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On a novel tentative stereochemical microstructure based explanation of β relaxation of poly(vinylchloride) (PVC)

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Abstract

A set of PVC samples with various stereochemical microstructures, especially the **mmmr** and the **mmmmrx** (**x** = **m** or **r** placement) repeating stereosequences, termini of isotactic sequences, has been prepared whether by changing the temperature of polymerization or by S_N2 substitution reaction which was demonstrated to occur through a highly stereospecific mechanism. The stereochemical microstructures were accurately analysed by ^{13}C NMR spectroscopy. For purposes of stating the microstructure/β relaxation relationship, the mechanical behaviour of all samples was studied by a dynamic mechanical thermal analyser (DMTA). The results are discussed on the ground of earlier fundamental contributions within the framework of the property/stereochemical microstructure relationships as abundantly studied in our laboratory. Basically it is shown that β relaxation decreases in both temperature and intensity with the content of the aforementioned microstructures, thereby suggesting that relaxation to stem from the enhanced free volume and favoured rotational motion facilities of the **mmmr** pentad under **GTGTTG$^-$TT** conformation.

Keywords: Poly(vinylchloride); Molecular microstructure; β relaxation; Local chain conformation; Nucleophilic substitution; Local rotational ability

1. Introduction

Secondary relaxation are known to be strongly related to the physical properties (i.e. the impact strength) of glassy polymers. The reasons for that are still to be wholly understood despite the research effort devoted to this matter [1–12]. The main difficulty arises from the fact that a comprehensive study on the specific chain parts involved in such relaxations has not been undertaken. In particular, the extent to which this relaxation relates to the specific molecular microstructures, which are the objective of our work, has not been so much taken into account.

An attempt to explain the so-called antiplasticization of polyvinylchloride (PVC) was published by our laboratory ten years ago [13]. This important phenomenon consists of an increase in modulus and a loss of β relaxation which is observed whenever some moieties of a plasticizer are present in the polymer. Since this effect is the reverse of that occurring with higher contents of plasticizer, which is known as plasticization, it was denoted by antiplasticization.

To do the above attempt the authors measured by dynamical mechanical thermal analysis (DMTA) the β

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relaxation of a PVC after either chemical modification to various extents or plasticization with distinct but small amounts of dioctyl phthalate. Interestingly both sets of experiments resulted in similar loss of β relaxation.

The chemical modification consisted of nucleophilic substitution, a reaction which has been extensively studied in our laboratory. According to the well stated substitution mechanisms [14–18] substitution extents up to around 7% molar conversion makes the **mmmr** isotactic pentads taking either of the **GTGTGT^{-}T** and **G^{-}GTTG^{-}TT** conformations to be converted into nucleophile centered pentads under the **GTTTTTTT** conformation of higher rigidity. Moreover, during the very first reaction steps (around 1% molar conversion) the **mmmr** pentads under **GTGTTG^{-}TT** conformation are the only to react. As proved by early work [14–18] such a specificity is connected with the occurrence of an isotactic sequence no shorter than one heptad associated with the **mmmr** pentad.

Only when these structures dissipate, other structures like the **rrmr** pentad, at the end of syndiotactic sequences, of much lesser reactivity, are able to react. This produces the shortening of the syndiotactic sequences by exchanging them for sequences of reduced rigidity. For purposes of further information the reader is kindly referred to the numerous publications around this matter [14,19–23].

Another course of action in our laboratory dealt with the nature of the PVC–plasticizer interaction. It was demonstrated by FTIR spectroscopy that the interaction between PVC and any carbonyl containing product, whether polymeric or not, occurs specifically through the **mmmr** pentads termini of isotactic sequences, whenever the content of the interacting agent does not exceed that of **mmmr** pentads under **GTGTTG^{-}TT** conformation. This interaction was shown to be stronger as the interacting agent is of a higher soft basic nature [14,24,25].

Turning to the above quoted attempt it is worthy to note that first β relaxation happened to shift to lower temperature as substitution progresses and secondly the peak height tends to vanish. Surprisingly these effects were both more accentuated for the lower substitution extents. However, what was really remarkable is that these behaviours were similar to those observed for the slightly plasticized polymers.

