Polymer Bulletin 32, 353–359 (1994)

Polymer Bulletin

On a novel interpretation of PVC antiplasticization based on some local chain conformations

P. Tiemblo, G. Martínez, J. M. Gómez-Elvira, and J. Millán*

CSIC, Instituto de Ciencia y Tecnología de Polímeros, Juan de la Cierva 3,
E-28006 Madrid, Spain

Summary

The β transition of a poly(vinyl chloride) after either nucleophilic substitution to various extents or plasticization with distinct amounts of dioctyl phthalate has been measured by Dynamical Mechanical Thermal Analysis. Both sets of experiments are shown to result in similar loss of β transition. The results are argued in the light of prior work on the substitution mechanism determining role of the **mmr** chain segments at the end of isotactic sequences. They strongly suggest the **mmr** structures to interact specifically with plasticizer thereby becoming stiffer (antiplasticization).

INTRODUCTION

Antiplasticization has been the main concern of a considerable number of papers for the last two decades. It has been often found that a few slightly plasticized polymers exhibit an increase in modulus and in tensile strength and a progressive disappearance of β transition (1-3). Since the effect that plasticizers have on the secondary relaxation is the reverse of that they have on the primary relaxation, i.e. plasticization, that behaviour is called antiplasticization. It is well known that the secondary relaxations influence strongly the physical properties (e.g. the impact strength) of glassy polymers. The great research effort devoted to clarify the antiplasticization mechanisms appears then justified.

The polymers that have most propensity to antiplasticization, at least the ones that have been most intensively studied, are polycarbonates (3,4) and poly(vinyl chloride) (PVC) (1,2,5). Up to date there is no satisfactory explanation as to why small quantities of plasticizer yields an increase in modulus and a loss of β transition. Attempts to relate it to a decrease in free volume and a subsequent suppresion of motions in the polymer chain have been published. According to these researchers it might be inferred that the local mobility in the plasticized polymer chains allows them to take a more ordered state (6) or that the plasticizer fills the specific hole free volume of the polymer glass (7,8). Also, specific interactions between the plasticizer and the polymer segments that are responsible for β transition, thereby hindering their motions, have been invoked (1,2,9). Most of the recent publications tend to agree with this belief. However, the type of interaction and the nature of the polymer segments that intervene in the interactions, remain quite unclear.

---

*Corresponding author

In this connection we have just demonstrated by FTIR spectroscopy that the structure in PVC most able to interact specifically with carbonyl containing solvents or with esters, whether polymeric or not, is the **mmr** located at the end of any isotactic sequence. This interaction was shown to be stronger as the solvent is of a higher soft basic nature, such that two distinct types of interaction could be evidenced depending on whether the solvent contains isolated carbonyls or it is of an aprotic basic nature (10). Also, as inferred from our studies on nucleophilic substitution, the longer the isotactic sequence associated with **mmr** the easier happens to be the interaction and the local mobility at this point. Interestingly indeed it was unambiguously shown that nucleophilic substitution with sodium benzene thiolate in cyclohexanone (CH) proceeds exclusively through **mmr** structures up to conversions of 7-10%. Then, the **rrm** structure which is necessarily located at the end of syndiotactic sequences, starts competing with the **mmr** although at lower rate. The whole mechanism and its implications have been extensively argued in a series of earlier publications (11-13). Two main features however are worth noting for the purpose of this work. One is that the **mmr** structures that react during the first period correspond to the isotactic sequences of at least a heptad long (11). The other feature is that out of the two likely conformations of **mmr**, i.e. GTGTTT and GTTG'TT, it is the latter conformation that has a high reactivity whereas the former is unreactive (14). Besides, because the polymer contains very little GTTG'TT conformations relative to the GTGTTT, the conformational change GTGTTT ⇒ GTTG'TT should occur for the reaction to proceed exclusively or preferably through the **mmr** structure as really happens on condition that a good solvent or at least a small amount of plasticizer is used in the reactions carried out in solution (14) or in the melt state (15) respectively.

As a result, it was our hypothesis that the above stereoselective substitution mechanism involves necessarily the occurrence of a specific interaction between **mmr** and the solvent or the plasticizer, so as to make the above conformational change possible. In fact the reaction proved not to occur in the melt when no plasticizer at all was present despite the severe conditions that are usually utilized (15). Only if one holds that such specific interactions occur, the stereospecificity of the substitution reaction, as experimentally found, can be understood.

