Dynamics of macromolecular chains—ultrasonic study of polystyrene in solution

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Ultrasonic relaxation measurements on 2,4,6,8-tetraphenylnonane and a series of narrow molecular weight samples of polystyrene dissolved in ethyl benzene are reported as a function of temperature and frequency. These data are compared with previous ultrasonic studies on the configurational isomers of 2,4-diphenylpentane and 2,4,6-triphenylheptane which have shown that the relaxation frequency of the isotactic triads or *meso* diads is always much lower than that determined for the syndiotactic triads or racemic diads. The ultrasonic spectra are thus resolved to give two relaxation processes. The origin of the highest frequency relaxation, which needs up to ten monomer units, is thought to be an intramolecular process of the syndiotactic sequences. In this model, several segments of the polymer chain independently undergo the conformational change:

$$\underline{\mathrm{gg}}\ tt\ gg\ tt\ \underline{\mathrm{gg}} \rightleftarrows \underline{\mathrm{tt}}\ tt\ gg\ tt\ \underline{\mathrm{tt}}$$

The absorption of energy in the low frequency range may be associated with a crankshaft motion.

INTRODUCTION

The study of macromolecular dynamics of ultrasonic relaxation has already been the subject of several investigations[1,2]. All the results on polystyrene solutions have shown a decrease in the ultrasonic absorption in the frequency range 1–150 MHz[3–7]. In an attempt to analyse more precisely the motions responsible for the relaxations observed, the ultrasonic attenuation of polystyrene has been investigated as a function of polymer concentration[8–10], molecular weight[9,11–13], thermodynamic solvent power[9,14–19], solvent viscosity[7] and temperature[3,12–17]. These measurements have clearly demonstrated the local character of the motions involved in the relaxation processes and conformational changes arising from rotational isomerism were thus postulated. However it was difficult to identify them for the following reasons: first, although acoustic relaxation is a powerful tool for studying rapid equilibration, the data yield no information on the nature of the species involved in the equilibrium; since vinyl polymers are subject to many different conformational changes by rotation around chain bonds, the choice of which one occurs in a given frequency range is uncertain. Moreover, the present accuracy of ultrasonic absorption measurements does not permit one even to determine whether two[5,6,13,19] or more[12] relaxation processes exist in the frequency range 1–150 MHz. Consequently, spectral decomposition is difficult and the values of the energies obtained from the temperature dependence of the ultrasonic spectra are, of course, highly dependent upon the choice of the model.

For these reasons, it appeared interesting to study the model molecules of polystyrene such as 2,4-diphenylpentane (DPP), 2,4,6-triphenylheptane (TPH) and 2,4,6,8-tetraphenylnonane (TPN). Indeed, these short chain molecules undergo only a small number of conformational changes and they can be separated into their configurational isomers, so that well-defined compounds may be studied.

For both meso and racemic isomers of DPP we have shown that a single relaxation process occurs in the frequency range of interest[20]. These equilibria have been assigned to rotational isomerism between the *gauche-trans* *g-t* (or *tg*+) state and the all *trans tt* conformation for the meso isomer and between *tt* and $g^- g^-$ conformations for the racemic isomer. The single relaxation observed for isotactic and syndiotactic isomers of TPH has been assigned to isomerism between the helix *tg* + *tg* + (or $g^-\ tg^-\ t$) and the transition form $g^-\ ttg$ + for the isotactic isomer and between *tttt* and *ttg* + *g* + (or $g^- g^-\ tt$) conformations for the syndiotactic isomer[21]. Two relaxation processes were needed for the heterotactic isomer, each involving one part of the molecule; the rotational isomerism of the meso diad is between $g^-\ ttt$ (or *tg* + *tttt* conformations while the racemic diad involves a relaxation between $g^-\ ttt$ and $g^-\ tg + g +$ conformations.

In the first part of this paper, the ultrasonic attenuation of TPN and three narrow fractions of polystyrene ($\bar{M}_w$ = 600, 2100, 2 x 10^5) is investigated as a function of temperature and frequency. The thermodynamic parameters related to the observed relaxation processes are also calculated. The second part is devoted to the ultrasonic spectra interpretation.

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EXPERIMENTAL

2,4,6,8-Tetraphenylnonane (TPN) was prepared by the method of Jasse[22]. TPN exhibits six different isomers, the amounts of which, as determined by gas chromatography, are 4% for the isotactic isomer, 15% for the syndiotactic isomer and 81% for the four heterotactic ones.

