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Molecular motion of polycarbonate in the vicinity of –60°C as revealed by broad-line n.m.r., magic angle spinning n.m.r. and conformational analysis

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On the basis of correlation of data obtained by broad-line n.m.r. and magic angle spinning n.m.r. analysis as well as conformational analysis, conclusions have been drawn concerning the nature of molecular motion occurring in a polycarbonate chain in the vicinity of –60°C. It is postulated that this motion is connected with conformational reorientation of bisphenol in unordered chains with a random conformation.

Keywords Polycarbonate; broad-line nuclear magnetic resonance; magic angle spinning n.m.r.; conformational analysis; molecular motion

INTRODUCTION

The occurrence of molecular motion in the bisphenol A polycarbonate (PC) chain near −60°C has frequently been observed by various methods[1–14]. Investigation has shown that the motion involves phenyl and methyl groups as well as carbonate groups. It has been suggested that these group motions should be cooperative and that they involve several recurrent units in the chain[5,7,10]. The objective of this work is to analyse the possible types of motions occurring in a PC chain in the vicinity of −60°C, correlating information gathered from broad-line nuclear magnetic resonance (BL n.m.r.), magic angle spinning nuclear matnetic resonance (MAS n.m.r.) and information of a dynamic nature obtained from conformational analysis.

BL N.M.R. and MAS N.M.R. ANALYSES

Correlation times of molecular motion

A thorough study of amorphous PC analysed by means of the BL n.m.r. method was presented in our previous work[14], which comprised also the analysis of PC swollen in CCl_4. In both cases, in the vicinity of −60°C the linewidth was found to decrease, the same phenomenon affecting the second moment. The values of these drops prove that they must be caused by activation of some specific motion concerning both phenyl and methyl groups. Activation energies of this motion calculated from the narrowing of the linewidth are 8.4 and 5.4 kcal mol^{-1} for unswollen PC and for PC swollen in CCl_4, respectively. This decrease of the motion's activation energy after swelling proves that the height of the energy barrier was lowered, the barrier being due to intermolecular interactions between the segments within either one or two different chains. *Figure 1* (open circles) presents

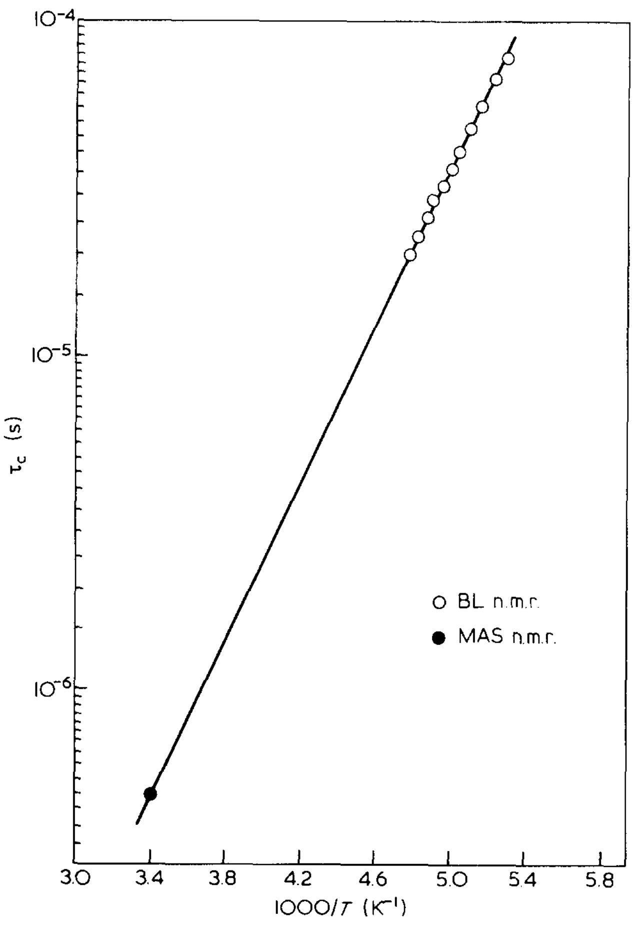

Figure 1 Variation of the correlation times near –60°C and at room temperature for polycarbonate swollen in CCl_4

