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Effect of $[CHCl]_{n\geq3}$-structures on the origin and relaxation of dipolar and trapped electric space charges in chlorinated PVC

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SUMMARY

The electric space charge behaviour of chlorinated PVC has been studied via thermal step (TS) and thermally stimulated discharge current (TSDC). Chlorination has been found to change strongly the ratio between polarization and injection charges in comparison with unmodified PVC. The results allow one to take the fundamentals of the space charge behaviour of PVC an important step further.

INTRODUCTION

Within the framework of the polymer property / molecular structure relationships the influence of some secondary structures on the electric space charge nature and distribution in insulating materials is of great significance scientifically and industrially (1). Space charges (electrons, ions, oriented dipoles, etc) which are trapped in certain parts of the insulator, specially when applying an electric field, are known to favour ageing and electrical breakdown and then to determine the electric properties and the performance in applications such as electric cable, transformers, electronic devices, power capacities, condensators, motors, etc. The basic phenomena of space charge storage in polymers and the methods for measuring charge distributions which have been developed for the last years have been conveyed by several authors (2-6).

The role of the specific molecular microstructure derived from tacticity (especially the isotactic **mmr** tetrad occurring whenever an isotactic sequence breaks off) (7), both in the chemical reaction mechanisms (7,8) and physical properties (9) has attracted our attention during the last years. The results obtained, coupled with the availability of first the so-called thermal step (TS) which allows an accurate and reproducible measurement of the space charges (10) and secondly the thermally stimulated discharge current (TSDC) technique to measure the thermal relaxations of those space charge containing polymer structures (11), made it greatly interesting to investigate the extent to which the found concepts hold for the space charge behaviour. By analogy with other properties (9) these studies were expected to provide novel information as to the mechanism of the processes involved in the space charge phenomenon and the nature of the space charge traps.

The results for poly (vinylchloride) (PVC) prior to and after gradually changing the tacticity-microstructure, either chemically (nucleophilic substitution) (12) or physically (stretching at temperatures near Tg) (13) have been recently published in detail. Also, some novel correlations for polypropylene have been disclosed (14).

From these studies some major conclusions have been drawn: 1) the magnitude of space charge trapping and the type of distribution, which emerge when applying an electric field depend strongly on the content of **mmr** configuration terminating every isotactic sequence (1,12-14); 2) the two chain conformations which are likely in **mmr** configuration, i.e. GTTGTT and GTGTTT, happen to be related to polarization charges and from electrodes injection charges respectively (15), thereby opening new prospects in the understanding of the space charge origin and trapping. Actually both conformations are molecular discontinuities with local excess free volume and enhanced mobility. Nevertheless, the distinct rotational capabilities of each conformation make the C-Cl dipoles orientate much more easily in GTTGTT conformation (12,13). Since chlorination of PVC proves to involve change in magnitude and nature of the same rotational motions (16) a study of the space charge behaviour of chlorinated PVC compared to pure PVC was outlined with the aim of confirming the local molecular requirements for each of the two types of space charges to be produced, as disclosed by the work above. This paper deals with the first results obtained.

EXPERIMENTAL

Materials

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

Samples B and C are the result of chlorination reaction of sample A, to 9.5 and 18.2 mol% as described by Contreras et al (16).

Both the degree of chlorination and the tacticity, were determined by the same authors by means of ^{13}C NMR spectroscopy (16). The values as kindly supplied by them, are given in Table 1.

Preparation of films

Films 100 µm thick (sample B) and 170 µm thick (samples A and C) were made by compression moulding at 150 °C at a pressure of 125 bar, using a Collin press Model 300.

Thermal Step (TS) method

The specific details have been described in previous papers (1,10). Basically, it consists in applying a sudden variation of temperature ($\Delta T = -35$ °C) to a one of the electrodes of the sample. The presence of charges Q_i in the insulator induces image charges on each electrode Q_{i1} and Q_{i2}; $(Q_i+Q_{i1}+Q_{i2})=0$. 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 the abscissa X_0 (see Fig. 1).

The current is: $I(t) = -\alpha . C . \int_0^D E(x) . \frac{\delta T}{\delta t} . dx$, where $\alpha = \alpha_x - \alpha_\varepsilon$, with α_x: linear expansion coefficient of material; α_ε: thermal dependence of permittivity coefficient; C: capacitance of sample; T: temperature; D: thickness of sample; E(x): electric field strength in elementary thickness dx; $\alpha_x = (1/l)\ \delta l/\delta T$ and $\alpha_\varepsilon = (1/\varepsilon)\ \delta\varepsilon/\delta T$.

