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On the coupling in molecular motions: A novel molecular micro-structure approach to the physical meaning of the Ngai's coupling parameter

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Summary

The dielectric behaviour through DETA system has been studied for six PVC samples of distinct molecular microstructure in terms of content and associated surroundings and conformation of the local configurations **mmr** termini of isotactic sequences. Both the dielectric studies and the microstructure of the samples, as obtained by stereospecific substitution reaction of an additive-free commercial PVC are to be published in detail separately. For purposes of clarity some of the results are mentioned in Experimental section.

The phenomenological correlation between the β parameter as defined by Ngai's theory and the microstructure of the samples, quantities both issued from the above quoted work, is considered in the present paper with the objective of providing some novel ideas on the physical meaning, at molecular level, of the Ngai's coupling parameter, in the light of mobility constraints and local free volume associated with **mmr** structure at its likely conformations.

Introduction

In a series of recent publications [1-13] we have experimentally demonstrated the straight relation between the physical properties and the stereochemical microstructure of poly (vinyl chloride) (PVC) as induced by the tacticity. This microstructure refers to the tactic sequences whether isotactic or syndiotactic, and especially the local configurations which occur necessarily whenever a tactic sequence breaks off, namely the **mmr** and the **rrm** tetrads repectively, and the conformations which are likely in them [1, 2]. It depends on the polymerization conditions which are suitable for every monomer and can be modelled through stereospecific chemical reactions [3-5] or physical treatments like stretching [6] or annealing [7].

Different studies have been performed on the microstructure dependence of the degradation [7, 8], the thermal relaxation properties [9, 10] and the electrical properties [11-13]. An overview of some of them has been published recently [1].

The explanation for the valuable correlations obtained rests upon the evidence that the mechanism of the process which each physical behaviour involves, can be understood only by assuming the occurrence of one of the foregoing specific microstructure features. The major conclusions can be summarized as follows: i) the **mmr** sequence appears to be the main driving force for properties like chemical reactivity [3-5], thermal degradation [7], dielectric relaxations [14, 15] and the electrical space charge nature and distribution [11-13]. Since they all depend on the occurrence of either local free volume excess or local molecular motions or both sequential and local dipole-dipole interchain interactions [9, 11], a possible explanation of the correlations found lies in the fluctuations of the latter quantities that would be expected to stem from the **mmr** associated with any isotactic sequence of at least one heptad in length [3]; ii) even if these fluctuations are intrinsic to **mmr,** they prove to depend to a substantial extent, on the conformation, whether **GTTG^{-}TT** or **GTGTTT**, which **mmr** is taking [16, 17]. As an example the latter conformations as controlled by modifying, chemically or physically a PVC of well known starting microstructure, prove to be sensitive to dipolar and injection space charge respectively [18]. Also, the dielectric molecular motions have been studied for firstly a PVC sample prepared at 70°C and the same polymer after substitution reaction to various molar percents with sodium benzenethiolate in the melt state [5], and, secondly a film of the same polymer prior to and after drawing at 90°C to elongation ratio of 1.5 [6]. These properties were measured by means of isothermal depolarization currents (TSDC) [14] and dielectric relaxation [15] techniques respectively. The results no matter how tentative, as interpreted according to the Ngai's coupling model [19], show alterations in the molecular motion parameters, e.g. the coupling between the moving units and the activation energy responsible for the motions, which would seemingly relate to the changes in **mmr** content, and especially in the corresponding **GTTG^{-}TT/GTGTTT** ratio as the result of the above-cited modifications.

The fundamental interest of these correlations encouraged us to attempt a more systematic research of the dielectric properties of a PVC sample and the same polymer after substitution reaction with sodium benzenethiolate [NaBT] in cyclohexanone solution to 0, 0.53, 0.7, 5, 8.5, and 15 molar percent (Table 1). As extensively conveyed [3, 4] these substitution conditions, unlike the ones utilised in the melt state, make it possible to remove selectively on the one hand the **mmr** at the end of isotactic sequences of at least one heptad in length, whether under **GTTG^{-}TT** conformation (0.7% substituted sample) or under **GTGTTT** conformation (samples of substitution degrees lower than roughly 8%), and on the other, either the **mmr** termini of short isotactic sequences or the **rrm** termini of syndiotactic sequences (15% substituted sample). By doing so the relation between each of the above types of microstructure and dielectric properties ought to be identified thereby furnishing some novel information as to the mechanisms at molecular level of the physical processes which are responsible for properties.