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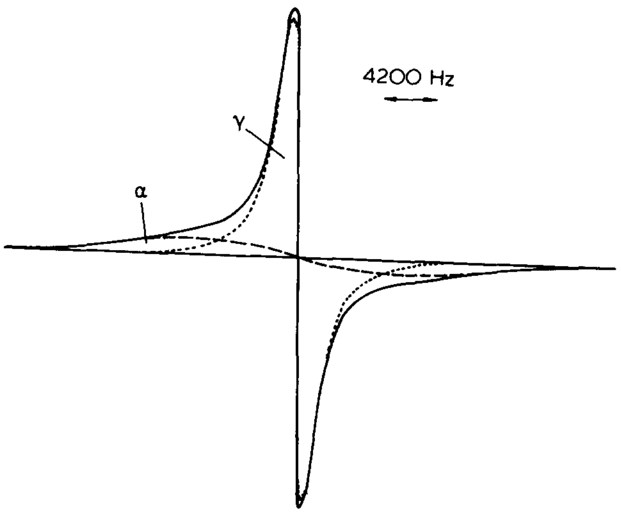


Figure 2 First derivative static sample n.m.r. absorption line of polycarbonate swollen in CCl_4

correlation times vs. temperature for PC swollen in CCl_4, calculated from linewidths on the basis of BPP theory[15]. The apparatus as well as sample preparation were described earlier[14].

To obtain additional information concerning the dynamics of PC chain motion, the MAS n.m.r. technique was used. For proton resonance this type of experiment may be performed exclusively in substances in which the resonance line is already partially narrowed because of limited molecular motions[16]. Such a situation is true in the case of PC swollen in CCl_4.

The static resonance line of the swollen PC recorded at room temperature is shown in *Figure 2*. It consists basically of two component lines, a narrow γ line with a width of ~1700 Hz, and a broad α line ~17 kHz wide. The occurrence of the narrow component line is due to the presence of chains with a random conformation in the system; these chains show a considerable freedom of motion. The broad component line α represents the areas of considerable chain ordering and relatively small mobility formed after swelling. The considerable increase in structural ordering in the PC after swelling in CCl_4 observed in the X-ray spectra[17] creates significant changes in the value of local field, which in turn gives large differences in the line broadening parameters. Because of its considerable width, the line α cannot be narrowed as a result of macroscopic rotation; therefore our attention is concentrated upon the narrow component line γ.

The n.m.r. linewidth of a static sample and a sample undergoing macroscopic rotation

In polymers at temperatures above the glass transition point T_g, the changes of local field are caused by two factors, namely by:

(1) relatively rapid conformational motion around single bonds that may be characterized by mean correlation time τ_a, and

(2) rotational and translational motions of larger fragments of molecules; these motions are much slower and may be characterized conventionally by mean correlation time τ_b.

The mean width of line $\delta\omega_s$ of the static sample may then be presented as[15,18]:

$$(\delta\omega_s)^2 = \omega_a^2 \int_{-\delta\omega_s}^{+\delta\omega_s} J_a(\omega)\mathrm{d}\omega + \omega_b^2 \int_{-\delta\omega_s}^{+\delta\omega_s} J_b(\omega)\mathrm{d}\omega \qquad (1)$$

where ω_a^2 and ω_b^2 are the intra- and intermolecular contributions to the second moment of the rigid lattice, respectively, and $J_a(\omega)$ and $J_b(\omega)$ are functions of spectral density representing two motions. Using the BPP relaxation model[18] for $J(\omega)$ and assuming that the motion around individual bonds is rapid enough to satisfy the inequality $\tau_a\delta\omega_s \ll 1$, the expression (1) takes the following form:

$$\delta\omega_s = \frac{2}{\pi}\omega_a^2\tau_a + \frac{2}{\pi}\frac{\omega_b^2}{\delta\omega_s}\text{arc tan}(\tau_b\delta\omega_s) \qquad (2)$$

In such a situation internal interactions in the chain are strongly reduced by the motion described by correlation time τ_a. Thus, weak interactions between segments may determine the width of the static line.

