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# On the $\beta$ relaxations in Poly(Butadiene) and Poly(Styrene-Butadiene) rubbers

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## ABSTRACT

The influence of the chemical microstructure on the secondary mechanical relaxations of PB and SBR has been studied by varying the content of vinyl, *cis*, *trans* butadiene and styrene groups. Two relaxational mechanisms are involved in their  $\beta$  mechanical relaxations with two distinct activation energies. The fitting by the summation of two Havriliak Negami functions of the experimental isochronal and isothermal curves prove that the vinyl groups are responsible for the contribution of the High Temperature part of the  $\beta$ -relaxation, whereas the butadiene 1,4 groups, *cis* and *trans* are at the origin of the low temperature part of this relaxation. Moreover, the intensity of the relaxation associated to each monomer appears to be proportional to their volume (and molar) fraction. Given the random characteristics of the studied copolymer, this suggest that the involved mechanisms are localized at the level of only one monomer unit.

**Keywords:** mechanical spectrometry; dielectric spectrometry; beta relaxation; styrene butadiene copolymer

# 1 Introduction

Styrene Butadiene rubber are mainly used at temperature well above their glass transition temperature; nevertheless, in some applications such as tires, the frequency domain at which they are dynamically deformed is so large that their mechanical response can involve relaxations usually occurring in the glass-rubber transition and also in the glassy state [1]. Moreover, these elastomers usually contain nanofillers. Their presence is known to decrease the polymer mobility in their surface neighborhood and as a consequence, should enhance the influence of these mechanical relaxations [2]. When these relaxations are activated, more viscoelastic dissipation occurs, which may be wished - for instance to promote traction or braking efficiency - or unwished on normal rolling, where energy saving is targeted. For sake of material optimization, the understanding of the microstructural parameters governing these relaxations is therefore mandatory.

The  $\alpha$ -relaxation is the dominating relaxation in glass-forming amorphous systems. It is highly cooperative and attributed to segmental relaxation of the main chain [3]. In the glassy state, additional relaxations, so called secondary relaxations (lettered  $\beta$ ,  $\gamma$  etc...when decreasing the temperature...), can be active on shorter time scales. Their characteristic time has an Arrhenius temperature dependence, and they have traditionally been related to local motion in the main chain consisting of twisting or crankshaft motions of the polymer backbone, or when they are present, to the local movements of side groups [4]. It has also been proposed that the  $\beta$ -relaxation, usually ascribed to crankshaft motions, is the precursor of the  $\alpha$  one, since local movements are first needed to enable larger scale movements [5].

Styrene Butadiene rubbers contain four specific groups which can be involved in the  $\beta$ -process, namely, (i) 1,2 butadiene (also called vinyl), (ii) *cis*-1,4 butadiene and (iii) *trans*-1,4 butadiene, and at last (iv) the styrene groups. Poly(butadiene) homopolymers, 1,2PB and 1,4 PB were studied by dielectric spectroscopy by Quan et al [6<sup>1</sup>. These authors ascribed the  $\beta$ -relaxation of the 1,4 PB to local rotations (crankshaft motions) of the main chain, whereas they proposed that the  $\beta$ -relaxation of the 1,2 PB is produced by the rotation of the vinyl pending group. Their study on different di-block copolymers was later completed by the work

of Hoffman et al [7], who systematically characterized the dielectric response of statistical PB copolymers with varying amount of 1,4 Cis and Trans Butadiene and of 1,2 Butadiene monomer units. They confirmed the existence of two different relaxation mechanisms, and in particular showed that the intensity of the dielectric relaxation is linearly related to the 1,4 butadiene content. They also established that very few monomer units are involved in the  $\beta$ -mechanisms. In dielectric measurements, it is expected that the trans units do not significantly contribute to the dielectric response. To the authors' knowledge, there is no similar study in the literature using mechanical spectroscopy, for which both trans and cis units should contribute to the  $\beta$ -relaxation. Moreover, the mechanical coupling of the polymer units being different from the dielectric one, the intensity of their mechanical relaxations might evolve differently with their content. The same questions arise when studying the  $\beta$ -relaxation of styrene-butadiene rubber, in which a fourth monomer unit, styrene, is added. Cervený et al. [8] concluded that the mechanical relaxation of their SBR could be ascribed to the rotation of the phenyl group, whereas two years later, the same authors suggested from dielectric spectroscopy that the  $\beta$ -relaxation of SBR originates solely from the butadiene units [9]. Unfortunately, they did not directly compare their dielectric and mechanical results as their mechanical study was performed on only one type of SBR.

Thus, our work aims at completing the Hoffman's study on polybutadiene by comparing his dielectric results to mechanical results obtained by mechanical spectroscopy. This work is also extended to the study of the  $\beta$ -relaxation of different styrene-butadiene rubbers, in order to better understand the contribution of the different monomer units of this copolymer - namely, styrene, butadiene 1,4 cis, and trans and butadiene 1,2, on this relaxation. Thanks to a phenomenological modelling approach, their contribution is then quantified and enable to understand the molecular origin of the  $\beta$ -relaxation mechanism.

## 2 Experiments

6 elastomers with different microstructures are studied: 3 poly(butadiene) and 3 poly(styrene-co butadiene) rubbers. Their different vinyl, cis, trans- and styrene unit contents (in

molar fraction) are reported in Table 1. They were measured by RMN 1D  $^{13}\text{C}$  with the following protocol:

The polymers were dissolved in  $\text{CDCl}_3$  to obtain 60 g/L solutions. All NMR experiments were recorded on a Bruker Avance III spectrometer operating at 11.7 T ( $^{13}\text{C}$  Larmor frequency of 125.83 MHz) at ambient temperature using a 5 mm broadband Helium cryoprobe. For all experiments  $^1\text{H}$  decoupling was applied only during signal acquisition. The  $^{13}\text{C}$  quantitative spectra were recorded using a flip angle of  $30^\circ$  (pulse length of 4us) and 4096 acquisitions were co-added using a recycle delay of 10 s to ensure complete recovering of the longitudinal magnetization. The  $^{13}\text{C}$  NMR spectra were referenced using the NMR resonance of  $\text{CDCl}_3$  at 77 ppm. Polymers microstructures were calculated according to the norm ISO 21561-2:16. The  $^{13}\text{C}$  NMR resonances between 43.5ppm and 45.2ppm were assigned to aliphatic CH of isolated vinyl units ( $V_{\text{isol}}$ ), i.e. vinyl units between two other units (butadiene 1,4 cis (C), butadiene 1,4 trans (T) and styrene (S)) as CVC, TVT, SVS, CVT, TVS, CVS, TVC, SVT and SVC.

The isolated vinyl fraction i.e. the fraction of the vinyl units ( $V_{\text{isol}}$ ) between two 1,4 butadiene units is calculated from the integration of the peaks of the aliphatic CH of the vinyl units between 43.5 ppm and 45.2 ppm by the integration of the carbon of all the vinyl units ( $V_{\text{total}}$ ) [10] following :

$$\%V_{\text{isol}} = \text{Int}V_{\text{isol}}/\text{Int}V_{\text{total}} \quad (\text{Eq.1})$$

This equation assumes that the resonances from SSS and SSV triad can be neglected. We have not detected these resonances with the  $^1\text{H}/^{13}\text{C}$  HSQC and HMBC NMR correlation experiments.

The average length of vinyl sequence and 1,4 butadiene sequence are conventionally calculated [11] as the ratio of the number of total vinyl units by half the number of vinyl units bonded to another polymer unit (C, T and S) and, the ratio of total 1,4 butadiene units (C+T) by half the number of 1,4 butadiene bonded to another polymer unit (V and S) respectively.

The materials glass transition temperature, measured by Differential Scanning Calorimetry (DSC, 10K/min heating ramp), is reported in the same table. The sample name is formatted as SBR x/y/z and PB x/y with x the vinyl weight fraction, y the cis unit weight fraction, and z the styrene weight fraction.

	SBR 42/15/25	SBR <sup>d</sup> 19/22,5/20	SBR 20/29/14	PB 5/59	PB 48/16	PB 81/11
Vinyl (%) <sup>a</sup>	42/44 (48)	19/19 (20)	20/20 (21)	5	48	81
Cis (%) <sup>a</sup>	15/15 (17)	22,5/23 (25)	29/29.5 (31)	59	16	11
Trans (%) <sup>a</sup>	18/18 (20)	38,5/40 (43)	37/38 (40)	36	36	8
Styrene (%)	25/22 (15)	20/18 (12)	14/12.5 (8)	-	-	-
% of vinyl monomer in sequence of 1 unit <sup>b</sup>	10 (13)	- (13)	18 (13)	5 (4)	21 (13)	32 (29)
	<b>20 (27)</b>	<b>- (62)</b>	<b>85 (62)</b>	<b>100 (90)</b>	<b>44 (27)</b>	<b>4 (1)</b>
% of CIS+TRANS monomer in sequence of 1 unit <sup>c</sup>	- (15)	- (7)	- (6)	- (0,3)	- (12)	- (12,5)
	<b>- (40)</b>	<b>- (10)</b>	<b>- (8)</b>	<b>- (0.2)</b>	<b>- (23)</b>	<b>- (65)</b>
Average length of Vinyl sequence <sup>d</sup>	1,6 (1,9)	- (1,2)	0,9 (1,3)	0,8 (1,1)	1,2 (1,9)	4,4 (5,3)
Average length of CIS+TRANS sequence <sup>d</sup>	1,2 (1,6)	- (3,1)	3,2 (3,5)	14,6 (20)	1,3 (2,1)	1,0 (1,2)
Tg <sub>DSC</sub> (K) <sup>e</sup>	248	225	208	173	217	251

<sup>a</sup> in parenthesis the % molar fraction, in italic the volume fraction taking 60cm<sup>3</sup>/mol for the butadiene units and 99cm<sup>3</sup>/mol for the styrene units.

