A study of molecular motion in polycarbonate by broad line nuclear magnetic resonance

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(Received 8 December 1976)

The nuclear magnetic resonance (n.m.r.) second moment has been measured for polycarbonate of bisphenol A over the temperature range 8 to 414K. An extensive study of the saturation behaviour has shown that the maximum previously reported for the second moment at low temperatures is incorrect and arises from selective saturation of the resonance. We have shown that at low radio-frequency power levels the second moment and line shape remain sensibly unchanged over the temperature range 8 to 80K. The rigid solid second moment has been considered theoretically from the intramonomer and interchain interactions with reference to the structures proposed by Prietzschk and by Bonart. We find that the structure of Bonart agrees best with a chain arrangement satisfying Van der Waals contact distances and that the rigid lattice second moment deduced correlates well with that measured for the rigid solid amorphous polymer. The temperature variation of the second moment shows two regions of relaxation processes, the low temperature one corresponding to the onset of methyl group rotations, followed by a region between 160K and the glass transition temperature in which the part of the monomer containing the phenyl and methyl groups acquires considerable mobility. These findings are in agreement with, and complementary to, previous suggestions that the toughness of amorphous polycarbonate of bisphenol A arises from extensive motion of the chains below the glass transition temperature.

INTRODUCTION

The origin of the mechanical toughness of polycarbonate of bisphenol A below its glass transition temperature at 422K (149°C) has been the subject of a number of investigations which have been reviewed by Locati and Tobolsky[1] who have ascribed it to the presence of chain backbone motions in the glassy amorphous state. A number of studies of the variation of the nuclear magnetic resonance (n.m.r.) absorption second moment with temperature down to 77K have shown the onset of molecular motions in the polymer, but these measurements do not go to sufficiently low temperatures to determine the rigid solid second moment[2-4]. It is not therefore possible to determine to what extent the decrease in second moment with increasing temperature is due to methyl group rotations and whether in addition chain backbone motions are involved. A further difficulty with the n.m.r. investigations cited is that there is considerable discrepancy in the values of second moment determined at about 77K.

Our object in this investigation was to extend the n.m.r. measurements to the liquid helium range to determine the rigid solid second moment and hence have a base from which to observe the change in second moment with increasing temperature, and apportion the decrease between methyl group and chain backbone motion. During the course of this work Kosfeld and von Mylius[5] reported the results of n.m.r. measurements in the same temperature range in which they observed the second moment of polycarbonate of bisphenol A to reach a maximum value of about 20 Gauss^2 at about 70K and then decrease to 15.2 Gauss^2 as the temperature was lowered to 5K. This effect was interpreted by them as arising from quantum

mechanical tunnelling of the methyl groups based on theoretical results of Allen[6] and of Clough[7]. Our own results showed that the second moments reached a constant value of about 16.4 Gauss^2 below 77K, a value in good agreement with theoretical estimates for the rigid solid polymer. Maxima in the values of low temperature second moments for solids containing methyl groups had previously been reported for poly(methyl α-chloroacrylate) by Powles[8], who attributed the effect to selective saturation, and for polypropylene by McDonald and Ward[19] who also ascribed the effect to saturation difficulties and hence not of significance. Because of the discrepancy between our own results and those of Kosfeld and von Mylius[5] we have made an extensive study of the effect of radio frequency power level on the spectra and second moments of polycarbonate of bisphenol A which confirm that the maximum in the second moment observed by Kosfeld and von Mylius does indeed arise from selective saturation similar to that postulated by Powles for poly(methyl α-chloroacrylate).

EXPERIMENTAL

For the temperature range 77 to 412K a Robinson[10] limited oscillator spectrometer operating at 24.5 MHz was used. The circuit included a vacuum tube voltmeter to monitor the oscillation level across the specimen coil so that measurements could be made at different power levels to test for saturation. In the range below 77K the Curie Law $1/T$ dependence of nuclear magnetization allowed a simple Q meter circuit (Rollin[11]) to be used, with its ease of adjustment for absorption signal and for setting the r.f. level. The r.f. level at the specimen coil was set using a cali-
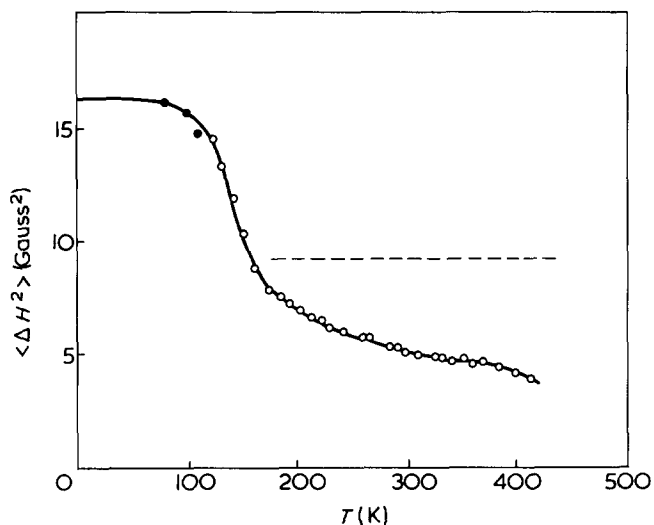
Figure 1 Variation with temperature of the n.m.r. second moment $\langle \Delta H^2 \rangle$ for isotropic Makrolon 3000: ●, measured with Q meter spectrometer; ○, measured with Robinson limited oscillator spectrometer. The horizontal full line for the results below 80K has been obtained from the results shown in *Figure 3*. The broken line at 9.2 Gauss² represents the second moment with rotating methyl groups

at 8K to determine the contribution of the isolated rigid molecular chains to the second moment of the solid material.

