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Molecular microstructure dependence of space charges in polymers. Coupling of thermal step and thermally stimulated discharge current methods in PVC after stretching at around 90°C

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A film of poly(vinyl chloride) (PVC) was stretched at 90°C under an inert atmosphere to an elongation ratio, λ, of 1.1, 1.2, 1.3 and 1.5. From the evolution of the dichroic ratio $R = A_{\parallel}/A_{\perp}$ of ν(C–Cl) 615 and 637 cm^{-1} frequencies and of relative absorbance A_{615}/A_{637} in the perpendicular direction, as measured by *FT*i.r. spectroscopy, it is concluded that stretching causes both the conformational change GTTG$^-$TT ⇒ GTGTTT for mmr isotactic tetrads, and the orientation of chains, to be operative, but the relative proportion of both phenomena varies with λ, the former one being the major effect up to $\lambda = 1.1$. The space charge distribution of all the samples has been studied by coupling the 'thermal step' (TS) and the 'thermal stimulated discharge current' (TSDC) techniques. The results, as analysed in the light of earlier work, show that the nature and distribution of the space charges which appear in the film submitted to high electric field, strongly depend on the GTTG$^-$TT and GTGTTT conformations of mmr, in particular the former. © 1997 Elsevier Science Ltd.

(Keywords: tacticity-microstructure; space charge; stretched PVC)

INTRODUCTION

In earlier work we investigated the influence of the tacticity-dependent microstructure on the space charge distribution in poly(vinyl chloride) films[1,2].

Space charges in insulating polymers are known to be of great importance in that they determine most of the electrical properties and failures of material submitted to a high electrical field in applications such as electric cable. The appearance of space charges inside an insulating polymer is known to favour ageing and electrical breakdown. Therefore, space charges appear to be an important challenge to the insulating material industry. Space charges are electrical charges (electrons, ions, dipole orientation, etc.) which are trapped in certain parts of the insulators, specially when applying an electrical field.

This phenomenon required first the availability of an appropriate method to measure accurately the space charges. Secondly, the question arose as to whether the charge trapping occurs randomly or specifically by well definite structures.

An answer to the first problem is the number of methods developed during recent years to determine the space charge distribution in a polymer. Of these, the so-called thermal step (TS) method as designed by Toureille *et al.*[3] is of high sensibility and reproducibility. In contrast, a great deal of research work is still to be done for the molecular grounds of the space charge trapping phenomenon to be thoroughly understood.

Based on the ability to prepare model polymers with well known tacticity induced molecular microstructures, resulting from our earlier work[4-7], an attempt to correlate this microstructure with the space charge distribution in PVC after an electric field having been applied, has been made recently with Toureille[1].

We designate by tacticity dependent microstructure, the local configurations terminal of isotactic and syndiotactic sequences, i.e. the isotactic mmr tetrad and the heterotactic rrmr pentad[4-6] in addition to the tactic sequences themselves and the local conformations characteristic of mmr and rrmr, in particular the former. Even though these local configurations and, specially, their respective likely conformations have been repeatedly considered elsewhere we think it helpful to reproduce them herein to avoid referring to earlier work[4,5,8] (*Figure 1*). It must be emphasized that mmr and rrmr (or rrmm) occur necessarily whenever an isotactic (...mmm) or a syndiotactic (...rrr) sequence breaks