<sup>b</sup> upper line: per 100 chain monomers ; lower line in bold: per 100 vinyl monomers; between parenthesis, theoretical values from random statistic

<sup>c</sup> upper line: per 100 chain monomers, no RMN data available, only calculated values from random statistics ; lower line in bold: per 100 CIS+TRANS monomers , between parenthesis: theoretical values from random statistics.

<sup>d</sup> in parenthesis the value calculated with random statistic from the formula 1/(1-%monomer)

<sup>e</sup> DSC : heating ramp 10K.min<sup>-1</sup>

<sup>f</sup> no structural analysis by NMR for this material. The composition is known from previous NMR experiments.

**Table 1: Microstructure and Tg<sub>DSC</sub> (K) of the studied PB (monomer content expressed in mass fraction). For SBR, the molar fraction of the different units is also reported between parentheses.**

The materials were processed following the Rauline patent [9]. First, the gum was introduced in an internal mixer and sheared for 2 min at 60°C. Then, the vulcanization recipe was added and the mix was sheared for 5 min, with the following composition: for 100 g of polymer, 1.5 g of DPG (diphenylguanidine), 3.8 g of CBS (n-cyclohexyl-2-benzothiazyl-sulfénamide), 1.5 g of Zinc oxide (ZnO), 1.5 g of ozone wax, 2 g of 6PPD (N-(1,3-dimethylbutyl-N'-phenyl-P-phenylenediamin), 2g of stearic acid, and 2.5 g of sulfur. The material was afterward sheared in an open mill for five minutes at 60°C. Sample sheets of 0.5 or 2 mm thickness were then obtained by hot pressing at 150°C during 90 min, which is the time needed to obtain 98% of the maximal torque during rheological measurement in plan/plan mount at 150°C.

Mechanical spectroscopy was performed in torsion mode with a Metravib apparatus enabling measurement in a frequency range [ $10^{-4}$  Hz; 1Hz] over a temperature range [100 K; 250 K] [10]. Samples were parallelepipeds with a  $0.5 \times 4 \times 10$  mm<sup>3</sup> or  $2 \times 6 \times 12$  mm<sup>3</sup> dimensions. Dielectric measurements were performed with a Novocontrol Concept 40 apparatus using sample disc film with 2cm diameter and 1 mm thickness. The frequency domain of this apparatus was set as [0,1 Hz, 1MHz], slightly overlapping with the frequency domain of the mechanical spectrometer. This overlap will be used in the following, to compare the material mechanical and dielectric responses at the same frequency. However, the much lower frequency domain of the mechanical spectrometer is an advantage compared to the one of the dielectric as it enables a better separation of the secondary relaxations. .

## 3 Results

### 3.1 Isochronal measurements

As shown in Figure 1a, PBs have two mechanical relaxations in the studied temperature range, namely, a relaxation at low temperature so called  $\beta$  and the  $\alpha$ -relaxation at higher temperature. The  $\beta$ -relaxation appears to be very wide, which might mean that it results from the overlapping of several contributions acting more or less independently the one from the other. Moreover, it is noteworthy that its width depends on the polymer chemical structure. The temperature of the  $G''$   $\beta$ -peak is reported in Table 2. At increasing vinyl content, i.e.

decreasing Cis/Trans units content, the  $\beta$  relaxation amplitude decreases, its maximum shifts towards higher temperature and its width increases. As this corresponds to a decrease of the low temperature part of this peak (90-135 K) and an increase of its high temperature part (135-200K), this suggests that two distinct mechanisms are involved in the secondary relaxation.

Sample name	$T_{\beta}$ (K)	Height of $G''$ $\beta$ peak ( $\pm 0,002$ ) /GPa
PB 5/59	129	0,029
PB 48/16	129	0,023
PB 81/11	157	0,019
SBR 20/29/14	122	0,03
SBR 19/22,5/20	123	0,026
SBR 42/15/25	142	0,022

Table 2: Height and temperature at the maximum of the  $\beta$  peak measured at 1Hz by mechanical spectroscopy .

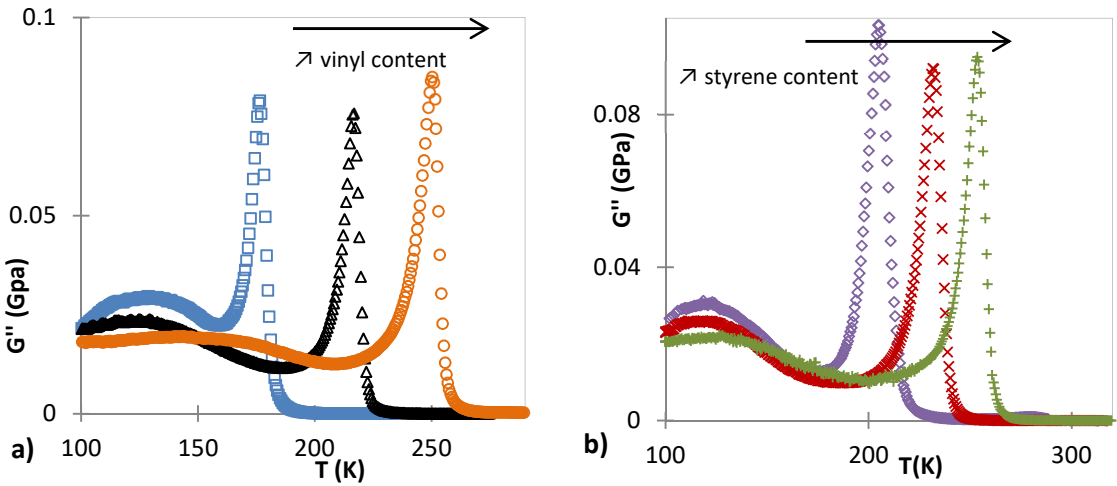


Figure 1: Dynamic loss modulus as a function of temperature, at 0.1 Hz a) for PB 5/59 ( $\square$ ), PB 48/16 ( $\triangle$ ), PB 81/11 ( $\circ$ ) b) for SBR 20/29/14 ( $\diamond$ ), for SBR 19/22,5/20 ( $\times$ ), for SBR 42/15/25 ( $+$ ).

Same experiments were performed with SBR samples and show  $\alpha$  and  $\beta$  relaxations (Figure 1b). As reported in Table 2, the temperature at the maximum of the  $G''$   $\beta$  peak is the same for SBR 19/22,5/20 and SBR 20/29/14, but is 20K higher for SBR 42/15/25. As for the



PBs, this peak amplitude varies with the copolymer microstructure. The significant difference between the SBR 20/29/14 and the two SBR 19/22,5/20 and SBR 42/15/25 might come from the difference in their styrene content, the increase of which necessarily decreases the relative amount of the other monomers and therefore the intensity of the relaxations in which they are involved.

Moreover, the  $\beta$  relaxation is weaker and more spread in temperature when the vinyl content increases while the Cis/Trans content decreases ; in other word, the evolution of the  $LT^\circ$  part and of the  $HT^\circ$  part of the relaxation are different. As previously for PBs, these results suggest that the increase of the vinyl content promotes the relaxational mechanism at high temperature, to the detriment of the low temperature mechanisms.

### 3.2 Isothermal measurements

#### 3.2.1 Mechanical spectroscopy

Frequency sweep curves [ $2 \cdot 10^{-3}$  ;  $4 \cdot 10^{-3}$  ;  $8 \cdot 10^{-3}$  ;  $1 \cdot 10^{-2}$  ;  $2 \cdot 10^{-2}$  ;  $4 \cdot 10^{-2}$  ;  $8 \cdot 10^{-2}$  ;  $1 \cdot 10^{-1}$  ;  $2 \cdot 10^{-1}$  ;  $4 \cdot 10^{-1}$  ;  $8 \cdot 10^{-1}$  ; 1 Hz] have been performed with the different materials over the temperature range of their  $\beta$  relaxation (temperature increment of 4K). Assuming the time-temperature equivalence, master curves were plotted at a given reference temperature. As an example, the  $G'$  and  $G''$  master curves of SBR 20/29/14 are presented in Figure 2 and validate the thermorheological simplicity assumption *as a first approximation*, taking as reference temperature,  $T_{ref} = 152K$ . The curves of the other materials are given as supporting information.