Taking into account that stereospecific reaction and polymer–plasticizer interaction proved both to relate to the **mmmr** pentads, especially when they take the **GTGTTG^{-}TT** conformation, the preliminary conclusion was drawn that the observed loss in β relaxation and then, the antiplasticization phenomenon ought to be connected with local motions occurring in that microstructure.

Since then a great amount of work has been focused on searching first the relationships between some fundamental physical properties like glass transition [19,20], ageing [26,27], degree of coupling [22,23], nature, distribution and stability of space charges [21,28–35] and the main repeating stereosequences, namely the **mmmr** pentad termini of isotactic sequences of at least one heptad long. And secondly the relationships between the same properties and either the same pentad associated with shorter isotactic sequences or the **rrmr** pentads termini of syndiotactic sequences. In addition, a likely explanation of the mechanisms of the physical properties driving processes was aimed. The results have been extensively conveyed [19–23,26–35]. They make it evident that the above microstructures are of fundamental interest to both explain the physical behaviours of polymers like PVC and PP and improve the technical performances of them.

In the basis of these results it seemed very interesting, scientifically, to examine whether the original property–microstructure relationships obtained, hold true for β relaxation of PVC such as suggested by the above mentioned attempt. This is the objective of the present work which stems from, on the one hand, a much real knowledge of the stereochemical pattern of the material, and, on the other hand, the above-cited original approaches which were performed for physical properties other than β relaxation.

2. Experimental

2.1. Materials

The PVC samples used were an-additive-free industrial PVC prepared in bulk polymerization at temperatures of 68 °C (sample X), 60 °C (sample Y) and 45 °C (sample Z). The samples were characterized as described elsewhere [14,18]. Cyclohexanone (CH) was purified as reported earlier [14]. Dioctyl phthalate (DOP) was used as received. Samples X, Y and Z were modified by nucleophilic substitution reaction with sodium benzenethiolate (NaBT) in CH and in the melt in the presence of DOP moieties following the methods described in previous papers [14,18]. The tacticity of modified samples was measured by means of ^{13}C NMR decoupled spectra as described elsewhere [14,18].

2.2. Mechanical properties

Dynamic mechanical measurements were carried out with a Polymer Laboratories MkII dynamic mechanical thermal analyser (DMTA) working in the tensile modulus at frequencies of 1, 3, 10 and 30 Hz. The temperature was varied from −130 to 90 °C at a heating rate of 2 °C/

min. The complex modulus and the loss tangent of each sample were determined at 10 Hz.

The samples were obtained by compression moulding of 0.1 g of material at temperature about 120 °C under a pressure of 1 MPa. The cooling process, under the same pressure, was carried out by quenching the molten polymer with water. All specimens were cut out into a rectangular strip 2.2 mm wide.

3. Results and discussion

The ^{13}C NMR measurements of samples X, Y and Z, prior to and after substitution to the indicated extents are presented in Tables 1 and 2. Two behaviours are worth mentioning. One is that the overall isotacticity decreases from sample X to sample Z, as easily observable from the **mm** value and specially the **mmmmrx** value; the other is that, as expected, these values are lower as the substitution extent increases. In addition, this decrease is much more accentuated for the lower substitution extents.

These behaviours are consistent with the above quoted substitution mechanisms [14–16,18]. Therefore the values in Tables 1 and 2 mean that the removal of **mmmr** pentads at the end of isotactic sequences of at least one heptad in length, is the only change in structure which has occurred. Moreover up to 1–1.5 substitution percent the only removed structures are the **mmmr** pentads under **GTGTTG^{-}TT** conformation [14,15]. Consequently, any change in property relevant to substitution, is to be attributed to a greatest extent, to the above changes in stereochemical composition.