On the other hand, the mean width of line $\delta\omega_r$ of sample rotating with frequency ω_r under the magic angle 54°44′ may be expressed, according to the above discussion and Andrew and Jasiński's calculation[19], as follows:

$$(\delta\omega_r)^2 = \omega_a^2\left(\frac{2}{3}\int_{\omega_r-\delta\omega_r}^{\omega_r+\delta\omega_r} J_a(\omega)\mathrm{d}\omega + \frac{1}{3}\int_{2\omega_r-\delta\omega_r}^{2\omega_r+\delta\omega_r} J_a(\omega)\mathrm{d}\omega\right)$$
$$+\,\omega_b^2\left(\frac{2}{3}\int_{\omega_r-\delta\omega_r}^{\omega_r+\delta\omega_r} J_b(\omega)\mathrm{d}\omega + \frac{1}{3}\int_{2\omega_r-\delta\omega_r}^{2\omega_r+\delta\omega_r} J_b(\omega)\mathrm{d}\omega\right) \qquad (3)$$

Assuming $\tau_a\omega_r \ll 1$ and applying the procedure applied earlier, we obtain[20]:

$$(\delta\omega_r)^2 = \frac{2}{\pi}\omega_a^2\tau_a\delta\omega_r + \frac{\omega_b^2}{\pi}\left(\tfrac{2}{3}\text{arc tan}\frac{2\tau_b\delta\omega_r}{1+(\omega_r^2+\delta\omega_r^2)\tau_b^2}\right.$$
$$\left.+\,\tfrac{1}{3}\text{arc tan}\frac{2\tau_b\delta\omega_r}{1+(4\omega_r^2-\delta\omega_r^2)\tau_b^2}\right) \qquad (4)$$

In particular, if $\omega_r\tau_b > 1$, the linewidth as a function of ω_r tends to a limiting value

$$\delta\omega_r^{rez} \simeq \frac{2}{\pi}\omega_a^2\tau_a \qquad (5)$$

The limiting value of the linewidth is observed in our experiment for the γ component of the line. We can estimate the time τ_a of the rapid motion around single bonds in the chain from expression (5). On the other hand, the linewidth given in expression (4) is found to narrow when $\omega_r \sim 1/\tau_b$, which allows us to determine the time τ_b of the slow motion.

We can assume that the inequality $\tau_a\delta\omega_s \ll 1$ is satisfied, as far as component γ of the line representing chains of great freedom of motion is concerned. This component's width for the static sample may then be described by equation (2). Narrowing of this line component is observed at relatively low frequencies of macroscopic rotation under the magic angle. The apparatus used in the study was described earlier[21].

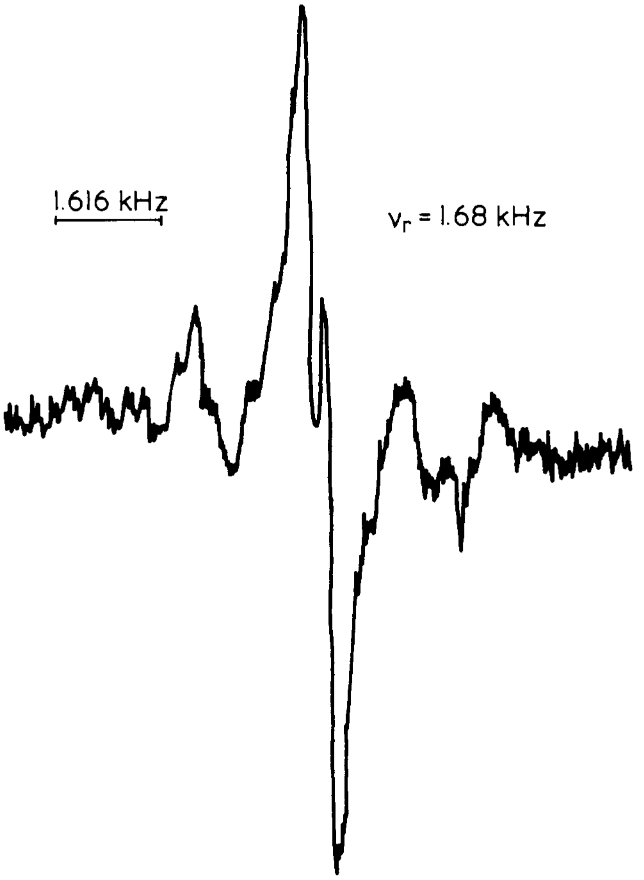


Figure 3 First derivative of the n.m.r. absorption line of polycarbonate swollen in CCl_4, rotated about the magic angle at 1680 Hz

As an example a line is shown in *Figure 3*, which was recorded at macroscopic rotation frequency $v_r = 1.68$ kHz. A significant narrowing of component γ of the line in comparison to the static spectrum presented in *Figure 2* can be seen.