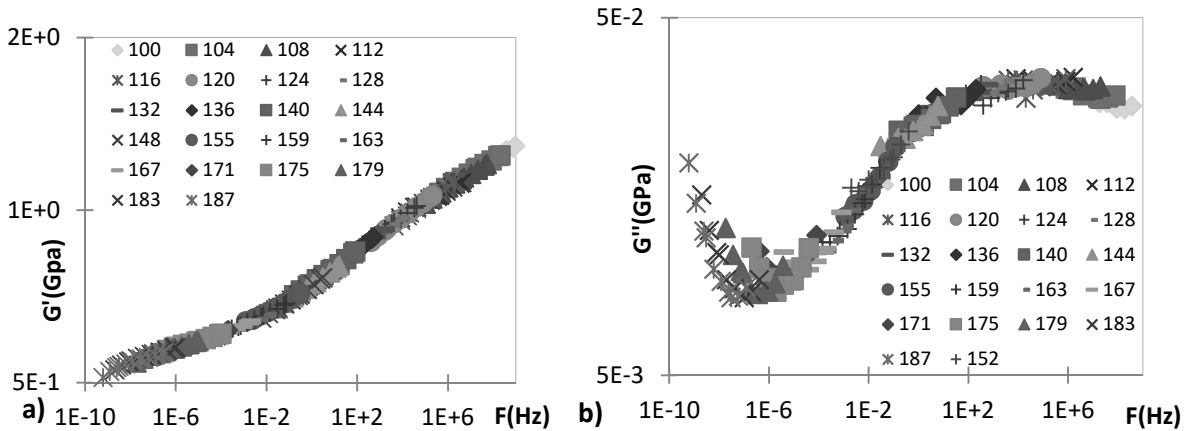
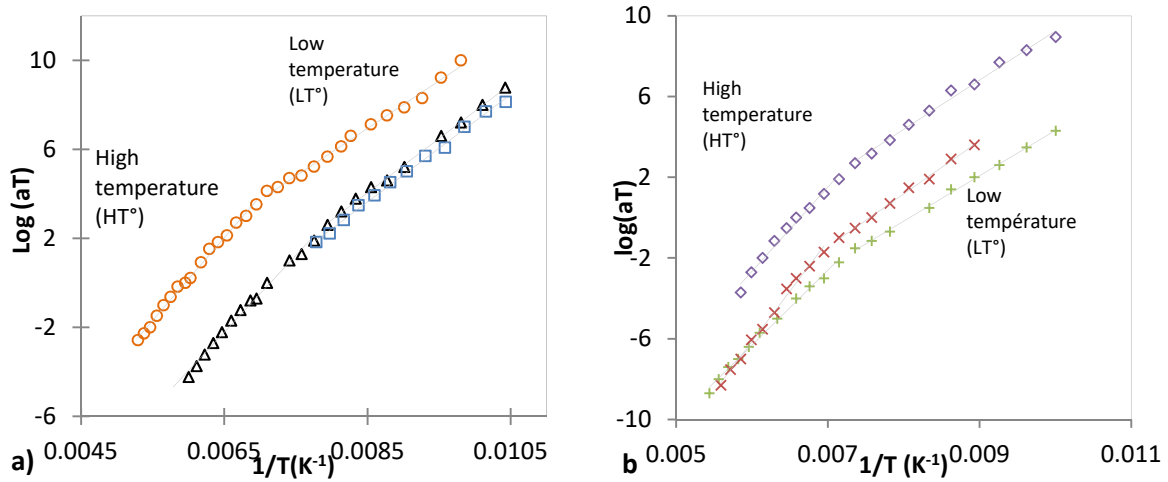


Figure 2:  $G'$  and  $G''$  master-curves for the SBR 20/29/14.  $T_{ref} = 152K$ .

The shift factors used for the master curve construction can be plotted, on a logarithmic scale, as a function of  $1/T$  (Figure 2a and 2b). For all the materials, except PB5/59 for which the high temperature part of the  $\beta$  relaxation overlaps with the  $\alpha$  relaxation, two slopes are visible. This confirms the presence of two Arrhenius mechanisms, the energy of which being higher for the high temperature mechanism.



**Figure 3: Shift factors as a function of  $1/T$  for a) for PB 5/59 ( $\square$ ), PB 48/16 ( $\triangle$ ), PB 81/11 ( $\circ$ ), b) for SBR 20/29/14 ( $\diamond$ ), for SBR 19/22,5/20 ( $\times$ ), for SBR 42/15/25 ( $+$ ), in the  $\beta$  relaxation temperature domain.**

The activation energies ( $E_{a\beta}$ ), are deduced from the Arrhenius law given by:

$$\tau(T) = \tau_o \exp\left(\frac{E_{a\beta}}{RT}\right) \quad (\text{Eq.2})$$

where  $R$  is the perfect gas constant,  $\tau$  is equal to  $1/2\pi f$ .  $f$  and  $T$  are the frequency and the temperature corresponding to the peak maximum. Defining the shift factors between two curves obtained at different temperatures, by  $a_T = \tau(T_1)/\tau(T_2)$ , it is then easy to determine  $E_{a\beta}$  (as displayed in Table 3).  $E_{a\beta}$  of the low temperature ( $LT^\circ$ ) mechanism are between 43 and 49  $\text{kJ}\cdot\text{mol}^{-1}$ ; the ones of the high temperature ( $HT^\circ$ ) mechanisms varie on a larger domain, between 62 and 90  $\text{kJ}\cdot\text{mol}^{-1}$ . Such result is explained by the proximity (in other word the partial overlapping) of the  $\alpha$  relaxation in the case of the materials with the lowest  $T_g$  (PB 5/59); this leads to an overestimate of the shift factors and consequently of the activation energy.

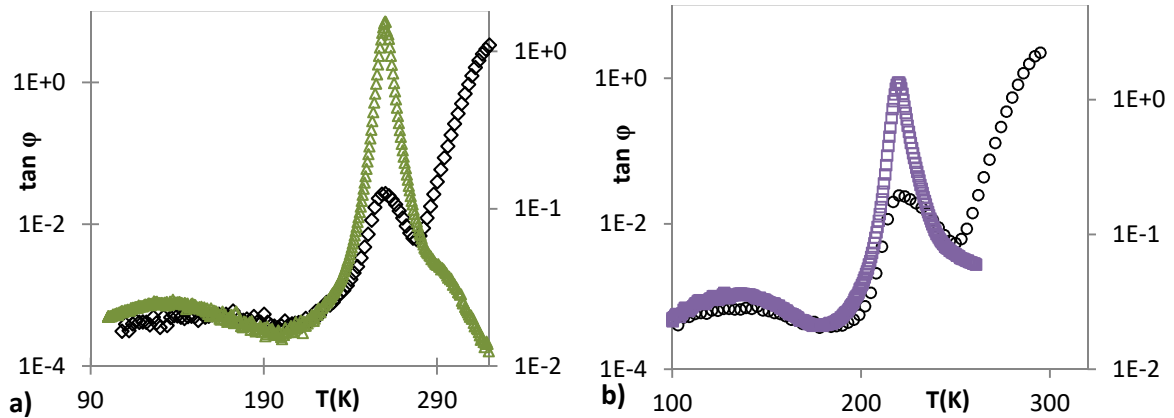
Materials	$E_{a\beta}$ HT*° (kJ.mol <sup>-1</sup> )	$E_{a\beta}$ LT*° (kJ.mol <sup>-1</sup> )
PB 5/59		<b>49</b>
PB 48/16	62	50
PB 81/11	<b>69</b>	43
SBR 42/15/25	69	43
SBR 19/22,5/20	80	50
SBR 20/29/14	75	47

\* HT° and LT° refer to High Temperature and Low Temperature side of the relaxations

**Table 3: Activation energy of the  $\beta$ -mechanical relaxation for the 6 different materials.**

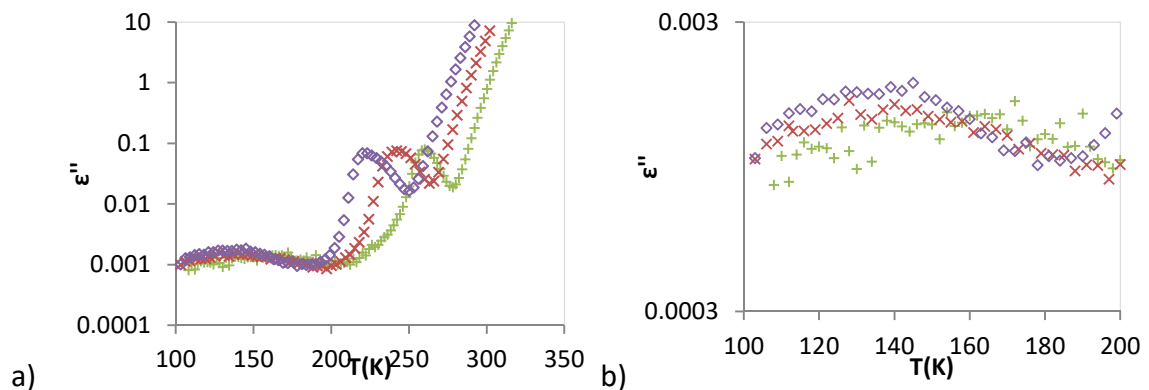
### 3.2.2 Dielectric spectroscopy

The isochronal curves of the loss factors obtained via the dielectric spectroscopy technique, at the same frequency 0,1Hz can be compared to the previous mechanical results (for instance Figure 4a and 4b). The HT° part of the dielectric  $\alpha$ -relaxation is masked by the increase in the ionic conductivity; nevertheless its peak maximum is observed at the same temperature as the one of the mechanical  $\alpha$  peak. At 0,1Hz, the dielectric and mechanical  $\beta$ -relaxation both spread over a same temperature domain, suggesting that they originate from very similar mechanisms. However, it must be recalled that the trans isomer being initially nonpolar, it does not significantly participate to the dielectric relaxations (its contribution coming only from induced polarization), conversely to the cis and vinyl monomers. Note also that for this reason, and given the different nature of the dielectric and mechanical solicitations, the very similar intensity of the mechanical and dielectric relaxation seen on the curve is fortuitous.



**Figure 4: Dielectric and mechanical loss factors as a function of temperature at 0.1 Hz: a) for SBR 42/15/25 (dielectric ( $\diamond$ ),DMA ( $\triangle$ )), b) for SBR 20/29/14 (dielectric ( $\circ$ ), DMA ( $\square$ )).**

Figure 5 presents the dielectric imaginary part of permittivity  $\epsilon''$  as a function of the temperature measured at 0.1 Hz for the 3 SBR. The height of the  $\epsilon''$   $\beta$  peak is lower and occurs at higher temperature for SBR 42/15/25 than for SBR 20/29/14 and SBR 19/22,5/20, as previously found with mechanical spectroscopy.



