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LOCAL STEREOCHEMICAL MICROSTRUCTURES DEPENDENCE OF β RELAXATION PROCESS IN SOME VINYL POLYMERS: FUNDAMENTALS AND CORRELATIONS

Key words: PVC, PMMA, β-relaxation, chain conformation, local motion, nucleophilic substitution, molecular microstructure.

Dynamic mechanical thermal analysis (DMTA) is an accessible and versatile analytical technique where a sample is submitted to an oscillating stress or strain as a function of oscillatory frequency and temperature. Through this non-destructive measurement, a comprehensive understanding of the dynamic mechanical properties of polymers may be obtained. In this context, two series of polymers having different tacticity-dependent stereochemical microstructures have been submitted to controlled dynamo-mechanical strength. One series consists of three different PVC samples prior to and after substitution reaction to various extents in solution and in melt state. And one series consists of three commercial PMMA samples. In this review, we provide a straight correlation between β-relaxation and the content of mmr tetrads termini of isotactic sequences of at least one heptad in length, especially with those mmr structures taking the GTTG^{-}*TT conformation. Basically it is demonstrated that β-relaxation both, temperature and intensity, decrease with the content of the aforementioned microstructures, giving further support to the implication of magnitudes such as free volume and of coupling degree of the local motions in the mechanisms of the physicochemical processes responsible of the PVC and PMMA mechanical behaviors.*

Ключевые слова: поливинилхлорид, полиметилметакрилат, релаксационный β-переход, конформация цепей, нуклеофильное замещение, молекулярная микроструктура.

Динамический механический анализ (ДМА) является доступным и универсальным аналитическим методом, в котором образец подвергают осциллирующему напряжению или деформации как функции от колебательной частоты и температуры. Благодаря этому неразрушающему измерению, может быть получено полное понимание о динамических механических свойствах полимеров. В связи с этим два типа полимеров, имеющих различные тактично-зависимые стереохимические микроструктуры, были представлены контролируемой динамо-механической прочностью. Один серия состоит из трех различных образцов ПВХ, до и после реакции замещения в различной степени концентрации и расплава. А другая серия состоит из трех коммерческих образцов ПММА. В данной работе, представлена прямая зависимость между β-переходом и содержанием ММР тетрад концов изотактических макромолекул, по меньшей мере одной гептады в длину, особенно с теми ММР структурами, принимающих GTTG^{-}*TT конформацию. В основном это свидетельствует о том, что β-переход как температуры, так и интенсивности, уменьшается с долей вышеупомянутых микроструктур, способствуя к вовлечению свободного объема и степени сцепления местных движений в механизмах физико-химических процессов, ответственных за механическое поведение ПВХ и ПММА.*

Introduction

The structure property relationships are greatly significant industrially and scientifically. Most of abundant research work in this field for the last years has dealt with approaches to the whole simulation of the physical behavior and, thence, to a macroscopic view of the related physical properties of polymers. In contrast, no attempts to correlate the physical properties with the molecular microstructure of polymers have been made. The implication is that little information as to the nature and the mechanisms of the molecular nature involvement in the physical behaviour of these materials is available. In fact, the studies to correlate every physical property with any specific molecular structure, in particular the local or sequential chain microstructure regardless of the type of vinyl polymer, are rather scarce if any. The difficulty lies in the fact that both the controlled formation of those microstructures along the polymer chain and their accurate determination are far from being successful.

Within this framework a rather abundant work in our laboratory has revealed that there exists a straight relation between some physical and chemical behaviours and the occurrence of a few repeating steresequences along the chain, especially the mmmr and the mmmmrx (x=m or r) which occur necessarily whenever an isotactic sequence breaks-off. The prominent role of them in a list of physical properties of poly(vinyl chloride) (PVC) including glass transitions, physical ageing, dielectrical relaxations and electrical space charge nature and distribution, has been extensively conveyed [1-5]. Most of the correlations found for PVC have been proved to hold true for poly(propylene) (PP) [6, 7]. They have been also extended to dynamic mechanical properties of PVC and PMMA. Actually, this paper deals with approaches to secondary relaxation knowledge as inferred from found correlations with the stereochemical microstructures mentioned below.