RESULTS AND DISCUSSION

Rigid solid second moment

The second moment variation with temperature of isotropic specimens of Makrolon 3000 from 8 to 412K is shown in *Figure 1*. The region below 80K is shown in more detail in *Figure 2* where results at different radio-frequency power levels are shown. The horizontal line at 16.4 Gauss² represents the average of the points at the three lowest power levels. The full curve with a maximum of 20 Gauss² at about 70K represents the results reported by Kosfeld and von Mylius. This curve is similar to the variation in second moment for our higher power results, for which the effects of saturation of the resonance become obvious. At the lowest temperatures near 10K, however, the second moments of the absorption curves decrease with increase in radio-frequency power.

The reason for this can be seen by examining the changes in n.m.r. line shape with power level at different temperatures. In *Figures 3* and *4* the normalized derivative absorption curves are shown for different power levels at 8.1K
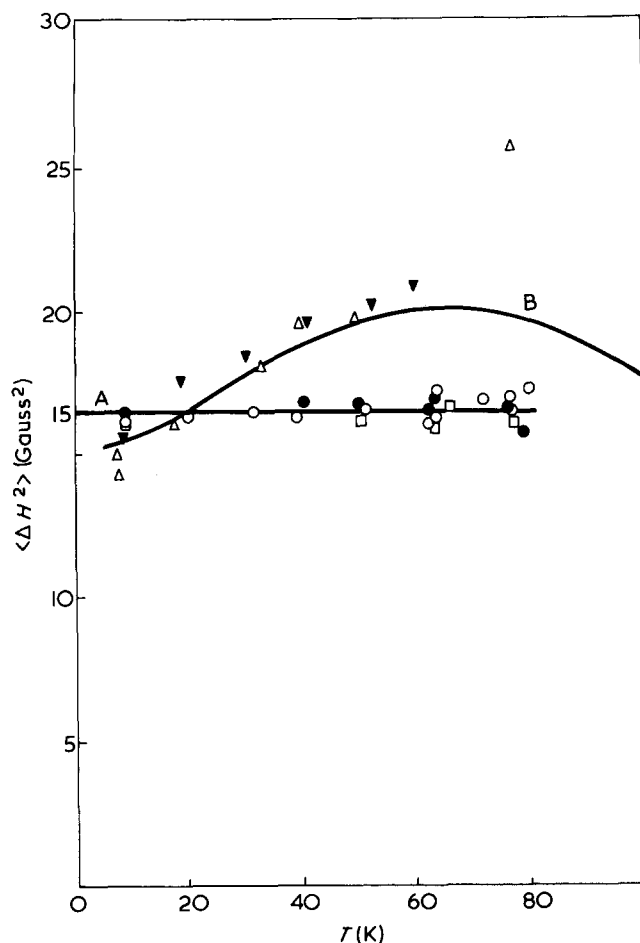
brated attenuator, and a second calibrated attenuator in the radio-frequency amplification circuit was then adjusted to make the total attenuation constant and at a value previously determined to give the best signal-to-noise ratio at the r.f. detector. The maximum setting used for the first attenuator was 50 dB corresponding to a maximum r.f. magnetic field at the centre of the specimen coil of 0.18 milliGauss.

A magnetic field modulation amplitude of 1 Gauss was used for all measurements giving an Andrew[12] correction to the second moment of 0.25 Gauss². This correction has been applied in the results presented here.

All spectra were recorded on a chart recorder linked to the field sweep calibrated with a Bell Model 640 Incremental Gauss meter. The accuracy of the Gaussmeter was checked with a variable-frequency nuclear magnetic resonance magnetometer. The low temperature results were also recorded digitally on paper tape at 0.1 Gauss intervals using a Solartron Digital Transfer Unit and a Facit tape punch. In addition to enabling rapid computation of second moments this also allowed us to produce the derivative absorption curves normalized to the same integrated intensity shown in *Figures 3* and *4* for comparison of line shapes at different power levels.

Temperature variation was achieved using gas-flow systems on both spectrometers. For the low temperature region where, because of the Curie Law dependence of the signal amplitude, the temperature must be kept steady during the recording of a spectrum, the gas flow cryostat system of Morris, Read and Temple[13] was used. Using this the temperature stability over the duration of a spectrum recording was 0.05 at 8K and 0.1 at 70K. Measurements were made on isotropic specimens of Makrolon 3000 (Bayer AG, Dormagen, W. Germany), prepared both by compression moulding and by melt extrusion. There was no difference in the results obtained from these two forms of specimen.