The implication is that the **mmr** structures that are located at the end of long isotactic sequences happen to be liable both for the specific interactions and for the motions involved in the conformational change. So, we judged it of great interest to profit from these results to elucidate the mechanism of antiplasticization of PVC, first by studying the evolution of β transition with stereoselective substitution, and secondly by comparing this behaviour with that of plasticization of the same PVC sample and of this sample after modification to various degrees. By doing that we expected to show the extent to which, if any, the specific structures above are responsible for the antiplasticization and to provide with some novel ideas on the mechanism involved. Some preliminary results are presented in this publication.

EXPERIMENTAL

Materials

The PVC sample used was prepared at 75°C in bulk using 2,2'-azoisobutyronitrile (AIBN) from Fluka as free radical initiator. The number-average molecular weight ($\overline{M}n$ = 27 900) was determined at 34°C in CH using a Knauer membrane osmometer. Tetrahydrofuran (THF) was distilled under nitrogen with lithium aluminium hydride (Merck) immediately before use to remove peroxides. CH and dioctyl phthalate (DOP) were purified by fractional distillation under nitrogen. Sodium benzenethiolate (NaBT) was prepared by the reaction of sodium (Merck) with thiophenol (Merck).

Table 1. Substitution reaction data[a)]

				Tacticity[c)]		
Sample No.	Temp., °C	Time,[b)] h	conversion, mol-%	P_{rr}	$P_{mr}+P_{rm}$	P_{mm}
0	-	0	0	0.303	0.496	0.201
1	-15	96.0	1.4	0.317	0.483	0.186
2	25	0.8	3.4	0.333	0.464	0.169
3	25	3.0	11.0	0.388	0.394	0.108
4	25	7.3	20.7	0.440	0.305	0.048

a) [PVC] = 6.4 10^{-2} mol/l, [C_6H_5SNa] = 7.6 10^{-2} mol/l

b) The time after which the sample was withdrawn

c) Probability of syndio (P_{rr}), hetero (P_{rm}) and isotactic (P_{mm}) triads

Substitution reaction with NaBT

The substitution reaction was carried out at -15° and 25°C in purified CH as solvent. The samples, withdrawn at the indicated reaction times (Table 1), were characterised by UV spectroscopy in order to determine the degree of substitution from the intensity of the benzenethiolate 256 nm band (12).

^{13}C NMR spectroscopy

The tacticity of both the starting and modified polymers 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 dioxane-d8 as solvent. The spectral width was 2500 mHz, a pulse repetition of 3 sec and 16K data points were used. The relative peak intensities were measured from the integrated peak area, calculated by means of an electronic integrator.

Mechanical Properties

The temperature dependence of the dynamic mechanical properties of the PVC, modified PVC and blends of PVC with DOP were studied with the Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA) operating in the tensile mode. The complex modulus and the loss tangent of each sample were determined at 3Hz over a temperature range from -120 to 80°C at a heating rate of 2°C/min. Samples for testing were obtained by compression moulding of 0.1g of material at temperature about 120°C under a pressure of 1MPa. The cooling process, under the same pressure, was carried out by quenching the molten polymer with water. All samples were rectangular strips, typical dimensions being 13.0 x 2.2 x 0.15 mm. The maximun value of the loss tangent is considered to measure the intensity of the relaxation.

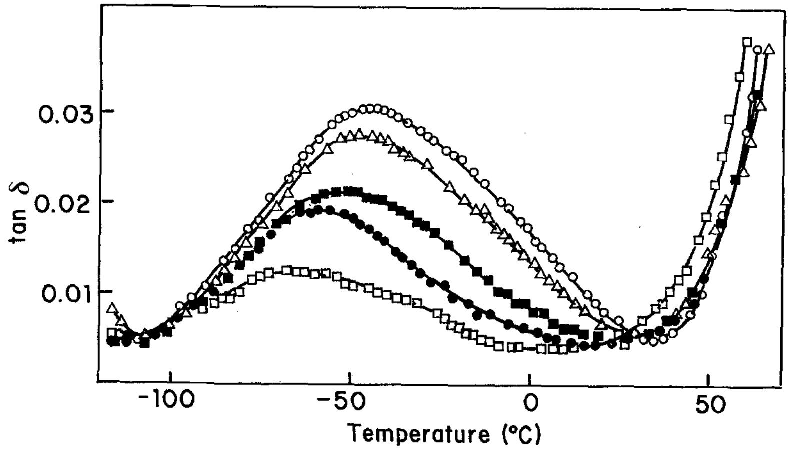

Figure 1. Effect of nucleophilic substitution on β transition of PVC. (○) 0%; (△) 1.4%; (■) 3.4%; (•) 11.0%, (□) 20.7%

RESULTS AND DISCUSSION

Figure 1 depicts the evolution of tan δ with temperature for samples 0 to 4 (Table 1). By inspection it is clear that the β peak shifts to lower temperature and that its hight tends to vanish progressively as the substitution progresses. Moreover, both effects of substitution on β transition happen to be more accentuated for the lower substitution extents. This holds particularly true for sample 1 where, on the other hand, the substitution was carried out at -15°C. Also, as can be seen, the curves hardly change on the low temperature side whereas the right-hand part is highly modified, that is, β transition is eliminated from the higher temperature side. Note that these parts are fairly parallel for samples 0 to 3 and that sample 4 deviates from this behaviour.