Fig. 1 displays the DMTA diagrams of samples X, Y and Z prior to and after substitution. By simple inspection it is evident that the β relaxation is lower as the substitution progresses. In addition the peak height decreases. These effects can both be better observed in Figs. 2 and 3, respectively. This allows one to asses that β peak and its intensity decrease both more markedly up

Table 1
^{13}C NMR data of PVC modified in cyclohexanone solution

Sample	Conversion, mol%	Triads			Tetrads	Pentads			Heptads	
		mm	**mr**	**rr**	**mmr**	**mmmm**	**mmmr**	**rmmr**	**mmmmrx**	**rmmmrx**
X	0	20.1	49.65	30.25	22.65	3.97	9.61	6.52	4.34	5.26
X1S	0.8	18.54	48.5	32.16	20.04	4.27	8.5	5.77	3.88	4.62
X2S	3.7	16.33	46.04	33.92	18.18	3.38	7.74	5.22	2.79	4.96
X3S	8.2	11.7	41.66	38.48	12.29	2.94	5.24	3.53	1.63	3.61
Y	0	18.89	49.38	31.72	20.31	4.21	9.06	5.63	4.02	5.03
Y1S	1.03	17.31	48.45	32.87	18.83	3.81	8.18	5.32	3.41	4.77
Y2S	3.1	15.22	46.76	34.93	16.07	3.66	7.06	4.5	2.49	4.57
Y3S	9.2	10.9	40.85	39.05	11.57	2.72	4.76	3.41	1.31	3.45
Z	0	18.66	49.36	31.99	20.68	3.77	9.11	5.79	3.87	5.24
Z1S	0.8	17.31	48.83	33.05	19.76	3.36	8.15	5.81	3.36	4.78
Z2S	3.7	14.86	45.81	35.57	16.76	3.15	6.65	5.06	2.59	4.06
Z3S	8.8	10.72	41.31	39.14	12.32	2.31	4.48	3.92	1.26	3.22

Table 2
^{13}C NMR data of PVC modified in melt state

Sample	Conversion, mol%	Triads			Tetrads	Pentads			Heptads	
		mm	**mr**	**rr**	**mmr**	**mmmm**	**mmmr**	**rmmr**	**mmmmrx**	**rmmmrx**
X	0	20.1	49.65	30.25	22.65	3.97	9.61	6.52	4.34	5.26
X1M	1.6	18.96	48.16	31.19	21.54	4.06	8.26	6.64	3.65	4.61
X2M	3.4	17.51	47.11	31.94	18.96	4.17	7.73	5.62	3.11	4.62
X3M	10.6	11.07	39.84	38.5	10.65	3.34	4.82	2.91	1.55	3.27
Z	0	18.66	49.36	31.99	20.68	3.77	9.11	5.79	3.87	5.24
Z1M	2.3	17	47.51	33.18	18.72	3.99	7.3	5.71	3.07	4.23
Z2M	3.2	16.43	46.79	33.54	17.51	4.22	6.88	5.31	2.91	3.95
Z3M	10.5	12.84	40.03	36.59	12.83	3.74	5.37	3.73	1.39	3.98