In addition the second moments of frozen solutions of the same polymer in deuterated chloroform were measured

Figure 2 Variation with temperature below 80K of the n.m.r. second moment $\langle \Delta H^2 \rangle$ for isotropic Makrolon 3000 at different r.f. power levels: △, 10 dB; ▼, 15 dB; ○, 35 dB; ●, 40 dB; □, 50 dB attenuation. A, represents the mean value of the low r.f. power measurements below 80K. B, Passing through a maximum of $\langle \Delta H^2 \rangle$ of about 20 Gauss² at 70K represents the results of Kosfeld and von Mylius
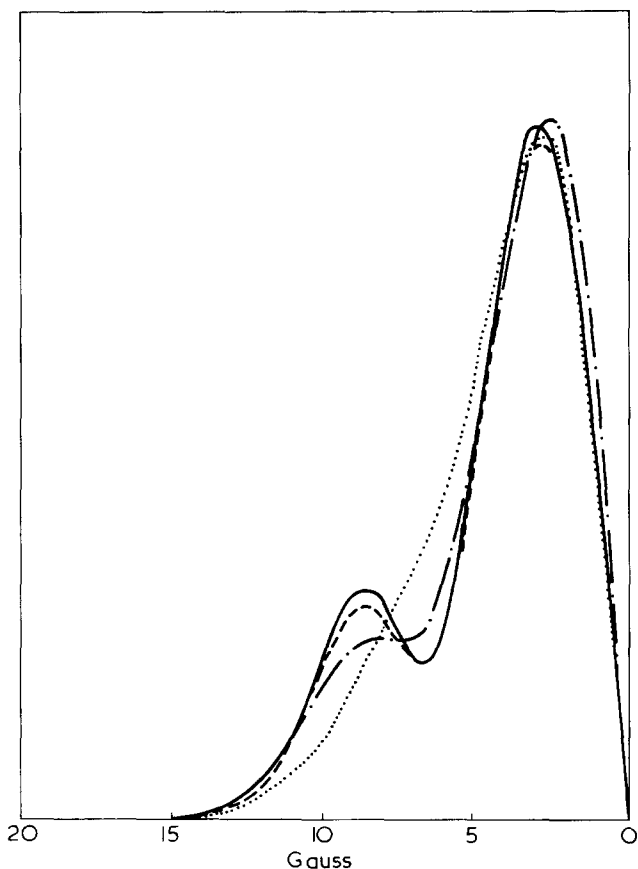
Figure 3 Variation with power level of the n.m.r. absorption derivative line shape at 8.1K; ...., 10 dB; —·—·—, 20 dB; — — —, 30 dB; ———, 50 dB

and in the vicinity of 77K. At the lowest power levels (50 dB attenuation at 8.1K and 40 dB attenuation at 75.8K) the spectra are sensibly identical and have the form expected for a polymer rich in methyl groups. The changes with increasing power level at the two temperatures are markedly different and may be explained by the different saturation behaviour of differently situated protons.

The n.m.r. signal in polycarbonate arises from methyl group protons and phenyl group protons whose numerical ratio is 3 to 4 with the same ratio of n.m.r. absorption signal intensities. The n.m.r. absorption spectrum of a dilute iso-tropic assembly of stationary methyl groups is a broad triplet with a second moment of 22.4 Gauss². The spectrum due to the 4 protons of a phenyl ring is much narrower with a second moment of 1.6 Gauss². The phenyl ring proton signal in polycarbonate is overlapped by the central com-ponent of the methyl group signal. In considering the derivative spectra of *Figures 3* and *4* it must be borne in mind that the inner component is dominated by the phenyl groups and the outer component is due to the methyl groups. The spectra in *Figure 4* for temperatures near 77K show a relative increase in the outer component with respect to the inner component as the radio-frequency power level is increased, indicating the onset of saturation of the phenyl ring proton resonance.

Consequently there is an increase in second moment. On the other hand at 8.1K the outer component decreases in relative height with increasing radio-frequency power indi-cating initial saturation of the methyl group proton reso-nance and a consequent decrease in the second moment.

A comparison of the normalized derivative absorption curves measured at the lowest power levels for temperatures between 8 and 77K shows that the line shape remains of the

form shown by the full lines in *Figures 3* and *4* over the whole temperature region and the second moment is sensibly constant at 16.4 Gauss². Above 77K the second moment decreases very rapidly with increasing temperature to about 7.5 Gauss² at 180K and then more slowly to 4 Gauss² at 400K (*Figure 1*). The fall in second moment between 77 and 180K and the values found above 180K are similar to the observations of previous workers. In order to interpret the decrease of the second moment with increasing temperature it is necessary to make some esti-mate of the rigid solid second moment and of the effect of molecular motion.