**Figure 5: a) Dielectric imaginary permittivity versus temperature for the 3 studied SBRs, at 0,1 Hz: SBR 20/29/14 ( $\diamond$ ), for SBR 19/22,5/20 ( $\times$ ), for SBR 42/15/25 (+); b) same figure with different scale**

The dependence of the dielectric relaxation time on temperature can be directly deduced from the peak maximum position on the isochronal curves like the one presented in Figure 6a for SBR 19/22,5/20. All these data show an Arrhenius behavior with only one slope; for the 3 SBRs, almost the same activation energies ( $48 < E_{a\beta} < 50 \text{ kJ.mol}^{-1}$ ) were calculated. They are close to the one found for the  $\text{LT}^\circ$  part of the  $\beta$ -mechanical relaxation (Table 3). The pre-exponential times are very close to each other:  $\tau_0$  is found equal to  $5 \cdot 10^{-19} \text{ s}$  for SBR 19/22,5/20 and SBR 20/29/14 and to  $1 \cdot 10^{-20} \text{ s}$  for SBR 42/15/25. Thus, these dielectric shift

factors does not enable to evidence two relaxational mechanisms, conversely to the previous mechanical measurements and to what is suggested by dielectric experiments on different materials (cf. introduction). This will be further commented in the discussion part.

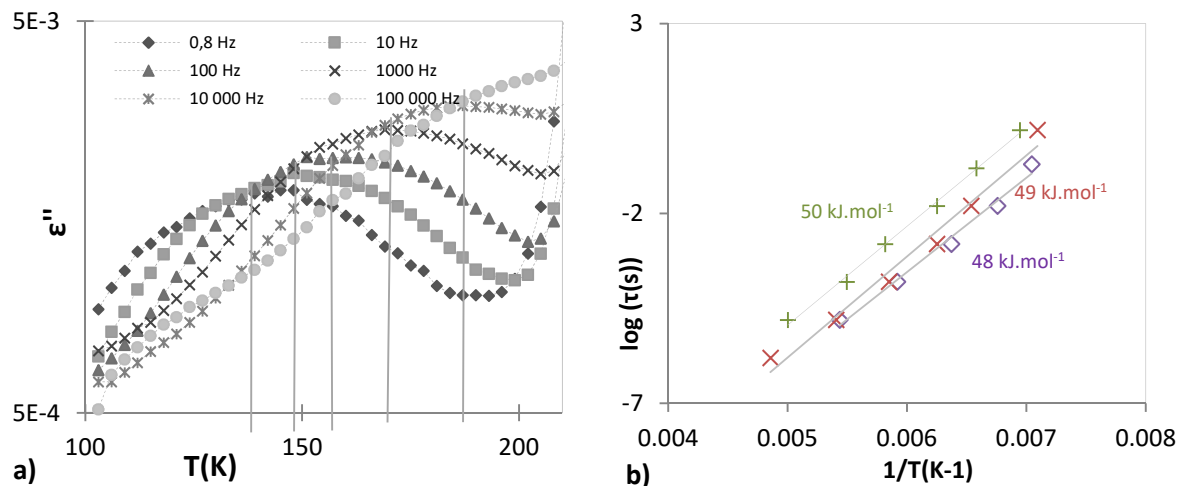


Figure 6: a) loss permittivity  $\epsilon''$  as a function of  $1/T$ , measured at different frequencies for SBR 19/22.5/20; b) dielectric  $\beta$ -relaxation times deduced from isochronal curves, for the 3 SBRs: for SBR 20/29/14 ( $\diamond$ ), for SBR 19/22,5/20 ( $\times$ ), for SBR 42/15/25 (+)

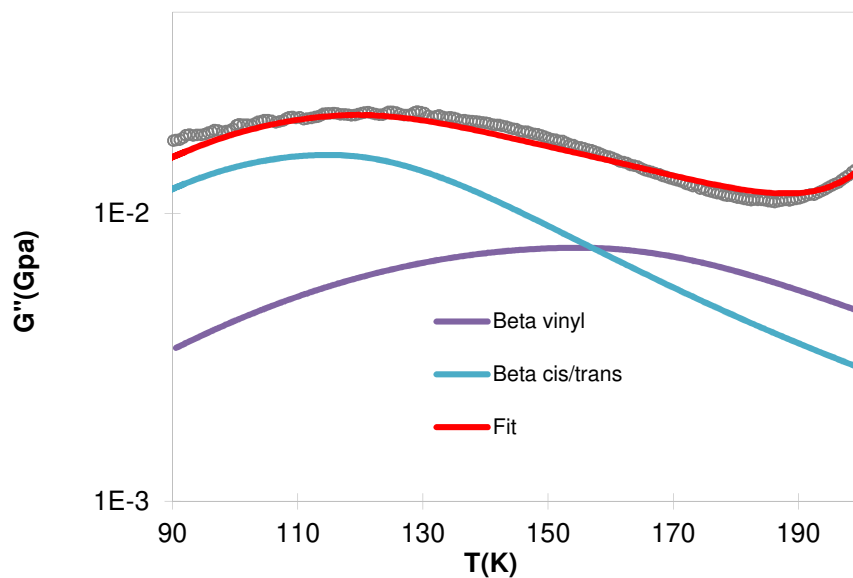
### 3.3 Discussion

As expected, the isochronal curves from both techniques have shown that a modification of the copolymers microstructure leads to a modification of the secondary relaxations. To sum up our experimental results, styrene has only a « diluting » effect as the increase in its content simply decreases the content of the other monomers and therefore the intensity of the relaxations in which they are involved (one can note however that this phenomenon is much less visible with dielectric spectroscopy; the authors having no explanation for this). In both PBs and SBRs, increasing the vinyl content shifts the position of the  $\beta$  relaxation peak towards higher temperatures and increases its width.

The evolution of the shift factors with temperature, deduced from mechanical spectroscopy, the large frequency domain on which the  $\beta$  relaxation spread in the “master curve”, as well as the large temperature domain over which it spreads in the isochronal curve, indicate that two mechanisms are involved in the  $\beta$  relaxation. Given the influence of the different monomers contents, the HT° mechanism can be ascribed to the vinyl isomers whereas the LT° one could be due to the movements of the *cis* and/or the *trans* units, whose respective contribution is impossible to distinguish from mechanical spectroscopy. The HT°

and  $LT^\circ$  contributions are difficult to characterize from the isothermal curves, as the frequency range over which the isothermal are performed are short, and as they seem to overlap over large temperature and frequency domains.

To solve this problem, we have chosen to deconvolute the  $G''$  contributions of the mechanical  $\beta$  relaxation. This deconvolution was performed thanks to PeakFit software ©. The isochronal curves at 0.1Hz of the different materials have been analyzed following the same method [7]: two peaks are defined with independent parameters, i.e. temperature at the peak maximum, the half widths for the left and the right side of the relaxation, and its amplitude A. The use of two peaks was motivated by the fact that the experimental peak is, for most of the materials, too large to be fitted by a single HN function (and, as said previously, by the fact that the previously seen influence of the comonomers contents on the shape of the  $\beta$  relaxation is incompatible with the assumption of a single process). The optimization of these parameters is based on the optimal fit of the experimental peak with the summation of the two simulated peaks. For instance, with PB 48/16, the two deconvoluted peaks have their maximum at 115K et 155K respectively (cf. Figure 7): other curves are presented as supporting information.



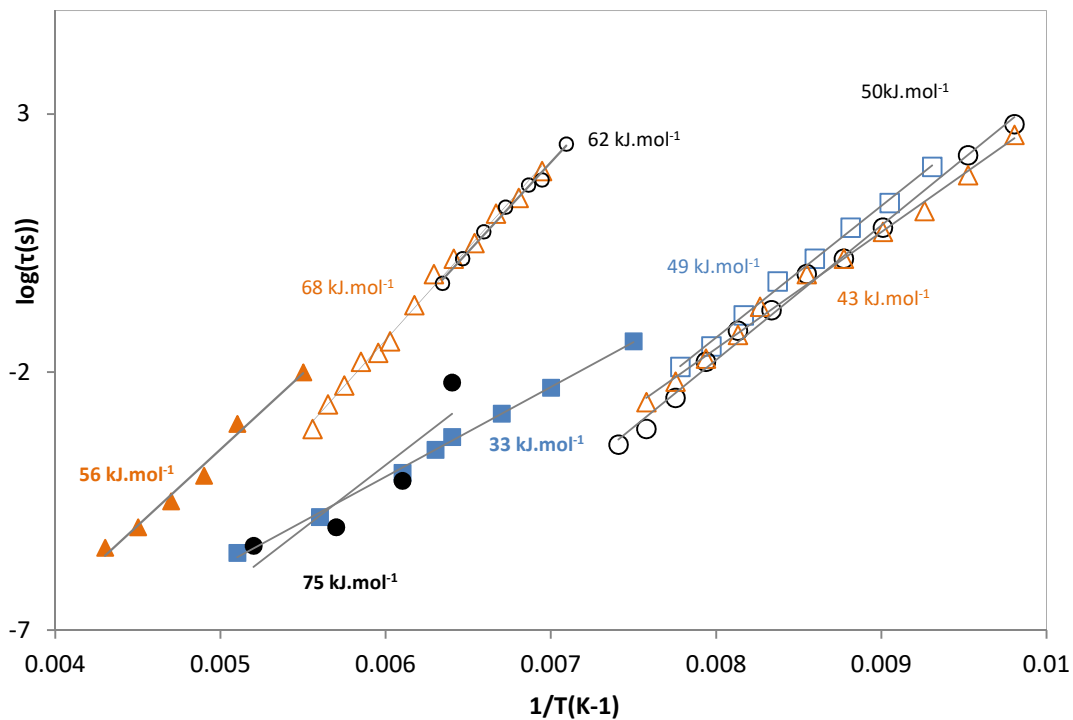
**Figure 7: Deconvolution of the  $\beta$ -peak mechanical relaxation of PB 48/16.**

From these temperature values at the peak maximum, one can deduce the value of the pre-exponential time in the Arrhenius expression of the relaxation time of the  $LT^\circ$  and  $HT^\circ$  mechanisms following:

$$\tau_o = \tau \cdot \exp\left(-\frac{E_{a\beta}}{RT}\right) \quad (\text{eq. 3})$$

R is the perfect gas constant ,  $\tau$  is equal to  $1/2\pi f$  with f the frequency of the test (0,1Hz) and T the temperature at the peak maximum. The activation energies are those previously deduced from the shift factors: we have assumed the same relaxation mechanisms in all the samples and therefore the same activation energy, i.e. 49 kJ/mol for the LT° mechanism and 69kJ/mol for the HT° one. As reported in Table 3, 49 kJ/mol is indeed the activation energy of the PB 5/59 which is the material which contains the largest amount of butadiene 1,4 (Cis or Trans) monomer (95 %), whereas 69kJ is the one of PB 81/11, which contains the largest amount of butadiene 1,2 (vinyl) monomer (81%).