The polystyrene samples were supplied by Pressure Chemical Co. The molecular weights and polydispersity indices of polymers are as follows:

	PS_1	PS_2	PS_3
$\bar{M}_w$	600	2100	200 000
$\bar{M}_w/\bar{M}_n$	1.06	1.10	1.06

The solvent used was ethyl benzene, except for sample PS_2 previously studied in toluene[23]. Nevertheless, the results can be compared since such solvents lead to similar ultrasonic absorption[23]. The concentrations were lower than 10^{-1} g/ml for TNP and PS_1, and equal to 5×10^{-2} g/ml for the higher molecular weight samples. Results are given for the standard concentration of 5×10^{-2} g/ml.

The ultrasonic absorption coefficient was measured by a pulse apparatus over the frequency range 3–200 MHz. The reverberation method[24] allowed some measurements between 0.6 and 1.2 MHz for sample PS_3. The temperature range was chosen to be as wide as possible and covered the range for which results have been previously obtained for DPP[20] and TPH[21]. For sample PS_3, the absorption has been measured from $-50°$ to $+60°$C.

RESULTS

The analysis of the data with a single relaxation process failed in most cases. The disagreement is all the more large as the molecular weight becomes high and the temperature is low. Since the single relaxation hypothesis is ruled out, the data were first analysed for a distribution of relaxation times, using the real part of the Cole–Cole distribution function, as proposed by Pethrick *et al.*[12].

$$\frac{\alpha}{f^2} = \frac{A\left[1 + \left(\frac{f}{f_c}\right)^{\beta}\cos\frac{\pi\beta}{2}\right]}{\left[1 + 2\left(\frac{f}{f_c}\right)^{\beta}\cos\frac{\pi\beta}{2} + \left(\frac{f}{f_c}\right)^{2\beta}\right]} + B$$

β is the distribution parameter, which equals unity for a single relaxation, f_c is the mean relaxation frequency, A is the relaxation amplitude and B represents the contributions to α/f^2 which are not related to the relaxation. The fit thus obtained is consistent with the accuracy of measurements, but the lowering of f_c with the temperature does not follow a regular pattern. An Arrhenius plot of $\log f_c$ *versus* $1/T$ is not linear, which means that the activation energies are not the same for each relaxation time.

We thus preferred an alternative analysis with two relaxation processes such as:

$$\frac{\alpha}{f^2} = \frac{A_1}{1 + \left(\frac{f}{f_{c_1}}\right)^2} + \frac{A_2}{1 + \left(\frac{f}{f_{c_2}}\right)^2} + B$$

This analysis is, in fact, suggested by the TPH spectra, where the characteristic frequencies of the meso diads are well separated from those of the racemic diads[21]. Since the number of parameters is increased as compared with the Cole–Cole function, such an analysis is allowed for each sample and temperature. The ultrasonic absorption at each frequency and temperature is a function of the thermodynamic and kinetic parameters of the two relaxations since, for a two-state model:

$$\mu_{\max} = n\frac{RT}{10^3 J}\left(\frac{\theta_v}{C_p}\right)^2\left(\frac{\Delta H}{RT}\right)^2\frac{\exp\left(-\frac{\Delta G}{RT}\right)}{\left[1 + \exp\left(-\frac{\Delta G}{RT}\right)\right]^2}$$

$$f_c = \frac{kT}{2\pi h}\exp\left(-\frac{\Delta H^*_{21}}{RT}\right)\exp\left(\frac{\Delta S^*_{21}}{R}\right)\left[1 + \exp\left(-\frac{\Delta G}{RT}\right)\right]$$

where ΔH^*_{21} and ΔS^*_{21} are the activation enthalpy and entropy differences between state 2 of higher energy to state 1, ΔH and ΔS the enthalpy and entropy differences between states 2 and 1; v, θ and C_p are the ultrasonic velocity, the expansivity and the specific heat of the solution. The low concentration used allowed us to take solvent values for v, θ and C_p. n is the concentration of relaxing systems and is unknown. It may be expressed as the number of monomer units required for one relaxing system (*Table 1*); this figure must not be confused with the number of monomer units involved in the relaxation process, a number which may be smaller than n. The volume change associated with the rotational isomeric process has been neglected in the $\mu_{\max}$ expression. In order to avoid intermediate calculations n, ΔH, ΔS, ΔH^*_{21}, ΔS^*_{21} and $B(T)$ were directly evaluated from the values of α/f^2, using a non-linear least-squares procedure[25]. In order to reduce the number of variables, B was given a quadratic dependence on temperature. As shown in *Figures 1, 2* and *3*, such an analysis is successful in the case of the shorter chain samples: TPN, PS_1 and PS_2 and results are given in *Tables 1* and *2*.

