# On the intermolecular order in amorphous polycarbonate. Neutron scattering results and model calculations*

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*(Received 16 October 1986; accepted 12 November 1986)*

Neutron scattering on isotopically substituted molecules has been used for exploration of the intermolecular order of amorphous polycarbonate (of bisphenol A). Low (wavevector) wide-angle neutron scattering experiments on differently deuterated versions of polycarbonate have been performed in the range $0.2 < q(\text{Å}^{-1}) < 3$. The scattering curves are compared with computer calculations assuming various model configurations of polycarbonate segments. Reasonable agreement was found for a model of three parallel segments each of two monomer units in a *trans–trans* conformation.

**(Keywords: polymers; neutron scattering; intermolecular order; polycarbonate)**

## INTRODUCTION

Polymer chains are internally mobile and often complicated in their monomer structure; intermolecular short-range order in their liquids is thus necessarily complex and difficult to analyse. The literature reflects the consequent reluctance of authors to propose definite models for the local structure of amorphous polymers[1].

The science of simple liquids of small, preferably rigid, molecules is comparatively far advanced; the liquids of some systems can now be considered known in detail on a molecular scale[2,3]. The route to success is a combination of neutron scattering experiments on a set of isotopic isomers of the substance in question and molecular dynamics (MD) computer calculation[4].

Most difficult to interpret is the scattering in the wavevector range $0.2 < q(\text{Å}^{-1}) < 2$, $q = (4\pi/\lambda)\sin(\theta/2)$, i.e. the low (wavevector) wide-angle neutron scattering (LWAS) range. The higher $q$ range (HWAS), $q > 2$ Å$^{-1}$, is dominated by intramolecular correlations due to the known chemical structure; the small $q$ range (SAS), $q < 0.1$ Å$^{-1}$, in non-critical liquids is dominated by random thermal fluctuations that obey the laws of thermodynamics[5]. It is the LWAS range defined above that reflects the elusive intermolecular correlations, where, even in the simplest liquids, only MD simulations can help to interpret the scattering results with a high degree of reliability.

Polymeric liquids do not form a fundamentally different class. The additional structure analysis problems encountered do not rest with the chain character of the molecules. Owing to almost perfect screening, the complicated single-chain structure[6] is not reflected in the SAS range[7]. Rather, the difficulties arise from the complexity of the local chemical structure and they are, therefore, also typical of liquids with complex and internally mobile small molecules:

(i) Generally, a large number of inter- as well as intramolecular correlations overlap to yield only poorly resolved LWAS curves, which are thus no longer a good test for MD simulation calculations.

(ii) MD simulations of liquids beyond a moderate degree of complexity are already beyond the capacity of available computers.

Even so, experimental[8] and MD[9] studies have been done on polymers with fairly simple repeat units.

The material studied in this paper is the polycarbonate of bisphenol A, a polymer with a complicated monomer unit. Different aspects of the structure of amorphous polycarbonate have been considered elsewhere: i.e. the single-chain structure[10,11], the long-range fluctuation behaviour[7], and the short-range order especially in the HWAS range[12,13].

This paper deals with the problematic LWAS range. An attempt was made to use the successful recipe of simple liquid structure analysis, but to replace the (impossible) MD simulations by model calculations. Neutron scattering experiments were done on amorphous polycarbonate and three differently deuterated derivatives thereof. Scattering from model groups of polycarbonate segments in assumed configurations was calculated by computer. The following is an account of the comparison of experimental and model results.

## POLYMERS

Differently deuterated derivatives of the polycarbonate (PC) of bisphenol A were synthesized in our laboratory via phase-transfer polymerization[14]. They will be denoted as follows (see *Figure 1*):

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*Dedicated to Professor K. Hamann on the occasion of his 80th birthday

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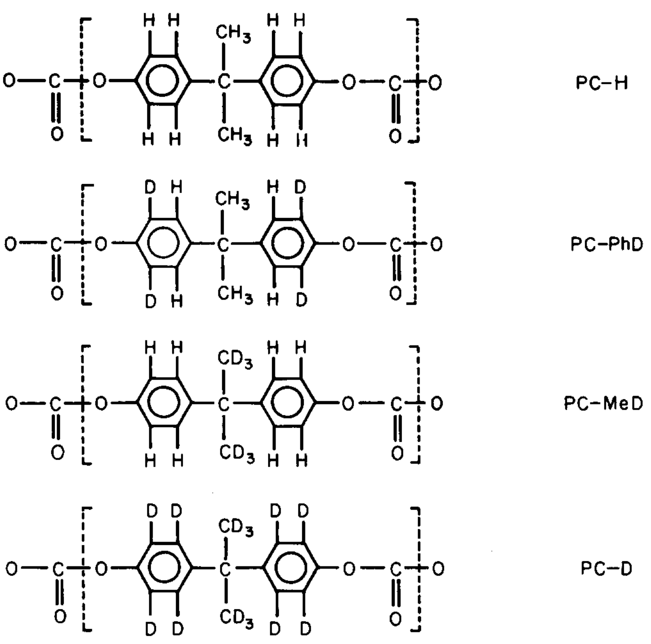

**Figure 1** Structure of the isotopic isomers of PC

| | |
|---|---|
| PC-H | normal PC, no deuteration |
| PC-PhD | phenyl rings deuterated in the positions *ortho* to the oxygen |
| PC-MeD | deuterated methyl groups |
| PC-D | perdeuterated PC |

According to $^1$H n.m.r. spectroscopy, the degree of deuteration exceeded 0.97 in all cases.

