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Exploration of the space charge behaviour of polyethylene using measurements of thermally stimulated discharge currents coupled with the determination of space charge distributions by the thermal step method in hydrogenated poly(vinyl chloride)

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Abstract

By using the thermally stimulated discharge currents (TSDC) technique and coupling it with the thermal step (TS) method, which allows accurate measurement of the space charge distribution (an outstanding electrical property), both the relaxation and the relative contribution of the intrinsic polarization charges and the extrinsic trapped charges have been analysed for a series of poly(vinyl chloride) (PVC) materials after partial hydrogenation as a precursor structure of polyethylene (PE). The α relaxation related to the release of frozen-in dipole orientation, and the ρ relaxation which is due to the trapping of extrinsic charges have been found to vary, both in intensity and in temperature, with the percentage of ethylene units. On the other hand, the TS measurement of the space charge distribution prior to and after destroying the polarization charges according to the TSDC behaviour, allows one to correlate, as a first approximation, those types of space charge with the molecular microstructure, of either PVC or PE parts. Even if further work remains to be done, the results, as discussed in the light of earlier work on tacticity-driven microstructure–PVC property relationships and on space charge distribution of PVC after hydrogenation, studied by the TS method, provide an original although still tentative interpretation of the space charge behaviour of PE.

Keywords: Hydrogenated PVC-space charges; Molecular microstructure; Relaxations

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1. Introduction

The relationship between the tacticity–microstructure of poly(vinyl choride) (PVC) and, on the one hand, the chemical behaviour of PVC, e.g. mechanisms of thermal degradation [1] or of analogous chemical reactions [2,3], and, on the other, some physical properties [4–9], have been studied extensively in our laboratory.

The specific details of the ‘‘tacticity–microstructure’’ concept have been widely conveyed [2,3]. It refers to a number of structural local peculiarities along the polymer chain induced by the tacticity without the occurrence of any change in the chemical composition. The most salient are the isotactic tetrad **mmr** and the heterotactic pentad **rrmr** which lie necessarily by the side of isotactic and syndiotactic sequences respectively regardless of their length [2,3]. In addition, the likely chain conformations of **mmr**, namely GTTG^{-}TT and GTGTTT, are of great importance.

The progressive removal of the above structures, whether through stereospecific nucleophilic substitution [2,3] or by stretching of films so as to provoke some definite conformational changes [9], enabled the availability of model polymers with well-known tacticity–microstructure, thereby making it possible to study the microstructure/property correlations.

As regards the space charges produced in the polymer upon application of an electrical field, some original correlations have been obtained recently [7,9]. Basically, it has been shown that the amount and distribution of the space charges in PVC relate both to the content of **mmr** structures and to the conformation that they are taking. On the other hand, the charges were found to stem from polarization (heterocharges) rather than from injection (homocharges) even if some injection was detected on the anode [8].

Since the hydrogenation reaction of PVC is also

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stereoselective in the way that it occurs preferably by the **mmr** structure terminal of isotactic sequences, some research work was outlined to examine the space charge behaviour of PVC after hydrogenation reaction with the purpose of corroborating earlier concepts on the microstructure dependence of space charge behaviour of PVC and of interpreting from a chemical point of view the space charge distribution pattern of PE. Indeed, hydrogenation of PVC involves the removal of **mmr** structures by exchanging them for ethylene units.

In a former paper the evolution of the space charge profile, as measured by the thermal step (TS) method [10–12], with degree of hydrogenation has been disclosed [13]. Interestingly, the contribution of a polyethylene (PE) sequence, as short as that formed by three methylene groups, to the space charge pattern of hydrogenated PVC was proved to be of the type known for pure PE and it could be differentiated from that of PVC parts. In addition, the correlation between tacticity-dependent microstructure (tacticity–microstructure from here on) and space charge behaviour of PVC, as stated by the above-mentioned work [7,9], was given additional proof [13]. After assessing the suitability of hydrogenated PVC for studying the molecular grounds of the space charge behaviour of PE, usually thought to be related to morphological features, it appeared of fundamental interest to investigate the relative contributions of the unmodified PVC parts and the PE-like structures to the content of intrinsic dipole polarization charges and of extrinsic injection charges from electrodes. This may be accomplished first by studying the evolution of α and ρ relaxations by the thermally stimulated discharge currents technique (TSDC), and second by coupling the TS and TSDC techniques so as to determine the content of extrinsic charges, mainly due to injection from electrodes, after destroying and measuring the polarization charges by TSDC. This coupling is the so-called ‘‘peak-cleaning’’ technique [14]. In addition, it appeared suitable to study the influence of the space charge creating electrical field on the shape of the distribution pattern. The changes in polarization and injection charges arisen from variations of electrical field are expected to occur at different rates and, consequently, can provide reliable information as to the molecular basis of the space charge behaviour of the PE-like structures and, thence, of PE itself.

The results obtained for 0 to 12% hydrogenated PVC are described in the present paper.

2. Experimental

2.1. Materials

Sample A was an additive-free commercial poly(vinyl chloride) (PVC) obtained in bulk polymerization at 70°C and the process was stopped at 62% conversion. The number-average molecular weight ($M_n = 44 \times 10^{-3}$) was determined osmometrically at 34°C with solutions in CH using a Knauer membrane osmometer.

Cyclohexanone (CH) was purified by fractional distillation under nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen with lithium aluminium hydride (Merck) immediately before use to remove peroxide.

2.2. Substitution reaction with $LiAlH_4$

The substitution reactions of PVC (sample A) with $LiAlH_4$ were carried out in THF solution at 40°C in an atmosphere of purified nitrogen. The products were withdrawn and purified twice with THF–methanol as the solvent–precipitant system and finally dried under vacuum at 50°C.

The degree of conversion was determined by ^{13}C NMR.