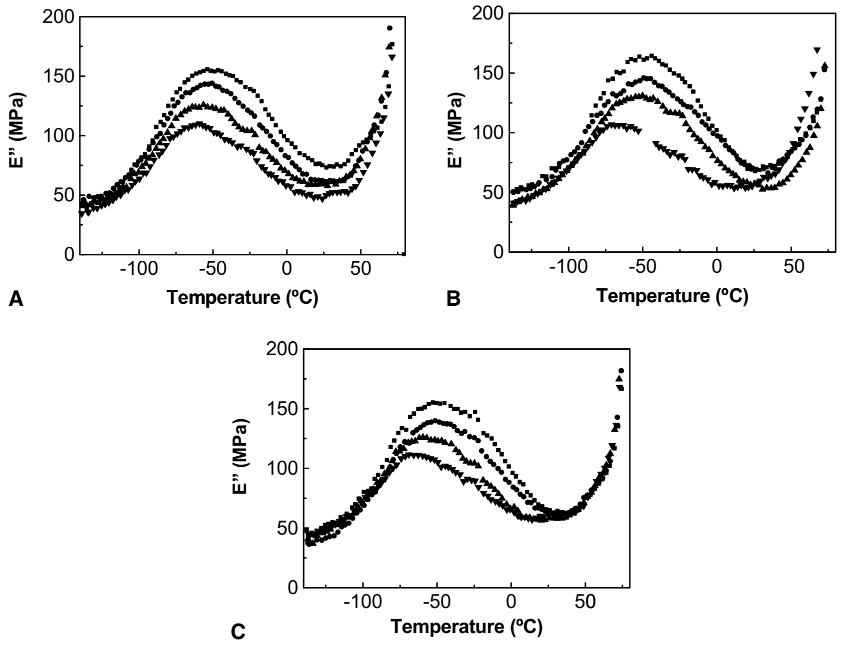

Fig. 1. Effect of nucleophilic substitution on β relaxation of PVC modified in cyclohexanone solution: (A) sample X: (■) 0%; (●) 0.8%; (▲) 3.7%; (▼) 8.2%, (B) sample Y: (■) 0%; (●) 1.03%; (▲) 3.1%; (▼) 9.2%, (C) sample Z: (■) 0%; (●) 0.8%; (▲) 3.7%; (▼) 8.8%.

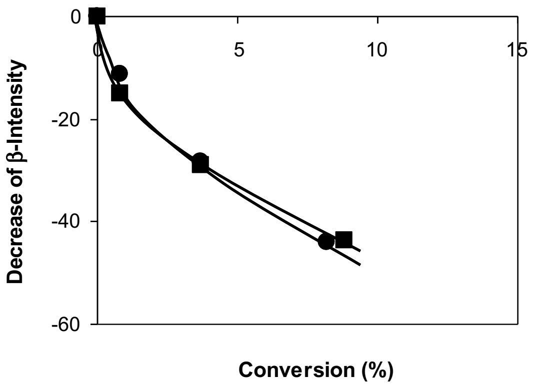

Fig. 2. Evolution of β-peak intensity versus degree of substitution of PVC in cyclohexanone solution: (●) sample X; (■) sample Z.

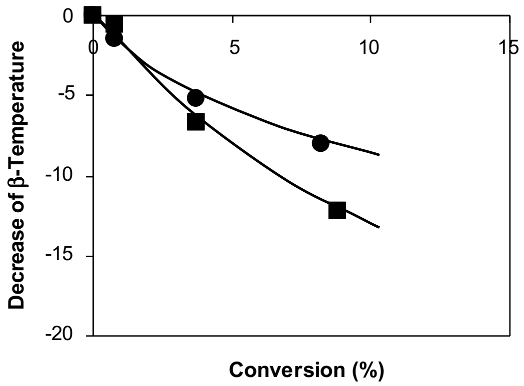

Fig. 3. Evolution of β-peak temperature versus degree of substitution of PVC in cyclohexanone solution: (●) sample X; (■) sample Z.

to roughly 3–4% conversion. Then, the trend is towards levelling off. Note that the left-hand and the right-hand parts of the curves in Fig. 1 hardly change, contrary to what happened when studying antiplasticization [24]. This accounts for the β relaxation processes to be independent of relaxations occurring at higher temperature, like T_g, and gives support for the existence of a straight relation between β relaxation and a well defined structure.

In this connection the decrease in peak height observed in Fig. 1 should be assumed as the result of the progressive disappearance of **mmmr** pentads related to long isotactic sequences.

With respect to the shifting to lower temperatures of β relaxation the more likely explanation lies in the fact that the length of the isotactic sequences bearing the reactive **mmmr** pentad is reduced as substitution advances. This agrees with some suggestions in the literature that β peak shifts to lower temperature as the length of the segment chain in motion decreases [36].

The higher decrease in both β temperature and peak height for the weakly substituted samples (1–1.5%) is

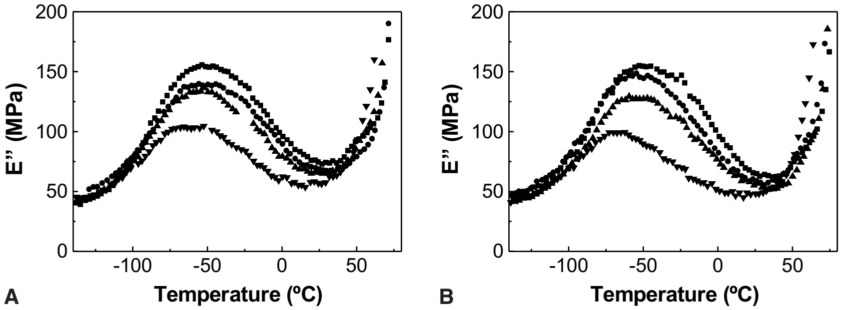

Fig. 4. Effect of nucleophilic substitution on β relaxation of PVC modified in melt state: (A) sample X: (■) 0%; (●) 1.6%; (▲) 3.4%; (▼) 10.6%, (B) sample Z: (■) 0%; (●) 2.3%; (▲) 3.2%; (▼) 10.5%.