In general the stereochemical microstructures that have been considered are: 1) the isotactic and syndiotactic sequences, that relate to the extent to which a polymer exhibits a non-Bernoullian tacticity distribution; 2) the mmr-based and the rrm-based local structures which occur necessarily whenever an isotactic sequence or a syndiotactic sequence breaks-off respectively; and 3) the atactic parts and the pure mrmr moieties.

It is well established that the rheological (mechanical) properties of polymeric materials directly affect their technical performance. Therefore, in order to ensure optimization of their design and application, it is important to accurately characterize their rheological properties and deeply understand the molecular implications on the physical processes involved in their dynamo-mechanical properties (β-relaxation). Among the several techniques used to mechanically characterize polymers, DMTA provides a rapid and non-destructive way to study and quantify the viscoelastic properties of polymeric materials [8-11]. Basically, DMTA involves the application of a sinusoidal stress (or strain) to a sample whilst measuring the mechanical response as a function of both oscillatory frequency and temperature. The dynamic storage modulus, E', and loss modulus, E", are among the most basic of all mechanical properties, and their importance in any structural property relationship is well applied.

The main purpose of this paper is to consider how far some local repeating stereochemical sequences of PVC and PMMA play a key role on impact strength and dynamic modulus, and to present some evidence that relaxation to stem from the enhanced free volume and the capability to local motions of mmmr structures relative to the remaining stereochemical microstructures in the polymer.

To do the above attempt the authors measured, by dynamic mechanical thermal analysis (DMTA), the β relaxation of: 1) PVC after chemical modification to various extents in solution and in melt state in the presence of some moieties of plasticizer (dioctyl phthalate, DOP), and 2) PMMA with different stereochemical compositions.

Experimental

Materials

Polyvinychloride. The PVC samples used were an-additive free industrial PVC prepared in bulk polymerization at temperatures of 68ºC (sample X), 60ºC (sample Y) and 45ºC (sample Z). The samples were characterized as described elsewhere [12, 13]. Cyclohexanone (CH) was purified as reported earlier [12]. 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 [12, 13]. The tacticity of modified samples was measured by means of ^{13}C NMR decoupled spectra as described elsewhere [12, 13].

Polymethylmethacrylate. Commercial PMMA (labeled as U, V and W) samples, obtained from Atochem, were purified using tetrahydrofuran (THF, Scharlau) as solvent and water as precipitating agent, washed in methanol and dried under vacuum at 40ºC for 48 hours. THF was distilled under nitrogen with aluminium lithium hydride (Aldrich) to remove peroxides immediately before use.

Characterization of Samples

Polyvinylchloride. The tacticities of both the starting (samples X, Y, and Z) and the modified polymers were measured by means of ^{13}C NMR decoupled spectra obtained at 80ºC on an Varian UNITY-500 instrument, operating at 125 MHz using 1,4-dioxane-d_8 as solvent under conditions described previously [12, 13]. The resonances used were those of methane carbons of the backbone ranging from 57 to 61 ppm. The 40000-50000 scans gave a very satisfactory signal-to-noise and the respective peak intensities were measured from the integrated areas, as calculated by means of an electronic integrator.

Polymethylmethacrylate. ^{1}H NMR spectra were recorded on a Varian UNITY-500 spectrometer operating at 499.88 MHz in $CDCl_3$ as solvent at 50ºC. The parameters of 8000 Hz spectral width and a 1.9s pulse repetition rate were used. The delay time was set to 0.5s. The spectra were obtaining after accumulating 64 scans with a sample concentration of 10 wt% solutions. The relative peak intensities were measured from the integrated peak areas, which were calculated with an electronic integrator. The content of the different triads were calculated by the electronic integration of the α-methyl signals which appear at (1.3-1.1ppm), at (1.1-0.9ppm) and at (0.9-0.7ppm) corresponding to isotactic (mm), heterotactic (mr) and syndiotactic (rr) triads, respectively.

Dynamic Mechanical Measurements

Polyvinylchloride. 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 90ºC at a heating rate of 2ºC/min. The complex modulus and the loss tangent of each sample were determined at 10Hz. All specimens were cut into a rectangular strip 2.2 mm wide.