2.3. ^{13}C NMR spectroscopy

The tacticity of all samples was measured by means of ^{13}C NMR decoupled spectra obtained at 85°C on an XL-300 Varian instrument, operating at 75.5 MHz using 1,4-dioxane-d_8 as solvent. The spectral width was 2500 MHz,

Table 1
Characteristics of polymers

Sample	Degree of hydrogenation (mol%)	Thickness (μm)	Tacticity (%)			
			mm	**mr**	**rr**	**m[mmr]**
A	0	100	20	49.7	30.3	9.2
B	1.3	160	18.5	49.3	32.2	8.7
B1	1.3	120	18.5	49.3	32.2	8.7
C	3.4	110	18.1	48.5	33.4	8.1
C1	9.4	110	15.6	49.2	35.2	8.1
D	7.1	160	16.6	48.5	34.9	7.2
E	9.4	120	15.6	49.2	35.2	6.4
F	12.3	220	14.8	49.2	36	6

Values taken from Ref. [15].
mm, isotactic triad; **mr**, heterotactic triad; **rr**, syndiotactic triad; **m[mmr]**, isotactic pentad.

and a pulse repetition rate of 3 s and 16K data points were used. The relative peak intensities were measured from the integrated peak area, calculated by means of an electronic integrator. The results are given in Table 1.

2.4. Preparation of films

All the films were made by compression moulding at 150°C at a pressure of 125 bar, using a Collin press Model 300.

The characteristics are given in Table 1.

The samples are provided with two identical electrodes (∅ = 20 mm). The usual method of metallization is to evaporate the electrode material (aluminium, which is resistant to oxidation) onto the sample under vacuum. The samples were conventionally polarized for 2 h. The polarizing field was 10 kV mm^{-1} (TSDC method) or 5 kV mm^{-1} (peak cleaning method) and the polarization temperature was 50°C.

2.5. Thermal step (TS) method

The specific details have been described in previous papers [7–9,13]. The presence of charges Q_i in the insulator induces image charges on each electrode Q_i1 and Q_i2 ($Q_\mathrm{i} + Q_\mathrm{i1} + Q_\mathrm{i2}) = 0$. The propagation of the thermal step modifies the equilibrium of the image charges and consequently a current appears in the external circuit. For the signal deconvolution, we consider that the insulator begins at X_0 on the abscissa (see Fig. 1).

The current is

$$I(t) = -\alpha C \int_0^D E(x) \frac{\delta T}{\delta t} \, \mathrm{d}x$$

where $\alpha = \alpha_x - \alpha_\varepsilon$, with α_x the linear expansion coefficient of the material, α_ε the thermal dependence of the permittivity coefficient, C the capacitance of the sample, T the temperature, D the thickness of the sample and $E(x)$ the electric field strength in elementary thickness dx. $\alpha_x = (1/l)\,\delta l/\delta T$ and $\alpha_\varepsilon = (1/\varepsilon)\,\delta\varepsilon/\delta T$. α is obtained by the measurement of capacitance at different temperatures.

After deconvolution by one of the different numeric treatments developed by Toureille et al. [10,12], the measurements give the resultant charge in the thickness direction:

$$\rho(x) = -\frac{\delta P}{\delta x}$$

where $\rho(x)$ is the remaining space charge and P is the remaining polarization.

Space charge measurements were performed after a short-circuit of 44 h.

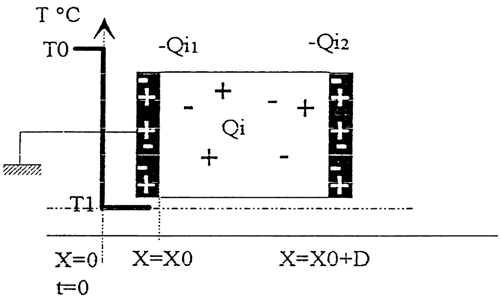


Fig. 1. The principle of the thermal step (TS) method.

2.6. Thermally stimulated discharge currents (TSDC) method: peak-cleaning technique

Although TSDC has a relatively short history, it has already evolved into a basic tool for the identification and evaluation of dipole reorientation processes and of trapping and recombination levels.

The sample is metallized on both sides, and charged by application of a DC field at a high temperature. This field is maintained, and the sample cooled to room temperature or below. Next, it is short-circuited and reheated at a linear rate of, say, 2°C min^{-1} (this being low enough to prevent temperature lags and to guarantee a good resolution of peaks) in the temperature range from 25 to 150°C, the discharge current generated being measured with an electrometer and recorded as a function of temperature by an x–y plotter. As will be explained later, the peak labelled α is mainly due to dipoles, whereas the ρ peaks are due to trapped space charge.

2.6.1. The peak-cleaning technique

The principle of this technique has been developed by Creswell and Perlman [14]. This method requires two similar films of the same polymer sample to be utilized, and it consists of coupling TS and TSDC methods as follows: first, TS and TSDC techniques are applied to one of the films in order to state the space charge distribution and to know whether or not the sample exhibits the peaks concerning the relaxations of different nature (α and ρ peaks), in particular the latter. Then, using the other film, polarized under the same conditions and exhibiting the same charge density, the TSDC spectra is registered up to a temperature higher that those of the α peak to ensure the dipole relaxation and elimination of its corresponding charges. The space charge distribution is then determined again by TS and compared to that measured prior to TSDC for the first film.

