately 50 Å fixed by the escape depth of the emitted photoelectrons is evidenced by the insignificant intensity of the nitrogen N 1s (400 eV) and oxygen O 1s (532 eV) lines, suggesting in particular the absence of contamination (incorporation) of the film by the supporting electrolyte, $(C_2H_5)_4N^+ClO_4^-$.

The details of the carbon 1s and chlorine 2p lines are shown in Figures 6(*b*) and (6(*c*). The presence of a single line centred at 286.1 eV [Figure 6(*b*)] does not allow distinction between different types of carbon in the molecule. On the other hand, the feature at 292.6 eV is attributed to the shake-up phenomenon, *i.e.*, a multielectronic process in which a $\pi \rightarrow \pi^*$ transition of the aromatic ring is induced simultaneously with the C 1s photoelectron emission. Thus, the kinetic energy of the latter is decreased. This phenomenon is already reported in an XPS study of poly(4-chlorostyrene).[17] In Figure 6(*c*) the chlorine 2p lines (Cl $2p_{3/2}$ 202.6 eV, Cl $2p_{1/2}$ 204 eV) show bond-energy values comparable to those found in the literature.[18] Most important to note in the total spectrum [Figure 6(*a*)] is the deficiency of chlorine atoms with respect to the molecular formula of poly(4-chlorostyrene). This reduction in the stoicheiometry of chlorine atoms in the surface film obtained electrochemically was emphasized when XPS spectra of a reference sample of poly(4-chlorostyrene) obtained by radical polymerization were recorded (Figure 7). The comparison of both spectra, Figure 6(*a*) and 7(*a*), indeed shows a significantly higher ratio, I[C 1s]/I[Cl 2p], of the intensities of the C 1s and Cl 2p lines of the polymer obtained electrochemically than in the reference sample obtained by radical polymerization. Inspection of the values summarized in Table 3 reveals a dependence of I[C 1s]/I[Cl 2p] on the electrochemical synthesis parameters (monomer concentration, electrode potential, amount of current passed through the film). The chlorine-atom deficit observed in the polymers obtained electrochemically