Starting from expressions (2), (4) and (5), and taking the experimental dependence $\delta\omega_r = f(\omega_r)$ into account, the inequality $\tau_a\omega_r \ll 1$ being satisfied, correlation times τ_a and τ_b may be estimated. *Table 1* presents the results obtained. The value of time τ_a is marked with a full circle in *Figure 1*.

CONFORMATIONAL ANALYSIS

Conformational analysis has its static and dynamic aspects. In the former case, it leads to the determination of the probability of the occurrence of various conformations around subsequent bonds. In the latter case, it enables us to evaluate the energy barrier for rotations around individual bonds. Conformational energy calculations of independent recurrent PC chain units were carried out earlier by Tonelli[22], with the use of the Lennard-Jones 6–12 potential. The accepted model of virtual bonds showed that free rotation occurs around these bonds. To obtain more detailed information concerning the dynamic behaviour of various PC chain fragments in the vicinity of −60°C, calculations of conformational energy were performed again.

At present many expressions are used to calculate conformational energy[23], the differences between them consisting in the choice of parameters and potentials. Most frequently conformational energy E^{conf} is calculated as the sum of torsional energy (6a), energy of interactions between unbonded groups (6b), electrostatic energy (6c) and hydrogen bonds energy (6d):

$$E^{\mathrm{conf}} = \sum_i \tfrac{1}{2} E_0 (1 - \cos N_i \theta_i) \tag{6a}$$

$$+ \sum_{ij} [A_{ij} \exp(-B_{ij} r_{ij}) - C_{ij} r_{ij}^{-6}] \tag{6b}$$

$$+ \sum_{ij} \frac{1}{\varepsilon} \left(\frac{\mu_i \cdot \mu_j}{t_{ij}^3} - 3 \frac{(\mu_i \mathrm{r}_{ij})(\mu_j \mathrm{r}_{ij}}{r_{ij}^5} \right) \tag{6c}$$

$$+ E_{\mathrm{H\text{-}H}} \tag{6d}$$

Expression (6a) takes into account the shape of atomic orbitals of bonded atoms, placed on the rotation axis. E_0 is the value of the inherent torsional barrier to rotation between bonded atoms. This barrier is the total effect of attractive and repulsive energy. Symbols N_i and θ_i designate rotation symmetry and rotation angle, respectively. Expression (6a) does not influence the static flexibility (static conformational probability) of a given chain element, as its contribution to the total energy in each conformation is equal. However, it influences the height of the potential barrier at the conformational change, i.e. it has an effect upon the dynamic flexibility of the chain element studied.

The second expression (6b) describes the energy of van der Waals interactions between unbonded atoms or groups. This energy is represented by one of the classic Buckingham (6b) or Lennard-Jones potentials. In the latter case the repulsive part takes the shape of $A_{ij} r_{ij}^{-12}$. Expression (6b) influences both static and dynamic flexibility of the chain unit analysed.

Expression (6c), denoting dipole interaction energy, is fundamental in the case of the occurrence of closely situated polar groups whereas the term (6d) must be taken into account when the conformation is stabilized by hydrogen bonds.