On the other hand, with the 200 000 molecular weight sample, the discrepancy between the measured absorption and the fitted curves exceeds the error bars. Several explanations can be sought in order to improve the model.

First, normal mode relaxation of the polymer chain may be taken into account. Such processes may be introduced into the equations describing classical acoustic absorption in the following manner:

$$\frac{\alpha}{f^2} = \frac{2\pi^2}{\rho V^3}\left(\frac{4}{3}\eta_s + \eta_v\right)$$

where ρ is the density, V is the propagation velocity of the longitudinal acoustic wave, η_s and η_v are, respectively, the shear and volume viscosities. The relaxational behaviour of the shear and volume viscosities are supposed to be very similar and the ratio η_v/η_s is usually assumed to be constant[12]. The frequency dependence of the viscoelastic contribution may be obtained from the classical expressions of Rouse or Zimm. However, such an analysis does not lead to a better agreement since the acoustic attenuation arising from these contributions is hardly larger than the error bars.

Secondly, the temperature dependence of the relaxation frequency may be changed, using an Arrhenius expression:

Table 1 Thermodynamic parameters of TPN, PS_1, PS_2 and PS_3

	TPN	PS_1	PS_2	PS_3
Low frequency:				
n_1 monomer units	10.0 ± 3.1	17.0 ± 8	14.3 ± 7.0	35.0 ± 9
ΔH (kcal mol^{-1})	1.3 ± 0.2	1.3 ± 0.3	2.2 ± 1.0	4.3 ± 0.5
ΔS (cal mol^{-1} K^{-1})	3.6 ± 1.5	5.3 ± 1.5	8.2 ± 4.3	15.6 ± 2.2
$\Delta H^{\ddagger}_{21}$ (kcal mol^{-1})	2.7 ± 2.3	1.8 ± 1.3	2.9 ± 2.8	–0.15 ± 1.0
ΔS^{*}_{21} (cal mol^{-1} K^{-1})	–11.5 ± 9.6	–17.8 ± 5.4	–14.3 ± 10.2	–26.0 ± 3.8
High frequency:				
n_2 monomer units	5.4 ± 2.7	5.3 ± 1.2	6.3 ± 3.1	8.0 ± 2.5
ΔH (kcal mol^{-1})	1.1 ± 0.4	1.4 ± 0.3	1.5 ± 0.4	2.3 ± 0.2
ΔS (cal mol^{-1} K^{-1})	5.6 ± 2.0	4.2 ± 0.7	4.6 ± 2.4	6.4 ± 1.0
$\Delta H^{\ddagger}_{21}$ (kcal mol^{-1})	1.8 ± 1.2	1.7 ± 0.7	1.0 ± 2.9	–0.1 ± 1.2
ΔS^{*}_{21} (cal mol^{-1} k^{-1})	–13.4 ± 5.2	–13.9 ± 3.2	–16.9 ± 3.7	–21.4 ± 4.3

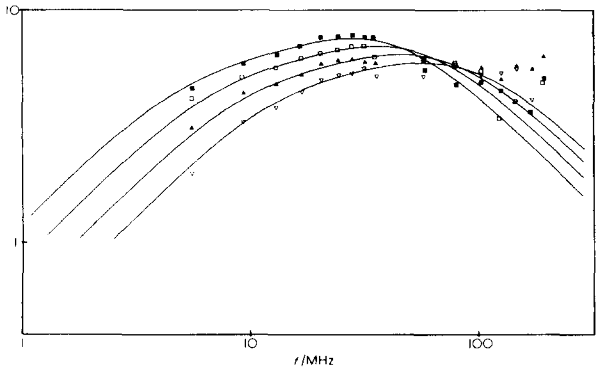

Figure 1 Ultrasonic relaxation spectra of 2,4,6,8-tetraphenylnonane in ethyl benzene. Concentration 5 x 10^{-2} g cm^{-3}. ■, –50°; □, –40°; ▲, –30°; ▽, –20°C

