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On a novel molecular microstructure based approach to the extrinsic space charges releasing in polypropylene (PP)

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SUMMARY

The release of the extrinsic charges produced when applying an electric stress has been studied for four polypropylene samples of distinct well controlled molecular microstructure by Thermal Stimulated Discharge Current (TSDC), with the aim of stating the correlation between the ρ relaxation (intensity and temperature) and the tacticity induced polymer microstructure, and of, demonstrating that the traps of space charges are not chain defects as usually proposed but that they relate to some normal local chain configurations.

The results are discussed in the light of the space charge distributions as measured in earlier recent work.

INTRODUCTION

The tacticity induced molecular microstructure / property relationships have been a major research concern of our laboratory. That microstructure, which will be referred to as "tacticity-microstructure" throughout this work, is understood as the local configurations occurring necessarily whenever an isotactic or syndiotactic sequence breaks off, i.e. the isotactic **mmr** tetrad and the heterotactic **rrmr** pentad respectively, in addition to the tactic sequences themselves and the local conformations characteristic of **mmr** and **rrmr**, in particular the former. The latter conformations, as widely considered previously (1,2), are reproduced in Fig. 1.

As extensively published the tacticity-microstructure was shown to be the main determining factor in chemical reactions (1,2) and physical properties (3,4) of poly (vinylchloride) (PVC). In this connection, an attempt to extend the above concepts to some electrical properties of PVC was made recently (5,6). In particular the space charges which originate upon application of a strong electric field were proved to relate straightforwardly to the content of **mmr** configuration, especially when adopting the GTTGTT chain conformation (Fig. 1).

Within this framework we thought it greatly interesting, scientifically and industrially, to investigate whether those original correlations found for PVC apply to polypropylene (PP), a highly important insulating material of extensive use in electrical and electronic engineering. Actually, PP exhibits the same tacticity-microstructure capabilities but quite different polarity to PVC so that distinct types and distributions of space charges should be expected. On the other hand the practical interest is such that some crucial electrical properties like electrical breakdown and ageing are known to depend on the sort and distribution of space charges.

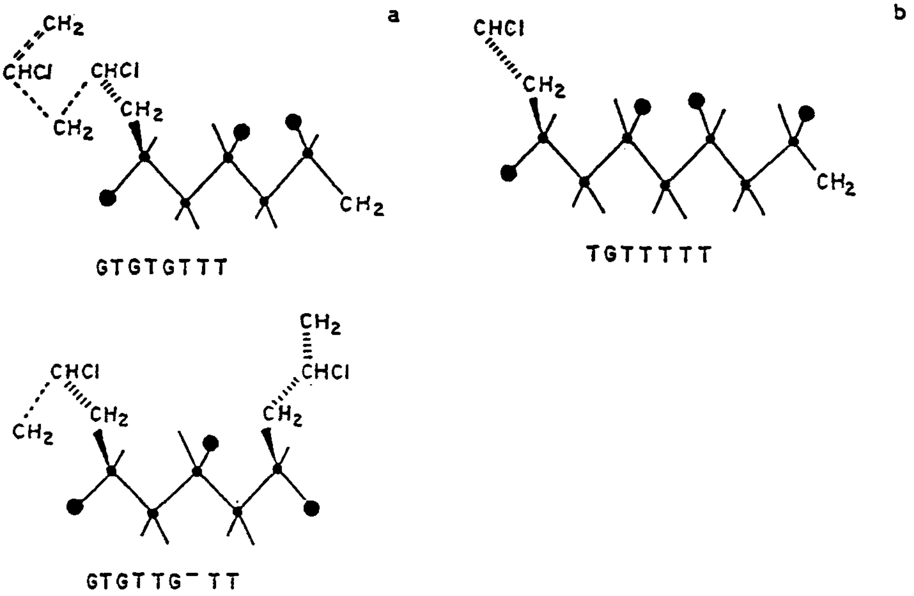

Figure 1: Conformations of *mmr* in *mmmr* pentad at the right side of an isotactic sequence (a) and of *rrmr* pentad at the right side of a syndiotactic sequence (b).

In a first work the distribution of space charges has been achieved through the Thermal Step (TS) method for four PP samples of different tacticity-microstructures. Of these, two samples obtained by fractionation according to isotacticity, consist basically in isotactic sequences separated by **mmr** structures. They differ in the average length of the isotactic sequences and, thus, in the frequency of occurrence of **mmr**. The other samples are unfractionated polymers and contain, in addition to the isotactic structure above, distinct moieties of atactic and syndiotactic parts.