also of high interest. It agrees with the specific disappearance of the **mmmr** pentads under **GTGTTG^{-}TT** conformation [14,15] thereby indicating that the local motion of this conformation is highly favoured compared to **GTGTGTTT** conformation. This fundamental feature is consistent with the polymer response to a rather great number of strengths other than that involved in β relaxation [19–23,26–32]. In all cases there appears to exist a straight relation between any physical behaviour and both free volume and the rotational motion facilities of the segment chain involved.

In support of the above interpretation are the results obtained for the same polymers after substitution in the melt in the presence of moieties of plasticizer (Figs. 4–6).

As can be seen the shift of β relaxation to lower values and the decrease of the peak height, both occur in a similar way to the reaction in solution from a qualitative point of view. Nevertheless these effects are somewhat less discriminated and significantly enhanced in the melt at low conversion rates of modification and at higher conversions respectively. This is consistent with our prior work on substitution in the melt [18]. It was actually shown that the **mmmr** pentads under **GTGTTG^{-}TT** conformation is able to react exclusively even in the absence of plasticizer [18]. In the same way, when using moieties of plasticizer, the remaining **mmmr** pentads, which are under **GTGTGTTT** conformation, happen to react until complete consumption without the other reactive structures starting to react. Owing to the severe conditions utilized, the reaction through the latter conformation might overlap, to some extent, that through the former conformation.

From the above results it follows that β relaxation of PVC is the response to a favoured mobility of the **mmmr** pentads specially when they are taking the **GTGTTG^{-}TT** conformation, provided that they should be located at the end of long isotactic sequences.

In this connection it has been repeatedly argued that first those structures exhibit enhanced free volume relative to the other; and secondly the coupling degree of the local motions, according to Ngai's theory is associated with the **mmmr** termini of long isotactic sequences and is the lowest when **mmmr** is taking the **GTGTTG^{-}TT** conformation [29,30].

In conclusion the results presented herein take the knowledge of the β relaxation process an important step

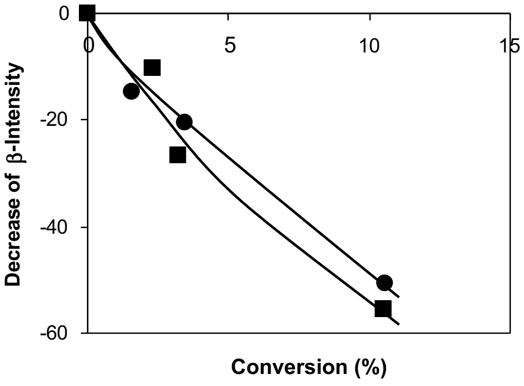

Fig. 5. Evolution of β-peak intensity versus degree of substitution of PVC in melt state: (●) sample X; (■) sample Z.

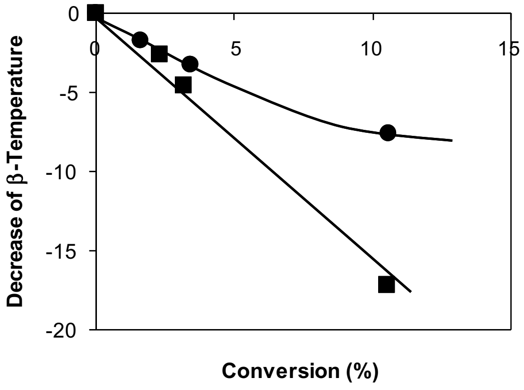

Fig. 6. Evolution of β-peak temperature versus degree of substitution of PVC in melt state: (●) sample X; (■) sample Z.

further. In addition, they shed further light on the property determining role of some local repeating stereochemical sequences as widely proposed in earlier work.

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