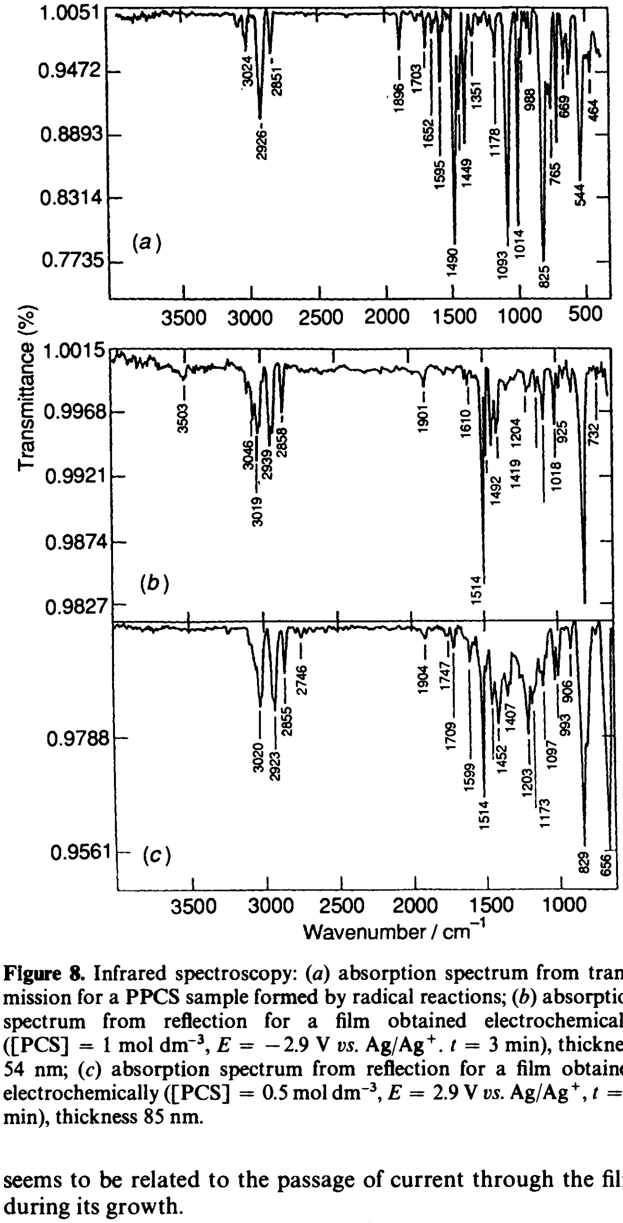


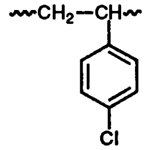
Figure 8. Infrared spectroscopy: (*a*) absorption spectrum from transmission for a PPCS sample formed by radical reactions; (*b*) absorption spectrum from reflection for a film obtained electrochemically ([PCS] = 1 mol dm^{-3}, $E = -2.9$ V *vs.* Ag/Ag$^+$. $t = 3$ min), thickness 54 nm; (*c*) absorption spectrum from reflection for a film obtained electrochemically ([PCS] = 0.5 mol dm^{-3}, $E = 2.9$ V *vs.* Ag/Ag$^+$, $t = 4$ min), thickness 85 nm.

seems to be related to the passage of current through the film during its growth.

Molecular structure (*infrared reflection–absorption spectroscopy*). Infrared measurements were made to determine the possible influence of the electrochemical parameters on the resulting molecular structure of the films. Accordingly, we compared the transmission spectrum of a polymer obtained by the radical process [Figure 8(*a*)] with the IR reflection–absorption spectra of polymer films obtained electrochemically [Figures 8(*b*) and 8(*c*)] under different conditions.

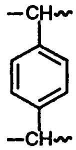
The characteristic bands at 2 940 (asymmetric ν_{C-H} of CH_2), 2 923 (ν_{C-H} of CH), 2 855 (symmetric ν_{C-H} of CH_2), and 1 452 cm^{-1} (scissoring δ_{C-H} of CH_2) in Figures 8(*b*) and 8(*c*) compared with those in Figure 8(*a*), show that the electropolymerized films include polymeric structures characterized by an aliphatic backbone of the type $-(CH_2CHR)_n-$. The existence of a chlorophenyl group is usually signalled by the bands at 3 080, 3 050, and 3 020 cm^{-1} characteristic of the vibrations of the aromatic C–H as well as the bands centred around 1 600, 1 514, 1 492, and 1 410 cm^{-1} characteristic of the stretching vibrations of the aromatic C–C bonds, $\nu_{C=C}$.[20a] The harmonic at 1 900 cm^{-1} and the γ_{C-H} out-of-plane deformation vibration at 825 cm^{-1} are typical of *para*-substitution on the phenyl ring. Most of these features are present in all spectra of Figure 8. The chlorine-atom deficiency already indicated in the ESCA of the electrochemical films can be correlated in the IR spectra by the low relative intensity of the band at 1 095 cm^{-1} attributed to the combination of the bands γ_{C-H} of the *para*-substituted aromatic nucleus and ν_{C-Cl} (X sensitive band; X = halogen).[20b]

Some differences between the spectrum of the reference sample, Figure 8(*a*), and those obtained for the electrochemical polymer films, Figures 8(*b*) and 8(*c*), are worthy of note. The electrochemical polymer samples strongly absorb at 1 514 cm^{-1} while the reference sample absorbs at 1 492 cm^{-1}. Moreover, for the electropolymerized films the band 1 492 cm^{-1} seems to decrease as a function of the amount of current passed through the film during its growth, Figures 8(*b*) and 8(*c*). Let us recall at this point that the absorption band at 1 492 cm^{-1} is attributed to a stretching vibration $\nu_{C=C}$ of the aromatic ring *para*-substituted by an alkyl chain and a chlorine atom and thus likely to correspond to the molecular structure element (**I**).



(**I**)

In the literature,[21] the absorption at 1 514 cm^{-1} is reported to characterize a phenyl ring *para*-substituted by two sp^3 carbon atoms which in our case could very well mean the existence of chains bridged by phenyl rings (**II**).



(**II**)

These points will be further considered, but it is reassuring at this point to note the consistency of ESCA and IR measurements regarding the question of the chlorine stoicheiometry in the electropolymerized films and their dependence on the current passed through the films.

Characterization of the Species Formed in the Cathode Compartment Solution.—The results presented so far relate to the modification of the cathode surface, the main characteristics being a very low growth rate of the polymer film and, compared with an ideal poly(4-chlorostyrene), the presence of alterations in the molecular structure of the film due to loss of chlorine atoms. These results obviously pose the problem of the reactive intermediates and the chemical stability of the functional group φ-Cl in the medium during the electrochemical process.