Although the comprehensive work is still to be completely analysed and is to be published separately we judge it interesting to take advantage of the values of the β parameter as defined by Ngai's theory [19, 20] and found therein for the samples of Table 1, to provide some novel ideas on the physical meaning of that parameter, in the light of its microstructure dependence. This would be of valuable help to better understand the real mechanisms of the molecular motions involved in most of the polymer physical properties.

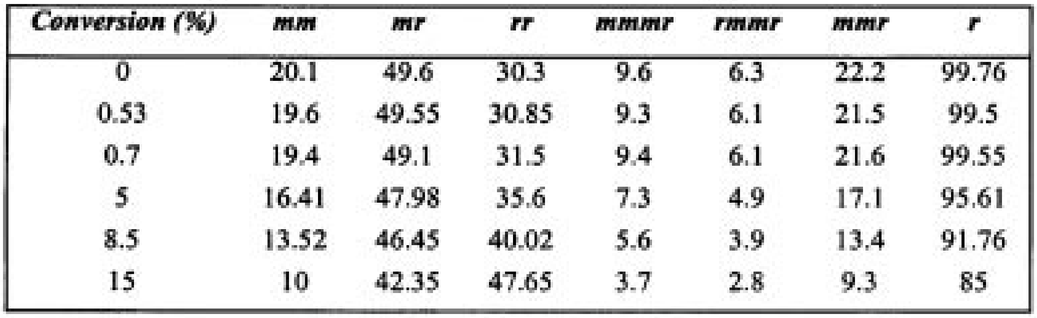
Experimental

Six PVC samples were used in this work (Table 1). Unmodified PVC (0%) was obtained by bulk polymerization at 70°C, and the process was stopped at a conversion of 62%. The number-average molecular weight (Mn = 44•10^3) was determined osmometrically at 34°C with solutions in CH using a Knauer membrane osmometer.

The substitution reactions of PVC (0%) with NaBT, to obtain the remaining samples were carried out in cyclohexanone solution at 25°C in an atmosphere of purified nitrogen. The products were purified by precipitation from THF in methanol, washed and finally dried under vacuum at 40°C.

The tacticity of the six PVC 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 spectra width was 2500 MHz, and a pulse repetition rate of 3s 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 shown in Table 1. They are consistent with the above mentioned changes in microstructure issued from stereospecific substitution [3, 4]. Actually up to 8.5% conversion the only reactive species proves to be **mmr** and most of the reacted **mmr** relate to either long isotactic sequences (loss of **mmmr** pentad) or isolated **mmr** (loss of **rmmr** pentad). This trend is clearly altered at 15% substitution so indicating that reactive species other than **mmr** have reacted. In fact, the complete validity of the stereoespecific nature of the mechanisms of this nucleophilic substitution has been repeatedly checked [3, 4].

Table 1: Tacticity characteristics of the PVC substituted samples



Conversion (%)	*mm*	*mr*	*rr*	*mmmr*	*rmmr*	*mmr*	*r*
0	20.1	49.6	30.3	9.6	6.3	22.2	99.76
0.53	19.6	49.55	30.85	9.3	6.1	21.5	99.5
0.7	19.4	49.1	31.5	9.4	6.1	21.6	99.55
5	16.41	47.98	35.6	7.3	4.9	17.1	95.61
8.5	13.52	46.45	40.02	5.6	3.9	13.4	91.76
15	10	42.35	47.65	3.7	2.8	9.3	85

The experimental DETA system has been already described in different works [15, 21, 22]. The set-up, consisting on a EG&G PAR 5208 two phase Lock-in analizer fully controlled by a computer, allows to measure simultaneously the real (ε') and imaginary (ε'') parts of the complex dielectric constant (ε* = ε' - iε'') of a given material (whose temperature is controlled within 0.1 K) under a controlled atmosphere of helium in a frequency range between 1 Hz and 10^6 Hz and a temperature range between 100 K and 600 K.