The space charge distribution of these samples after subjecting them to an electric field was found to depend strongly on the tacticity-microstructure in the way that the injection of positive charges from the anode and of negative charges from the cathode relate to the presence of moieties of atactic and syndiotactic sequences and to the above mentioned pure isotactic microstructure respectively. Furthermore, both the accumulation of negative charges in the proximity to the cathode and their extending through the inside of the film, proved to depend on the frequency of occurrence of **mmr** structures and thence on the average length of the isotactic sequences by either side (7).

A tentative explanation for these original behaviours was proposed to lie in the fact that as can be seen from Fig. 1, **mmr** is a local molecular discontinuity capable of forming a sort of cavity trap. The charge trapping depth would thus depend mainly on the extent to which a definite regular fragment of chain is distorted by **mmr**, which would account for the observed stronger accumulation and stability of negative charges as the content of **mmr** increases up to a certain value (7).

One way to elucidate those proposals is that of investigating whether the so called ρ relaxation of Thermal Stimulated Discharge Currents (TSDC) spectra for the same PP samples, relates to the tacticity-microstructure. Indeed, ρ relaxation is known to arise from the motion of the local specific chain sites carrying extrinsic charges. They are usually viewed as material defects. On the other hand, **mmr** surrounded with two isotactic sequences is a local structure of excess free volume, enhanced mobility and null or little interaction with vicinal chains (3,8). Thus, if they were preferential traps of charges, as suggested by the above quoted work (5,6) then both the intensity and the temperature of ρ relaxation would have to change with the tacticity-microstructure of PP, and the correlations so obtained would take the space charge behaviour of PP an important step further.

The present paper deals with the results obtained in this matter for the same PP samples as previously studied by TS method.

EXPERIMENTAL

Materials

Samples A and D were commercial polymers after purification by dissolution and precipitation. Samples B and C were obtained by controlled fractionation of a commercial polymer (PP050 supplied by Repsol) after purification, using a polar/non polar pair of solvents in various proportions. The methodology was previously reported (7). The overall isotactic triad content decreases in the order A (92.3 %) > B (90.6 %) > C (75.7 %) > D (59.3 %). Samples A and D, furnished as isotactic and atactic polymers, contain atactic and syndiotactic parts. Samples B and C are pure isotactic in character in that they arise from fractionation according to isotacticity. They consist basically in **mmr** configuration surrounded with isotactic sequences, the frequency of the former and, then, the average length of the isotactic sequences being respectively higher and lower for sample C.

Characterization

The tacticity of the four distinct PP samples was measured by ^{13}C-NMR spectroscopy on an Bruker DRX400 instrument. The specific details have been provided in prior publication (7).

Preparation of the films

PP samples were processed from powder by compression moulding at 165± 5 °C and at a pressure of 125 bar to prepare films of 300 μm thickness (sample A and D), 225 μm thickness (sample B) and 350 μm thickness (sample C), using a Collin press Model 300.

The films were provided with two identical aluminium electrodes (ϕ = 20 mm) which were deposited through evaporation of the electrode material (aluminium, which is resistent to oxidation) on each side of the samples under vacuum.

Thermal Stimulated Discharge Currents (TSDC) method

In the TSDC technique, the sample, a thin polymer film of a few square centimeters area (electrodes, ϕ = 20 mm), is poled submitted, in parallel, to an electric stress of 10 kV/mm at a temperature of 90 °C during 2 hours in order to form an electret that is, a sample exhibiting an electrical charge which decays with a time constant much longer than the time scale of experiments (9). The thermoelectret may be stored between two shorted electrodes. When the study of TSDC is to be carried out the electret is reheated at a linear heating rate and the discharge current generated is measured with an electrometer and recorded. The plot of the discharge current as a function of temperature is called a thermogram. A thermogram exhibits one or several peaks and is characteristic of the material. For this reason, the TSDC method is also called dielectric depolarization spectroscopy and it has been largely used as a basic tool for the study of dipole reorientation and of trapping and recombination processes. The first theoretical basis for the TSDC phenomena was established by Bucci and Fieschi (10) for dipolar reorientation and then by Perlman (11) for extrinsic space charges.

The TSDC measurements were made on four different polypropylene films at a temperature range from 25°C to 160°C. A heating rate of 2°C/ min was retained as the most suitable (this being low enough to prevent temperature lags and to guarantee a good resolution of peaks). The current measurement requires a sensitive Keithley electrometer, which has a lower detection limit of 10^{-15} A.

RESULTS AND DISCUSSION

Fig. 2 depicting the TSDC spectra obtained under similar conditions clearly indicate that the PP samples (see experimental section) are different in behaviour. Owing to the fact that PP is poorly polar, the α transition, corresponding to the relaxation of dipoles and then to the intrinsic polarization charges relevant to the electret formation, was scarcely observable, so the TSDC spectra were registered from 25 °C. Neither the section of TSDC spectrum after the maxima of ρ relaxation could be registered due to the overlapping effect of the incipient melting process. Nevertheless, the ρ relaxation could be repeatedly registered with resolution enough for both the intensity and the temperature at the maxima to be reliably stated within the experimental uncertainties.