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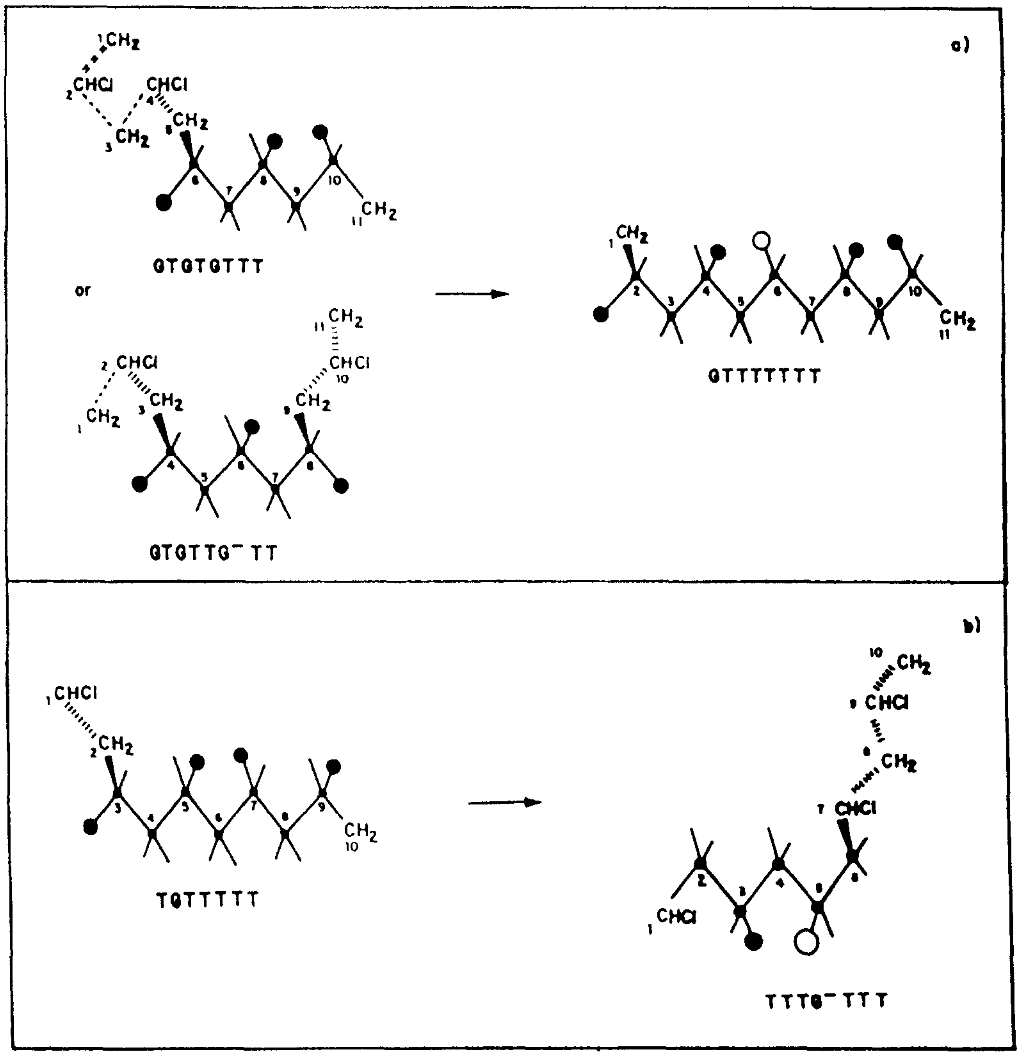

Figure 1 Likely conformations (left side) and conformational changes (right side) involved in substitution of PVC on the central C–Cl bond of: (a) mmmr pentad, (b) rrmr pentad; Cl (●); nucleophile group (○)

off along the chain, respectively. Such a microstructure may be controlled through stereospecific nucleophilic substitution reactions. The specific details of these reactions and the implications as to the changes both in mmr and rrmr content and in the respective likely conformations have been extensively argued[4,5,8] and are also depicted by *Figure 1*.

Comparing the differences in overall microstructure of three PVC samples with the changes in space charge distribution, as measured by the thermal step (TS) method of Toureille *et al.* it has been suggested, recently, that the space charge increases substantially as the content of mmr at the end of isotactic sequences increases[1]. This tentative and hitherto unknown correlation prompted us to attempt some more systematic studies using a single PVC sample with well defined microstructure, after accurate removal of mmr by stereospecific nucleophilic substitution reaction to various extents. In addition we thought it of great interest to investigate the space charge distribution in films of the same polymer after stretching to various degrees so as to make the mmr under GTTG$^-$TT conformation adopt the more stable GTGTTT conformation in an irreversible way according to some preliminary results[9,10].

These two courses of action were considered to be an appropriate route to demonstrate, that the accumulation of space charges is not a random phenomenon but that it occurs preferably by specific points of higher free volume and local mobility such as mmr at the end of isotactic sequences and, to a lesser extent, the rrmr terminal of syndiotactic sequences, which are characteristic of any vinyl polymer[8,9]. From the influence of stretching on the quantity of space charges, some valuable information as to local free volume and mobility dependence of space charge trapping was expected. Actually, mmr under GTTG$^-$TT conformation is known to exhibit excess free volume, high mobility and reduced ability to interact with other chains compared to the same mmr taking the GTGTTT conformation[8–11].

The space charges of the chemically modified PVC have been recently studied by coupling the TS and the thermally stimulated discharge currents (TSDC) techniques. This procedure allows one to investigate whether there are charges injected on the electrode–polymer interphase (homocharges) in addition to the space charges relevant to polarization of permanent dipoles (heterocharges) which are typical of polymers like PVC.

As published elsewhere the amplitude of the space charge distribution decreases as the degree of substitution increases and this effect is much more marked in the proximity of the cathode thereby indicating that space charges other than those arising from the polarization of permanent dipoles, namely the injected charges, are contributing to the observed distributions. This is confirmed by the results from the TSDC study for all the samples, and by applying the peak cleaning technique[12] to one of them. On the other hand, the decrease in overall space charge is particularly abrupt for as low degrees of substitution as 1.1%, which agrees with the removal of mmr under the GTTG$^-$TT conformation[2]. Even though more research work remains to be done the obtained results clearly indicate that space charges, whether induced by permanent dipole polarization or injected from electrodes, in PVC after electrical constraint, strongly depend on the local configurations terminal of isotactic and syndiotactic sequences, in particular the former. Moreover, the fraction of mmr taking the GTTG$^-$TT conformation as a result of polymerization, appeared to be specially sensitive to space charges trapping.