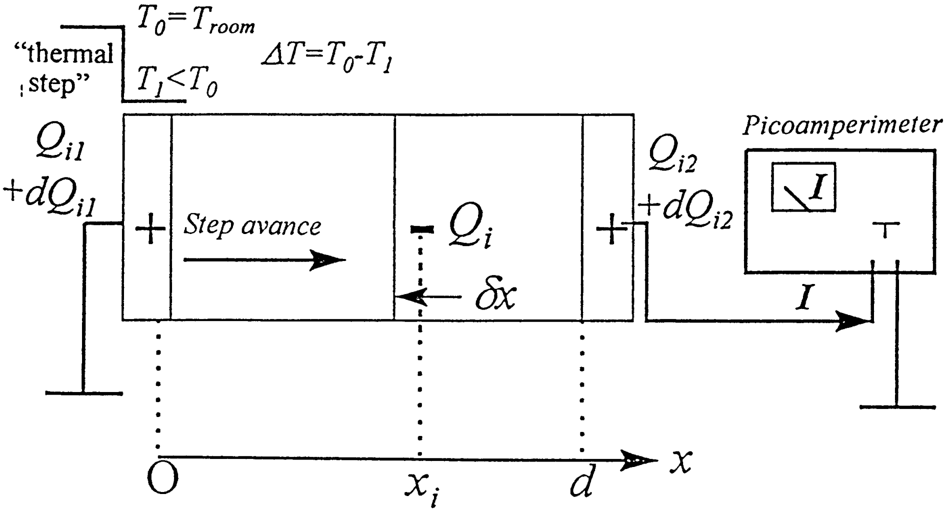

Figure 1: The principle of thermal step method.

α is obtained by the measurement of capacitance at different temperatures.

The current is amplified and recorded on a computer and then there is a deconvolution by one of the different numeric treatments (Fourier series or derivation) which have been described in previous papers (6).

Aluminium electrodes (Φ = 20 mm) have been deposited under vacuum on each side of the samples. These were conventionally polarized. The polarizing field and polarization temperature were 10 kV/mm at 50 °C during 2 hours.

Space charge measurements have been performed after a short-circuit of 44 hours. This period was usual in earlier work regardless of the type of polymer after proving that no change in space charge density occurs.

Thermally Stimulated Discharge Current (TSDC) method

This method is based on the fact that each of the microscopic processes that lead to polarization has a characteristic relaxation time. Usually thermally stimulated experiment is carried out by heating the sample at a constant heating rate while the sample is shortcircuited through an ampermeter. The resulting current is recorded as a function of the temperature and the charge relaxation processes are reflected as current peaks in the TSDC spectrum.

Thermally stimulated discharge current measurements have been performed with a heating rate of 2 °C/min (this being low enough to prevent temperature lags and to guarantee a good resolution of peaks) on a temperature range of 25 °C to 160 °C.

RESULTS AND DISCUSSION

As shown by Table 1, the samples A, B and C differ both in chlorination degree and in tacticity. The trend of the latter with increasing chlorination has been argued to obey the preferential chlorination through the **mmr** tetrad, at least to a substantial extent (16). Also, chlorination up to roughly 9% was found to involve isolated monomer units, so giving birth to -[CHCl]$_3$-structures (16). Conversely, at higher chlorination degrees -[CHCl]$_{3>}$-structures are produced. This makes the difference between samples B and C.

Table 1: Characteristics of samples[a]

Sample	Chlorination degree (mol%)	Tacticity		
		mm (%)	*mr+rm (%)*	*rr (%)*
A	0	20.1	49.6	30.3
B	9.5	19.7	48.7	31.6
C	18.2	19.4	47.7	32.9

[a]Values taken from ref. 16

mm: isotactic triad; *mr+rm*: heterotactic triad; *rr*: syndiotactic triad

Thermal Step (TS) results

Fig. 2 depicts the current measured on the anode and the cathode for the samples of Table 1. The corresponding space charge distributions as deduced through deconvolution of the measured currents of Fig. 2 (6) are presented in Fig. 3.

Overall, the space charge pattern for samples A and B (Fig. 3) are of the type found for a priority polarization mechanism (1,12). Still, significant differences are quite apparent doubtless because of the isolated -[CHCl]$_3$-structures in the case of sample B. In agreement with prior work (1,12,13), the distribution for sample A, a pure PVC, shows a higher amplitude by the side of cathode so suggesting the occurrence of some positive charge injection from the anode. Sample B shows an amplitude significantly lower than sample A, and then a lower amount of charges.