The whole results of Figure 1 can be accounted for straightforwardly by the molecular changes that originate from the stereospecific substitution reaction. Actually, as reliably stated previously (16) what has happened for samples 1 and 2 is that PVC mmmr pentads taking either of the GTGTGTTT and GTGTTGTT conformations are converted into benzenethiolate centered pentads addopting the much more rigid GTTTTTTT conformation (In the case of sample 1 this process affects more specially the GTGTTGTT conformations). In contrast, for conversions higher than roughly 10%, as is the case of sample 4, the substitution by rrmr pentads at the end of syndiotactic sequences, operates too. This causes the latter all-trans syndiotactic sequences to be shortened by exchanging for sequences with gauche conformations thereby decreasing the local rigidity (16). The latter substitution, unlike that at **mmmr** pentads, brings about a substantial decrease in Tg what would disturb the high temperature side of the corresponding curve of Figure 1. This certainly accounts for the deviation of sample 4 from the behaviour of sample 1-3 (Figure 1). The boundary between the above two distinct behaviours is that of sample 3 (16).

Finally, the higher propensity of the right-hand part of the curves, as compared with the left-hand, to change with substitution as the result of the β peak shift, is consistent with the higher reactivity of **mmr** as the length of the associated isotactic sequence increases (13). It has been indeed suggested that β peak shifts to lower temperature as the length of the segment chain in motion decreases (17).

The influence of plasticization on the dynamic mechanical properties of PVC sample 0 (Table 1) is shown in Figure 2. From a qualitative point of view, plasticized PVC behaves similarly to modified PVC (Figure. 1) in that the β transition shifts to lower temperatures and the hight of the β peak becomes lower. Also, plasticization, likewise stereoselective substitution, modifies much more the right-hand part of the β transition than the left-hand part. Nevertheless, for plasticized PVC (Figure 2) the steepness of the former part of the spectrum decreases drastically as the amount of plasticizer increases, while in the case of the modified samples (Table 1) that decrease is observed only for sample 4 (Figure. 1). These changes in steepness are doubtless due to the intrusion of the α transition when it becomes lower whether as the result of plasticization (2) or because the substitution attains the less reactive **rrmr** pentads (16). Interestingly, the superiority of **rrmr** pentad, relative to **mmmr** pentad in nucleophilic substitution occurs only at conversions near 20% (16).

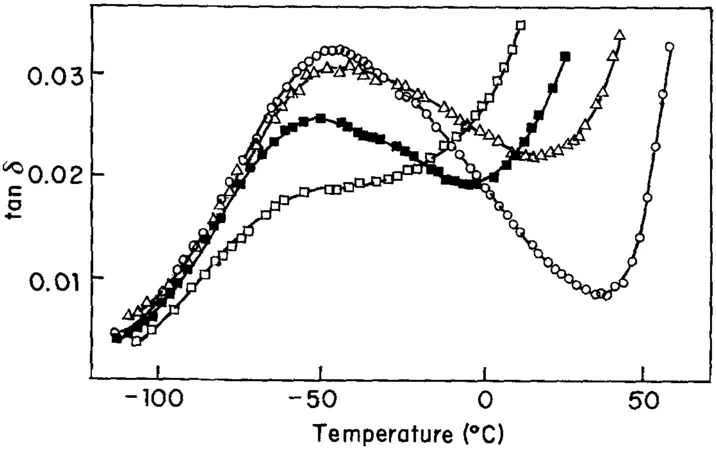

Figure 2. Effect of plasticization on β transition of PVC. [DOP]: (o) 0 wt%; (△) 2.5 wt%; (■) 5 wt%; (□) 10 wt%

From the above results it follows that similar decrease in β transition is obtained either by forcing some **mmmr** pentads to take a more rigid local conformation through stereoselective substitution reaction (16) or by slightly plasticizing PVC. Such an analogy strongly suggests the antiplasticization to originate from the occurrence of strong and specific interactions between the **mmr** structures associated with long isotactic sequences and the plasticizer, thereby hindering the motions at the latter structures. On the ground of prior work these motions are to be related to the above quoted conformational change between the two likely conformations of **mmr** (13).