3. Results and discussion

Fig. 2 displays the TSDC spectra of the samples (Table 1). All the spectra exhibit two peaks: one is the α relaxation corresponding to the dipole reorientation when at the glass transition temperature the frozen-in orientation of dipoles while application of the electric field (polarization process) is released. The other is the ρ relaxation which is believed to be related to space charges other than those derived from dipole orientation, presumably charges of extrinsic nature

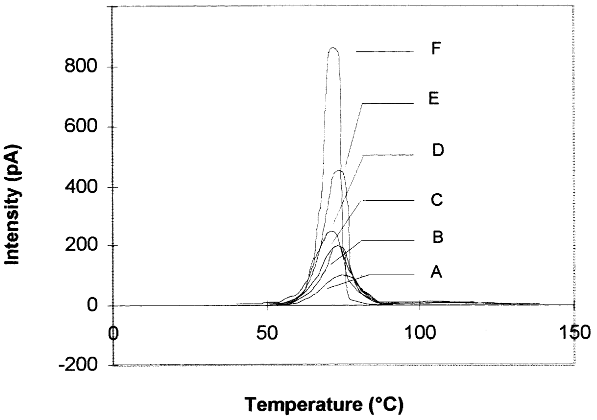


Fig. 2. TSDC whole spectra in polarized PVC hydrogenated to different degrees: (A) 0%; (B) 1.3%; (C) 3.4%; (D) 7.1%; (E) 9.4%; (F) 12.3% (10 kV mm^{-1}, 50°C, 2 h).

produced by electrode injection. As can be seen the intensity of α relaxation is very high relative to that of ρ relaxation. To make it possible to compare the latter relaxation for the samples studied, the ρ peaks at a larger scale are shown in Fig. 5. From Fig. 2, two conclusions may be drawn. One is that, as in the evolution of the overall space charges as shown previously [13], the intensity of the α peak increases with hydrogenation, but clearly this happens at a different rate depending on the conversion range. Another conclusion is that the temperature of the α peak decreases with hydrogenation.

This behaviour is more accurately apparent in Figs 3 and 4, plotting the evolution of intensity and temperature versus the percentage of ethylene units respectively. Interestingly, as can be seen from Fig. 3, the early stage of hydrogenation (1.3%) involves an appreciable increase in intensity; then, after a conversion range from 1.3% to about 7% where the intensity increase is rather slow, a steep and linear slope is observed.

This behaviour is the reverse of that found for nucleophilic substitution reactions, as was the case for the amplitude of the space charge distribution which was shown to decrease and to increase with substitution [8] and with hydrogenation [13] respectively. However, both substitution and hydrogenation reactions involve the preferential removal of **mmr** structures linked to isotactic sequences [2,3,13], so giving rise to similar changes in the tacticity–microstructure of PVC parts. Instead, those reactions induce reverse effects on the modified parts. As has been extensively argued [2,3], the nucleophilic substitution makes the **mmr**-containing sequence adopt a stiff all-trans conformation without appreciably changing the chemical nature of the polymer units involved, because polar and bulky chemical groups have been substituted for chlorine atoms. In contrast, the replacement of chlorine atoms by hydrogen atoms, as when hydrogenating PVC, strongly increases the ability of C–C bonds to rotate along the same **mmr**-based sequence by exchanging it for a PE-like short sequence (appearance of three consecutive methylene groups) which, in addition, produces a significant reduction in dipole content.

The above implications of substitution and hydrogenation by the **mmr**-containing isotactic pentad are illustrated by Scheme 1 and Scheme 2 respectively.

The above reverse implication of the chemical-based microstructure compared to the tacticity–microstructure lends further support for the occurrence of two processes of opposite effects on the overall space charge accumulation in hydrogenated PVC, as inferred from the TS study earlier [13] for the samples of Table 1 and suggested by the slowing down of the α intensity increase between 1.3 and 7% hydrogenation range (Figs 2 and 3). Instead, the observed increase of α relaxation throughout the hydrogenation reaction, unlike substitution, is at variance with the augmentation of ethylene units at the expense of vinyl chloride units, because α relaxation is known to be due to dipole orientation only. Thus, some new dipoles should be expected to arise from the hydrogenation reaction.

As can be seen from Scheme 2 and is easily observable with appropriate atomic models, the explanation lies in the huge propensity to orientation that the two C–Cl bonds have by either side of any sequence of CH_2 groups. Moreover,

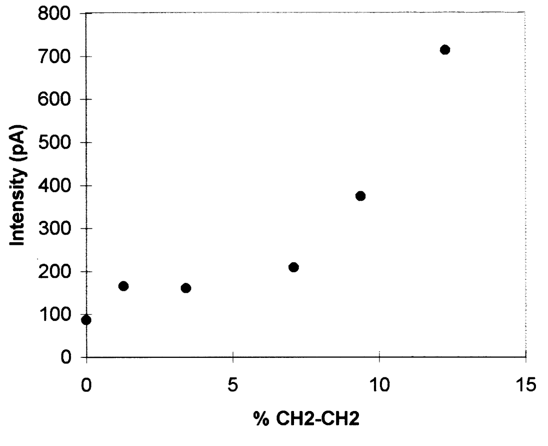


Fig. 3. Evolution of the polarization peak intensity (α) of PVC samples with degree of hydrogenation.

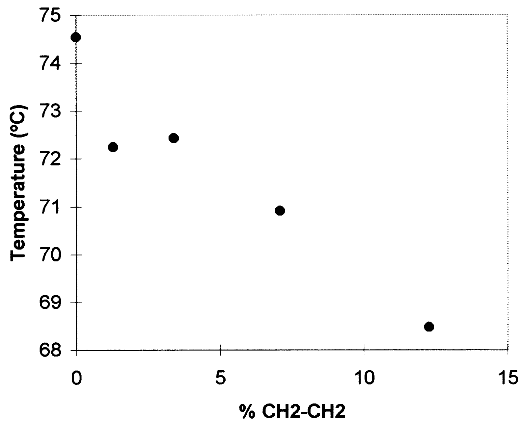
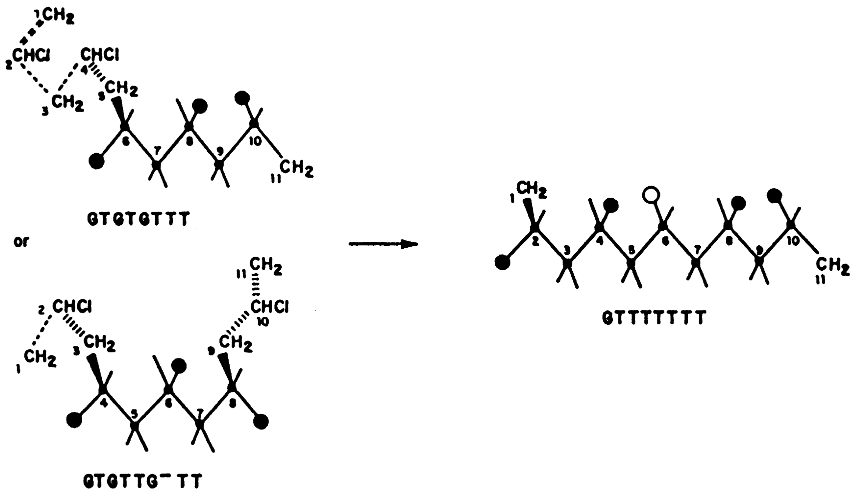


Fig. 4. Evolution of the polarization peak temperature (α) of PVC samples with degree of hydrogenation.