In order to clarify these correlations we designed a parallel study for the same polymer after stretching to various degrees, where the only microstructural change consists of gradually removing the permanent GTTG$^-$TT conformations of mmr by exchanging them for GTGTTT conformations in an irreversible way. This paper deals with the results obtained.

EXPERIMENTAL

Materials

PVC was obtained by bulk polymerization at 70°C and the process was stopped at a conversion of 62%. The number-average molecular mass ($M_n = 44 \times 10^{-3}$) was determined osmometrically at 34°C with solutions in CH using a Knauer membrane osmometer.

The tacticity data, as obtained by ^{13}C n.m.r. spectroscopy, have been published elsewhere[2]. The found values are 0.314 (rr triad); 0.496 (mr and rm triad) and 0.190 (mm triad). The probability of mmr and rrmr structures is 0.215 and 0.155, respectively.

Preparation of films

Films of $140 \pm 20\,\mu$m were made by compression moulding at 150°C and at 150 bar of pressure, using a Collin press Model 300 with well defined temperature and pressure programs applied to the plates.

Stretching polymers

Rectangular strips with dimensions 2 cm × 3 cm and thickness $100 \pm 5\,\mu$m were uniaxially drawn in an Instron dynamometer at 0.1 cm min^{-1}. The samples were stretched at 90 ± 1°C after previous conditioning at this temperature in a thermostatic chamber. They were quenched in ambient air under tension, when the programmed elongation ratio, λ, was reached; λ is defined by:

λ = final stretched length/initial unstretched length

The values of λ for the stretched polymers utilized were: $\lambda = 1$ (unstretched PVC sample); $\lambda = 1.1$, 1.2, 1.3 and 1.5.

Infrared measurements

A *FT*i.r. Nicolet 520 spectrometer, equipped with a polarizer was used. The peak absorbances were determined from a tangent baseline. From them, the dichroic ratios $R = A_\parallel / A_\perp$ of 615 and 637 cm^{-1} bands were determined for all the films.

The thermal step method

There exist several methods to measure the space charge distribution. The fundamental principle of them lies in first, making the changes move somewhat for them to create image charge changes in the aluminium electrodes deposited on each side of the sample, and second, measuring the current produced by the above image charge variations in the external circuit.

Of the known methods, we utilized the so called 'thermal step' developed by Toureille *et al.*[1,3] where the space charge shift is obtained by circulating a cold liquid in a radiator which is in contact with one of the sample electrodes. The space charge distribution is obtained from the measurement of the current vs time by a deconvolution method.

After deconvolution by one of the different numeric treatments (Fourier series or derivation) developed by Toureille *et al.*[1,3], the measurements give the following charge in the thick direction:

$$\rho(x) = \delta P / \delta x$$

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

Aluminium electrodes were deposited under vacuum on each side of the samples. These were polarized at 50°C for 2 h under a 10 kV mm^{-1} electric field. Space charges measurements were performed after a short-circuit of 44 h.

Thermal stimulated depolarization current method

The thermal stimulated discharge current (TSDC) method is a destructive method based on a depolarization of the sample by thermal activation. The sample is heated to a temperature T_p, then a d.c. voltage V_p is applied for a time t_p. After rapid cooling to room temperature, under V_p, the sample is short-circuited through an electrometer, in an oven which is programmed to rise linearly in time. The first theoretical basis for the TSDC phenomenon was established by Bucci and Fieschi[12].

TSDC provides information of relaxation processes that occur in polymers. Two of these processes are the depolarization of permanent dipoles and the release of charges from traps.

For a current due to dipolar reorientation, Bucci and Fieschi[12] give the following expression:

$$J(t) = A \exp\left[-E_a/kT - 1/v\tau_o \int_{T_o}^{T} \exp(-E_a/kT)\mathrm{d}T\right]$$

with $\tau = \tau_0 \exp(-E_a/kT)$ the relaxation time of dipoles at temperature T

A: constant (pre-exponential factor); E_a: the activation energy; k: Boltzmann constant; T_o: room temperature, and T: temperature in time t, v: heating rate (d_o/s), τ_o: characteristic relaxation time.

Perlmann[13] has given an identical expression for a current due to space charge. The total charge released during TSDC is the area delimited by $j(t)$:

$$Q(t) = \int_{\mathrm{to}}^{t} j(t)\mathrm{d}t$$

The polarization of the samples was carried out as indicated for TS measurements. The thermostimulated discharge measurements were scanned at 2°C min^{-1} at a heating rate from 25 to 150°C.