Theoretical aspects of second moments

The theoretical expression due to Van Vleck[14] for the n.m.r. second moment of a rigid solid may be written:

$$\langle \Delta H^2 \rangle = (G/N) \sum_{j>k} r_{jk}^{-6} (3 \cos^2 \theta_{jk} - 1)^2 \qquad (1)$$

where $G = 3/2\, I(I + 1)g^2\mu_n^2$, I is the nuclear spin number, g the nuclear g factor, μ_n the nuclear magneton, N the num-ber of nuclei over which the sum is taken, r_{jk} the length of the vector joining protons j and k, and θ_{jk} the angle between the vector r_{jk} and the externally applied magnetic field. For an isotropic specimen expression (1) must be averaged over all θ_{jk} and leads to the expression:
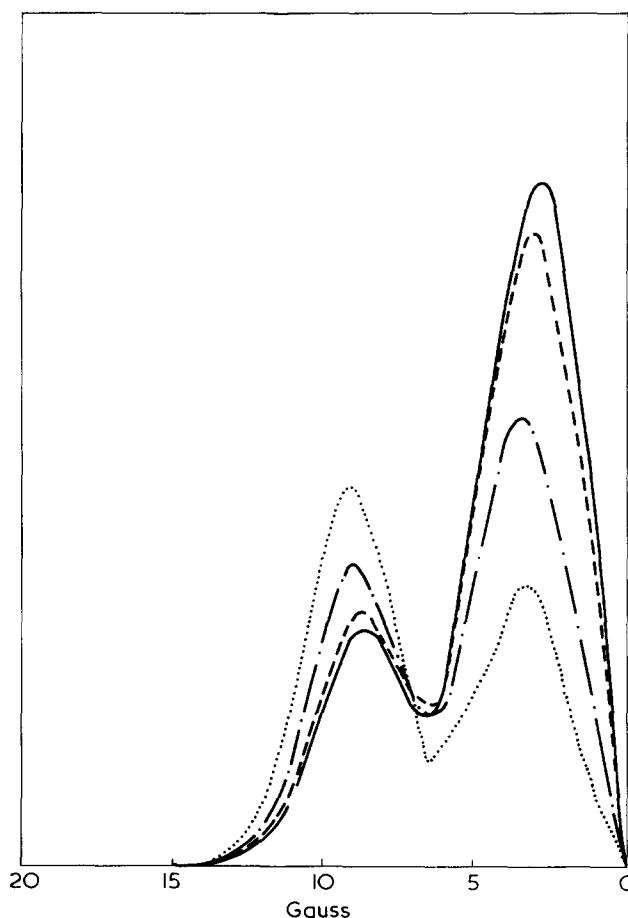

Figure 4 Variation with power level of the n.m.r. absorption derivative line shape at temperatures near 77K: ...., 10 dB, 77.2K; —·—·—, 20 dB, 78K; — — —, 30 dB, 75.6K; ———, 40 dB, 75.8K

$$\langle \Delta H^2 \rangle_{\text{iso}} = \frac{4}{5} \frac{G}{N} \sum_{j>k} r_{jk}^{-6} \qquad (2)$$

The effect of molecular motion can be observed as a reduction in the second moment when the frequency associated with the motion exceeds the width of the resonance spectrum measured in frequency units. Experimentally the reduction in second moment is observed as the temperature of the specimen is raised and the frequencies associated with the molecular motion increase. The theoretical calculation of second moments of rotating molecules is made by taking the time averages of r_{jk} and θ_{jk} in equation (1) and again averaging over all directions for isotropic specimens. Because of the r_{jk}^{-6} dependence in equation (1) the accuracy to which theoretical values of second moments can be calculated depends on how well the hydrogen nuclei positions and hence the separations r_{jk} can be determined. This means that in general even for a crystalline polymer whose crystal structure is well known, the hydrogen positions have to be deduced from assumptions about bond lengths and angles relating them to the position of heavier atoms, such as carbon, determined by X-ray crystallography. For non-crystalline polymers although rather more assumptions are necessary the calculation of satisfactory second-moment values is achieved because of the dominance through the r_{jk}^{-6} dependence of the interaction between hydrogen atoms bonded to the polymer chains over the contributions of interactions between different chains, for which the minimum values of r_{jk} are of the order of the Van der Waals' separations. For example the hydrogen nuclei separation in methyl groups is 1.79 Å compared with the normal 2.4 Å Van der Waals' separation of hydrogen atoms. Because of the r_{jk}^{-6} dependence the contribution to the isotropic second moment of a pair of hydrogen atoms at the Van der Waals' separation is only 18% of that of a pair of hydrogen atoms in a methyl group. Where there is a well established structure for the crystalline form of a polymer the calculation of the second moment can be carried out directly provided care is taken to check that the hydrogen nuclei positions determined with assumed bond lengths and valence angles do not lead to unrealistic internuclear separations. Such calculations have been very successful for long chain alkanes and high density polyethylene[15-18]. The calculations for crystalline material may also be decomposed into intermolecular contributions and the results used in estimating the second moments of non-crystalline forms of the polymer.