Polymethylmethacrylate. Mechanical measurements were carried out on rectangular strips of 2.2 mm wide with a Polymer Laboratories MkII dynamic mechanical thermal analyser (DMTA) working in the tensile modulus at a frequency of 10Hz. The measurements were performed in the temperature range -100 to 140ºC at a heating rate of 2ºC/min. The complex-modulus and the loss tangent of each sample were determined.

The PVC and PMMA samples were obtained by compression moulding of 0.1g of materials at temperature about 120ºC and 1MPa of pressure for PVC and around 140ºC and 50bar of pressure for PMMA The cooling process, under the same pressure, was carried out by quenching the molten polymer with water.

Results and discussion

The PVC and PMMA stereochemical microstructures

The NMR spectroscopies allow one to state and to measure the above quoted microstructures [14]. ^{13}C NMR and ^{1}H NMR spectroscopies were used to analyse the sorts of mmr- and rrm- based stereochemical sequences and their surroundings for one series of PVC samples and one series of PMMA samples, of different tacticities. Basically, the spectra allow to determine the content of isotactic (mm), heterotactic (mr & rm) and syndiotactic (rr) triads. In fact, what is directly measured on the spectra are the integrated areas of signals belonging to the corresponding pentads. In the case of the isotactic pentad of PVC the spectra resolution is good enough for the content of the three sorts of pentad, mmmm, mmmr and rmmr to be determined accurately. From the triad content it is possible to calculate on the one hand the content of isotactic (m), heterotactic (h) and syndiotactic (r) dyads and on the other hand, the probability that one placement r follows one m placement or one r placement, P_{mr} and P_{rr} respectively. The corresponding equations have been given previously [14]. Obviously, if Bernoullian statistics applies then $P_{mr}=P_{rr}$. Therefore, P_{mr}-P_{rr} is an accurate measure of the sample departure from Bernoullian behavior (Note that the same is valid for P_{mm} and P_{rm} denoting the probability that one m placement follows one m or one r placement, respectively). In addition in case of Bernoullian behavior the probability of occurrence of any repeating sequence may be obtained through universal relations [14]. The results so obtained for the samples of this work are presented in Table 1. As can be seen PVC samples, prior to modification (Table 1) are all Bernoullian. Thus there appear to be not so different in tacticity arrangement. Nevertheless the whole isotacticity clearly decreases from sample X to sample Z. As widely argued [14] this means that the isotactic sequences of at least one heptad in length decreases in the same order and so does the content of the conformation GTTG$^-$TT of the tetrad mmr which occurs necessarily whenever an isotactic sequence breaks off, relative to the other likely conformation, the GTGTTT [14]. The content of GTTG$^-$TT conformation may be determined by means of substitution reaction at as low temperature as -15ºC. The values so obtained are denoted by *h* in Table 1. The implications of the substitution reaction to the tacticity arrangement are commented below.

Table 1 - The content of GTTG$^-$TT conformation at low temperature (-15ºC)

	Samples	Mn	Triads			Tetrads	Pentads			Bernoullian Probabilities			
			mm	mr	rr	mmr	mmmm	mmmr	rmmr	P_{mm}	P_{rm}	P_{mm}-P_{rm}	*h*
PVC	X	42000	20.1	49.65	30.25	22.65	3.97	9.61	6.52	0.447	0.451	(0)0.004	0.8
	Y	53500	18.89	49.38	31.72	20.31	4.21	9.06	5.63	0.443	0.438	0.005	0.6
	Z	64000	18.66	49.36	31.99	20.68	3.77	9.11	5.79	0.421	0.431	(-)0.01	0.5

	Samples	Mn	Triads			Diads		Bernoullian Probabilities		
			mm	mr	rr	m	r	P_{mm}	P_{rm}	P_{mm}-P_{rm}
PMMA	U	45503	8.56	41.81	49.63	29.46	70.53	0.291	0.296	(-0)0.005
	V	43131	12.8	39.92	47.28	32.27	67.24	0.391	0.297	0.094
	W	44868	20.97	36.5	42.53	39.22	60.78	0.535	0.535	0.235

With reference to the PMMA tacticity it appears clear that samples U and V are totally isotactic particularly sample U, while sample W is non Bernoullian syndiotactic (Table 1). The overall isotactic content decreases from sample U to sample V. Therefore what has been said in the precedent paragraphs applies to PMMA. Sample W will exhibit more syndiotactic sequence content. On the other hand, the content of rrm tetrad, which occurs whenever one syndiotactic sequence breaks off, will be greater. More details concerning PMMA tacticity are given below. To the above considerations it should be added the chain conformations which each structure may adopt.