RESULTS AND DISCUSSION

Stretching induced microstructure changes

It is well known, that stretching a polymer film in one direction causes the polymer chains to tend to orientate themselves in the stretching direction. The orientation phenomena are usually investigated by *FT*i.r. dichroism. The dichroic ratio between the absorption intensities for the polarization directions ($R = A_{\parallel}/A_{\perp}$) parallel and perpendicular to the stretching direction provides useful information as to the geometrical structure of the polymer chain.

The orientation is generally assumed to disappear when the temperature is raised above T_g so as to allow the polymer chains to be released from the constraints induced by orientation and, consequently, to recover the initial state. In this respect the possible occurrence of some irreversible conformational changes during stretching has been a persistent concern in our laboratory. Of all the conformational changes that are possible in PVC, the GTTG$^-$TT ⇒ GTGTTT in the mmr sequence is the only one to involve a local lengthening of the chain. On the other hand, the GTTG$^-$ conformation has been widely argued to be of much higher potential energy and to possess higher mobility and weaker interchain interaction than the GTGT conformation[14]. Based on these concepts, it is our belief that the above conformational change is irreversible in nature so that the GTTG$^-$TT conformation should not be recovered after the disappearance of orientation, whether by heating at moderate temperatures or by dissolution of the films. That this proves to be so, has been strongly suggested by two recent papers[9,10]. Because the depletion of the mmr fraction taking the GTTG$^-$TT conformation was required for its effect on space charge distribution to be demonstrated, we have investigated by *FT*i.r. dichroism the evolution of 615 and 637 cm^{-1} bands of the C–Cl bond with degree of stretching (λ = final stretched length/initial unstretched length). The details of this research work lie outside the aim of the present paper and are to be published separately. What is worth mentioning here is that 615 and 637 cm^{-1}, unlike the bands at 695 and 685 cm^{-1} not considered herein which are due to S_{CH} modes, obey both S_{HH} absorption modes of the C–Cl bond (the suffix refers to the *trans* substituents on both C–C bonds adjacent to the C–Cl bond[5]). These bands are therefore very sensitive to chain conformations. Besides, each of these frequencies is known to depend on the local environment in which the bands find themselves. Thus, the 637 and 615 cm^{-1} bands have been assigned to S_{HH} flanked by two S_{HH} modes [S_{HH} $(S_{HH})_a$ S_{HH}] and S_{HH} flanked by one S_{CH} mode and one S_{HH} mode [S_{CH} $(S_{HH})_c$ S_{HH}], respectively. As to the S_{HH} mode flanked by two S_{CH} modes, this has been assigned to a band at 622 cm^{-1}, which is usually overlapped by that, stronger band, at 615 cm^{-1}. We denote these frequencies $(S_{HH})_a$, $(S_{HH})_c$ and $(S_{HH})_b$, respectively. Interestingly, as extensively documented[6,9] they are likely only in the TTTT syndiotactic triad, GTTT heterotactic triad and GTTG$^-$ isotactic triad, respectively.

Bearing these concepts in mind, the GTTG$^-$TT ⇒ GTGTTT conformational change ought to involve the following change in the C–Cl stretching vibration modes:

$$S_{CH}S_{CH}(S_{HH})_bS_{HC}S_{HH} \Rightarrow S_{CH}S_{CH}S_{CH}(S_{HH})_cS_{HH}$$

As argued elsewhere[5,9] the appearance of one $(S_{HH})_c$ mode at the expense of one $(S_{HH})_b$ mode infers that the mmr is lengthened and that two consecutive C–Cl bonds perpendicular to the chain axis appear, which ought to result in a moderately enhanced absorption intensity of the 615 cm^{-1} band in the perpendicular direction. It should be noted that no conformational change is possible at all-*trans* syndiotactic sequences, the absorption mode of which is $(S_{HH})_a$ corresponding to the 637 cm^{-1} band. Nevertheless, the orientation of these sequences as the result of stretching make the C–Cl bonds tend to be perpendicular to the chain axis and, thence, the absorption intensity of the 637 cm^{-1} band in the perpendicular direction will increase. Thus, stretching is expected to produce perpendicular behaviour in both 615 and 637 cm^{-1} bands but this effect is different in nature for the two bands in that it obeys the conformational change and chain orientation, respectively.

The results given by *Figures 2* and *3* agree thoroughly with expectations. As can be seen from *Figure 2*, the dichroic ratio $R = A_{\parallel}/A_{\perp}$ of 615 and 637 cm^{-1} decreases up to $\lambda = 1.3$ so indicating a perpendicular behaviour of both bands; then the dichroic ratio of 615 cm^{-1}, unlike that of 637 cm^{-1} which goes on decreasing, stabilizes. On the other hand, during the first stage of stretching, the perpendicular behaviour of 615 cm^{-1} band strongly prevails over that of the 637 cm^{-1} band as it does between $\lambda = 1.2$ and 1.3. Thus, up to $\lambda = 1.3$ the above conformational change at mmr predominates over orientation of all-*trans* syndiotactic sequences.