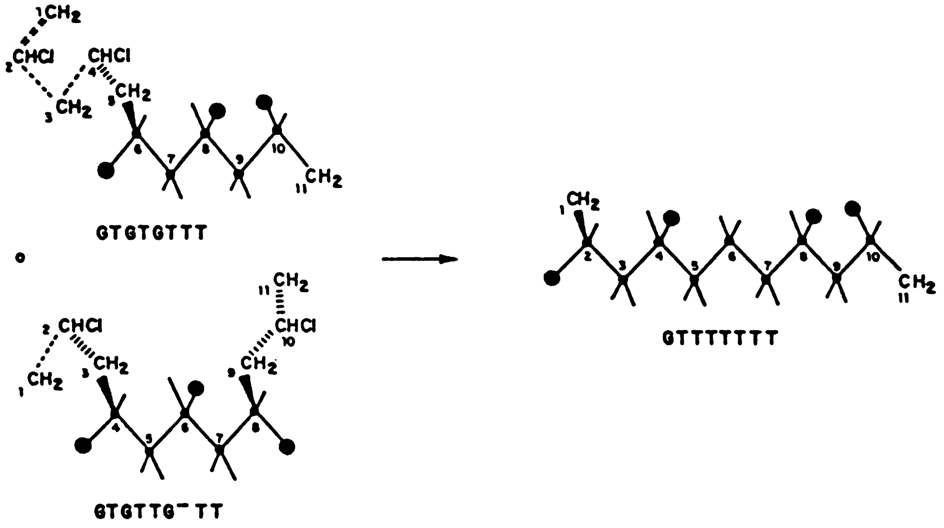
Scheme 1. Conformational changes involved in substitution of PVC on the central C–Cl of the **mmmr** pentad. Cl (●); nucleophile group (○). (Ref. [2].)

their ability to orientation is higher as the length of the sequence of the CH$_2$ group increases, which accounts for the steep increase in α relaxation intensity for hydrogenation degrees over 9.4% (Figs 2 and 3), i.e. when polyethylene triads are formed [15]. Moreover, the latter effect agrees with the reaction period where the removal of **mmr** starts vanishing [15].The conclusion we come to is that new C–Cl dipoles of much enhanced polarizability relative to those of PVC are formed in parallel to the ethylene units even though the total number of C–Cl bonds decreases. The evolution of the α transition with hydrogenation, as revealed by Figs 2 and 3, can thus be explained satisfactorily.

The evolution of the α temperature with conversion as given in Figs 2, and 4 clearly indicates a progressive decrease in agreement with expectations from the increasing content of ethylene units along the chain. As argued elsewhere [15], the presence of chain segments, making the formation of successive hydrogen bonds scarce in PVC, involves a marked decrease of the glass transition temperature. This is certainly the case for the segments of at least three CH$_2$ groups which are formed during hydrogenation from the very beginning. As a consequence, a lower energy is required for the chain segments to move cooperatively.

In conclusion, the results of Figs 3 and 4 as regards the space charges characteristic of PVC, namely polarization charges, are consistent with the evolution of molecular microstructure during the hydrogenation reaction which causes a new kind of C–Cl easily polarizable bonds to appear, so compensating the loss of less polarizable C–Cl bonds at the **mmr** structure, of high reactivity up to 9.4% conversion [15].

As to the changes in the ρ peak (Fig. 5), these can be seen in Figs 6 and 7 showing the intensities and temperatures as a function of hydrogenation degree. Clearly, the intensity (Fig. 6) experiences fairly steady behaviour up to near



Scheme 2. Conformational changes involved in the hydrogenation of PVC on the central C–Cl of the **mmmr** pentad. Cl (●). (Ref. [15].)

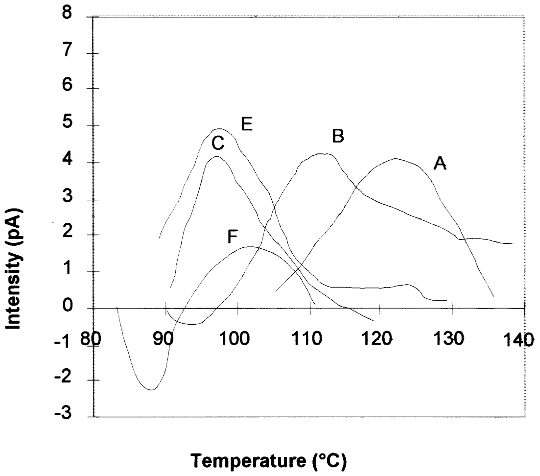


Fig. 5. TSDC ρ relaxation region in polarized PVC hydrogenated to different degrees: (A) 0%; (B) 1.3%; (C) 3.4%; (E) 9.4%; (F) 12.3% (10 kV mm^{-1}, 50°C, 2 h).

10% conversions and then it changes abruptly and turns to be negative. Such behaviour is again at variance with that found for nucleophilic substitution where the ρ peak was found to decrease markedly up to conversions of about 10% after which it tended to increase [8]. This was tentatively thought to agree with the progressive disappearance of the **mmr** structure because of the contribution of the latter to the minority homocharges near both electrodes as proved by the peak-cleaning technique [8]. On these grounds, and taking into account that the intensity of the ρ peak is proportional to the number of space charge trapping sites, the steady behaviour of Fig. 6 would indicate that the decrease of injection charges as the result of the removal of **mmr** structures is balanced by the injection charges relevant to the PE-like parts, in agreement with the proposals issued from the TS study [13].