The isothermal ε’’ curves obtained in the temperature region where α-relaxation of PVC appears, after being substracted from the DC conductivity and β-relaxation contributions, were used to built master curves for each sample. As it is obtained over all the glassy polymers, these master curves were fitted to the phenomenological Havriliak-Negami (HN) function [23] (depicting the relaxation in the frequency domain) that, as it has been demonstrated in the last decade [24], can be considered in good approximation as the Fourier transform of the well known Kohlrausch-Williams-Watts (KWW) function [25] (that describes the relaxation in the time domain). This fact allows to calculate easily the non-exponential parameter β of the KWW function from the shape parameters of the HN function obtained from the fits of the experimental curves. Note that KWW function and Ngai’s relaxation function [19, 20] are formally the same. The above procedure is the usually utilized way to obtain the Ngai's β values [14, 19, 20, 22].

Results and discussion

The evolution of Ngai’s β parameter with substitution extent, as determined through samples of Table 1, is depicted by Figure 1. Interestingly, there are three distinct behaviours which are characterized by a rather abrupt decrease (between 0 and 0.7% conversion), an accentuated increase (between 0.7 and 8% conversion) and a slowing down (conversions higher than 8%) respectively. This means that the coupling degree of the local motions, according to Ngai’s theory, is the highest for 0.7% substituted sample and the lowest as substitution exceeds 8%. Comparing this behaviour and the corresponding evolution of microstructure as well stated in earlier work [3, 4] it is evident that: a) the lowest value of β agrees with the highest content of the long isotactic-based **mmr** structures taking **GTGTTT** conformation which thus appear to experience the most coupled motions; b) the **mmr** taking **GTTG^{-}TT**, also associated with long isotactic sequences, which vanish from the unmodified sample to the 0.7 substituted sample, is drastically less sensitive to coupling; and c) the coupling is anyway associated with the **mmr** termini of long isotactic sequences and is little significant after the removal of them (substitution degrees higher than 8%).

The physical meaning of the coupling parameter $n=1-\beta$, according to Ngai’s model [19, 20] arises from the argument that, unlike in the remaining theories, the relaxation of a “primitive species” is considered to depend on its surroundings. Parameter n ($0<n<1$) means the strength of the coupling of this primitive species to its environment, the strength of the coupling increasing with n. Whether the coupling of the primitive species is to vicinal chains (interchain interactions) or to adjacent units on the same chain (intramolecular interactions) has not been disclosed by Ngai’s model. Coupling has been anyway identified as the result of local free volume and its fluctuations in size, which would produce changes in the dynamical nature of the constraints and consequently in the relaxation rate. It is however worth mentioning that these phenomena have been always treated under a macroscopic point of view and that no specific relations with microscopic molecular features of structural nature have been invoked.

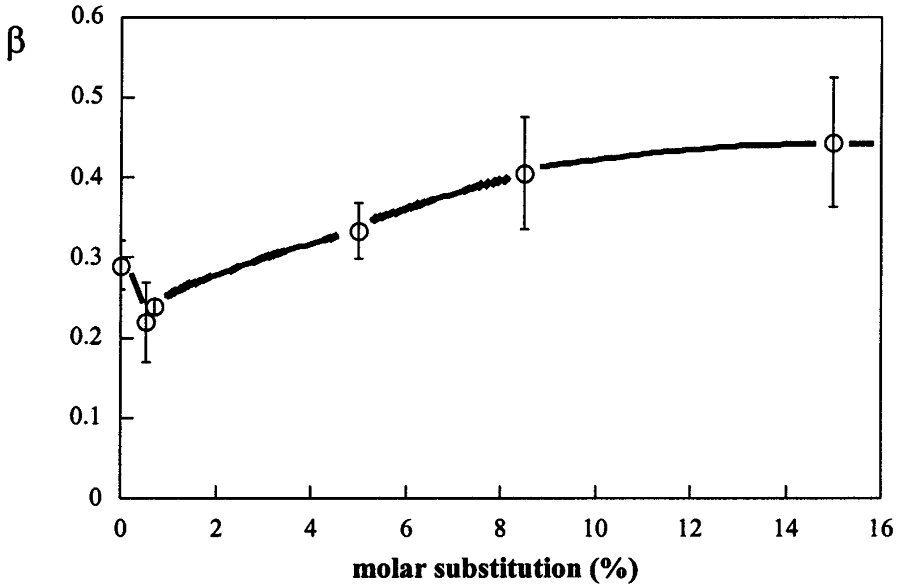


Figure 1: Non-exponential β parameter of each sample plotted versus the substitution percentage