Crystal structure of polycarbonate

The crystal structure of polycarbonate of bisphenol A is not sufficiently well known for direct calculation of the overall rigid solid second moment. Crystal structure investigations have been carried out by Prietzschk[19] who proposed an orthorhombic lattice with $a = 11.8$ Å, $b = 10.1$ Å and $c = 21.5$ Å, and by Bonart[20] who put forward a monoclinic lattice with $a = 12.3$ Å, $b = 10.1$ Å and $c = 20.8$ Å and $\gamma = 84°$. In both structures each unit cell contains 8 monomer units on 4 polymer chains. The dimensions of the cells are not very dissimilar but the arrangement of the chains in the cells proposed by Bonart is quite different from that of Prietzschk. They are shown in *Figures 6a* and *6b* which are sections perpendicular to the c axis. In both models the chains are rotated about and displaced along the c axis with respect to each other. The relative orientations are shown

by the arrows on the chain axes and the displacements are indicated as fractions of c. In the Prietzschk structure the chains form a rectangular array whereas Bonart concludes that they lie on a pseudo-hexagonal net. Bonart discusses the structure in terms of layers as indicated in *Figure 6b* in which neighbouring chains in each layer are displaced by about $c/8$, although not exactly $c/8$, with respect to each other along the z axis and alternate layers are rotated by $180°$ and displaced by $a/4$ in the x direction and $c/4$ along the z direction. We have examined the feasibility of the spatial arrangements of chains by calculating the separations of atoms on different chains and comparing them with the Van der Waals' separations. For the Van der Waals' radii we have used 1.20 Å for H, 1.80 Å for C and 1.40 Å for O (Kitaigorodskii[21]). We have used a chain conformation proposed by Williams and Flory[22] in their discussion of the chain statistics and shown in *Figure 5*. The carbonate group is planar and in the *trans, trans* position and Williams and Flory state that the carbonate groups will prefer orientation with their plane perpendicular to the plane of the adjoining phenylene groups giving two energy minima in these positions and the $C-C_1-C_4-O$ axis may be treated as an axis of free rotation subject to a twofold symmetric potential. The rotation of the phenylene groups about this axis is restricted by steric hindrance of the phenyl and methyl protons such that the phenyl group cannot at the same time have ϕ and ϕ' less than $\pm 30°$ when the signs of ϕ are the same, or less than $\pm 60°$ when ϕ and ϕ' are of opposite sign, where ϕ and ϕ' are measured from the position in which the phenyl groups are coplanar. The length of one
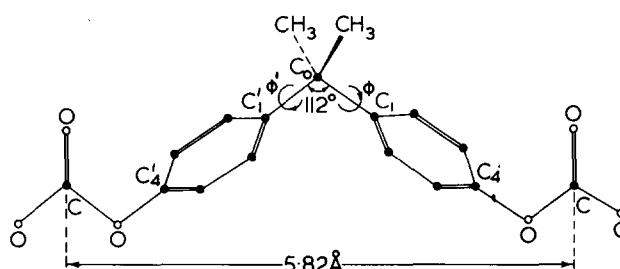
Figure 5 Chain configuration proposed by Williams and Flory[22] and used as a basis for studying atomic hindrance between adjacent chains
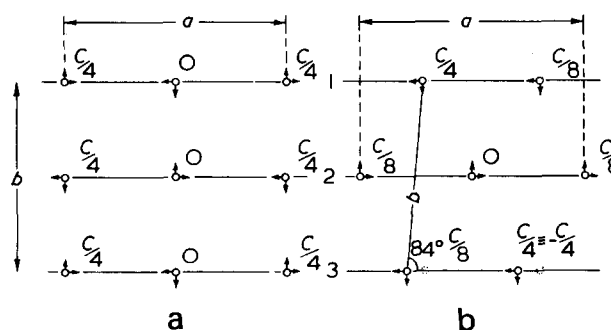
Figure 6 Projection of the arrangement of chains in the crystalline lattice proposed by (a) Prietzschk: orthorhombic lattice $a = 11.8$ Å, $b = 10.1$ Å, $c = 21.5$ Å; (b) Bonart: monoclinic lattice $a = 12.3$ Å, $b = 10.1$ Å, $c = 20.8$ Å and $\gamma = 84°$. The arrows on the chains represent the relative orientations of adjacent chains with respect to each other. The numbers 1, 2 and 3 refer to the layers discussed in the text. The fractions of c against the chains represent the displacement of chains in the z direction with respect to the central chain
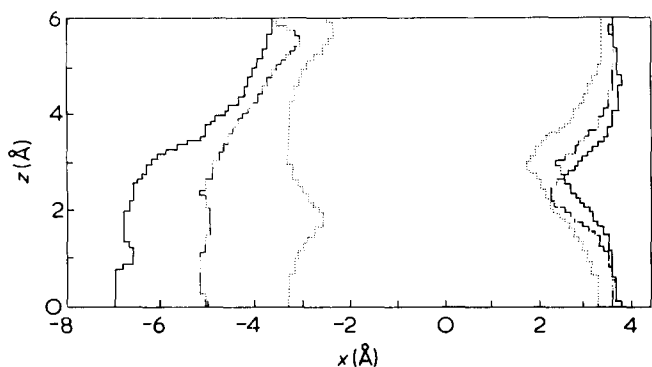
Figure 7 Combinations of displacements in the layer (x) and chain (z) directions to avoid Van der Waals contacts with: ...., C—C = 3.6 Å; —·—·—, HC = 3.0 Å; — — —, H—H = 2.4 Å. ———, Boundary for all contacts