This procedure enables to plot the relaxation times in absolute values for both mechanisms and for all the samples on Figure 8. The average relaxation times of the HT° mechanisms of PB 48/16 and PB 81/11 are superimposed (those of PB5/59 cannot be deduced with enough certainty from the data as the  $\alpha$  relaxation is too close from the  $\beta$ -one). The same superimposition is found for the relaxation times of the LT° mechanisms.



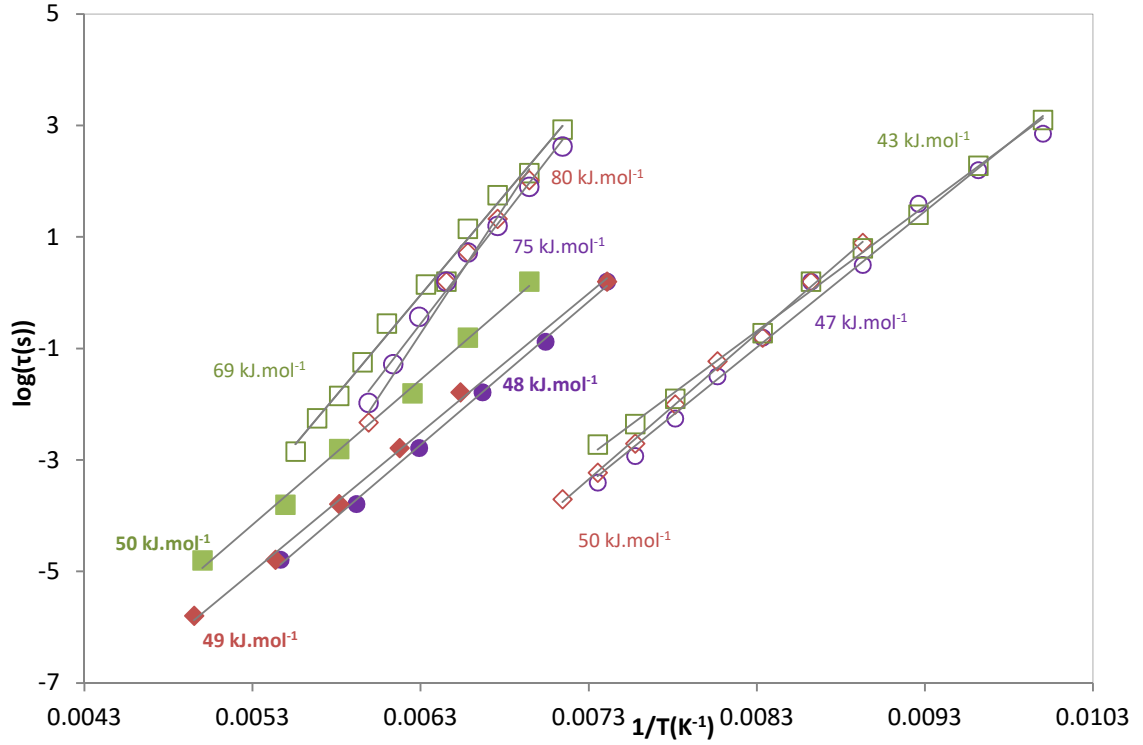
**Figure 8: Arrhenius plot of the PBs  $\beta$ -relaxation times deduced from mechanical spectroscopy (PB 81/11 ( $\Delta$ ), PB48/16( $\circ$ ), PB 5/59 ( $\square$ )) and dielectric spectroscopy (full symbols: PB 86/6 ( $\blacktriangle$ ), PB 52/19( $\bullet$ ), PB 7/41( $\blacksquare$  ) (Hoffman data, from Fig 7(b) in reference 7).**

For the three SBRs, the mechanical relaxation times of the HT° contributions are superimposed; the same result is found for the mechanical relaxation times of the LT° contributions (Figure 9).

Now that we have obtained more information on the relaxation times of both mechanisms, and therefore less free parameters, the mechanical isochrones and isothermal curves can be fitted with the sum of two Havriliak-Negami functions (HN) with the two following assumptions:

- Two different contributions exist in the  $\beta$ -relaxation of PBs and SBRs : one at HT° due to the relaxations of the 1,2 butadiene units (vinyl) and one at LT° due to the relaxation of the 1,4 butadiene *cis/trans*.
- From a polymer to another, i.e. from a chemical microstructure to another, the width, the asymmetry and the peak positions (in other word the relaxation times) of each contribution does not change.





**Figure 9: Arrhenius plot of the SBRs  $\beta$ -relaxation times deduced from mechanical spectroscopy (SBR 20/29/14 (○), for SBR 19/22,5/20 (◇), for SBR 42/15/25 (□)) and dielectric spectroscopy (same full symbols).**

The HN function for the complex modulus is:

$$G^*(\omega) = G_{\infty} + \frac{\Delta G}{(1 + (i\omega\tau_{HN})^{\alpha_{HN}})^{\gamma_{HN}}} \quad (\text{eq. 4})$$

with  $\alpha$  controlling the peak asymmetry,  $\gamma$  its width and  $\Delta G$  its amplitude. The real and imaginary parts are given by:

$$G'(\omega) = G_{\infty} + \Delta G \frac{\cos(\gamma_{HN}\varphi)}{\left[1 + 2(\omega\tau)^{\alpha_{HN}} \cdot \sin\left(\frac{\pi(1 - \alpha_{HN})}{2}\right) + (\omega\tau)^{2\alpha_{HN}}\right]^{\frac{\gamma_{HN}}{2}}} \quad (\text{eq. 5})$$

And

$$G''(\omega) = \Delta G \frac{\sin(\gamma_{HN}\varphi)}{\left[1 + 2(\omega\tau)^{\alpha_{HN}} \cdot \sin\left(\frac{\pi(1 - \alpha_{HN})}{2}\right) + (\omega\tau)^{2\alpha_{HN}}\right]^{\frac{\gamma_{HN}}{2}}} \quad (\text{eq. 6})$$

With

$$\varphi = \arctan \left[ \frac{(\omega\tau)^{\alpha_{HN}} \cdot \cos\left(\frac{\pi(1-\alpha_{HN})}{2}\right)}{1 + (\omega\tau)^{\alpha_{HN}} \cdot \sin\left(\frac{\pi(1-\alpha_{HN})}{2}\right)} \right] \quad (\text{eq. 7})$$

At the loss peak,

$$\omega\tau = \left( \frac{\sin\left(\frac{\pi\alpha}{2(\beta+1)}\right)}{\sin\left(\frac{\pi\alpha\beta}{2(\beta+1)}\right)} \right)^{\frac{1}{\alpha}} \quad (\text{eq. 8})$$

The evolution of the complex modulus with temperature is therefore the consequence of the evolution of the relaxation times ( $\tau$ ). As suggested by the previous results, these times follow the Arrhenius equation in which the activation energies are fixed at 69kJ.mol<sup>-1</sup> for the HT° contribution and at 49kJ.mol<sup>-1</sup> for the LT° contribution.. The fixed pre-exponential times are also the ones deduced from equation 8, for these two materials (table 4). Our second assumption is that  $\alpha_{HN}$  and  $\gamma_{HN}$  are constants for each contribution, whatever the polymers. Their value is fixed from the fitting of the isochronal curves obtained at  $f = 0.1\text{Hz}$  (helped by the initial curve fitting with peakfit). It is indeed impossible to estimate them from the isothermal curves since the frequency domain tested is too small.