Figure 1 reproduces the picture of the two indicated repeating stereosequences as built up with CPK models. By simply manipulating them, it can be seen that the isotactic sequence cannot adopt a conformation other than …GTGTGT… . The occurrence of a conformation other than GTGT implies the planar coexistence of bulky atomic groups, which is highly unlikely and is to be discarded [15].

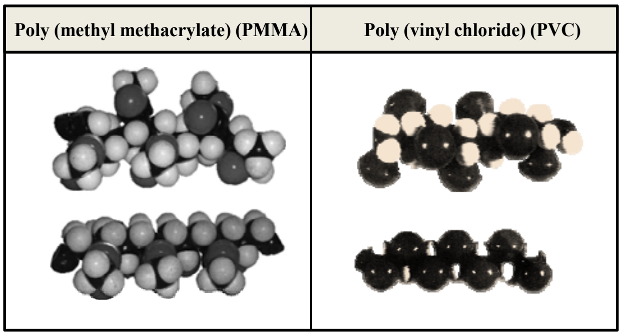

Fig. 1 - Some repeating sequences of equal length of PMMA (left side) and PVC (right side): all isotactic ~GTGT~ conformation (upper) and all ~TT~ conformation (bottom). (CPK molecular models)

As widely conveyed for PVC [13, 16] the last triad (i.e. the mm in mmr tetrad) is the only likely triad to adopt, incidentally, the GTTG$^-$ conformation. In fact there is an equilibrium GTGT ↔ GTTG$^-$ which in both polymer PVC and PMMA, strongly lies over GTGT conformation. Nevertheless some important differences between both polymers are evident: PMMA shows large free volume, more hindered rotation and much lesser possibility of interchain hydrogen bonds. As a result the occurrence of GTTG$^-$ conformation at the end of isotactic sequences will be more restricted and of lower content than in PVC. In order to compare both conformations, which may occur in the mmr tetrad terminating any isotactic sequence, they are reproduced in Figure 2.

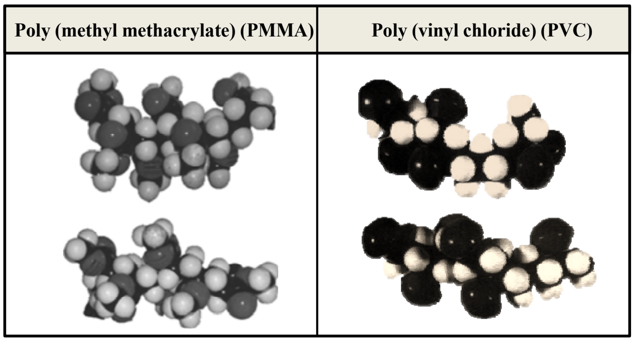

Fig. 2 - Some repeating sequences of equal length of PMMA (left side) and (PVC (right side): ~GTTG$^-$TT conformation (upper) and ~GTGTTT conformation (bottom). (CPK molecular models)

As can be seen from Figures 1 and 2, it holds that: (a) the mmr repeating sequence is shorter and of greater volume than mmm or rrr sequences. Moreover, these differences are considerably enhanced for GTTG$^-$TT conformation relative to GTGTTT conformation. Considering that mmr is a local helix-coiled regularity disruption, the GTTG$^-$TT involves higher local change in both free volume and rotational motion; (b) the rotational motions are favoured and are less dependent on the adjacent isotactic sequences in GTTG$^-$TT conformation, therefore GTTG$^-$TT motion exhibits less coupled nature than GTGTTT conformation; and (c) turning to the syndiotactic TTTT sequence, it appears evident that it is longer and exhibits lower free volume and more reduced ability to rotate as compared to isotactic GTGT sequence.

The role of some stereochemical microstructures on the PVC and PMMA dynamo mechanical properties

The results obtained for the PVC samples prior to and after substitution (Table 1) are displayed in Figures 3A-C. By simple inspection it is evident that the β relaxation shifts to lower temperature and its height tends to vanish progressively as the substitution progresses. A more detailed observation of both effects, in Figures 3D and 3E, allows one to asses that they decrease both more markedly for the lower substitution extents (0-4 %). Then, the trend is towards levelling off.