monomer unit of this chain is 5.82 Å which is slightly greater than $c/4$ for the structures of both Prietzschk and Bonart. The distance between the oxygen atoms attached to C_4 and C_4' is determined by the bond angle at C_0 which is not very flexible so that the shortening of the chain in the crystal lattice is most likely to be due to some distortion of the carbonate group bonds. This is not likely to influence the calculation of second moments since the significant proton interactions are intramonomer and interchain. The method of examining realistic arrangements of chains is illustrated in *Figure 7* for two chains lying in adjacent layers (1 and 2 of *Figure 6b*) at a separation $y = b/2$ with the chain in layer 2 rotated through 180° about an axis passing through the centre of the phenyl rings. The lines on the Figure represent the limits of the displacements of the chain in layer 1 in the x and z directions with respect to a chain in layer 2, which keep the interatomic distances between the chains above the Van der Waals values. On this basis positions given by displacements in the region between the solid line boundaries in the positive and negative x directions are not possible. It is clear immediately that the minimum separation between two chains in layer 1 which are not to interfere with a chain in layer 2 is given when the two chains in layer 1 are displaced distances $x = +2.55$ Å, $z = 2.6$ Å, and $x = -3.65$ Å, $z = 5.8$ Å respectively. The separation of the chains in layer 1 in the x direction becomes 6.20 Å which is very close to half the lattice parameter $a = 12.3$ Å and the displacements in the z direction correspond approximately to $c/4$ and $c/8$ in good agreement with the deduction of Bonart. The minimum distance between the two neighbouring chains of layer 1 is governed by contacts of hydrogen atoms on these chains with hydrogen atoms on a chain of layer 2. These hydrogen—hydrogen interactions are also important for the interchain n.m.r. second-moment contributions.

An examination of the case where chains in layer 2 are not rotated with respect to those in layer 1 gives a minimum separation between chains in layer 1 which is clearly in disagreement with the X-ray results referred to earlier. The corresponding study for chains in the same layer rules out the arrangement in which adjacent chains are rotated by 180 degrees with respect to each other. For chains in the same layer displaced without rotation, the minimum separation is least for no relative displacement in the z direction and increases to 6.15 Å for a z-displacement of 1.6 Å rather less than the $c/8 = 2.6$ Å of Bonart's structure. The atomic contacts which become equal to the nominal Van der

Waals separation are between two of the hydrogen atoms of the methyl groups on one chain and two of the carbon atoms of a phenyl group on the other chain. By rotating the methyl groups and relaxing the allowed contact distance between hydrogen and carbon atoms to 2.7 Å the two chains may be displaced by $c/8$ in the z direction at a separation of 6.15 Å. Atomic separation less than the nominal Van der Waals separation are commonly observed when an overall improvement in the molecular packing results (Kitaigorodskii[21]). The displacement of chains in the same layer by about $c/8$ with respect to each other is determined by the requirements of the interactions between adjacent layers, a point which Bonart makes in describing the interlocking of the layers with the methyl groups projecting from one layer into spaces between them in the adjacent layer. Since the contacts governing the separation of the chains are between carbon and hydrogen atoms, the interchain contribution to the n.m.r. second moments is relatively insensitive to small changes in the relative positions of adjacent chains in the same layer.

In two respects the above analysis leads to differences from Bonart's model. First, chains of atoms in the same layer are displaced progressively by $c/8$ with respect to each other, whereas Bonart shows them displaced alternatively in opposite directions by $c/8$ although this does not appear to be essential to his model. Secondly, because alternate layers of chains are rotated by 180° they should lie on a net with a rectangular base, indicated in *Figure 6b* by the displacement of the chains in layer 3 to the positions shown as broken circles.

Rigid solid second moment calculation for polycarbonate

The discussion of the preceding section allows us to calculate the interchain contribution to the n.m.r. second moment for polycarbonate. It amounts to 2.8 Gauss^2 for the six nearest neighbour chains to a given chain. More distant chains give negligible contribution to the second moment. The intrachain contribution depends on the rotational positions assumed for the methyl and phenyl groups which must be such that the separations of hydrogen atoms bonded to different groups must not be unrealistically small, leading to excessively high values of second moments. We have calculated interatomic separations and second-moment contributions for symmetrically disposed rotational positions of both methyl and phenyl groups at 5° intervals over the complete range of rotational displacements, and find for all combinations that there is at least one pair of hydrogen atoms on different groups with a separation of less than or equal to 2.04 Å. This is 0.36 Å less than the nominal Van der Waals separation for non-bonded hydrogen atoms and appears to be a practical lower limit for these separations (Kitaigarodskii[21]). The intramonomer second moment corresponding to the conformation for which the minimum hydrogen—hydrogen separation is 2.04 Å is 15.08 Gauss^2 and occurs for $\phi = \phi' = 60°$ in *Figure 5*. The calculated second moment remains below 16.0 Gauss^2 for rotational displacements of both the phenyl and methyl groups of ±10° but these rotational displacements lead to physically unrealistic minimum separations between non-bonded hydrogen atoms. The rotational displacements could occur with some distortion of the monomer unit, which indeed must happen when rotational motion of the methyl groups sets in at high temperature. Such distortion must reduce the second moment to a

value corresponding to minimum hydrogen—hydrogen separation of about 2.0 Å.