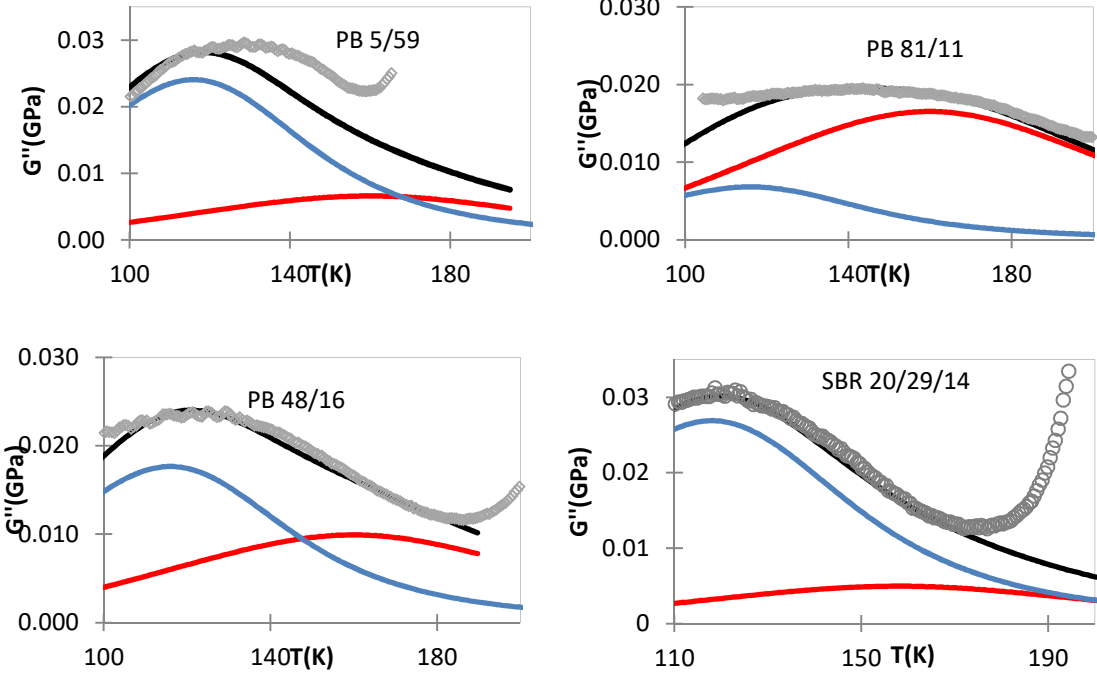
Note also that these two parameters are deduced with the assumption that the width of the times distribution of the relaxational processes do not depend on the temperature. Such dependence was discussed in literature, for instance, for the modelling of the  $\beta$  relaxations of PMMA [15] or PVC [16]. It is related to the distribution of the activation entropy of the relaxations. Taking into account such dependence add more complexity and an additional parameter to the fitting procedure. Moreover, in references 15 and 16, the found dependence seems difficult to characterize (the data are scattered), and in any case relatively small (less than 10% variation of the width of the time Gaussian distribution over the whole temperature range of the relaxation). For these reasons, neglecting it seems very reasonable, and to our opinion, has no significant influence on the conclusion of our work.

Given the fact that there are two contributions within the  $\beta$  relaxation, it is not satisfactory to use the fitting of the built master curves, as these ones assume a time-temperature equivalence which is a rough approximation. However, the amplitude of each relaxation can be deduced from the simultaneous fitting of the isothermal and isochronal data. A satisfactory fit of both isothermal *and* isochronal curves is usually difficult to obtain and its success must always be seen as strong support of the employed procedure.

	HT°	BT°
$E_{a\beta}$ (kJ.mol <sup>-1</sup> )	69	49
$\tau_{\beta_0}$ (s)	$2.10^{-19}$	$3.10^{-19}$
$\alpha_{HN}$	0,2	0,23
$\gamma_{HN}$	0,18	0,2

**Table 4: parameters used for the HN fitting of the isochronal curves**

For all the studied materials, the isochronal fitting is very satisfactory given the simplicity of the procedure, except for PB 5/59 (Figure 10). It is indeed difficult to fit its HT° contribution because it merges with the  $\alpha$ -relaxation.



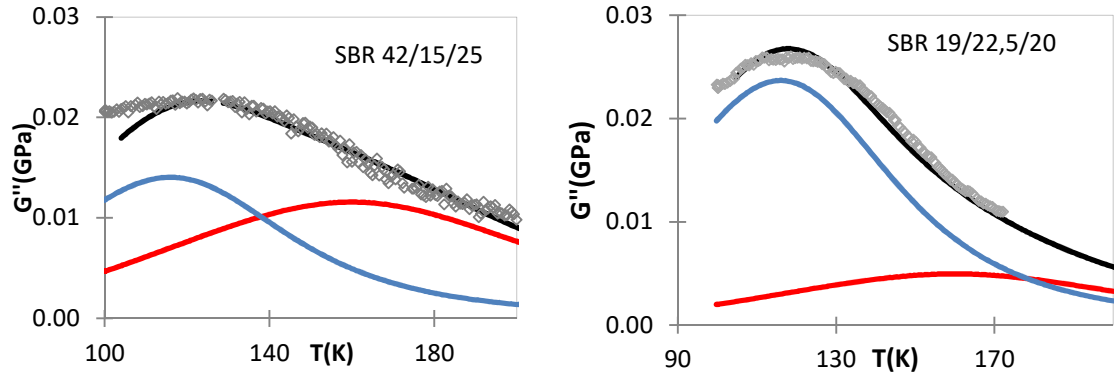
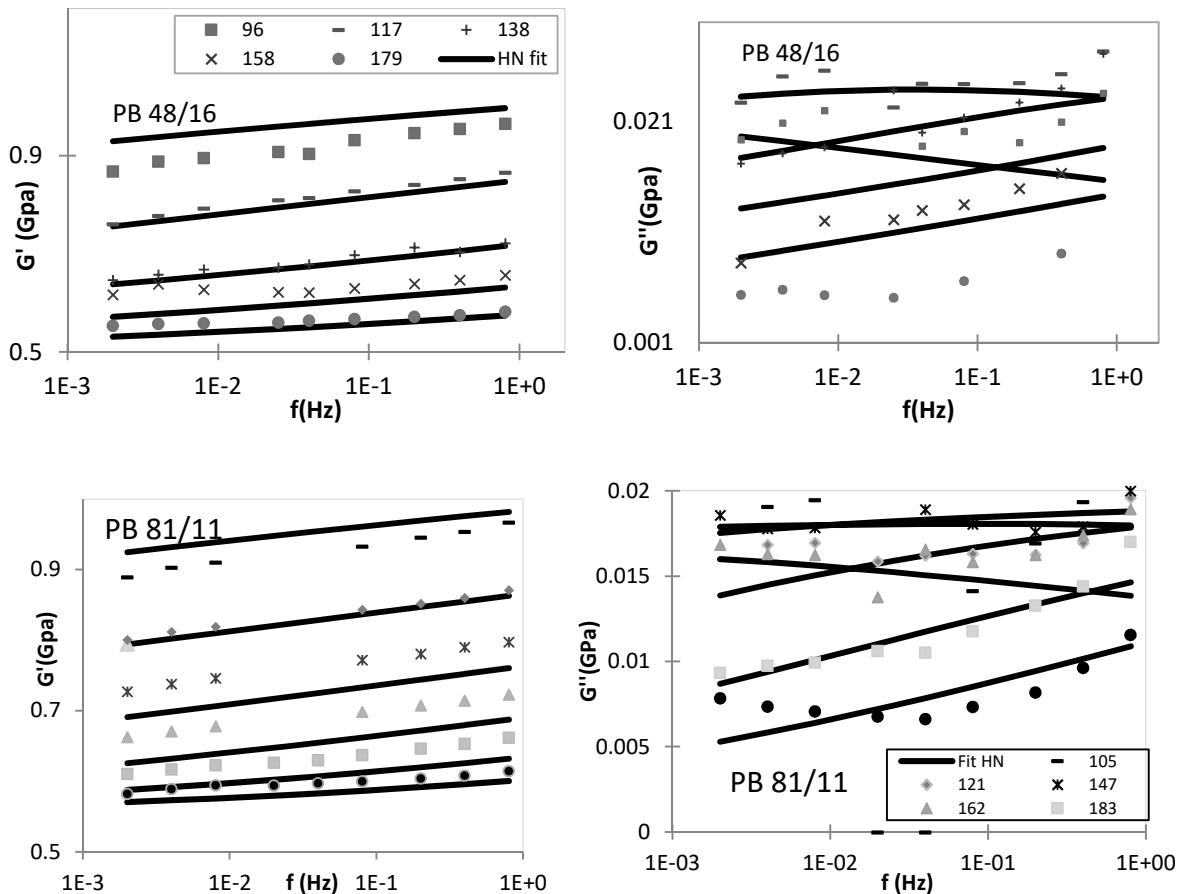
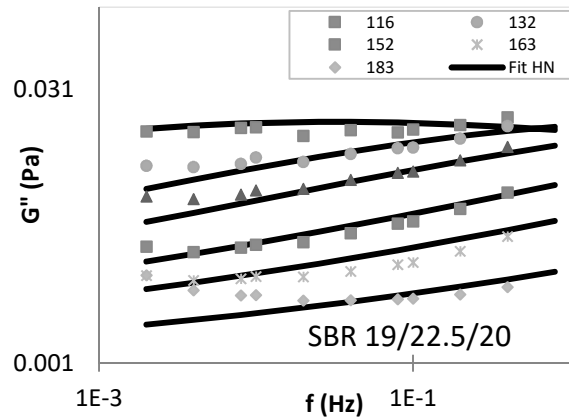
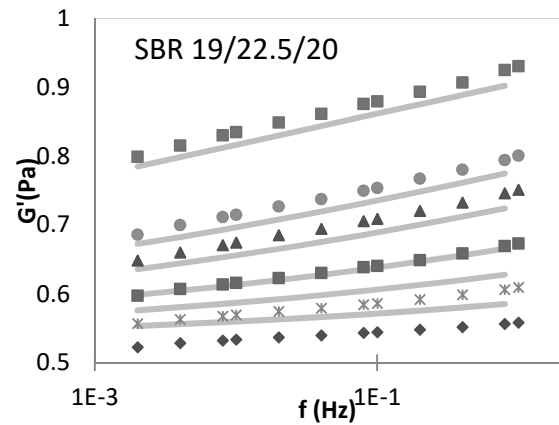
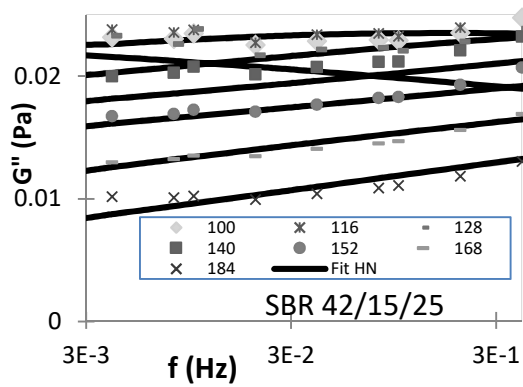
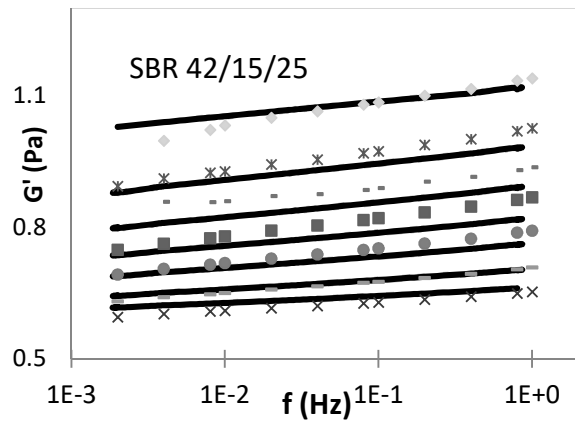
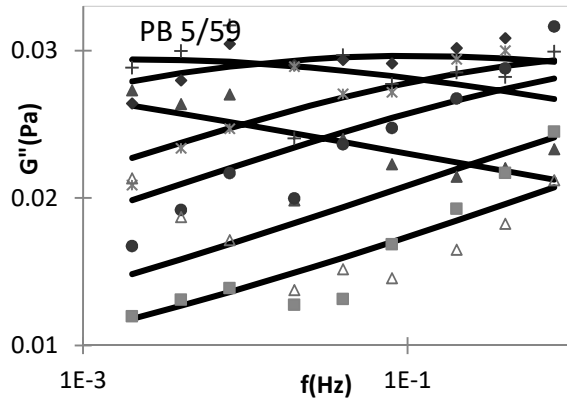
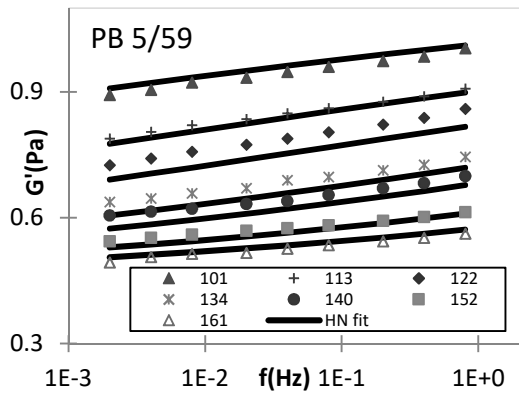
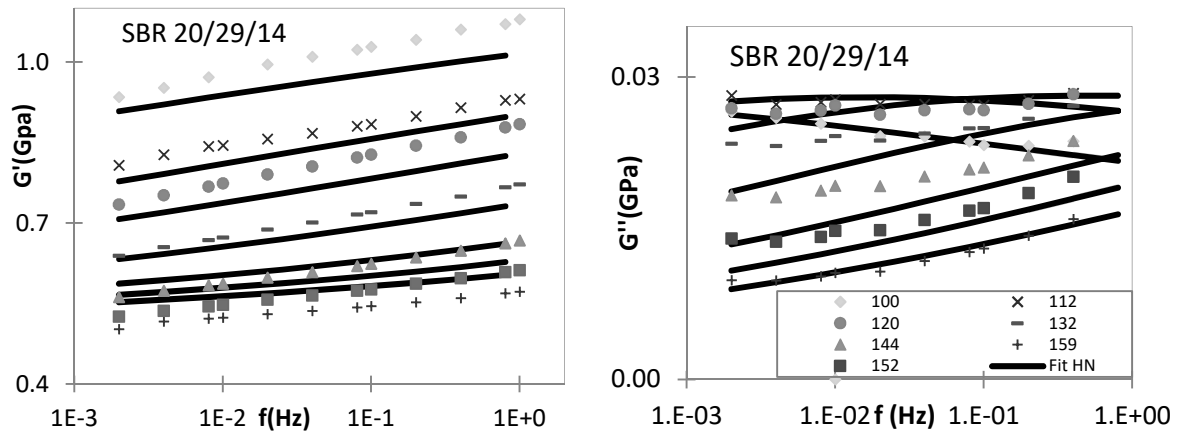