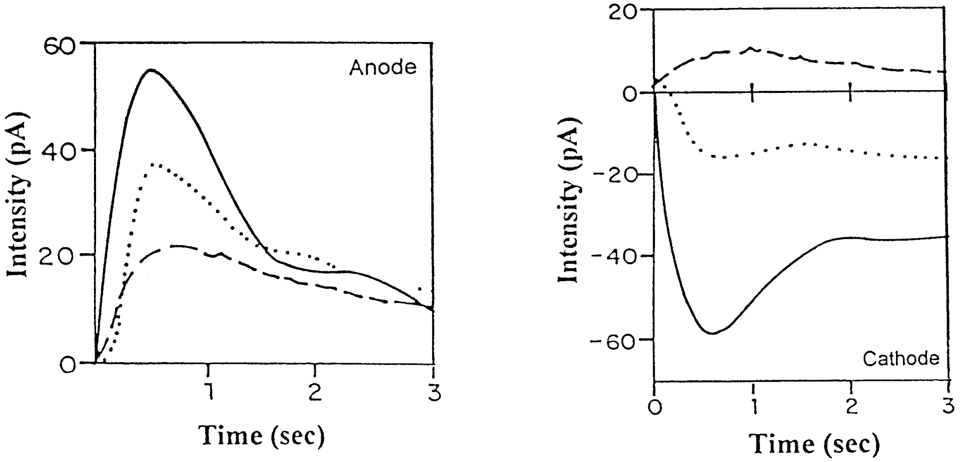

Figure 2: Intensity of the thermal step induced currents vs time for chlorinated PVC to various degrees (Tab. 1): (——) 0%; (·····) 9.5%; (- - -) 18.2% (10 kV/mm, 50 °C, 2h.).

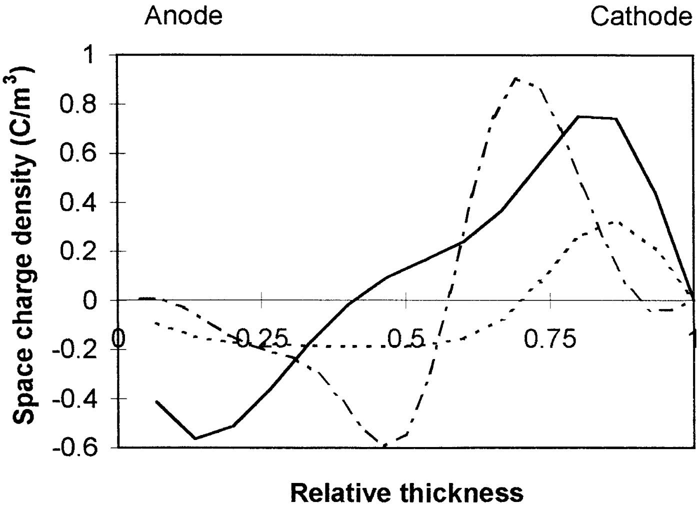

Figure 3: Space charge density in polarized chlorinated PVC to different degrees: (—) 0%; (······) 9.5%; (- - -) 18.2% (10 kV/mm, 50 °C, 2h.).

This can be due either to a lower number of dipoles or to a higher contribution of injection charges which would neutralize the polarization ones. As can be seen there is a negative charge accumulation extending through the sample between the anode side and the proximity to the cathode where a heterocharge accumulation is produced. Clearly the summation of negative charges is higher than that of positive charges thereby suggesting that there is negative charge-injection from the cathode.

The interpretation above of the results of Fig. 3 is given further support by the current intensity curves of Fig. 2. These curves are of positive and negative sign for both samples and the intensity at the maximum is substantially higher for sample A in either electrode. In addition, the ratio between the surface areas of anode and cathode is lower and considerably higher than unity for samples A and B respectively, so indicating that even if sample B keeps up a majority polarization pattern, the injection produced through the cathode in sample B, unlike sample A, prevails over that from the anode, as the result of chlorination.

Sample C behaves in a different way to sample B. As can be seen from Fig. 2 the TS current intensities on the anode and the cathode are both of positive sign which is characteristic for an injection process from the cathode in polar polymers like PVC. Correspondingly, the space charge distribution (Fig. 3) shows a slight and strong accumulation of homocharges on the cathode and in the middle of the sample respectively.

In addition, a rather great amount of positive charges gather in the region next to that trapping most of the negative charges (Fig. 3). The fact that the maxima of the two latter accumulations lie near the middle of the sample, makes it unlikely to relate them to polarization charges. The accumulation of negative charges like those observed in Fig. 3 occurs usually when the negative charge injection from the cathode is accompanied by the migration of these charges towards the middle of the sample (14). Conversely, since no appreciable injection from the anode is apparent, the massive accumulation of positive charges as observed for sample C (Fig. 3) can hardly be attributed to any migration process. Thus, we believe it more probable that those positive charges have been induced by the massive injection of negative charges from the cathode.

As a first approximation the results of Figs. 2 and 3 are a clear indication that the chlorination of PVC favours the occurrence of negative charge-injection from the cathode but they give no information about the extent to which these homocharges can offset or even exceed the heterocharges relevant to polarization. This can be achieved by coupling the TS method with the TSDC, a method which makes it feasible to distinguish between both types of charges (12). On the other hand such a complementary study proves useful to state the local molecular features which are sensitive to either polarization or injection charges (12,15).