A value of about 15.0 Gauss^2 would therefore appear to be an upper limit for the intramonomer contribution to the second moment even if molecular distortions of bond angles allowed other conformations of the monomer since the minimum hydrogen atoms separations would still be expected to be of the order of 2.0 Å. A guide to the reasonableness of the order of magnitude of this upper limit of 15 Gauss^2 can be obtained by comparing it with the intragroup contribution. For an isotropic assembly, the rigid solid second moment contribution of a methyl group is 22.4 Gauss^2 and for a phenyl group 1.6 Gauss^2. An assembly of the two groups in equal numbers as in polycarbonate would therefore contribute $1/14$ ($6 \times 22.4 + 8 \times 1.6$) = 10.5 Gauss^2, leaving 4.5 Gauss^2 for the intergroup contributions. A separate calculation of the intermethyl group contribution of a dimethyl group gives a range of values of 1.41 to 3.02 Gauss^2 with an average over all pairs of rotational angles for the methyl groups of 1.88 Gauss^2. In polycarbonate the intermethyl contribution would be $6/14$ of these values, ranging from 0.6 to 1.29 Gauss^2 with an average value of 0.81 Gauss^2. An upper limit for the monomer of 15.0 Gauss^2 allows at least 3.2 Gauss^2 for the interphenyl and phenyl—methyl interaction contribution and this appears to be ample. Adding in the interchain contribution, an upper limit for the theoretical rigid-lattice second moment of crystalline polycarbonate of 17.8 Gauss^2 is obtained. The value of 16.4 Gauss^2 measured for the rigid solid amorphous material is quite consistent with this theoretical estimate.

Additional second-moment measurements were made to test some of the theoretical conclusions. A solution of the polymer in deuterated chloroform with 1 part of polycarbonate to 7 parts of $CDCl_3$ by volume was prepared and the n.m.r. second moment measured in the frozen solution at 8K. In this solution the average interchain proton separations were approximately doubled, reducing the interchain second-moment contribution to a negligible amount. The measured second moment was 14.3 Gauss^2, a reduction of 2.1 Gauss^2 from that of the solid polymer, confirming the correct calculated order of magnitude of the interchain contribution. To compare the second moments of crystalline and amorphous polycarbonate the second moment of material crystallized from solution was measured at room temperature. The crystalline second moment was 6.5 Gauss^2 compared with 5 Gauss^2 for the amorphous material which parallels the difference between the theoretically estimated 17.8 Gauss^2 for rigid crystalline material and the measured low temperature value of 16.4 Gauss^2 for non-crystalline material.

Temperature dependence of the second moment

The decrease in the second moment with increasing temperature is caused by thermal motion of the atoms leading to a reduction in the average value of the $(1 - 3 \cos^2 \theta_{jk})$ and r_{jk}^6 terms in equation (1). The effect of rotational motion of methyl groups in solids has been discussed by Gutowsky and Pake[23] who show that for a random assembly of isolated rotating methyl groups the second moment can be reduced to ¼ of its rigid solid value of 22.4 Gauss^2, that is by 16.8 Gauss^2. The sharp decrease in the second moment of polycarbonate between 80 and 150K is typical of the effect of methyl group rotation. The contribution of full rotation of the methyl groups to the reduction of the

second moment in polycarbonate below its rigid lattice value is therefore $6/14$ of 16.8 Gauss^2 which would thus account for a reduction of the second moment from 16.4 to 9.2 Gauss^2, the value at about 150K. The broken line in *Figure 1* is drawn at $\langle \Delta H^2 \rangle$ = 9.2 Gauss^2. Between 150 and 414K the second moment falls from 9.2 to 3.8 Gauss^2 indicating considerably more relative motion of the hydrogen atoms in the polymer than can be accounted for by the methyl group rotations alone.

The theory of the motional narrowing of n.m.r. resonance lines was first discussed by Bloembergen, Purcell and Pound[24] for the case of liquids with molecules in rotational motion. The Bloembergen, Purcell and Pound formula was given an *ad hoc* modification by Gutowsky and Pake[23] for a change from a wide to a narrow absorption line. Recently Hendrickson and Bray[25] have developed a phenomological equation for motional narrowing in solids. As in previous theories the development is based on the Bloch equations which lead to Lorentzian line shapes but Hendrickson and Bray have applied their equation successfully to the case in which the rigid lattice line shape was Gaussian. In the absence of inhomogeneous broadening they can express the motional narrowing by the following equation:

$$\ln \left[\frac{1}{W} - \frac{1}{A} \right] = - \frac{E_a}{kT} - \ln \left[\frac{1}{B} - \frac{1}{A} \right] \tag{3}$$