Chosen fragments of PC chain, taking into account the first two terms of conformational energy exclusively, were subjected to the type of calculations presented above. The terms (6c) and (6d) that were left do not play any significant role in the case analysed because of the lack of hydrogen bonds and closely situated polar groups. At the first stage bisphenol A (4,4′-dihydroxydiphenylpropane-2,2) was analysed. Its conformation may be defined by the two angles θ and Θ (*Figure 4*). Angle θ characterizes

Table 1 N.m.r. characteristic of the γ line component of PC swollen in CCl_4

ω_0^2 (kHz²)	ω_a^2 (kHz²)	ω_b^2 (kHz²)	$\delta\omega^{st}/2\pi$ (Hz)	$\delta\omega^{rez}/2\pi$ (Hz)	τ_a (s)	τ_b (s)
262	259.6	2.38	1700	500	4.8×10^{-7}	4×10^{-4}

ω_0^2 = the second moment of the rigid lattice
ω_b^2 = the second moment of the static line
$\delta\omega^{st}/2\pi$ = the static width of the line
$\delta\omega^{rez}/2\pi$ = the limiting width of the line

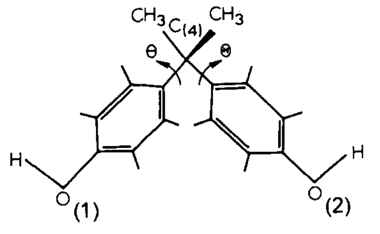


Figure 4 Schematic representation of bisphenol A and its conformation defined by the two angles θ and Θ

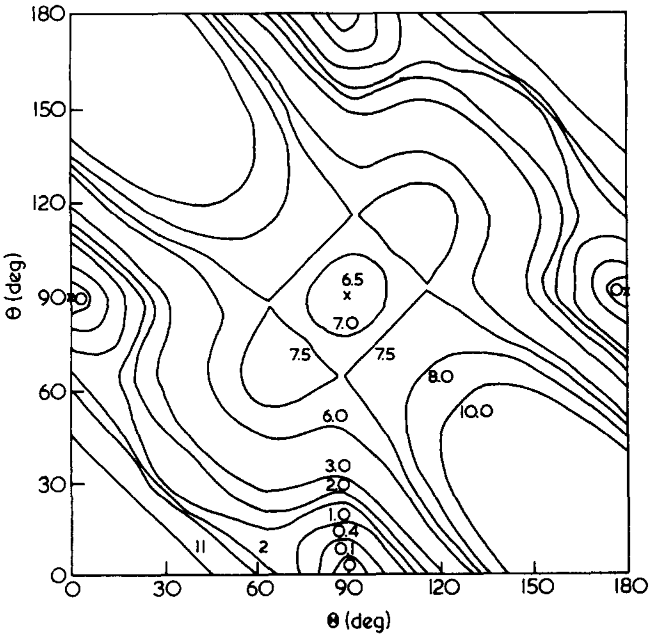


Figure 5 Conformational energy contours (in kcal mol^{-1}) for bisphenol A drawn relative to the minimum energy conformations

rotation round axis $O_{(1)}C_{(4)}$, i.e. oxygen $O_{(2)}$ positioning on the valency sphere of axis $O_{(1)}C_{(4)}$; angle Θ defines rotation of the right ring around axis $C_{(4)}O_{(2)}$. In the initial position accepted for calculations ($\theta = \Theta = 0°$) the rings and OH gro8ups are coplanar.

The value of Buckingham potential coefficients for individual atoms and groups, the value of E_0, as well as values of angles in the chain and lengths of bonds were taken from previous works[24-27]. The effect of calculations is shown in *Figure 5*.

At the second stage the carbonate group conformation (*Figure 6*) was analysed, considering rotation around axis $C'O_{(2)}$, i.e. the change of a *trans–trans* conformation into a *trans–cis* one (or *cis–trans*, when rotating around axis $C'O_{(1)}$). In the *trans* and *cis* positions the carbonyl and phenyl groups are mutually perpendicular. It is assumed that γ_1 = constant during the conformational change. The *cis–cis* conformation is excluded. The potential barrier appearing at the *trans–cis* change is about 9 kcal mol^{-1}. As the value of E_0 is difficult to estimate for the C'O bond[23,24], the error in estimating the height of that barrier may be considerable.

It is also evident from our calculations that E^{conf}_{cis} in position *cis* is higher by 1.82 kcal mol^{-1} than E^{conf}_{trans} in position *trans*. Statistical weights calculated in relation to *trans* conformation for C'O bond in *cis* conformation are presented in *Table 2*.