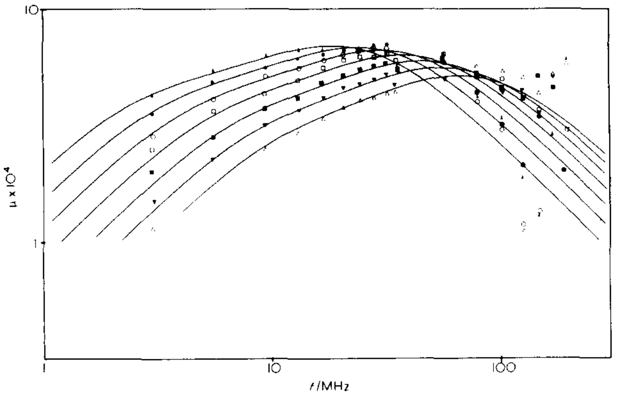

Figure 2 Ultrasonic relaxation spectra of polystyrene (M_w: 600) in ethyl benzene. Concentration 5 x 10^{-2} g cm^{-3}. ▲, –50°; ●, –40°; ○, –30°; □, –20°; ■, –10°; ▼, 0°; △, +10°C

$$f_c = C\exp\left(-\frac{\Delta H^{*}_{21}}{RT}\right)\left[1+\exp\left(-\frac{\Delta G}{RT}\right)\right]$$

Such a slight difference with the previously used relation is, however, insufficient and the accuracy of data cannot resolve these alternative descriptions.

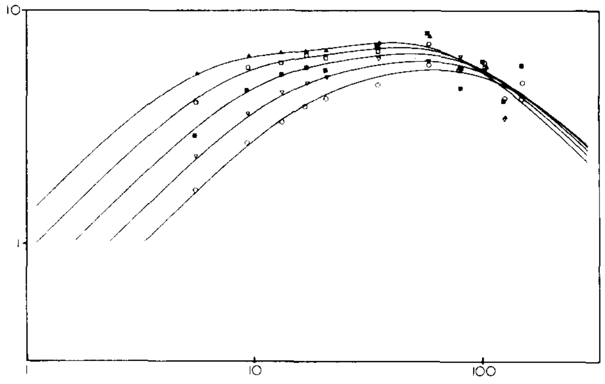

Figure 3 Ultrasonic relaxation spectra of polystyrene (M_w: 2100) in ethyl benzene. Concentration 5 x 10^{-2} g cm^{-3}. ▲, 0°; □, +10°; ■, +20°; ▽, +30°; ○, +40°C

Thus, we went back to the first analysis but without taking into account the measurements carried out at the lowest temperatures (–50° and –40°C) for which the discrepancy between the measured absorption and the fitted curve was the most important. The sum of the squares of the residuals is then strongly reduced and the values obtained are given in *Tables 1* and *2* and shown in *Figure 4*. An additional relaxation process may explain the gap between the fitted curves and the measured absorption for the lowest temperatures.

Influence of molecular weight

The μ_1 and μ_2 values are given in *Figure 5 versus* molecular weight, at 0°C. For TPN, the amplitudes have been calculated by extrapolating the data of *Table 1*. The curves have been drawn assuming that the ultrasonic absorption is insensitive to molecular weight above 5000, as shown by several studies[9,11,12]. As we already noted[13], it may be seen that the high and low relaxation behaviours are quite different.

The strong lowering of μ_1 from molecular weight 5000 to 2100 means that the low frequency relaxation involves

Table 2 Relaxation amplitudes and frequencies

T (°C)	A_1 (10^{-17} cm^{-1} s^2)	f_1 (MHz)	μ_1 (10^{-4})	A_2 (10^{-17} cm^{-1} s^2)	f_2 (MHz)	μ_2 (10^{-4})	B (10^{-17} cm^{-1} s^2)
2,4,6,8-Tetraphenylnonane							
−20	19.2	17.3	2.52	8.3	73.3	4.62	2.8
−30	26.3	12.8	2.63	11.5	57.3	5.15	3.1
−40	36.3	9.4	2.73	16.2	43.9	5.71	4.3
−50	50.7	6.7	2.78	23.1	33.1	6.30	6.5
PS_1							
+10	16.7	13.2	1.53	8.9	73.6	4.55	2.2
0	22.1	10.8	1.71	11.2	61.4	4.93	2.0
−10	29.3	8.8	1.90	14.0	50.8	5.25	2.3
−20	39.1	7.0	2.08	17.6	41.5	5.55	3.2
−30	52.5	5.5	2.26	22.1	33.5	5.78	4.5
−40	70.9	4.3	2.45	27.7	26.7	5.93	6.3
−50	96.6	3.3	2.63	34.9	20.9	6.01	8.7
PS_2							
+40	17.4	23.3	2.55	7.8	84.8	4.17	1.8
+30	25.1	18.0	2.94	9.4	75.2	4.61	2.8
+20	36.5	13.8	3.39	11.3	66.3	5.04	3.5
+10	53.1	10.3	3.80	13.6	58.1	5.49	3.9
0	77.6	7.7	4.28	16.4	50.6	5.95	4.0
PS_3							
+60	24.7	16.5	2.39	15.0	53.1	4.68	7.9
+40	52.3	11.5	3.79	19.9	45.9	5.76	7.4
+20	104	7.9	5.53	25.2	39.6	6.72	7.0
0	184	5.6	7.38	30.2	34.2	7.40	6.8
−10	226	4.7	7.84	32.2	31.8	7.56	6.7
−20	261	4.1	8.13	33.7	29.6	7.58	6.7
−30	279	3.5	7.63	34.4	27.5	7.39	6.7
−40	272	3.1	6.77	34.5	25.5	7.06	6.9
−50	243	2.8	5.61	33.5	23.9	6.60	10.4