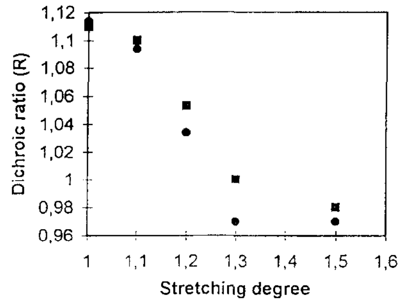

Figure 2 Dichroic ratio (R) of the bands at 615 cm^{-1} (●) and 637 cm^{-1} (■) vs stretching

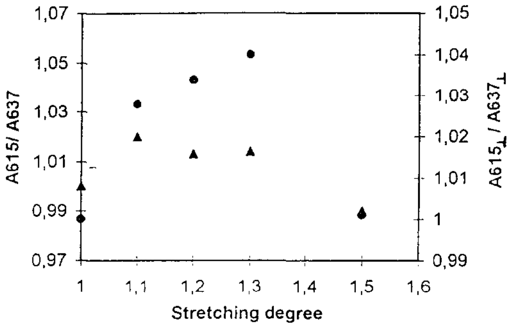

Figure 3 Relative absorbance of A_{615}/A_{637} (●) and $A_{615}\perp/A_{637}\perp$ (▲) vs stretching

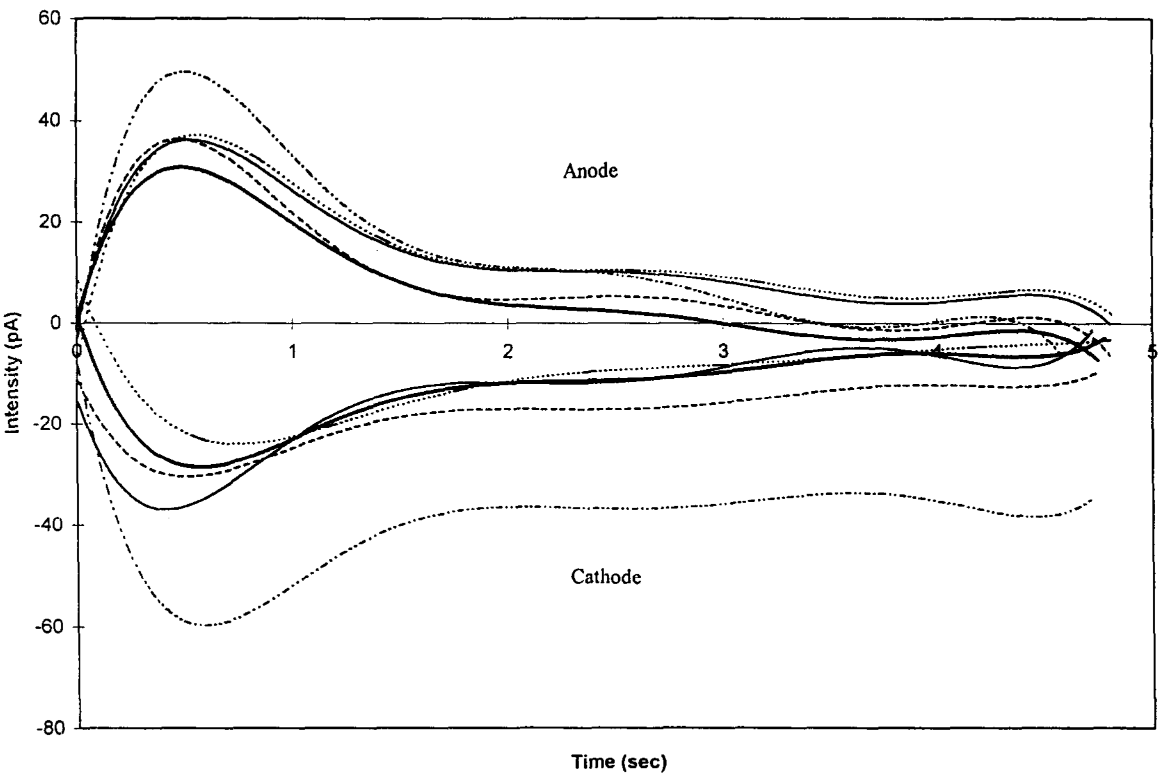

Figure 4 Intensity of the thermal step induced currents vs time for PVC with stretching. λ: (– · ·) 1; (······) 1.1; (——) 1.2; (——) 1.3; (– –) 1.5

Further support for this conclusion is given by the results in *Figure 3*. Actually, when the relative absorbance A_{615}/A_{637} as taken from the spectra registered without a polarizer, is plotted against the degree of stretching, it is evident that at $\lambda = 1.1$ the band at $615\,\mathrm{cm}^{-1}$ increases abruptly; then, that increase is balanced and surpassed by that of $637\,\mathrm{cm}^{-1}$ before and after $\lambda = 1.3$, respectively. A similar plot with the absorption intensities at $615\,\mathrm{cm}^{-1}$ and $637\,\mathrm{cm}^{-1}$ in the perpendicular direction (*Figure 3*) shows that the perpendicular behaviour of the band at $615\,\mathrm{cm}^{-1}$ strongly prevails over that of $637\,\mathrm{cm}^{-1}$, while the reverse occurs as the stretching surpasses the 1.3 value because of the GTTG$^-$TT conformation depletion by exchanging it for GTGTTT conformation.