Finally, Figure 3 shows the effect of 2.5 wt% plasticization on β transition for samples 1 and 3 (Table 1). From mere observation it straighforwardly follows that plasticization of PVC after partial selective elimination of **mmr** structures, causes the loss of β transition that has arised from the substitution reaction, to prosecute in the same sense, irrespective of the substitution degree.

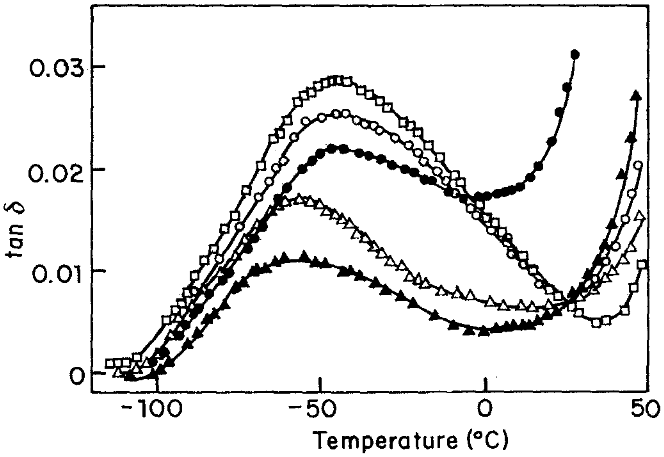

Figure 3. Effect of 2.5 wt% plasticization on β transition of the modified samples 1 (○) and 3 (△) (Table 1): (●) sample 1; (▲) sample 3. The spectrum of unmodified sample (□) is included for comparison.

Such behaviour is a further support for our above conclusion as to the prevailing role of **mmr** structure in the antiplasticization mechanism of PVC.

These are but a few preliminary results of our current research work to further establish that some crucial physical properties are related to the local conformations that will occur at the end of either syndiotactic sequences or, especially, isotactic sequences in tendentially bernoullian polymers. More comprehensive publications concerning antiplasticization, molecular motions and molecular interactions are to appear.

ACKNOWLEDGEMENT

The authors are grateful to the CICYT (MAT 381/91) for financial support.

REFERENCES

1. Pezzin G, Ajroldi G, Garbuglio C (1967) J.Appl.Polym.Sci. **11**:2553
2. Kinjo N, Nakagawa T (1973) Polym.J. **4**:143
3. Ngai KL, Rendel RW, Yee AF, Plazek DJ (1991) Macromolecules **24**:61
4. Jones AA (1985) Macromolecules **18**:902
5. Mikhailov GP, Mirkamilov DM, Gotlib Yu Yu, Lobanov AM, Volchek BZ (1967) Polym.Sci.URSS **9**:2219
6. Fischer EW, Hellman GP, Spiess HW, Horth FJ, Ecarius U, Wherle M (1985) Macromol.Chem.Phys. Suppl.No. **12**:189
7. Robeson LM, Faucher JA (1969) J.Polym.Sci., Part B **7**:59
8. Anderson SL, Grulke EA, DeLassus PT (1992) ACS Polym.Preprints **33**:128
9. Suvorova AI, Hannanova EG (1990) Makromol.Chem. **191**:993
10. Tiemblo P, Martínez G, Millán J J.Polym.Sci.,Polym.Chem.Ed. (in press)
11. Millán J, Martínez G, Jimeno ML (1991) Eur.Polym J. **27**:483
12. Martínez G, Guarrotxena N, Gómez-Elvira JM, Millán J (1992) Polym.Bull. **28**:427
13. Guarrotxena N, Martínez G, Gómez-Elvira JM, Millán J (1993) Eur.PolymJ. **29**:685
14. Millán J, Martínez G, Mijangos C (1985) J.Polym.Sci.,Polym.Chem.Ed. **23**:1077
15. Millán J, 33rd IUPAC Int.Symp. on Macromolecules, Montreal, Canada (1990); Guarrotxena N, Martínez G, Gómez-Elvira JM, Millán J (to appear)
16. Guarrotxena N, Martínez G, Gómez-Elvira JM, Millán J Makromol.Chem.,Rapid Comm. (in press)
17. Wada Y, Tsuge K, Arisawa K, Ohzawa Y, Shida K, Hotta Y, Hayakawa R, Nishi T (1966) J.Polym.Sci. Part C **15**:101

Accepted January 21, 1994 C