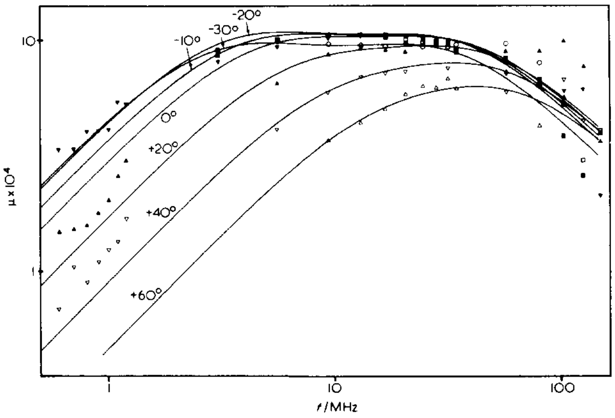

Figure 4 Ultrasonic relaxation spectra of polystyrene (M_w: 2 x 10^5) in ethyl benzene. Concentration 5 x 10^{-2} g cm^{-3}

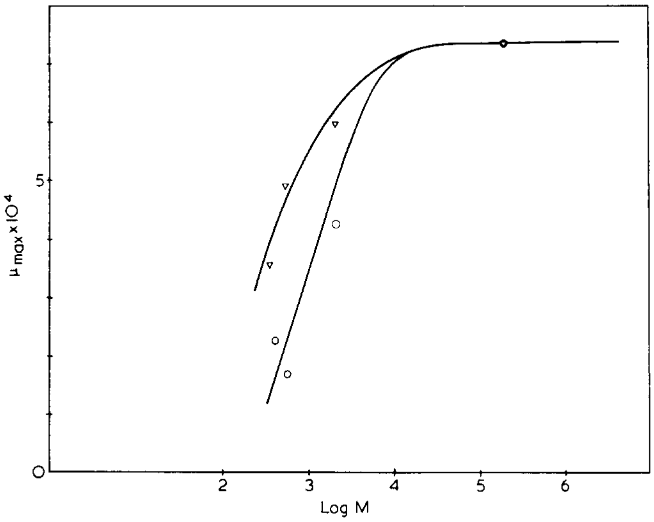

Figure 5 Dependence of μ_{max} on molecular weight at 0° C. ○, Low frequency relaxation; △, high frequency relaxation

about 20 monomer units. The amplitude of μ_2 decreases more slowly and less than 10 monomer units seem to be affected by the high frequency relaxation. The studies of DPP[20] and TPH[21] have shown that the tacticity plays a prominent part in the conformational dynamics and ultrasonic relaxation. Thereafter, each subchain made up of the required number of monomer units may not give rise to a relaxation, and the n_1 and n_2 values may be larger than 20 and 10 monomer units respectively. This actually occurs for the low frequency relaxation of sample PS_3 (n_1 = 35) while the n_2 value appearing in *Table 1* (n_2 = 8) is in good agreement with the critical value of 10 monomer units.