Figure 10: fitting of the  $G''$  isochronal curves at 0.1Hz with the HN model: data (circle symbol), HN fit of the  $HT^\circ$  contribution (red line), HN fit of the  $LT^\circ$  contribution (blue line), HN fit with both contributions (dark line)

The fitting of the isothermal curves is also satisfactory, as shown on figure 11. *Still with the same parameters*, this procedure has been also applied to the isochronal curves obtained at  $2.10^{-3}$  Hz (cf. Supporting Information) and gives very good results, which also validates our approach.





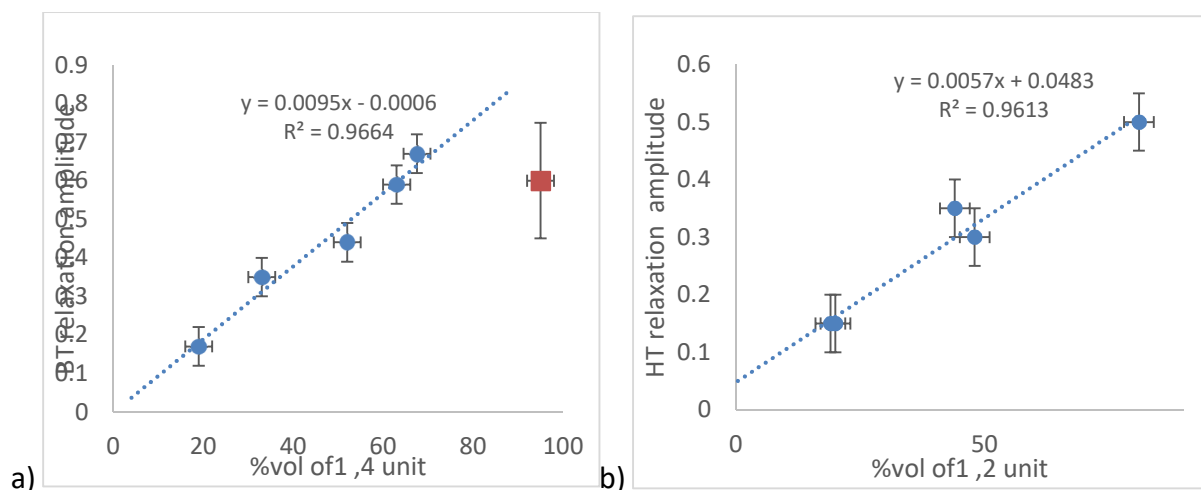


**Figure 11: fitting of the isothermal curves of the different materials with the HN model (some temperatures have been selected in order to ease an easier comparison between the fitting line and the HN model; it is important to recall that fitting has been performed simultaneously on the isothermal and isochronal curves).**

The amplitude found for each contribution can now be plotted on figure 12 as a function of the volume fraction of the 1,2 butadiene (*vinyl*) and 1,4 butadiene (cis and trans) content. The volume fraction is preferred to other parameter (weight or molar fraction) as the mechanical response of a material is usually related to the volume fraction of its different phases. To calculate this volume fraction, we have assumed that each unit has the molar volume of its homopolymer (60 cm<sup>3</sup>/mol for butadiene, and 99 cm<sup>3</sup>/mol for styrene). A linear relationship is found for both HT° and LT° contributions. (Note that the data for PB5/59 is not included in the trend curve calculation as its value is calculated with a more important error (+ 0.1), due to the proximity of the  $\alpha$  and  $\beta$  relaxation in this material). A plot as a function of the molar fraction of the butadiene units leads to the same conclusion (see Supporting Information Figure SI17). This is not surprising as there is very small difference between molar, volume and weight fractions in the considered materials, (the styrene content being low in the studied SBRs). As seen in Figure 12, the fitting line passing close to the origin, this nicely confirms that the HT° contribution is due to the movements of the 1,2 units and the LT° contribution to those of the 1,4 units. Moreover, it must be emphasized that our results also prove that both cis and trans units are involved in the LT° contribution of the mechanical relaxation, for two reasons. First, a plot of the LT° relaxation amplitude as a function of only the trans units volume fraction cannot be fitted by a straight line (see Figure SI16 Supporting Information). Moreover, as also shown in the Supporting Information (Figure SI15), the amplitude of the  $\beta$ -

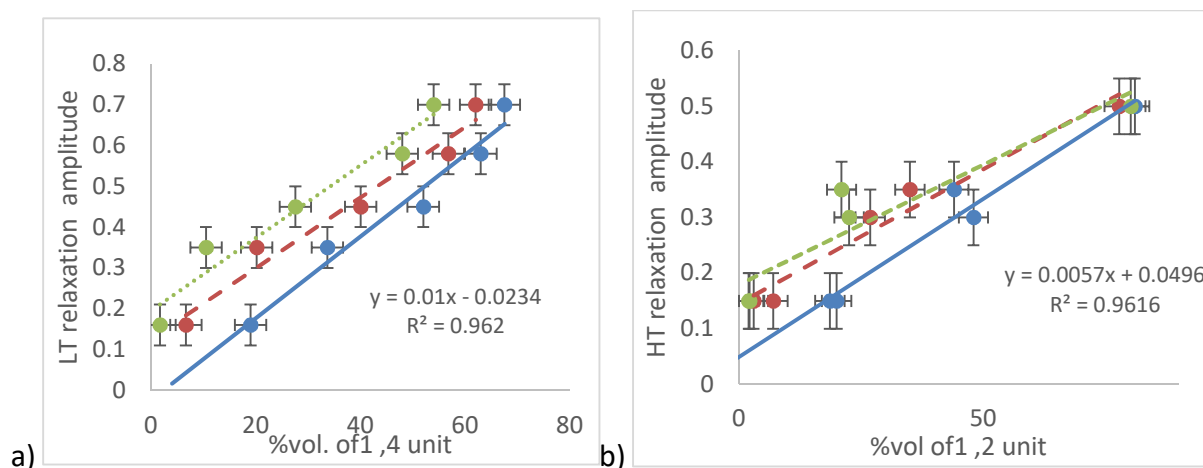
relaxation of the PB5/59, of the order of 0.7, is not compatible with a linear plot of the LT° relaxation contribution as a function of only the cis units volume fraction.