The spectra of Fig. 2 shows two ranges of temperature for the ρ relaxations, each range embracing the temperatures higher or lower than 120°C. The first range includes samples B and C and the second range includes sample D. Interestingly, sample A exhibits two peaks, each located at one of the temperature ranges.

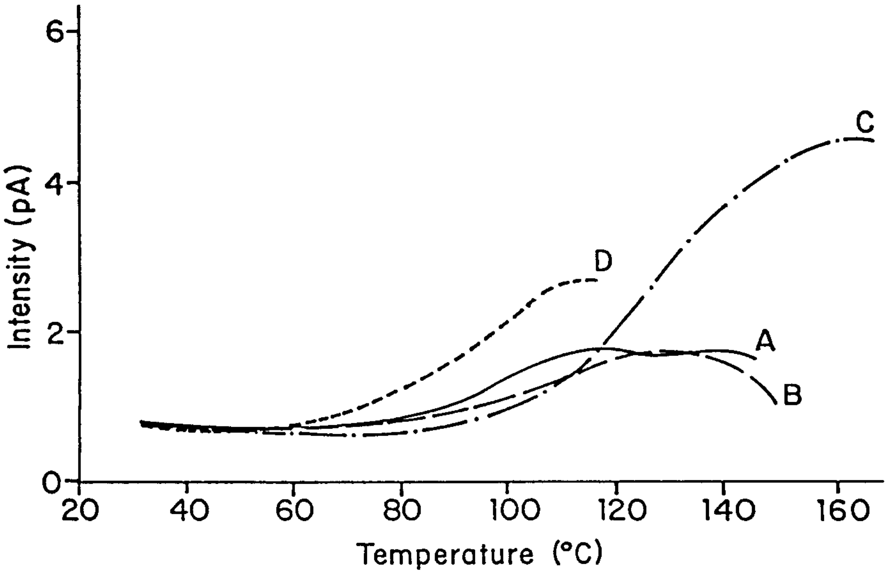

Figure 2 : TSDC spectra in polarized PP to different isotactic triad content, *mm*: (——) 92.3%; (----) 90.6%; (– · –) 75.7%; (······) 59.3%. (10 kV/mm, 90 °C, 2h).

According to the specific microstructure of the samples (Experimental section; (7)) those temperature ranges may be considered to relate respectively to the **mmr** based pure isotactic microstructure (which is the unique structure in samples B and C, and the majority structure in sample A) and to the atactic sequences (which are abundant and scarce in samples D and A, respectively). Further support for these correlations is given by the high intensity both of the ρ peak of sample C relative to sample B, and to sample A (higher peak), and of sample D relative to sample A (lower peak), as illustrated by Fig. 3 showing the intensity of the ρ peaks for the B-C and A-D pairs of polymers versus the isotactic triad content. Actually, these differences in intensity of the peaks agree with the respective contents either of **mmr** based pure isotactic microstructure (samples B and C, and, to a greatest extent, sample A), or of atactic sequences (sample D and, to a little extent, sample A) (Experimental section and ref. 7). It is worth noticing that the two peaks of sample A are roughly similar in intensity (Fig. 2); so, a single value, common to both relaxations is given in Fig. 3.

In regard to samples B and C, the results of Figs. 2 and 3 agree with the occurrence of strong injection of negative charges from the cathode as unique response of sample C to the electric field (7). In this respect sample B was proved to behave, qualitatively, in a similar way to sample C in that only injection from the cathode was observed. Nevertheless, the amplitude of space charge distribution was found to be very low for sample B compared to sample C what was attributed to the little content of **mmr** structures and the subsequent lengthening of the associated isotactic sequences in sample B (7) without, as it is the case for sample C, any structure other than the latter one, being appreciably likely (7).

These conclusions are consistent with the strong difference in ρ intensity between samples C and B (Fig. 3).

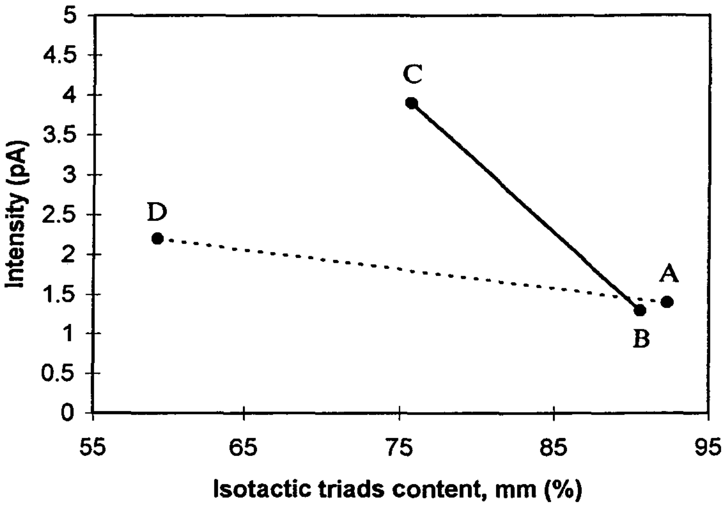

Figure 3 : Evolution of the space charge peak intensity (ρ) of PP samples with isotactic triad content, *mm*.