The results of *Figures 2* and *3* are more significant as the number of C–Cl bonds able to become perpendicular to the chain axis as the result of stretching is much lower at mmr than at all-*trans* syndiotactic sequences.

From the above results it may be concluded that stretching up to about $\lambda = 1.3$ causes the conformational change GTTG$^-$TT $\Rightarrow$ GTGTTT at mmr to operate, thereby involving GTTG$^-$TT conformation depletion. Accordingly, any variation in behaviour as the result of stretching up to 1.3 is to be attributed chiefly to the gradual disappearance of that conformation.

Space charge distribution from thermal step measurements

The current intensities vs time, as measured by the thermal step (TS) method both in the anode and in the cathode for all the samples, are given in *Figure 4*. Overall, the curves are similar in shape. As can be seen, the intensity of the maxima of the curve changes markedly from one sample to another, and this occurs in a different order in each electrode. This can be appreciated in *Figure 5* plotting the intensity at the maxima of *Figure 4* vs λ. The most salient point is the marked decrease of intensity for $\lambda = 1.1$. In the light of the above results (*Figures 2* and *3*) this must be assumed to be due to the removal of GTTG$^-$TT conformations without appreciable orientation of the all-*trans* sequences which are responsible for the $637\,\mathrm{cm}^{-1}$ band. Actually, it is from $\lambda = 1.1$ that the dichroic ratio of $637\,\mathrm{cm}^{-1}$ band starts decreasing. Thus, the two competing processes, i.e. the conformational change by mmr and the orientation of chains, are operative at stretching degrees higher than 1.1 even if until $\lambda = 1.3$ the former process predominates over the latter. As will be seen below, this point is of great importance in interpreting the evolution of both distribution and nature of space charges with stretching.

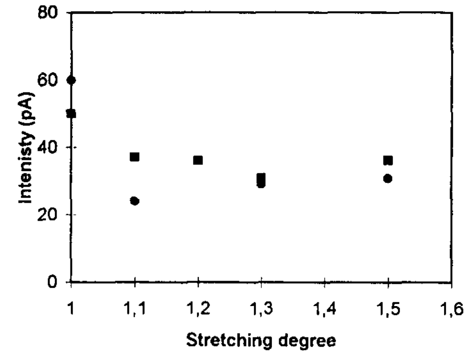

Figure 5 Evolution of the current intensity at the maxima of *Figure 2* with degree of stretching (λ). Anode (■); cathode (●)

Figures 4 and *5* also show that, overall, the current intensities are higher at the anode than at the cathode. This is known to obey the occurrence of charge injections (homocharges) which are assumed to be compensated by those of polarization when applying the TS method to polar material[3]. That behaviour agrees with what was found for PVC after removal of mmr by substitution reaction. Nevertheless, the evolution of intensity with stretching degree (*Figure 4*), deviates substantially from the same evolution with degree of substitution[2].

In this connection, *Figure 5* shows how unlike PVC, after substitution where the intensities decrease with degree of substitution, the intensities after $\lambda = 1.1$ either stabilize or increase slightly with stretching. Besides, the decrease in intensity up to $\lambda = 1.1$ is much more pronounced and occurs much faster in the cathode compared to the anode.

The first behaviour clearly indicates that conformational change and chain orientation are processes of reverse effect on current intensity, probably because the chain orientation in the stretching direction causes the rrmr terminal of syndiotactic sequences to be released from entanglement constraints so showing local excess free volume and enhanced mobility. As to the second behaviour, this clearly shows the GTTG$^-$TT conformation to be sensitive to charge injection in the proximity of the anode.

However, the results of *Figures 4* and *5* strongly suggest that the permanent GTTG$^-$TT conformations in some of the mmr terminal of isotactic sequences, are the main responsible structures for the space charge, in PVC. As extensively argued[8,11] this conformation exhibits higher free volume and mobility, and lower ability for interchain interaction than any structure in a vinyl polymer like PVC.

The whole space charge distribution is deduced by means of a deconvolution of the measured currents, after amplification on a computer by one of the numeric treatments (Fourier series or derivation) developed by Toureille *et al.*[3]. *Figure 6* depicts the results obtained from the deconvolution of the currents corresponding to the measurements at the anode (*Figure 4*). Note that the plots for $\lambda = 1.3$ and 1.5 are shifted towards the right side because of their greater thickness.