UV–VIS spectroscopy study of the reaction intermediates. In an attempt to specify the nature of the growth rate of the film, UV–VIS spectroscopic studies of the cathode solution were conducted after electrolysis for different electrode polarization values (Figure 9). To follow the influence of the imposed potential on the reaction medium and thus to specify the nature of the mechanisms, a series of spectra was recorded setting the potential at the half-wave value of the monomer reduction ($E = -2.60$ V *vs.* Ag/Ag$^+$). The spectra in Figure 9(*a*) shows two absorption bands in the visible region at 475 and 410 nm and a shoulder centred at 340 nm next to the characteristic UV absorption region of the monomer (PCS) (293, 283, and 248 nm). These absorptions are typical of different negatively charged species (anions, radical anions, and dianions).[22] The

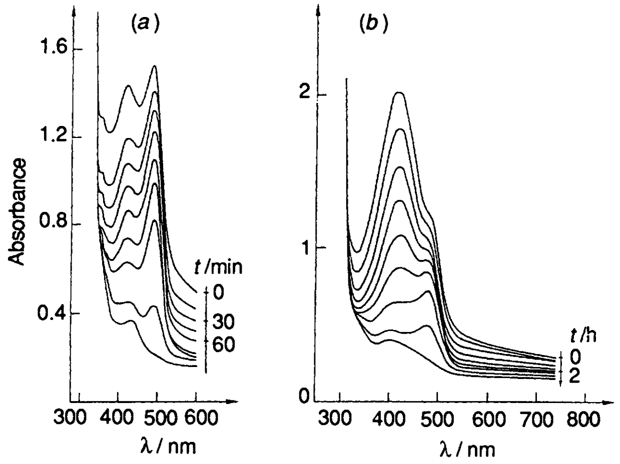


Figure 9. UV-VIS spectroscopy of the cathodic compartment solution after electrolysis (carried out in a closed cell): (*a*) time interval between readings 15 min, spectra obtained after cathodic polarization, $E = -2.6$ V *vs.* Ag/Ag$^+$, [PCS] = 1 mol dm^{-3}, $Q = 1.3$ C; (*b*) time interval between the readings 30 min, spectra obtained after cathodic polarization, $E = -2.9$ V *vs.* Ag/Ag$^+$, [PCS] = 1 mol dm^{-3}, $Q = 1.3$ C.

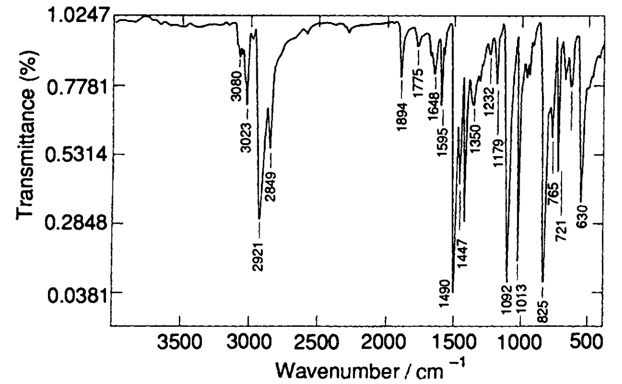


Figure 10. IR transmission spectrum of the polymer formed in the cathodic solution.

anionic nature of the species formed has been verified by recording the absorption spectra of a solution analogous to the previous one, but this time with 5 mm^3 of water added. In this case, the decay kinetics were very rapid and the above-mentioned absorption lines completely disappeared within 1 min. The presence of such species suggests an anionic nature for the polymerization mechanism.[23] This will be further discussed.