As shown in Fig. 7, the temperature corresponding to ρ relaxation decreases with hydrogenation, but it does so more steeply during the early stages by exchanging them for ethylene units, that is when the removal of the more reactive **mmr** isotactic tetrads, namely those under GTTG^{-}TT conformation [15], occurs in a preferential way. This suggests that the energy which is required for the relaxation of the extrinsic charge traps to occur decreases with hydrogenation, which is consistent with the progressive change in nature of the traps both for the PVC unreacted parts (removal of **mmr** structures) and for the modified parts (PE-like structures).

From the foregoing results and the above-quoted work [13] on space charge distribution of samples of Table 1, it follows that, first, the overall space charge behaviour is strongly influenced by the presence of PE-like sequences along the chain of PVC, and, second, the major contribution of the latter sequences relates to the extrinsic charges probably arising from injection from electrodes.

An appropriate way to state the real evolution of the content of the space charges, other than those stemming from dipole polarization when applying TS and TSDC methods separately, is that of the so-called peak-cleaning method, a useful technique developed by Creswell and Perlman [14] as described in the previous section.

Fig. 8 exhibits the intensity currents prior to and after application of peak cleaning for two hydrogenated samples with 1.3 and 9.4% content of ethylene units. As can be seen in both samples, the sign of the currents as measured at the cathode is reversed, contrary to what happens at the anode where both currents are positive. In principle, this would indicate the occurrence of charges other than those from dipole polarization in the cathode.

On the other hand, comparing the intensities of the curves, it is apparent that the intensity at the anode, prior to peak cleaning, is higher than that at the cathode for two samples. That is, a certain dissymmetry revealing the presence of space charges of a distinct nature [7,8] takes place. Instead, after peak cleaning, the intensity order is reversed in the case of sample B1 (1.3%), whereas sample C1 (9.4%) shows similar values at both electrodes. In addition, the decrease in intensity as the result of peak cleaning, i.e. once the dipole constraints have been released (α relaxation), is more significant at the anode compared to the cathode for both samples, so indicating a higher contribution of polarization-induced charges at the anode.

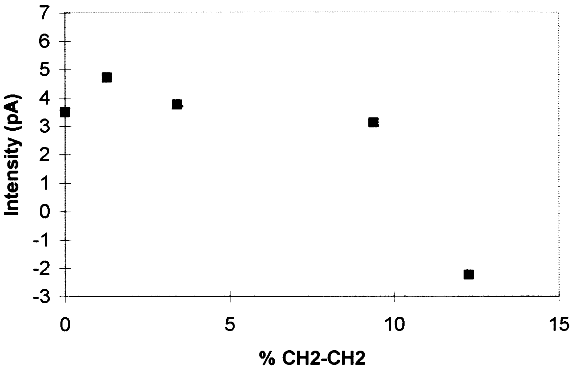


Fig. 6. Evolution of the space charge peak intensity (ρ) of PVC samples with degree of hydrogenation.

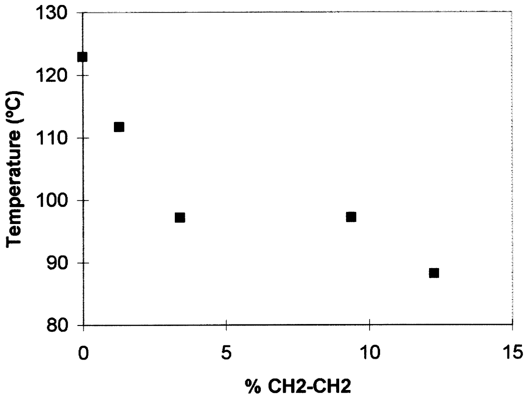


Fig. 7. Evolution of the space charge peak temperature (ρ) of PVC samples with degree of hydrogenation.

These changes, together with the sign inversion in the cathode, clearly confirm that space charges other than those from polarization appear by the side of the cathode and they suggest that this effect is more pronounced for sample B1 than for sample C1.

In order to obtain more specific details of the foregoing results it is necessary to compare the space charge distribution of each sample prior to and after the peak-cleaning operation. The results are displayed by Fig. 9a and Fig. 9b for samples B1 and C1, respectively.

As can be seen, both samples before peak cleaning exhibit a profile characteristic of priority polarization, as expected from the predominance of the vinyl chloride structure over the ethylene structure. Nevertheless, a somewhat pronounced departure from the behaviour of pure PVC [7] is apparent in that a strong broadening of the profile by the side of either electrode is found to arise as the result of hydrogenation. The modification of the profile is such that a trend towards the appearance of two maxima is often observed [13], thereby suggesting that there are space charges of different behaviour. Taking into account the profile of pure PVC [7], it seems reasonable to correlate the maxima in the nearest proximity to either electrode with this polymer. Conversely, the maxima nearer the middle of the film ought to be due to ethylene units. This clearly agrees with the distortion at the middle of the film, relevant to the ethylene units, which is found to overlap the profile typical of PVC [13].

As shown by Fig. 9a for sample B1, the space charge distribution after peak cleaning reveals a rather large amount of homocharges together with a little heterocharge by the side of the anode. The former is probably associated with the low incursion of the corresponding intensity current into negative values (Fig. 8a), whereas the latter should be more directly linked to the remaining positive values of the corresponding current induced by TS, and it should be attributed to some residual polarization. As to the rather abundant homocharges, this could be thought to be due to two factors. Of these, one factor is the contribution of the PE-like structures exhibiting injection charges from the anode [10,11]. The position of the maximum of the homocharges (Fig. 9) could result from their migration.