The enthalpy differences ΔH quoted in *Table 1* increase with molecular weight. This effect may be attributed to the larger number of conformational changes associated with the larger number of monomer units involved in the relaxation process. On the other hand, the activation energies ΔH^*_{21} seem to decrease, although the confidence interval is such that it is difficult to ascertain whether they reach negative values. This results from the small shift of the relaxation frequency with temperature which is rather unexpected. In order to take into account similar effects, Cerf[2,26] has proposed a model involving a negative activation energy in such a way that f_c goes through a minimum. More likely, the analysis with only two relaxation processes seems questionable. First, the lowest temperature behaviour suggests

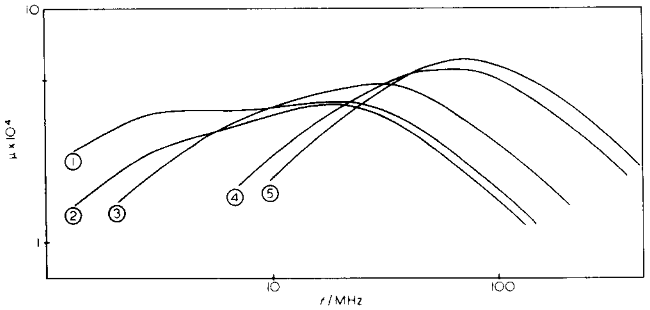

Figure 6 Ultrasonic relaxation spectra at –50°C for solutions of polystyrene [Molecular weight: 2 x 10^5 ^{1}, 600^2], 2,4,6,8-tetraphenylnonane^3, 2,4,6-triphenylheptane^4 and 2,4-diphenylpentane^5 at the same diad concentration. For 2,4-diphenylpentane and 2,4,6-triphenylheptane, data are for an equimolecular mixture of the isomers. The ultrasonic spectrum for polystyrene of molecular weight 2 x 10^5 is calculated from *Tables 1* and *2*

the occurrence of an additional process. Then, four different relaxations are already needed for the TPH isomers. It is expected that one or several extra relaxation processes would lead to higher ΔH^*_{21} values than those of *Table 1*, but the accuracy of the data makes illusive any analysis involving more than two relaxations. The results reported here must be considered as a first approximation.

INTERPRETATION OF POLYSTYRENE RELAXATION

We may try to understand the ultrasonic behaviour of polystyrene arising as a consequence of local conformational changes, by comparing the spectra of model molecules to that of the polymer.

The ultrasonic absorptions of DPP, TPH, TPN and polystyrene samples PS_1 and PS_3 are plotted at –50°C in *Figure 6*. This low temperature permits precision for the DPP and TPH spectra but, as seen above, the experimental data are troublesome for sample PS_3 so that the spectrum given in *Figure 6* for this sample has been calculated using the values of *Tables 1* and *2*. As the diad is the smallest unit with regard to the molecular dynamics, these spectra are given for the same diad concentration. For DPP and TPH, the results are for an equimolecular mixture of the isomers, meso and racemic in the first case, iso, syndio and heterotactic in the last case. Thus, the ratio of the meso and racemic diads is 50% for both compounds.

Figure 6 shows that the spectra are continuously shifted towards the lower frequencies as the molecular weight increases. This effect may be ascribed to the decrease of the characteristic frequencies. The amplitude of the high frequency side of the spectrum is only slightly affected, first decreasing from DPP to sample PS_1, then slightly increasing with the high molecular weight sample PS_3. On the other hand, the low frequency amplitude strongly and continuously increases with number of monomer units in the chain. This becomes clear in *Figure 7*, where the same spectra have been translated along the axis in order to superpose the high frequency limits.

The molecular interpretation of the relaxation processes must be consistent with these results. Moreover the selected conformational changes must satisfy some further conditions.

(i) the ultrasonic selection rule needs an enthalpy change ΔH different from zero;

(ii) then, in order to give rise to significant relaxation amplitudes the conformational equilibria must involve states with non-zero probability with respect to energy and tacticity since polystyrene is atactic. As an example, we cannot consider a stereoregular sequence which is too long or a high energy conformation such as $g+g^-$ which leads to steric overlap. In fact, the ultrasonic relaxations of DPP[20] and TPH[21] have been assigned to the most likely states, as displayed by calculations and n.m.r. experiments. These conformations are g^-t, $tg+$ and tt for a meso diad, tt and gg for a racemate:

(iii) for a macromolecular chain the rotation of only one conformational angle implies that one part of the chain sweeps across the solvent. Such motion cannot occur on the time scale considered here and, moreover, is very sensitive to the solvent viscosity contrary to earlier experiments[7]. The conformational change needs the cooperative rotation of two angles or more in order to leave unchanged the parts of the chain which are not involved in the motion.