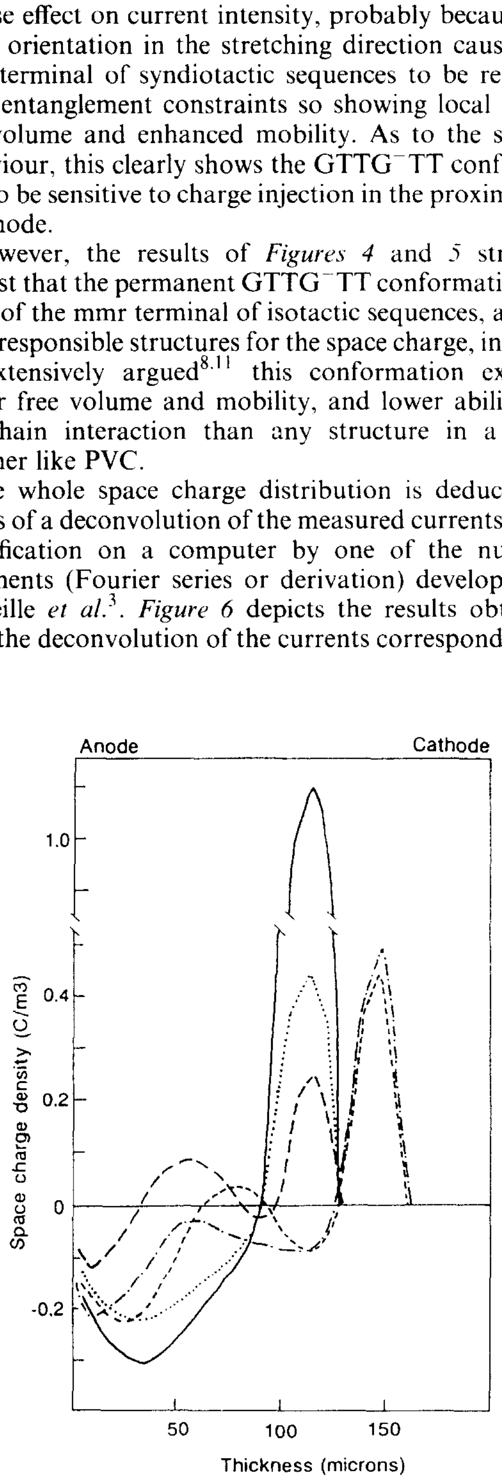

Figure 6 Space charge distribution in polarized PVC with degree of stretching (λ). Value of λ: (——) 1; (······) 1.1; (– – –) 1.2; (— -) 1.3; (– · –·) 1.5 (10 kV mm^{-1}, 50°C, 2 h)

Two conclusions may be drawn: first, the amplitude decreases strongly and weakly along the stretching ranges $\lambda = 1$–1.1 and 1.1–1.2, respectively. Then, the amplitude increases again, especially by the cathode side. Secondly, some positive space charges appear near the centre of the sample and the quantity of them increases up to $\lambda = 1.3$, then it decreases markedly.

The former conclusion obviously agrees with expectations on the basis of the *Figure 4*. The above correlation with the disappearance of GTTG$^-$TT conformations is thus confirmed. As to the second conclusion, this appears difficult to explain at the current state of our work. Its connection with mmr taking the GTTG$^-$TT or GTGTTT conformation, seems not to be so because no positive charge appear before $\lambda = 1.1$. Instead, along the 1.1–1.3 stretching range, the chain orientation which is related to the perpendicular dichroism of the 637 cm^{-1} band, parallels the conformational change resulting in the perpendicular dichroism of 615 cm^{-1} band (*Figures 1* and *2*). It seems therefore, reasonable to assign the occurrence of positive charges to the chain orientation during stretching. As already indicated, the orientation of syndiotactic sequences could be thought to release the terminal rrmr configuration from entanglement constraints, thereby creating sites of high mobility and free volume. Further work is expected to provide a complete understanding of such an important behaviour.

Thermal stimulated discharge current results

It is well known that TSDC provides information about relaxation processes in polymers. This technique is also utilized to examine the so called ρ peak which, unlike α relaxation, a characteristic intrinsic to the material, is generally believed to obey the release of space charges trapped in the polymer and therefore is an extrinsic phenomenon which can be observed only through TSDC. The ρ peak usually appears at temperatures above T_g.

This is the reason why TSDC is generally coupled with the TS method to obtain a complete insight into the space charge nature and distribution. Indeed, the TS method provides the localization of the whole charges without it being possible to differentiate, in an accurate way, the charges injected from electrodes (homocharges) from those induced by dipole polarization (heterocharges).