The situation by the cathode side of the same profile is appreciably different. On the one hand, there are some homocharges in agreement with prior results showing the occurrence of a small injection from the cathode in PVC [8,9]. In this respect it should be noted that sample B1 is only very slightly hydrogenated PVC (Table 1). On the other hand, the presence of a considerable amount of heterocharges is quite apparent. This behaviour is of the type observed for pure PE [10,11] and, surprisingly, it is observed at as short and isolated a PE sequence as that arising in the early hydrogenation period [15].

Based on these considerations we are inclined to think that those heterocharges are the result of migration of a part

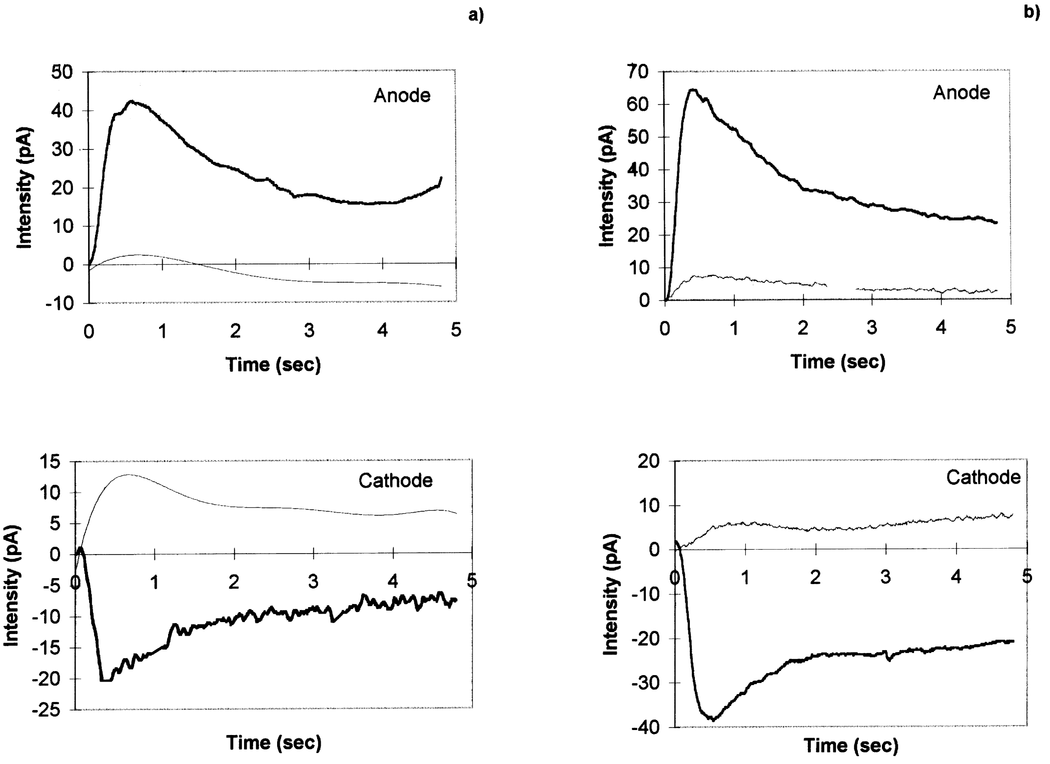


Fig. 8. Intensity of the thermal step-induced currents vs. time for polarized hydrogenated PVC samples B1 (a) and C1 (b), prior to (———) and after (———) peak cleaning (5 kV mm^{-1}, 50°C, 2 h) (see Table 1).

of the injected charges (positive charges) from the anode in exchange for the migration of injection charges from the cathode (negative charges) towards the inside of the film (Fig. 9).

In support of this interpretation is the fact that profiles like that of Fig. 9a for sample B1 after peak cleaning are obtained for pure PE, on condition that sufficiently high electric fields are utilized in the TS method [10,11]. Moreover, very complicated profiles suggesting the occurrence of space charge migrations to different extents were obtained when the strength of the electric field was lowered [10].

Turning to sample C1 (Fig. 9b) it appears evident, first, that within the experimental and calculation uncertainties, the overall profile prior to peak cleaning may be considered to be of the same type found for sample B1. And second that, as inferred from the profile after peak cleaning, both the residual polarization and the small homocharges content by the side of the anode and the cathode, respectively, are absent. The reason for the latter should lie in the fact that in sample C1, unlike sample B1, most of the **mmr** structures relevant to long isotactic sequences have been removed by exchanging them for sequences of three CH_2 groups [13]. If this correlation holds true, then the results of Fig. 9 will provide new reliable support for the role of GTTG^{-}TT and GTGTTT conformations of the **mmr** terminal of isotactic sequences of at least one heptad length in the priority dipole polarization charges and the minority injection charges respectively in PVC [8,9].

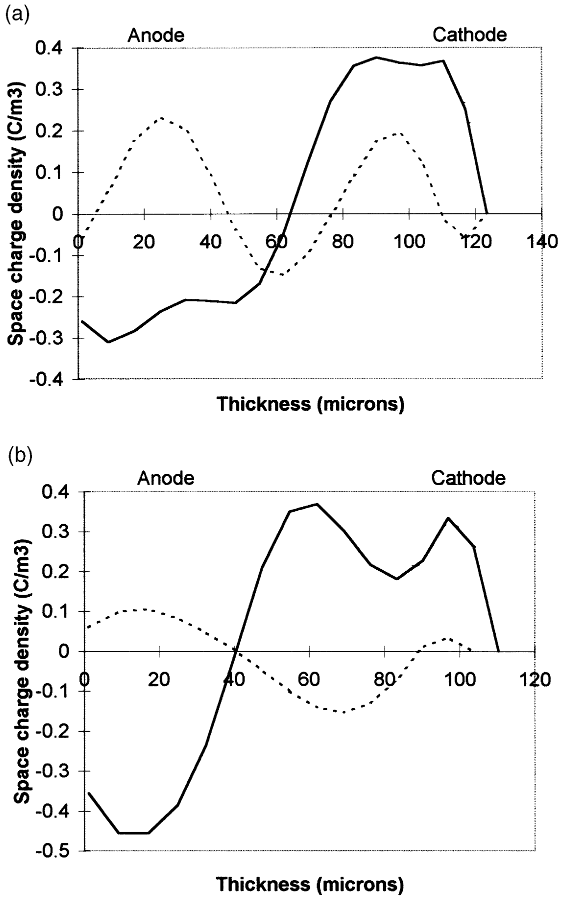


Fig. 9. Space charge distribution in polarized hydrogenated PVC samples B1 (a) and C1 (b), prior to (———) and after (- - -) peak cleaning (5 kV mm^{-1}, 50°C, 2 h) (see Table 1).