High frequency relaxation

The ultrasonic study of DPP and TPH has shown that the racemic diads are relaxing at frequencies about three times larger than the meso diads. In the case of polymer, the higher relaxation frequency has a value close to that of the meso DPP at –50°C; but as it is hardly to be expected that the meso diads are not slowed down when inserted in the chain, the purely syndiotactic sequences only can give rise to the high frequency part of the polymer spectrum. At this time scale, the meso diads may be viewed as frozen.

The preferred conformations of syndiotactic diads are *tt* and *gg*, and the steric interactions prevent the occurrence of two adjacent *gg* states. In the diamond lattice, such a chain is made up of planar zig-zag, the vertical planes of which are at 90° with each other (*Figure 8*). The right angles arise from the *gg* diads. Projected on an horizontal plane, the chain appears in a square lattice. It may be seen that two different motions are allowed with such a geometry. The motion $\underline{gg}\ tt\ gg\ tt\ \underline{tt} \rightleftarrows \underline{tt}\ tt\ gg\ tt\ \underline{gg}$ moves the two *gg* defects along the chain. Such a motion however, is inefficient with respect to the ultrasonic absorption since it does not change the chain energy.

The other motion $\underline{gg}\ tt\ gg\ tt\ \underline{gg} \rightleftarrows \underline{tt}\ tt\ gg\ tt\ \underline{tt}$ changes the position of four monomer units. Two conformations *gg* disappear and it may give rise to an ultrasonic relaxation process. The enthalpy difference ΔH is expected to be twice the racemic DPP value, that is to say 3 kcal mol^{-1} in agreement with the 2.3 kcal mol^{-1} given in *Table 1*. The number of monomer units involved, i.e. 5, is also consistent with the value obtained by considering the molecular weight effect. Moreover, the atactic polystyrene is actually rather syndiotactic so that such stereoregular sequences are not unlikely.

The activation energy for this motion is difficult to esti-

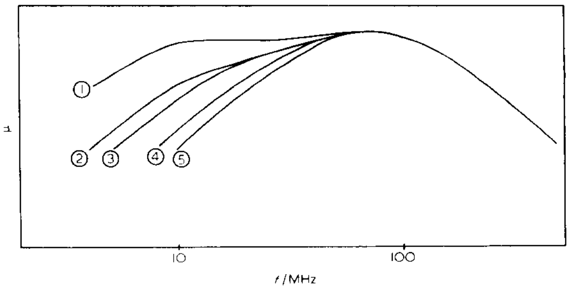

Figure 7 Ultrasonic relaxation spectra shifted in order to make the high frequency limits superposed. Key as in *Figure 6*

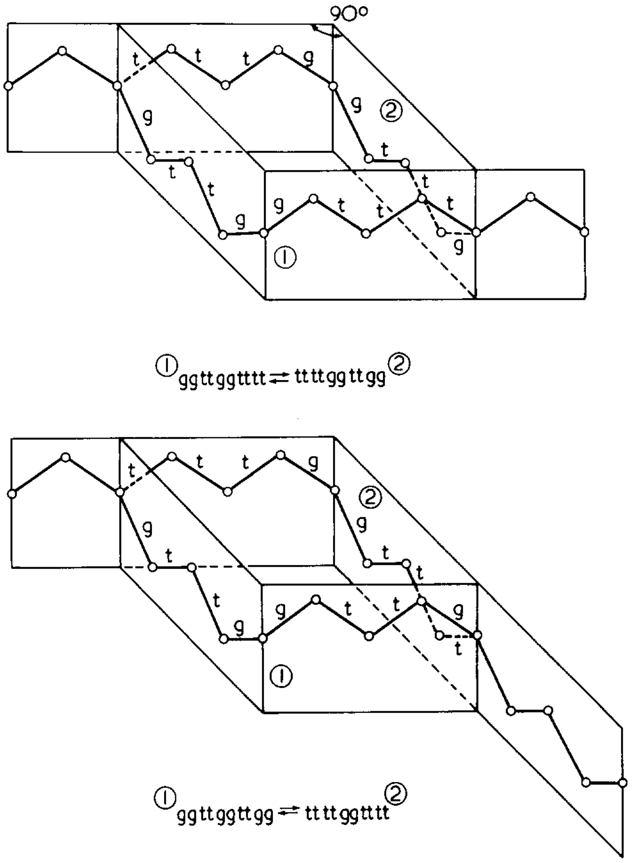

Figure 8 Two possible motions in a syndiotactic polystyrene chain

mate. It may be seen that the rotation of only four angles cannot ensure the crossover from one position to the other. But, the involved range of five monomer units has ten conformational angles and ten valence angles along the main chain and small deviations from their values may lower the activation energy.