The TSDC spectra obtained for the stretched films are given in *Figure 7*. Interestingly, the intensity of α relaxation decreases strongly from $\lambda = 1$ to 1.1–1.2; then it tends to increase again. Taking into account that the α peak is proportional to the number of aligned dipoles, that behaviour is a clear indication that the mmr taking the GTTG$^-$TT conformation is the structure most able to polarize upon the action of an electrical field. Indeed, from $\lambda = 1.1$ to 1.2 the conformational change is the only significant implication of stretching, whereas it is from roughly $\lambda = 1.2$ that the chain orientation competes against the conformational change in mmr. Moreover, orientation becomes the major event as stretching surpasses $\lambda = 1.3$ (*Figures 2* and *3*). Thus, the increase in intensity of α relaxation for $\lambda = 1.3$–1.5 (*Figure 7*) should be assigned to the chain orientation, which lends support to our tentative

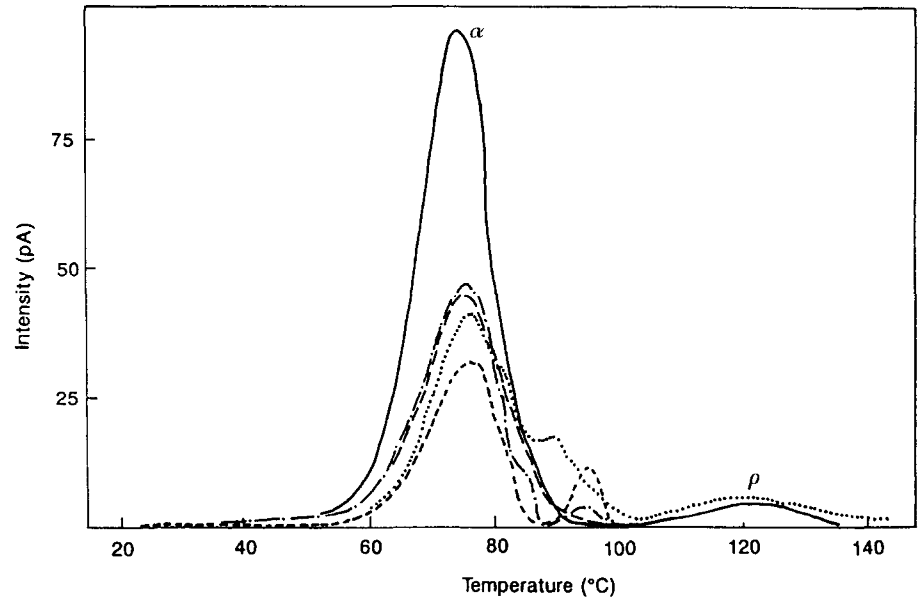

Figure 7 TSDC spectra in polarized PVC with distinct degrees of stretching (λ). Value of λ: (——) 1; (······) 1.1, (– – –) 1.2; (— —) 1.3; (– · –) 1.5 (10 kV mm^{-1}, 50°C, 2 h)

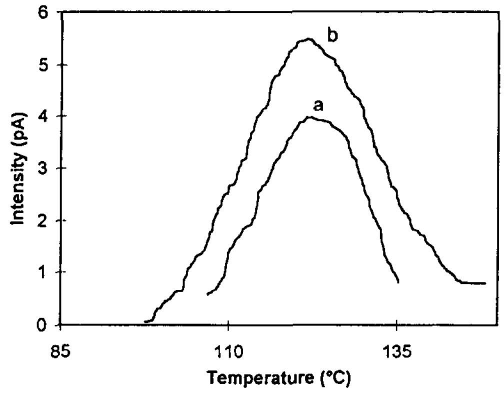

Figure 8 ρ peak of TSDC spectra for the unstretched PVC (a) and to $\lambda = 1.1$ stretched PVC (b)

proposal that orientation of syndiotactic sequences should make the terminal rrmr local configuration become increasingly able to move and polarization.

The ρ peak evolution with stretching remains to be studied thoroughly. Owing to the recovering of films when T_g is surpassed, we failed to obtain a systematic measure of the films stretched at $\lambda > 1.1$. A detailed study is now under way.

Figure 8 shows the ρ peak for $\lambda = 1.1$. Interestingly, the intensity increases markedly with stretching but once again this tendency seems to reverse at higher λ values (results not shown herein). Therefore, the results of *Figure 8* tentatively suggest a higher propensity of the GTGTTT conformation to charge trapping than the GTTG$^-$TT conformation, contrary to what happens for dipole polarization (*Figure 8*).

CONCLUSION

The results obtained herein give further evidence of the crucial role of the mmr and rrmr terminals of isotactic and syndiotactic sequences, respectively, in the nature and distribution of the space charges trapped by the material upon application of an electrical field. The fact that stretching causes the conformational change GTTG$^-$TT $\Rightarrow$ GTGTTT in mmr to be operative as the unique or the major process depending on the stretching extent, allows one to distinguish between the effects of each conformation. It appears apparent that GTTG$^-$TT favours dipole polarization over trapping of charges injected from electrodes, while the opposite seems true for GTGTTT conformation. Further work currently under way, is expected to further assess the space charge/microstructure relationship.

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