The lower amplitude of the space charge distribution profile after peak cleaning for sample C1 (Fig. 9b) relative to sample B1 (Fig. 9a) is somewhat surprising because of the higher content of ethylene units of the former sample. Even if an appreciable amount of work on this matter remains to be done, two important points are worth mentioning. One is that the contribution of the PVC parts to the whole homocharges by the side of the anode is significantly lower in sample C1 due to the removal of the injection space charges sensitive **mmr** structures under GTGTTT conformation [8,9].

The other point is that the migration of homocharges, in particular the positive ones, might be favoured as the result of the changes in chemical composition microstructure, so allowing the charges to disappear partly through the electrodes. The TSDC results above lend support to this interpretation.

What is worth emphasizing is that, on the one hand, the space charge distribution after peak cleaning agrees thoroughly with that of PE irrespective of the hydrogenation degree (Fig. 9a, Fig. 9b), and, on the other, the elimination of the polarization charges relevant to PVC parts, by applying that technique, provide an original local molecular microstructure-based insight into the space charge behaviour of PE, in that the profile of PVC containing short PE-like sequences, after peak-cleaning, agrees with that of PE.

The electric field dependence of the space charge nature and distribution as measured by the TS method is depicted by Fig. 10a and Fig. 10b. To accomplish this, hydrogenated samples with 1.3 and 9.4% content of ethylene units were submitted to electric fields of 5 and 10 kV mm^{-1}, the remaining experimental conditions (polarization temperature, T_p, 50°C and polarization time, t_p, 2 h) being unaltered. Note that the former field is the one utilized in the foregoing peak-cleaning study.

As shown by Fig. 10, the currents measured on the anode and the cathode are of positive and negative sign respectively, so indicating a priority polarization regime.

Comparing the intensities it is apparent that on raising the electric field to a value twice as high as that initially used, the intensities on the anode increase at the same rate, whereas on the cathode they increase according to a substantially higher proportion, so indicating that the whole amount of space charges is higher by the side of cathode. In this respect, the number of oriented dipoles and, hence, of polarization charges are known to be proportional to the electric field with a similar coefficient for either electrode. As a consequence, if there were only polarization charges then the currents of the anode and the cathode would have to be symmetrical. Thus, the above difference between the anode and the cathode relates certainly to charges other than the polarization ones, namely homocharges as the result of injection from electrodes, which agrees with the foregoing results on peak cleaning.

More specific details about this matter are available from the space charge distributions in the material as deduced from the currents of Fig. 10 through the usual deconvolution method. They are given in Fig. 11. As argued elsewhere [13], the patterns corresponding to the $5\,\mathrm{kV\,mm^{-1}}$ field consist of the overlapping of the space charge distributions typical of PVC and PE. Even though, as a whole, the distributions are of the type obtained when polarization predominates over injection, the occurrence of the latter is evidenced by, on the one hand, the clear superiority of positive charges compared to the negative, and, on the other, the fact that the charges are spread from the surface to the middle of the film. The above events are at variance with the occurrence of a priority polarization pattern with little or no injection, which usually exhibits two well-defined maxima of similar amplitude in proximity to the anode and the cathode.

When raising the field to $10\,\mathrm{kV\,mm^{-1}}$ (Fig. 11), a sharp increase in the space charge density occurs near either the anode or the cathode, similarly to what happens with pure polarization.

Thus, a major effect of increasing the electric field is found to be that of increasing the space charges derived from dipole polarization, even though the overall number of C–Cl bonds decreases. This confirms the enhancement of polarizability of the C–Cl bonds by the side of every PE-like sequence as inferred both from the TSDC results and from TS earlier work [13]. However, the fact that this effect is higher near the cathode is consistent with the occurrence of injection charges from the anode, relevant to PVC parts [8].

It should also be added that the positive and negative space charges around the middle of the film change both in position and in relative density when increasing the field. As suggested by earlier work [13], these charges are to be associated with the presence of ethylene units and are the result of migration of extrinsic charges (injection from either electrode). As may be seen from Fig. 11, increasing the electrical field brings about, on average, an increase in density of positive charges, doubtless because of an increase in injection related to the ethylene units.

Therefore, the increase in current intensities with increasing field, as shown in Fig. 10, seem to obey two factors: one, of greater significance, is the increase in polarization charges related to the PVC C–Cl bonds vicinal to the PE-like sequences; the other is the occurrence of additional extrinsic charges, especially by injection from the anode. The latter are due to a great extent to the ethylene units and, to a smaller extent, to PVC parts [13].