a) b)



**Figure 12: a) Amplitude of the LT° contribution in the  $\beta$  mechanical relaxation as a function of the cis/trans 1,4 butadiene volume fraction, full square symbol for PB 5/59 (the data for PB5/59 is not included in the trend curve calculation as its value is estimated with a more important error (+0.1)) ; b) Amplitude of the HT° contribution in the  $\beta$  mechanical relaxation as a function of the 1,2 butadiene volume fraction .**

In random copolymers, a low molar fraction of one monomer leads to a large number of isolated units of this monomer in the polymer chains. As reported in table 1 the average length of the vinyl, and of the cis+trans sequences in the studied copolymer measured by NMR, as well as the % of isolated vinyl units are in relatively good agreement with the theoretical values calculated for perfectly random copolymers. The LT° and HT° relaxation amplitudes have been plotted (Figure 13) as a function of the volume fraction of units in sequence of more than one units and in sequence of more than two units (using, when available, the experimental data from NMR, otherwise theoretical values for random copolymer, reported in Table 1). Clearly, for both LT° and HT° mechanical  $\beta$ -relaxation, not taking into account the fraction of isolated units immediately shifts the fitting linear curve far from the origin (again, a plot as a function of molar fractions would lead to the same conclusion, as seen in Supporting Information (cf. Figure SI18)). These results strongly suggest that both LT° and HT° mechanisms only need one butadiene unit to occur.



**Figure 13: a) Amplitude of the LT<sup>o</sup> contribution in the β-mechanical relaxation as a function of vol. fraction of cis/trans 1,4 butadiene units in sequence of more than 0 unit (●), more than 1 unit (■), more than 2 units (▲) ; b) Amplitude of the HT<sup>o</sup> contribution in the β mechanical relaxation function of vol.% fraction 1,2 butadiene units in sequence of more than 0 unit (●), more than 1 unit (■), more than 2 units (▲) .**

Some comments can finally be made concerning the dielectric data. Our analysis of the mechanical relaxation of the three PB materials is consistent with the one performed by Hoffman on the dielectric response of PB with different comonomers contents. Moreover, as said in the experimental part, both dielectric and mechanical relaxations are, at the same frequency of 0,1 HZ (figure 5) , similar for all the SBR materials. In both cases, the β relaxation is the narrowest and at lower temperature for the material having the highest Cis unit content (SBR 20/29/14), whereas it is spread over a larger temperature domain for the material having a high Vinyl unit content (SBR 42/15/25). The influence of the Cis and Vinyl units content on the LT<sup>o</sup> and HT<sup>o</sup> parts of the relaxation is therefore the same in dielectric measurements, the difference with the mechanical response being that the Trans units do not have a significant dielectric response, whereas they participate to the mechanical relaxation.

This conclusion is also supported by the characterization of the relaxation times. The dielectric ones found by Hoffman have been plotted on Figure 8 with our mechanical relaxation times. Depending on the PB, they are either in between the LT<sup>o</sup> and HT<sup>o</sup> mechanical relaxation times (PB 7/41 and PB52/19) or close to the HT<sup>o</sup> mechanical relaxation times (PB 86/6). The activation energy is found equal to 56 kJ.mol<sup>-1</sup> for PB 86/6, that is comparable with the



68kJ/mol found for PB 81/11 by mechanical spectroscopy. 75 kJ/mol is found for the PB 52/19 ; this is much higher than what we found for PB 48/16 but is explained by the few data of Hoffman which in addition, hardly follow an Arrhenius law. The activation energy of the PB 7/41 was found equal to 33 kJ.mol<sup>-1</sup> , which is not so far from the 49 kJ/mol found for the PB 5/59. Note that conversely to our mechanical data, the dielectric ones of Hoffman do not enable to evidence a clear difference of activation energy of the LT° and HT° part of the relaxation (a slight difference can however be observed in figure 7 of Hoffman's article, between its PB07 and PB95 materials). This might be partly explained by the fact that in dielectric measurements, the data used to extract the relaxation times (from the frequency at which the  $\beta$  peak maximum is observed) are in a temperature/frequency domain where the the LT° and HT° relaxation times are closer (cf. Figure 8). Despite this remark, the comparison of the dielectric and mechanical relaxation times of the PB suggests a same molecular origin for both relaxations. The dielectric and mechanical relaxation time of the SBR can be compared on figure 9. Having deduced the dielectric relaxation times from the isothermal curves, without any deconvolution, it is expected for their value to be significant of the relaxation process with the largest amplitude (as the signatures of both processes overlap). As said previously, the Trans unit does not participate to the dielectric response. Therefore, the dielectric response depends on the CIS and Vynil units. Two of the SBRs (SBR 20/29/14 and SBR 19/22,5,20) tested contains slightly more CIS units than vinyl ones, and present an activation energy very close to the one of the LT° process of the mechanical relaxation. This is consistent with Hoffman's finding that the dielectric response of the Cis unit is much more intense than the one related to the Vinyl ones [7]; the main contribution in the dielectric peak, which therefore mainly influences the peak maximum position is indeed that of the Cis unit relaxation. The deduced activation energy for the dielectric relaxation of the SBR 42/15/25 is close to the one of the other SBR, in spite of the fact that the vynil unit content is 3 times the one of the Cis unit, also confirming (like the figure 5b) the main role of the Cis units in the dielectric  $\beta$ -relaxation.

## 4 Conclusion

The influence of the chemical microstructure on the secondary mechanical relaxations of PB and SBR has been studied by varying the content of vinyl, cis, trans butadiene and styrene

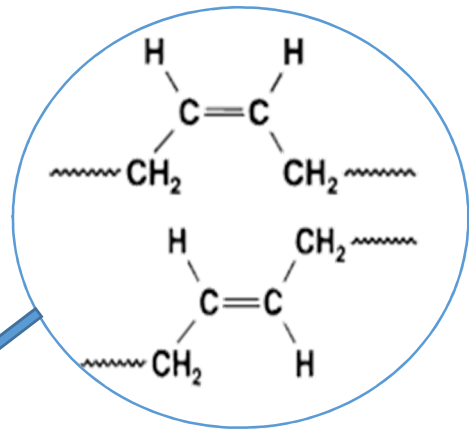
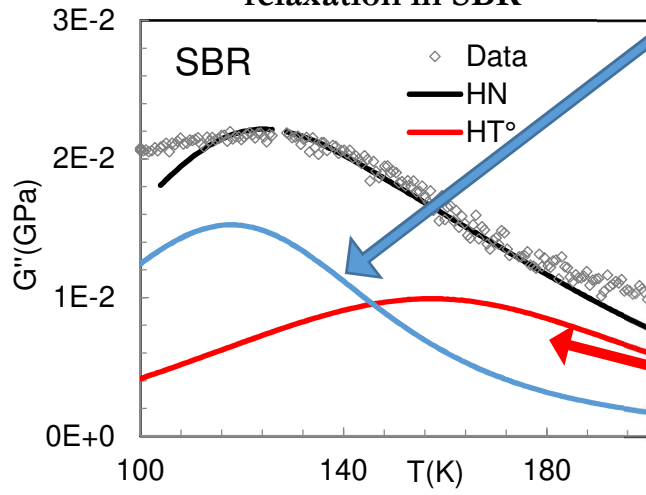
groups. First, the addition of styrene decreases its amplitude without modifying the other characteristics. The plot of the master curves and of the evolution of the  $\beta$ -relaxation times of the different materials from dielectric and mechanical spectroscopies confirms the existence of two relaxational mechanisms with two distinct activation energies. Based on this result, the experimental isochronal and isothermal curves obtained by mechanical spectroscopy were fitted thanks to the summation of two Havriliak Negami functions. This enables to prove that the vinyl groups are responsible for the contribution of the HT° part of the  $\beta$ -relaxation, whereas the butadiene 1,4 groups, *cis* and *trans* are at the origin of the low temperature part of this relaxation. Contribution of the *trans* unit in the SBR dielectric  $\beta$  relaxation does not exist, whereas it is significant in the LT° part of the  $\beta$  mechanical relaxation. Like in the dielectric response, the intensity of  $\beta$  mechanical relaxation of the *Cis* units is more intense than the one of the vinyl units. Moreover, the intensity of the  $\beta$  mechanical relaxation associated to each monomer appears to be proportional to their volume (and molar) fraction. Given the random characteristics of the studied copolymer, this suggests that the involved mechanisms are localized at the level of only one monomer unit. Finally, this shows that it is relatively easy, by playing with the content of the butadiene 1,2 and butadiene 1,4 monomers, to pilot the width and intensity of the  $\beta$  mechanical relaxation of the styrene-butadiene copolymers and rubbers.

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### Origin of the $\beta$ mechanical relaxation in SBR



Scale of the movement : one monomer unit