At the third stage the analysis of rotation around axis $O_{(2)}C_{(ar)}$ was performed. It proves that there occurs an unusually high potential barrier, which precludes uncorrelated rotational motion of carbonate groups and its neighbouring rings. Conformational calculations of a hypothetical chain fragment shown in *Figure 7* confirm this conclusion.

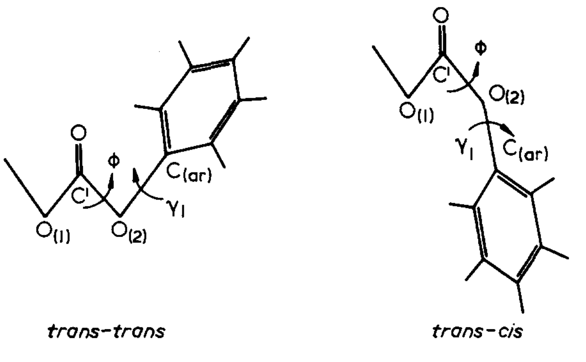
Figure 8 presents the effect of these calculations. The values of conformation energies presented were calculated on the assumption that in the analysed chain fragment all bonds have conformations of the *trans* type. Angles ψ_1 and ψ_2 characterize ring oscillation around axis $C_{(4)}O$.

In *Figure 8* there is visible only one position of minimum energy for $\psi_1 = \psi_2 = 90°$, i.e. when the rings are placed in planes perpendicular to carbonate groups. The rings are not then in the mutual position of minimum energy (see *Figure 5*). To obtain the lowest possible energy E^{conf} of the analysed fragment, we can no longer assume the coplanar *trans* conformation.

CORRELATION OF RESULTS AND CONCLUSIONS

We have presented analyses by BL n.m.r. and MAS n.m.r. methods of PC swollen in CCl_4. The analyses by means of BL n.m.r. dealing with the change of the static width of the line make it possible to draw the temperature dependence of correlation times. This dependence is shown in *Figure 1*. The experiment of macroscopic rotation under the magic angle enabled us to evaluate correlation times of rapid and slow molecular motions of chains represented in the static line at room temperature by the narrow component γ.

It is evident from calculations that the correlation time of rapid molecular motions has the value of 4.8×10^{-7} s at room temperature. This value was also marked in *Figure 1*.



trans-trans *trans-cis*

Figure 6 Schematic representation of a portion of the polycarbonate chain with two conformations of the carbonate group

Table 2 Statistical weights of C'O bonds in *cis* conformation

T (°C)	u_{cis}
−60	0.013
+22	0.045
+150	0.11
+200	0.14

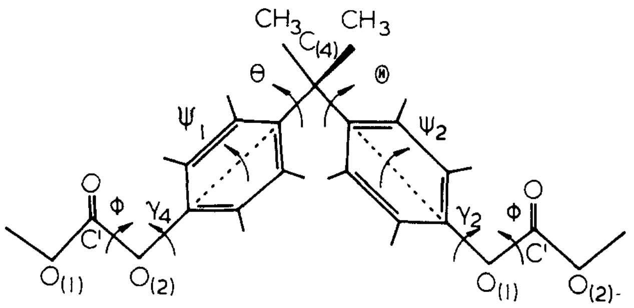


Figure 7 A portion of the polycarbonate chain in the planar zig-zag conformation. The phenylene rings are coplanar in this reference conformation

As the points obtained by means of both methods are clearly colinear, it is evident that the molecular motion characterized by the temperature dependence of the static linewidth in the vicinity of -60°C is identical with the rapid conformational motion around individual bonds determined by MAS n.m.r. measurements.

Therefore, the conclusion may be drawn that the narrowing of the static line observed in the vicinity of −60°C is due to this type of motion only in chains represented at higher temperatures by the narrow component γ of the line, i.e. in unordered chains of random conformation.

The conformational analysis that was performed provided information concerning the fragments of the chain that may undergo reorientation of this type. From calculations it is evident that in bisphenol A there occur four conformational positions of equal energy. Transitions between them are subject to a potential barrier of about 2 kcal mol^{-1} to about 6 kcal mol^{-1}, dependent on this motion's correlation with the rotation of phenyl rings. It gives a high frequency of motion at the temperatures considered. This result is in good agreement with the work of Tonelli[22]. Moreover, calculations proved that from a dynamic point of view the carbonate group should be treated as being remarkably rigid (*Table 2*). At −60°C, according to our calculations, conformational reorientation between *trans* and *cis* positions does not occur, because of static rigidity. In the case of Williams and Flory's evaluation[27], the number of carbonate groups undergoing reorientation at these temperatures may increase to about 5%.