In the second series of measurements [Figure 9(*b*)] carried out on the cathode solution with a more negative potential (-2.9 V instead of -2.6 V *vs.* Ag/Ag$^+$), two absorption bands are also present in the visible region at 475 and 410 nm, but in this case they have opposite intensities compared with those recorded at lower potential (-2.6 V *vs.* Ag/Ag$^+$). The formation kinetics of the reaction intermediates thus appear to be dependent on the imposed potential. Tables in reference 22 assign the absorption band at 475 nm to the PCS radical anion (dominant species at low potential). The band at 400–410 nm probably corresponds to a parent anionic species of styrene, and the shoulder centred at 340 nm is indicative of an anion of the 4-chlorostyryl type.[24]

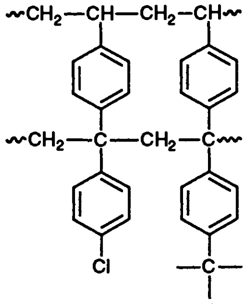
IR transmission spectroscopy study. At the end of the electrochemical process, the cathode compartment solution exhibited a yellow–orange colour which progressively disappeared with time and was replaced by a white deposit. The structural alterations in the grafted films on the cathode surface can obviously be related to some of the reactions (competing, parasitic, *etc.*). occurring in the medium. In the hope of finding clues to this interdependence, the deposit was studied by IR spectroscopy 24 h after its formation. After being rinsed several times with acetonitrile and evaporation in vacuum, the deposit was broken up and dissolved in KBr.

The IR spectrum was recorded in transmission and is shown in Figure 10. With a few exceptions, this spectrum is completely analogous to that of the reference polymer sample obtained by radical polymerization. Differences are in the higher relative intensity of the cluster of lines at 3 000 cm^{-1} ($\nu_{C\text{-}H}$ of CH_2) which are probably indicative of short oligomer chains in a head-to-head configuration.[25] Noteworthy in the spectrum of Figure 10, is that the C–Cl bond vibration (1 092 cm^{-1}) has a relative intensity comparable to that of the reference sample [Figure 8(*a*)] obtained by radical polymerization and thus different from that observed in the spectra of films formed on the cathode surface [Figures 8(*b*) and 8(*c*)]. This structural difference in the materials formed in solution and at the cathode further supports the hypothesis that the charge transfer through the polymer film influences the chlorine atom deficiency in the electropolymerized film.

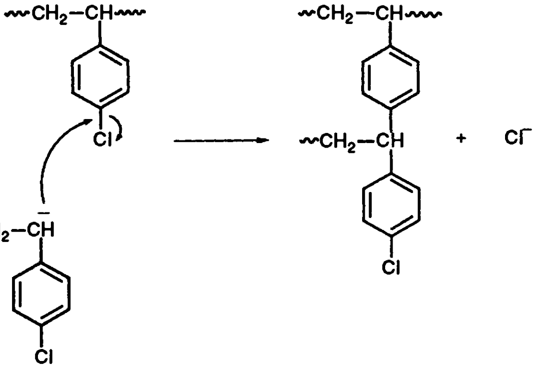
Reaction Mechanisms.—On the basis of the above results we can conclude at the first electrochemical synthesis of a polymer film on the surface of a cathodically polarized electrode in the presence of 4-chlorostyrene, a monomer differing in its molecular and electronic structure from acrylonitrile. We have shown the existence of a secondary electrode reaction which is at the origin of the formation of the polymer film, and, in parallel, a Faradaic transfer to the monomer molecules in solution leading to coupled chemical reactions. The functional group (4-chlorophenyl) carried by the molecule initiates of the slow polymerization and also the reactions leading to the loss of chlorine atoms both from the polymer film and from the molecules that undergo the Faradaic transfer in solution (anionic species derived from styrene). As indicated by various spectroscopic measurements, the electropolymerized film departs somewhat from a poly(4-chlorostyrene) obtained by the classical bulk radical polymerization. To understand these differences as well as to optimize and control future syntheses of polymer films on oxidizable cathodes, the reaction mechanisms should be described in the greatest possible detail. In spite of the limited information available from this first work, we discuss the main reaction mechanisms involved in the electrochemical process and propose a first picture of the synthesis.

Mechanisms of the formation of polymer films on the cathode surface. Under the influence of the electrode polarization a double-layer electric field forms and the surface oxides are reduced. The PCS molecule is oriented according to the direction of the cathode field and its dipole moment: the vinyl end (CH_2) is oriented towards the cathode surface. Closer to the cathode surface, the combined action of the reactive atomic fields and the electron attractive inductive effect of the chlorophenyl group results in a gradual electron depopulation of the CH_2 end. At reactive distances from the cathode, this situation ultimately leads to a chemical bonding interaction between the nickel electrode surface (the oxides of which have been reduced) and the vinyl end of PCS. This chemisorbed PCS molecule reacts subsequently *via* an anionic polymerization process with a new molecule of PCS, oriented and activated as just described, with this new surface to lead (propagation step) to the formation of the polymer.