In this connection, the tacticity-governed molecular microstructure, as defined in our work, has been shown to involve changes in local free volume and in sequential inter-chain interactions through successive hydrogen bonds. On the other hand, the constraints of the adjacent isotactic ....**GTGT** section on the terminal **mmr**, slowing down the rotation facilities of the latter structure, have been proved to be near nil or very strong depending on whether mmr is taking **GTTG^{-}TT** or **GTGTTT** conformation respectively [7]. A plausible explanation lies in the fact that, first the only likely rotation motion of **mmr** is that of converting the two latter conformations into each other, and, secondly, as extensively shown experimentally [3, 5] these two conformations are extremely unstable and very stable respectively. The above sorts of change have provided satisfactory explanations of the straight relations between microstructure and properties, as repeatedly found, so allowing the knowledge of the mechanisms of the respective physical processes to take a step further. These conclusions, coupled with the results depicted by Figure 1 and the molecular microstructure of the polymers listed in Table 1, as described in detail elsewhere [2], make it possible to get a novel insight into the very physical meaning of the coupling parameter. It is summarised in what follows.

i) The increase of n to attain a maximum at 0.7% conversion is concomitant with the removal of **GTTG^{-}TT** by exchanging for **GTGTTT** conformation in **mmr** associated with long isotactic sequences. As argued elsewhere [1, 9, 10] this agrees with on the one side a substantial decrease in local free volume, a quantity which is higher in the former conformation, and on the other an extension of the **GTGT** sequence, of higher length and more liable to form repeated hydrogen bonds with neighbouring isotactic sequences than **GTTG**$^-$ sequence. In addition, and this is a crucial point, it is easy to observe with appropriate atomic models [26] that, owing to the distinct constraints on **mmr** depending on its conformation as discussed above, the rotational motion in **mmr** (**GTGTTT**) is much hindered and requires the involvement of the adjacent units compared to that of **mmr** (**GTTG**$^-$**TT**), of much lesser stability. The explanation of such an important behaviour lies in de fact that the equilibrium GTTG$^-$TT ⇔ **GTGTTT** leans strongly to the right side [3, 6].

ii) The drastic fall of n between 0.7 and roughly 7% substitution percent and the slowing down observed afterwards can be related only to those effects inherent to the isotactic sequence length, namely the ability to form successive hydrogen bonds and the hindering of the rotation motion of the **mmr** breaking off the isotactic sequence. Obviously the effect of the free volume of **mmr** should be discarded because the **mmr** structures are all under **GTGTTT** conformation throughout this conversion rate [3, 9, 10].

iii) On the ground of the two above points the conclusion may be drawn that, firstly the real factor which determines the coupling is the **mmr** whenever it is associated with an isotactic sequence of at least an heptad in length; and secondly, of the above quoted implications of this structure the rotation motion facilities, as determined by the constraints of the isotactic .....**GTGT** sequences which neighbour necessarily upon it, are the main factor influencing the coupling. It is worth mentioning that according to these conclusions, the main effect of **mmr** (**GTTG**$^-$**TT**) producing lower values of n would relate to its favourable rotation motion to adopt **GTGTTT** conformation rather than to its higher free volume.

As widely considered in our work, **mmr** is a local structure which breaks off a regular segment of chain , namely an isotactic helix-coiled sequence, and its potential interchain interactions, a situation which is common to many materials irrespective of the nature of either the chain disruption or the chain regularity and intra-molecular interactions which are characteristic of each material. Therefore, the proposals given herein about the physical meaning of Ngai’s parameter, would apply to non-crystalline polymer materials other than PVC.

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