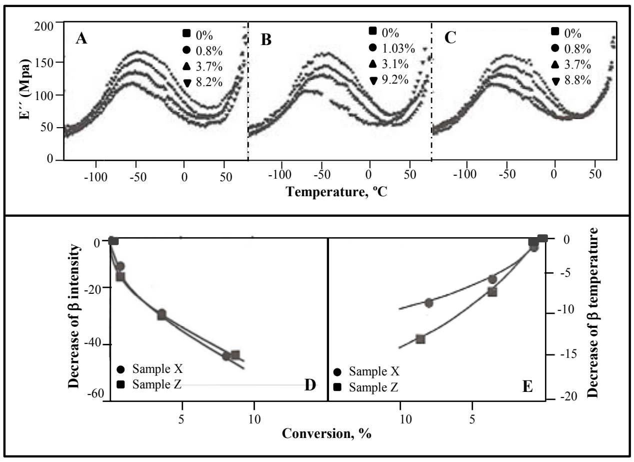

Fig. 3 - Effect of nucleophilic substitution on β relaxation of PVC modified in cyclohexanone solution: (A) sample X, (B) sample Y, (C) sample Z. Evolution of β peak intensity (D) and β peak temperature (E) versus degree of substitution of PVC in cyclohexanone solution. [(f= 10Hz)]

In this connection the decrease in peak height observed in Figure 3D should be assumed as the result of the progressive disappearance of mmmr pentads associated with 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 [17].

The higher decrease in both β temperature and peak height for the weakly substituted samples (1–1.5%) is also of high interest. It agrees with the specific disappearance of the mmmr pentads under GTGTTG$^-$TT conformation [12, 13] 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 [1-3, 5, 18-25]. 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.

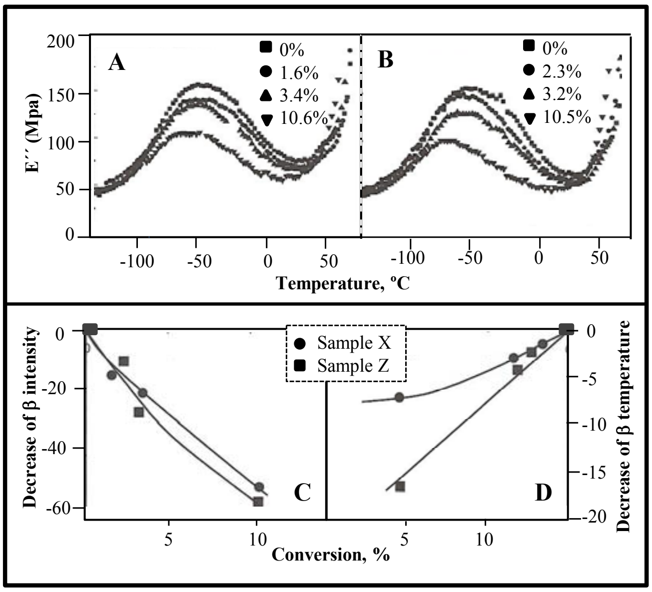

Fig. 4 - Effect of nucleophilic substitution on β relaxation of PVC modified in melt state: (A) sample X, (B) sample Z. Evolution of β peak intensity (C) and β peak temperature (D) versus degree of substitution of PVC in melt state. [(f= 10Hz)]

The same PVC polymers after substitution in the melt with DOP proved to behave similarly from a qualitative point a view in that the β-transition shifts to lower temperatures and the height of the β peak becomes lower (Figures 4A-B and 4C-D). 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 [15]. It was actually shown that the mmmr pentads under GTGTTG$^-$TT conformation is able to react exclusively even in the absence of plasticizer [15]. 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 strongly responds to the tacticity dependent microstructure, in particular, the favoured mobility of local configurations (mmmr pentads) termini of long isotactic sequences when they are taking the GTGTTG$^-$TT conformation.

Figure 5A plots the DMTA diagrams for samples U, V and W of polymethylmethacrylate. By inspection it is clear that the β position and the height for sample U are both higher than those of samples V and W. A better comparison of both magnitudes can be obtained by plotting them against the overall isotactic content in Figure 5B. The absence of curves symmetry suggests that the right-hand is influenced by α relaxation occurring at higher temperature, certainly Tg.