According to this description of the reaction events at the molecular scale, the structure of the polymer formed should have a regular head-to-tail sequence, characteristic of anionic-type polymerization.[26] Unfortunately, the very low amount of electrodeposited substance and the film adherence precludes successful verification of this hypothesis by the otherwise most appropriate NMR spectroscopy. Furthermore, the results obtained by ESCA and IR spectroscopy show considerable deviation from a pure poly(4-chlorostyrene) film. This points to the existence of defects related to segmentation reactions (chain terminations), and presence of residual vinyl structures (*e.g.* monomer molecules trapped in the film). Another type of defect corresponding to the loss of chlorine atoms in the polymer film was noted. This last phenomenon is function of the electrode potential, its amplitude being significant at -2.4 V *vs.* Ag/Ag$^+$, and lower potential values, and is conjectued to originate from the interchain links in the 1,4-position of the aromatic ring as shown.



The formation of interchain phenyl bridges can be viewed in two ways: (*a*) a nucleophilic aromatic substitution reaction during the film growth according to Scheme 1;[27] (*b*) a reaction related to the charge transport through the film which is required to keep the electrolytic cell in operation. A reaction scheme analogous to that proposed for the reduction of halobenzenes[28] is suggested. The mechanism outlined in Scheme 2 is justified by the dependence of the structural changes in the film on the amount of current passing through it.

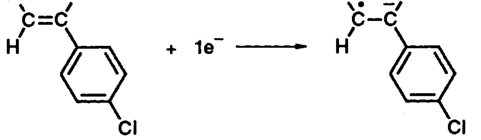


Scheme 1.

In both cases, the mechanisms advocated imply transfer of an electron which will most probably be confined to the phenyl ring. Due to the electron-donating character of both the alkyl chain (polymer backbone) and the chlorine atom, this excess of charge cannot be sufficiently delocalized to form a stable anionic structure and a more stable species is produced by the negative charge being lost as the departing chloride ion. Quantum-mechanical calculations on model anionic structures are planned to assess this destabilization.

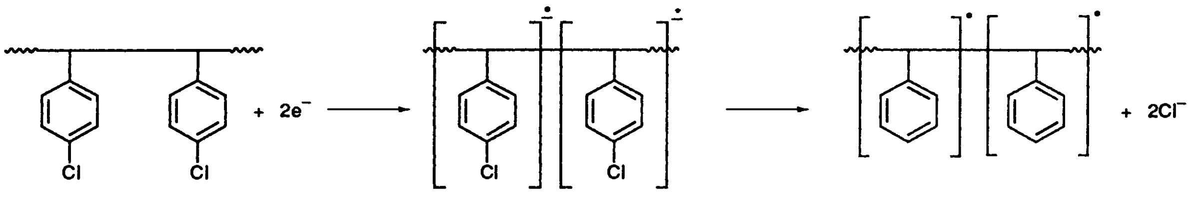
Mechanisms related to charge transfer in solution. The low values observed for the kinetics of growth of the films on the electrode, compared with those found for the formation of polyacrylonitrile films obtained under analogous conditions[15] are controlled, to a large extent, by the stability of the anionic reaction intermediates. The role of the stability of the anionic species has been proved indirectly by the results of the UV-VIS studies (see earlier). Simple considerations such as the possibility of delocalization of the excess negative charge support the idea that PCS has greater stabilizing abilities than acrylonitrile. As already noted however, the chlorine atom in PCS acts as a donor and therefore it is hazardous to base stability predictions on rules of thumb; quantum-chemistry calculations would be very helpful in this context. The question of the stability of anionic species arises also for the chemical reactions connected to charge transfer in solution which take place along with the film-growth process.

Thus, the stability of anionic species and the presence of a chlorine atom on the aromatic ring favour the occurrence of parasitical mechanisms in competition with electropolymerization in solution. It is generally agreed[29] that the first step in the reduction is the formation of a radical anion by the transfer of an electron to the lowest unoccupied molecular orbital (LUMO) of the PCS (Scheme 3). Assuming the validity of this picture, considering that the LUMO of PCS has an energy comparable to that of acrylonitrile and noting that the moiety adds to the delocalizability of the electronic charge, one can argue that the anionic species above is quite stable and is the one responsible for the yellow–orange colour observed in solution. It absorbs in the visible region at 475 nm. According to the electronic structure drawn above, the vinyl radical end is the reactive part of the molecule and accounts for the rapid formation of dianionic dimer (Scheme 4). This is in competition with a direct initiation of a polymer chain by reaction of the anionic end. This dimer absorbs at *ca.* 340 nm, is stabilized by charge delocalization, and can initiate a polymerization reaction in solution according to the Scheme 5.