In this connection sample A was found to exhibit priority injection of negative charges from the cathode, associated with its pure isotactic part, together with a little injection of positive charges from the anode, resulting from the atactic moieties which are present in this sample (7). These results agree with the occurrence of two peaks in it (Fig. 2).

Finally, sample D proved to experience positive charge injection from the anode, which was assigned to the rather abundant atactic sequences in it (7). As it is the case for the lower ρ peak of sample A, the ρ peak of sample D is to be related to the latter sort of microstructure.

Therefore, two well differentiated space charge behaviours may be stated depending on whether the polymer consists in **mmr** based pure isotactic microstructure (like samples B and C) or whether it contains, in addition to that microstructure, substantial amounts or some moieties of atactic sequences, which is the case for samples D and A, respectively.

The foregoing structures are responsible for the trapping either of negative charges injected from the cathode or of positive charges injected from the anode, respectively (7).

Comparing the behaviours of samples B and C in Fig. 3, it is apparent that the ρ peak intensity is higher as the number of **mmr** based local configurations surrounded by two isotactic sequences increases, as it does from sample B to sample C. It is then this specific microstructure that must be viewed as the usual trap of negative charges.

As to the ρ peaks of samples A and D, these are relevant to the competing processes of injection from the anode and the cathode (7) and, then, to the ratio between the content of the two types of microstructure in each of the samples. The higher intensity of ρ peak of sample D, compared to sample A (lower peak), clearly obeys the much higher content of atactic sequences of the former sample, so indicating that the traps of positive charges are located at those sequences. Nevertheless, the real microstructure of these traps cannot be assessed at the current state of our work. On the other hand, the increase in ρ intensity from sample A to sample C happens to be less significant than that from sample B to sample C. However, whether this obeys a lower trapping efficiency of the atactic sequences, compared to the **mmr** based traps, or whether it is due to the competing trapping action of the latter traps cannot be disclosed either.

Fig. 4 displays the temperature at the highest intensity of ρ versus the overall isotactic triad content. Since, unlike the intensities, the temperatures of the two peaks of sample A are different, they are both included.

Overall, the temperatures in Fig.4 are an indication that the negative charges injected from the cathode are more deeply trapped by the **mmr** based isotactic microstructure than are the positive charges injected from the anode, trapped by non-isotactic structures. This is particularly evident by considering both the higher temperature and the highly restricted migration of the negative charges injected from the cathode as observed in Fig. 4 and found in the above quoted work (7) respectively. The higher temperature of the ρ peak relevant to the **mmr** based traps in sample A, lends further support for that conclusion.

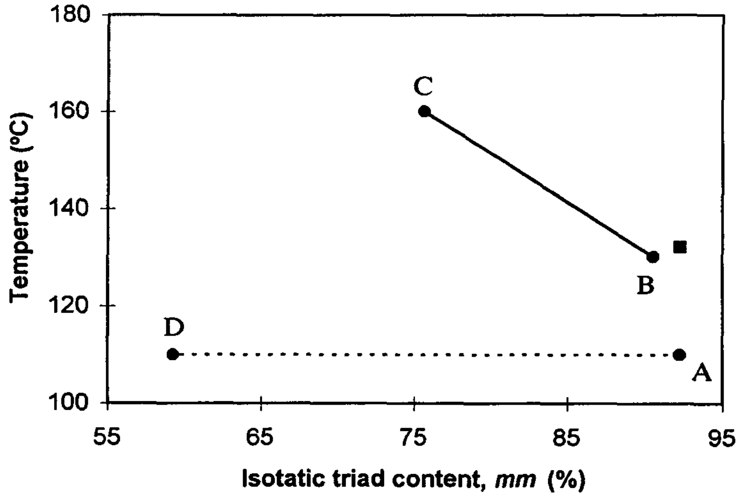

Figure 4 : Evolution of the space charge peak temperature (ρ) of PP samples with different isotactic triad content, *mm*. [■] corresponds to the second ρ peak for sample A (92.3%).

In conclusion, the results obtained herein allow one to explain the differences in space charge distribution as obtained previously for the same samples (7) and enable for the definite **mmr** based isotactic microstructural units to be the prevailing traps of the extrinsic negative charges created in PP upon application of an electric field.

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