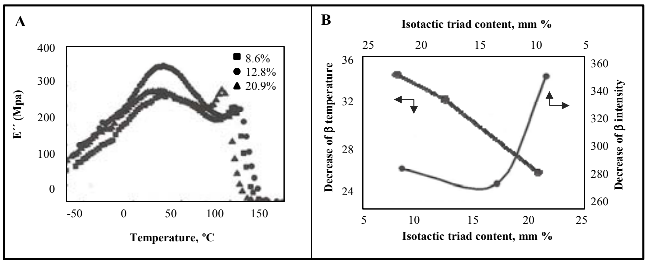

Fig. 5 - Effect of isotactic triad content (mm) on β ρelaxation of PMMA (A). Evolution of β peak intensity and β peak temperature versus overall isotactic triad content, mm of PMMA samples (B). [(f= 10Hz)]

Sample U exhibits the higher intensity of the maximum (Figure 5B) relative to samples V and W. In addition the intensity of sample W is somewhat higher than that of sample V. The results in Figure 5B seem to be at variance with a simple correlation with the overall isotactic content (Table 1). A likely explanation can be given in the light of P_{mm} and P_{mr} values reported in Table 1. In sample W, the increase in average length of the isotactic sequences is accompanied by a decrease in frequency of the same sequences, so that the number of mmr structures does not increase or even decrease somewhat with respect to sample V. On these grounds it may be concluded, at least in a tentative way, that the number of mmmr microstructures should vary in the sense: U>V≈W.

Assuming the above argument, the results in Figure 5B would indicate the occurrence of a clear correlation between the intensity of β relaxation and the content of mmmr microstructures. This would account for the β transition to obey the capability of motion of mmmr, Figure 5B depicts the evolution of β temperature with the overall isotactic content. Even through the shift of β temperature seems like the evolution of the intensity (Figure 5B), it cannot be attributed to the amount of mmmr microstructures because β temperature value relates chiefly to the nature of the structure that is able to motion. Since, this structure is mmmr, the shift of β temperature must obey the differences in surrounding of mmmr in the samples. In this connection it may be assumed from P_{mm} and P_{mr} values that the length of the isotactic sequence, concomitant with any mmmr microstructure, increases from sample U to sample V and from this to W sample, the latter change being much more marked than the former. On the other hand the isotactic sequence is more rigid as its length increases. This might cause the capability to motion of the corresponding mmmr microstructure to increase in the same sense.

Actually, the degree of coupling of mmmr motion with that of the adjacent units should be higher as the rigidity of the latter units decreases. As a consequence, the mmmr with the little rigid adjacent units, as a whole, would merge into a new microstructure of lower capability of motion relative to the uncoupled mmmr microstructure.

The results on β transition of PMMA, despite preliminary nature, give evidence of the straight relation between β transition and the mmmr-based microstructures in PMMA. Further results are expected to shed light on the very nature of that relation as issued from the results obtained so far.

Comparing these behaviours and those previous reported for PVC prior to and after substitution it is evident that the initial drop of the β relaxation intensity and temperature can be attributed to the disappearance of mmmr under GTGTTG^{-}TT conformation of very low degree of coupling with the vicinal isotactic sequence, and then, of enhanced capability of motion. As above indicated, the occurrence of that conformation in PMMA is very unlikely. Thus, its influence on β transition should be discarded.

On the contrary, it was well shown in PVC that β temperature decreases with the decreasing length of the isotactic sequences, which gives support to the above explanation of the results in Figure 5B showing the β temperature shift with the overall isotactic content of PMMA.

Conclusion

From the above results it may be concluded that some normal stereochemical microstructures namely the mmrnr repeating isotactic sequence are a major driving force for the physical processes involved in the dynamic mechanical properties of PMMA and PVC. Actually, the β relaxation is the result of the progressive disappearance of mmmr, where the GTGTTG^{-}TT conformation exhibits a highly favoured local motion and free volume compared to GTGTGTTT conformation [22, 23].

In conclusion these results take the knowledge of the β relaxation process an important step further and shed further light on the property determining role of some local repeating stereochemical sequences as widely proposed in earlier work.

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