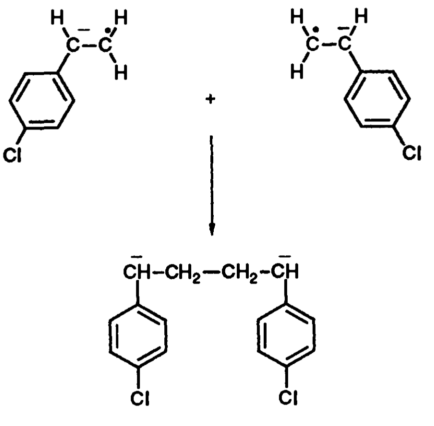


Scheme 3.

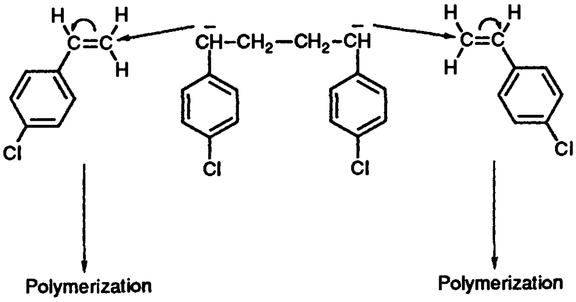
A second step in the reduction, in competition with the dimerization, is favoured by use of more negative potentials which amounts to an increase of the basicity of the solution (by increasing the carbanion concentration). This step can be written in the form of a combined mechanism (Scheme 6). The styrene anion thus formed absorbs at about 400 nm. It is deactivated after proton capture to give styrene, which has been



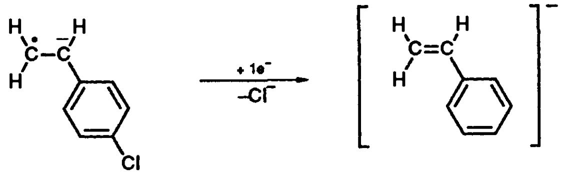
Scheme 2.



Scheme 4.



Scheme 5.



Scheme 6.

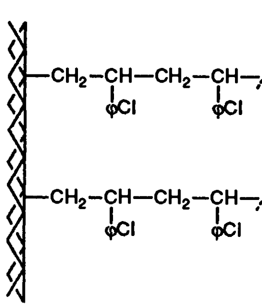


Figure 11. Schematic diagram of the molecular structure of the polymer film on the electrode surface.

detected in solution by using high-resolution gas-phase chromatography.

The ensemble of the processes, including the radical anion formation step, can be compared with an ECEC type mechanism.[30] The species undergoing a second electron transfer (radical) are probably more easily reduced than the initial PCS. This proves the occurrence of a single diffusion-controlled reduction.

Conclusion

The role played by the functional chlorophenyl group in the formation of the polymer film on a nickel surface (cathodically polarized) has been revealed by a study combining experiment and theory. Information was obtained from a study of the molecular structure of the film and the reactions occurring in solution. The reaction products formed in the cathodic compartment are precursors of the reactive intermediates involved in the growth of the polymeric film.

On the basis of simple rules governing their molecular structure (delocalizability over the phenyl ring conjugated to a vinylic moiety) and preliminary quantum-chemistry calculations on neutral molecules, we conclude that the stability of the anion radicals form by Faradaic transfer in solution accounts for the slow film-growth kinetics.

A defect in the chlorine atoms in the polymer films has been shown by comparison of the results of spectroscopic measurements on the modified electrode with those on both phases (solid and liquid) in the cathodic compartment after polarization of the medium. The loss of chlorine atoms is explained by the fragility of the C–Cl bond under electronic transfer. Furthermore, the migration of the charges through the film and their transfer to the monomer molecules in solution can induce lability of these atoms.

The first study, which has shown the complexity of the process, is far from being complete and calls for further studies, experimental and theoretical, to fully disentangle the problem. The role of the stability of the anionic species stressed for PCS also raises new questions in the case of acrylonitrile.

Acknowledgements

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