where W is the line width at temperature T, A is the line width at low temperatures and B the high temperature line width. In examples of the application of their formula they have shown that a semilogarithmic plot of equation (3) can show up the presence of different relaxation mechanisms. We have plotted our data according to equation (3) except that we have used the square roots of second moments instead of line widths, as the latter are not well defined for our absorption curves. The semi-logarithmic plot of *Figure 8* shows that the data can be divided into two regions represented by two straight lines with different slopes for temperatures below and above 160K. Although the slopes of the straight-line portions of the graphs correspond to activation energies of 1.86 kcal/mol and 0.47 kcal/mol for the low temperature and high temperature relaxation process respectively the numerical values must be treated with caution in view of the assumptions of the theory. The value of 1.86 kcal/mol is however consistent with other n.m.r. results of activation energies for methyl group rotation in low molecular weight compounds (Powles and Gutowsky[26]). These results suggest that between 160K and the glass transition temperature a low activation energy process enables the development of considerable motion of the hydrogen nuclei. Since by far the largest contribution to the second moment of polycarbonate arises from the intramonomer interactions, the reduction in the second moment between 160K and T_g must come mainly from a reduction of the intramonomer contribution. The calculations of minimum hydrogen atom separations and second-moment contributions discussed in an earlier section show that apart from the reduction of the second moment due to methyl group rotations already discussed, there is little possibility of further reduction through changes in r_{jk} of equation (1) by relative displacements of groups in the monomer with respect to each other. The large decreases in $\langle \Delta H^2 \rangle$ between 160K and T_g must therefore entail a substantial decrease in the time average of the $(1 - 3 \cos^2 \theta_{jk})$ of equation (1), consequent on bodily motion of the monomer
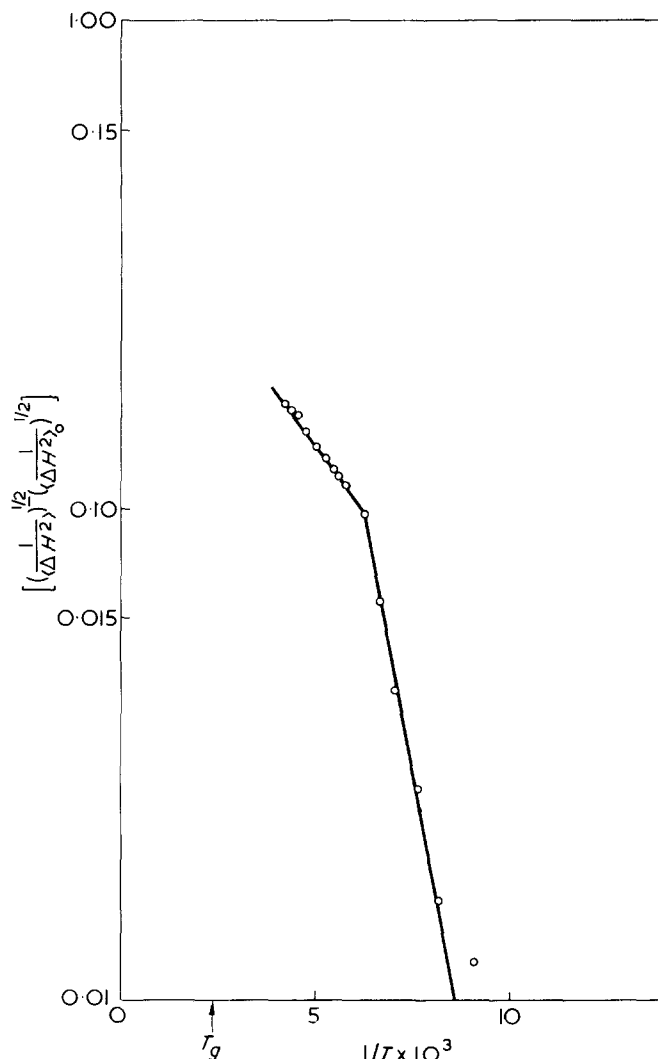
Figure 8 Semi-logarithmic plot of $[(1/\langle\Delta H^2\rangle)^{1/2} - (1/\langle\Delta H^2\rangle_0)^{1/2}]$ against $1/T$. $\langle\Delta H^2\rangle$ = second moment at temperature T, $\langle\Delta H^2\rangle_0$ rigid lattice second moment

methyl and two phenyl groups as a unit is necessary as discussed above.

The evidence of the n.m.r. and dielectric measurements is complementary and permits the conclusion that in the secondary transition region general motion of the polycarbonate backbone chain becomes possible and provides a molecular mechanism which could contribute to the toughness of the material below the glass transition point.

ACKNOWLEDGEMENTS

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as a whole, probably by torsional oscillation about the chain axis either coherently with the chain or involving some flexibility of the carbonate bonds between the hydrogen containing groups.

In their review of the experimental evidence on the secondary transition in polycarbonate Locati and Tobolsky[1] discuss the hypothesis that the broad secondary transition observed consists of two secondary transitions, which have been resolved in creep and stress relaxation measurements, and that from dielectric and n.m.r. evidence these two transitions represent relaxation of the carbonate group and the phenyl group respectively. The fall in second moment observed by us is too large to be attributed to motion of the phenyl groups alone which contribute only a small amount to the second moment. The motion of the two