The analysis indicates also that independent motion of carbonate groups and phenyl rings is impossible (*Figure 8*).

The above data make it possible to determine the permissible types of motions at the transition from the state of a rigid lattice to the more mobile higher temperature state. Their identification is possible by the experimental data obtained from n.m.r. analyses.

Besides full rotation of methyl groups around the threefold reorientation axis C_3,[14] at low temperatures oscillations of phenyl rings around $C_{(4)}O$ axis and oscillations of carbonate groups are possible within a limited angle range. Ring oscillation in PC chain does not change radically either the width of the static n.m.r. line or the value of the second moment, and cannot be responsible for the observed lowering of these characteristics in the analysed temperature range. In the vicinity of −60°C a new type of motion is activated. In our opinion that motion may be connected only with conformational transitions between four equilibrium positions of bisphenol. This motion should be associated by a reorientation of methyl groups around axis $C_{(4)}C_{(ar)}$ and a correlated rotation of phenyl rings and carbonate groups. As already mentioned above, it can be inferred from the conformational analysis that this type of reorientation is subject to a potential barrier from 2 to 6 kcal mol^{-1}. The calculated activation energy of motion that brings about the narrowing of the static n.m.r. line in the vicinity of −60°C is about 5.4 kcal mol^{-1} for PC swollen in CCl_4 (*Figure 1*). This value is in good agreement with the height of the potential barrier for conformational transitions of bisphenol. Intermolecular interactions may contribute to the potential barrier of 5.4 kcal mol^{-1}; this interaction can raise the barrier's value to 8.4 kcal mol^{-1} for unswollen PC[14]. A considerable contribution of intermolecular interactions to the potential barrier in this type of reorientation is understandable because, owing to the length of the $C_{(4)}O$ bonds, the reorienting fragments occupy a relatively large space. For the same reasons this motion will be hindered in areas with ordered chains.

Finally, we suggest that the molecular motion occurring in the vicinity of −60°C is connected with a conformational reorientation of bisphenol in unordered chains of random conformation.

Magnetic, dielectric and mechanical relaxation observed at these temperatures results from a strong correlation between this type of reorientation and a rotation of phenyl and carbonate groups.

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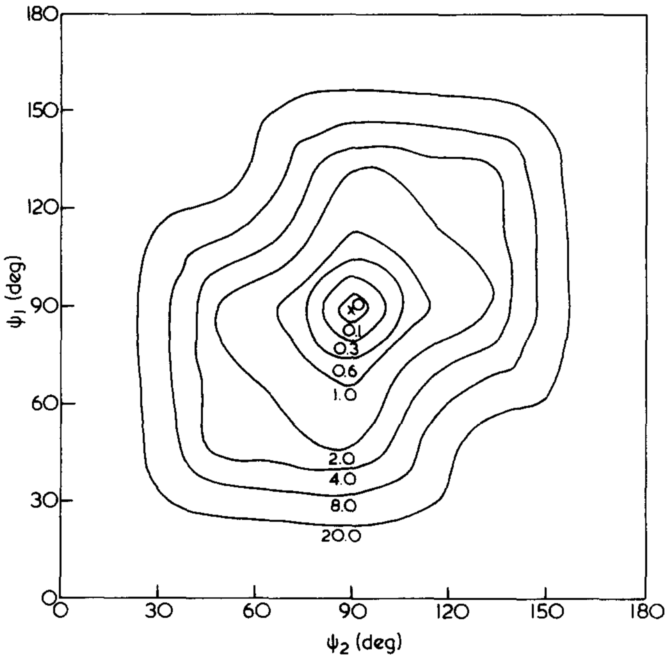

Figure 8 Conformational energy contours (in kcal mol^{-1}) for oscillations of phenylene rings in a polycarbonate chain with the planar zig-zag conformation

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