In support of these conclusions are the foregoing results obtained through the peak-cleaning study. They also allow

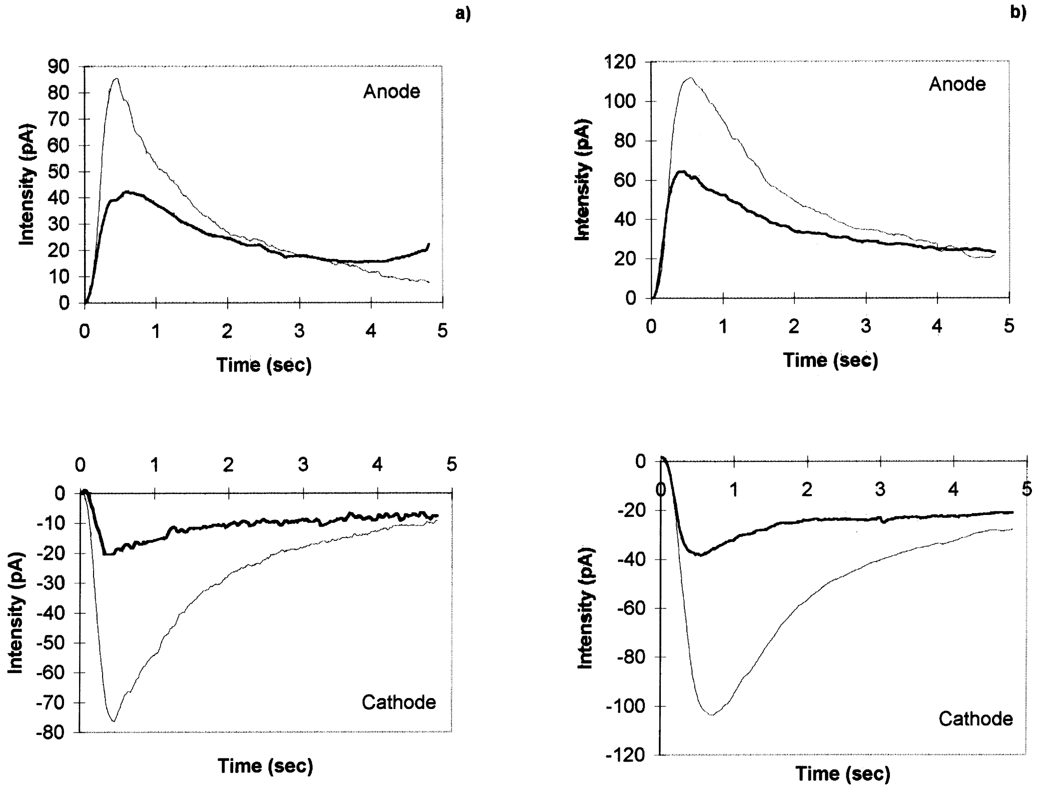


Fig. 10. Intensity of the thermal step-induced currents vs. time for 1.3 and 9.4% hydrogenated PVC, polarized (50°C, 2 h) at different electric fields: (a) 1.3% ((——) sample B1, $5\,\mathrm{kV\,mm^{-1}}$; (——) sample B, $10\,\mathrm{kV\,mm^{-1}}$) and (b) 9.4% ((——) sample C1, $5\,\mathrm{kV\,mm^{-1}}$; (——) sample C, $10\,\mathrm{kV\,mm^{-1}}$) (see Table 1).

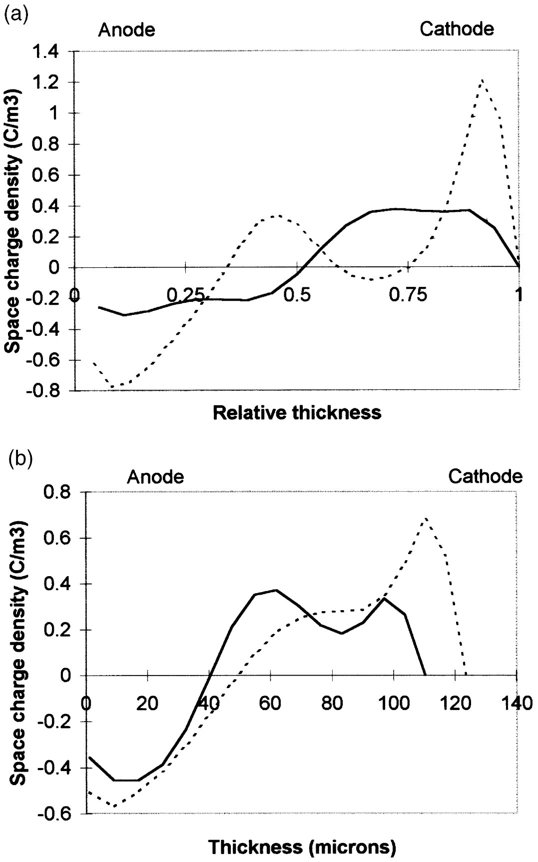


Fig. 11. Space charge distribution in polarized PVC after 1.3 and 9.4% hydrogenation, submitted to different electric fields: (a) (———) sample B1, 5 kV mm^{-1}; (- - -) sample B, 10 kV mm^{-1} and (b) (———) sample C1, 5 kV mm^{-1}; (- - -) sample C, 10 kV mm^{-1} (see Table 1).

one to go further into the knowledge of the respective contributions of PVC and PE structures to the space charge distribution as measured for PVC after hydrogenation, thereby providing further evidence of the relationship between nature and quantity of space charges and molecular microstructure both for PVC and for PE.

4. Conclusions

The coupling of TSDC and TS techniques for electrical studies on hydrogenated PVC, a particular PVC containing short PE-like sequences, leads to a novel insight into, first, the space charge behaviour of both PVC and PE materials and, second, the nature of the microstructure-based sites where the charges, whether polarization or injection charges, originate and are trapped.

Comparing the relative contributions of PVC and PE parts in hydrogenated PVC it is apparent that: (i) the polarization charges relate to isolated short polar chain segments exhibiting free rotation capabilities, as is the case of the **mmr** tetrad under the GTTG^{-}TT conformation (Scheme 1) or C–Cl bonds adjacent to short PE-like sequences (Scheme 2); and (ii) the trapping of charge from electrode injection charges seems to occur in short sequences with both little propensity to rotation and excess free volume, surrounded by rather motionless segments as the result of either interchain interactions or entanglement. Examples of those sites are the mmr tetrad under the GTGT^{-}TT conformation (Scheme 1) and the short PE-like sequences surrounded by PVC sequences (Scheme 2). It is notable that the latter may also occur in pure PE as the result of molecular entanglement.

Further results of some work currently under way are expected to confirm these preliminary conclusions.

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