Low frequency relaxation

In this case, the problem is much more complicated. First, the relaxation time is long enough so that both meso and racemic diads may be involved. If, however, we restrict our investigation to purely isotactic sequences, it can be seen that a straightforward extension of the motion previously proposed for the TPH to longer chains is the following:

$$g^- t\, g^- t --- g^- t \rightleftarrows g^- t\, g^- t --- g^- t\, tg^+ \rightleftarrows$$

$$--- \rightleftarrows g^- t\, tg^+ --- tg^+ \rightleftarrows tg^+ --- tg^+$$

Such conformational changes rotate one part of the chain with respect to the other and should not occur at these frequencies in a polymer. Thus, any local motion inside an isotactic chain must involve at least a third state: the conformation *tt*.

In order to investigate such motions we made the following assumptions: the macromolecule is described in a tetrahedral lattice; the chain is isotactic and three diads are allowed tg^+, $g^- t$ and tt, with the exclusion of the sequence $tg^+ - g^- t$ because the steric interaction is too strong.

We looked for all the subchains made of *N* monomer units such that their ends are fixed. This investigation has been carried out on a computer for *N* up to 7 (*Table 3*). Motions which can be considered as a combination of smaller motions have been excluded. Most of the possible conformational changes thus selected involve many angular rotations and are thus rather unlikely. However, the first one is the well-known crankshaft involving four monomer units. It shifts a *tt* defect along the chain with only two rotations. Moreover, these rotations are made around two colinear bonds and thus, the activation energy is at most twice the activation energy of the free diad. Such motion appears to be easiest in an isotactic chain.

Table 3 Possible conformational changes involving *N* monomer units in an isotactic chain

N	Conformational equilibria		
4	*tg+ tg+ tg+ tt*	⇄	*tt tg+ tg+ tg+* Crankshaft
5	*tg+ tt tg+ tg+ tt*	⇄	*tt tg+ tt tg+ tg+*
	tg+ tg+ tg+ tg+ tg+	⇄	*tt tg+ tt tg+ tt*
6	*tg+ tt tt tg+ tg+ tt*	⇄	*tt tg+ tt tt tg+ tg+*
	tg+ tt tg+ tt tg+ tt	⇄	*tt tg+ tt tg+ tt tg+*
	tg+ tt tg+ tg+ tg+ tg+	⇄	*tt tg+ tt tt tg+ tt*
	g − t tt g − t tg+ tt tg+	⇄	*tt g − t g − t tg+ tg+ tt*
7	*tg+ tt tt tt tg+ tg+ tt*	⇄	*tt tg+ tt tt tt tg+ tg+*
	tg+ tt tt tg+ tt tg+ tt	⇄	*tt tg+ tt tt tg+ tt tg+*
	tg+ tt tt tg+ tg+ tg+ tg+	⇄	*tt tg+ tt tt tt tg+ tt*
	tg+ tt tt tt g − t tg+ tt	⇄	*tt tg+ tt g − t tt tg+*
	tg+ tt tt g − t g − t tg+ tt	⇄	*tt tg+ tt g − t g − t tt tg+*
	tg+ tg+ tg+ tt g − t g − t g − t	⇄	*tt g − t g − t g − t tg+ tg+ tg+*
	g − t tt g − t tt tg+ tt tt	⇄	*tt g − t g − t tg+ tg+ tg+ tg+*
	tg+ tt tg+ tt g − t tt g − t	⇄	*tt tg+ tg+ tt g − t g − t tt*
	g − t tt tt g − t tg+ tt tg+	⇄	*tt g − t tt g − t tg+ tg+ tt*

Concerning the enthalpy change ΔH, it may be seen at first sight that it is zero. However, if the subchain energy is considered to be the sum of its triad energy it appears that ΔH is different from 0, since the triads $tg + tt$ and $tttg+$ are not symmetrical and their energy difference is 0.4 kcal mol^{-1} as previously calculated[21]. Nomura *et al.*[18] have performed very simple conformational energy calculations on polystyrene and showed the existence of a low potential height difference ΔH of 0.4 kcal/mol and an activation energy ΔH_{21} of only 0.8 kcal/mol^{-1}. Therefore, the crankshaft motion could account for a part of the low frequency ultrasonic relaxation.

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