Thermally Stimulated Discharge Current (TSDC) results

The TSDC spectra of sample A, B and C are displayed in Fig. 4. They show the evolution of α and ρ relaxations which are relevant respectively to glass transition and to the release of cavity traps carrying space charges other than the polarization ones (11).

Comparing the spectra it is evident that the intensity of α relaxation and consequently the number of C-Cl bonds capable of orientation, increases strongly from sample A to sample B and it drastically drops to a very low value for sample C even if the overall number of C-Cl bonds increases steadily from sample A to sample C.

ρ relaxation is found to behave otherwise in that it is of little significance for sample A compared with those of samples B and C. It is noteworthy that the temperature increases in the order A < B < C so suggesting that the charge retention increases in the same order. Even though more work remains to be done, this seems to indicate that the capability of charge trapping decreases in the order **mmr** under GTGTTT conformation in pure PVC > isolated -$[CHCl]_3$-structures > -$[CHCl]_{n>3}$-sequences. On the other hand the difference in intensity between the ρ peaks of samples B and C, might be due to the change in the ratio between the contents of $[CHCl]_3$ and $[CHCl]_{n>3}$ structures.

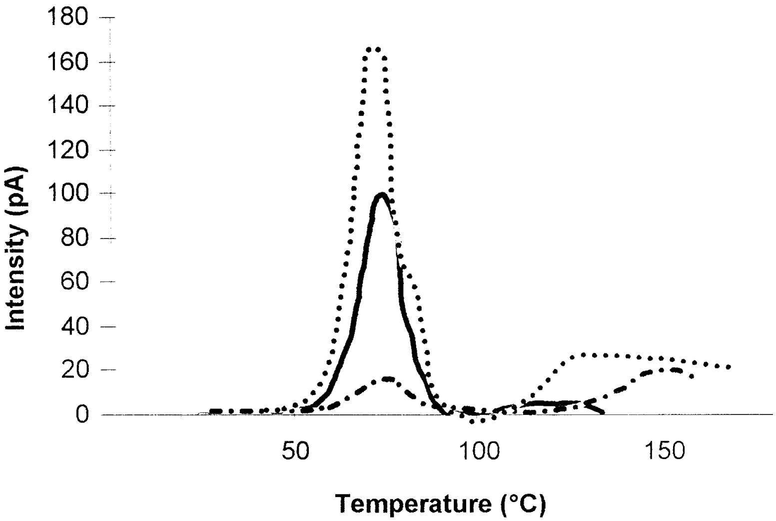

Figure 4: TSDC spectra in polarized chlorinated PVC to different degrees: (—) 0%, (···) 9.5%; (- · -) 18.2% (10 kV/mm, 50 °C, 2h.).

The behaviours of α and ρ relaxations (Fig. 4) lend further support for the TS results as tentatively explained above. First, the occurrence of space charge-injection from the electrodes is confirmed by the high intensity of the ρ peak for samples B and C relative to sample A. Secondly, the higher or the almost-null content of polarizable C-Cl dipoles, found for samples B or C respectively compared with sample A (Fig. 4, α relaxation) is consistent with the prevailing polarization or injection space charge distribution of samples B and C (Fig. 3) despite the substantial injection charges in sample B.

CONCLUSIONS

The foregoing results not only enable the space charge behaviour to be correlated with the specific chlorinated structures but can give further support for the local microstructural features which make a definite material produce either polarization or injection space charges according to earlier work.

Actually these results allow one to assign the high injection from the cathode in samples B and C, relative to pure PVC, to both -$[CHCl]_3$- and -$[CHCl]_{n>3}$-structures. In addition, the former structure contains more polarizable C-Cl dipoles than PVC.

As argued elsewhere (16) and easily observable with appropriate atomic models -$[CHCl]_3$- and -$[CHCl]_{n>3}$-structures are, likewise GTTGTT and GTGTTT conformations of **mmr**, local chain discontinuities involving excess free volume and an enhanced and localized mobility. Moreover, the magnitude of the latter proves to depend on the ability that the chain segment has to experience a conformational change through the rotational motion of the involved C-C bonds. It is this feature that causes the -$[CHCl]_3$-structure to be more polarizable and the -$[CHCl]_{n>3}$-to have a more restricted rotational motion than GTTG$^-$TT and GTGTTT conformation respectively in pure PVC (16).

Therefore the results obtained herein provide new evidence of the specific conditions, which a local molecular microstructure ought to fulfil to produce either polarization or injection space charges, as put forward for PVC (1, 12, 13, 15) and PP (14).

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