## NEUTRON SCATTERING

The neutron scattering experiments were done using the wide-angle diffractometer D1B at the high-flux reactor of the Institute Laue–Langevin (ILL) in Grenoble. The neutron wavelength was 2.5 Å, the detector distance 1.5 m. The data treatment is discussed elsewhere[11]. The scattering curves of PC-H, PC-PhD, PC-MeD and PC-D are displayed in *Figure 2*. The four curves are markedly different: the main maximum ($q = 1.25$ Å$^{-1}$ for PC-H) is split into two in the cases of PC-MeD and PC-D, and smaller maxima on both sides of the main peak appear at different positions with varying intensity (e.g. $q = 0.63$ Å$^{-1}$ for PC-PhD and $q = 1.87$ Å$^{-1}$ for PC-D).

The scattering curve obtained by X-ray scattering[12] is rather similar to that of PC-H within the $q$ range considered here. As demonstrated by *Figure 2* the method of isotopic substitution and application of neutron scattering dramatically expands the scale of information. So the full set of scattering curves should constitute a sensitive test for the model calculations described below.

## MODEL CALCULATIONS

At first glance, it seems rash to assume certain intermolecular configurations of polymer segments to model an amorphous structure. However, the incentive to undertake this study was the observation that the X-ray and neutron LWAS curves of amorphous and crystalline PC are quite similar, differing only in that the moderately narrow peaks produced by crystalline PC are broadened into halos for amorphous PC. This offers the tentative assumption, which is also suggested by studies on oriented and on annealed PC[15,16], that the short-range order of amorphous PC is similar to that in the crystalline state. The following treatment starts from this assumption.

Small highly ordered units of one, two or, in most cases, three neighbouring PC segments were designed, where each 'segment' is a sequence of two PC monomers. The scattering from these units was calculated on the computer using the Debye formula:

$$I(q)=\sum_{m}\sum_{n} b_m b_n \frac{\sin(qr_{mn})}{qr_{mn}}$$

where $m$ and $n$ denote different atoms, $b_m$ and $b_n$ are their neutron scattering lengths, $r_{mn}$ is their mutual distance, and $q$ is the absolute value of the scattering vector. Scattering curves were calculated for all four isotopic isomers of PC of all model units considered.

### *Conformation of one PC segment*

*Figure 3* shows the PC segment (67 atoms) in its 'all-*trans*' (*tt*) conformation, i.e. the planar *trans* sequence of the axes $f_{1-4}$ in the $xz$ plane. The phenyl rings are tilted at $\theta = \pm 45°$ out of the $xz$ plane[17] in a sequence of alternating sign. Bond lengths and bond angles were taken from refs. 17, 18 and 20. Following ref. 17 the angles between the axes were chosen to be $\alpha(f_{1,2}) = 134.0°$ and $\alpha(f_{2,3}) = 109.5°$. This *tt* conformation was used exclusively in the calculations for the following reasons.

The distribution of intramolecular conformations in amorphous PC is not yet accurately known, but there is little doubt that the *tt* conformation is the most stable

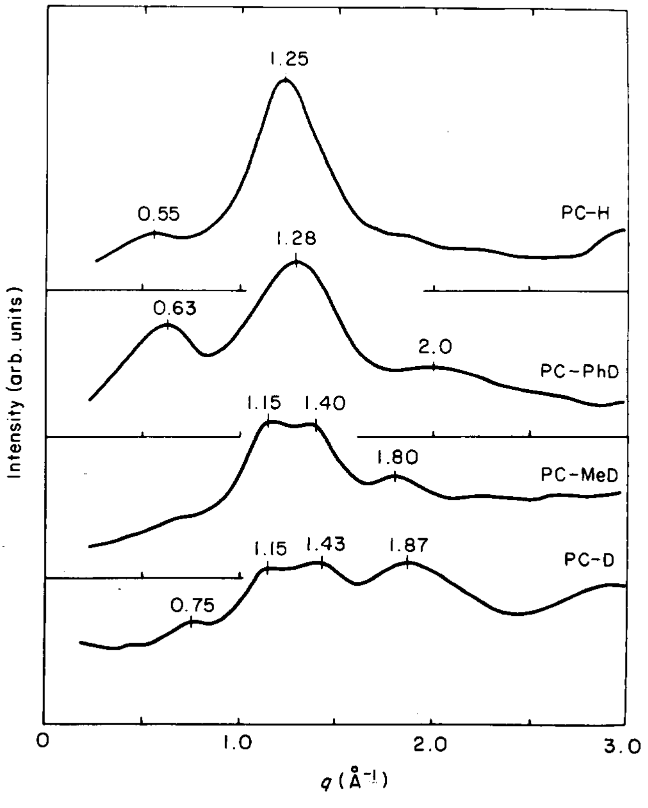

**Figure 2** Neutron scattering curves of amorphous PC-H, PC-PhD, PC-MeD and PC-D

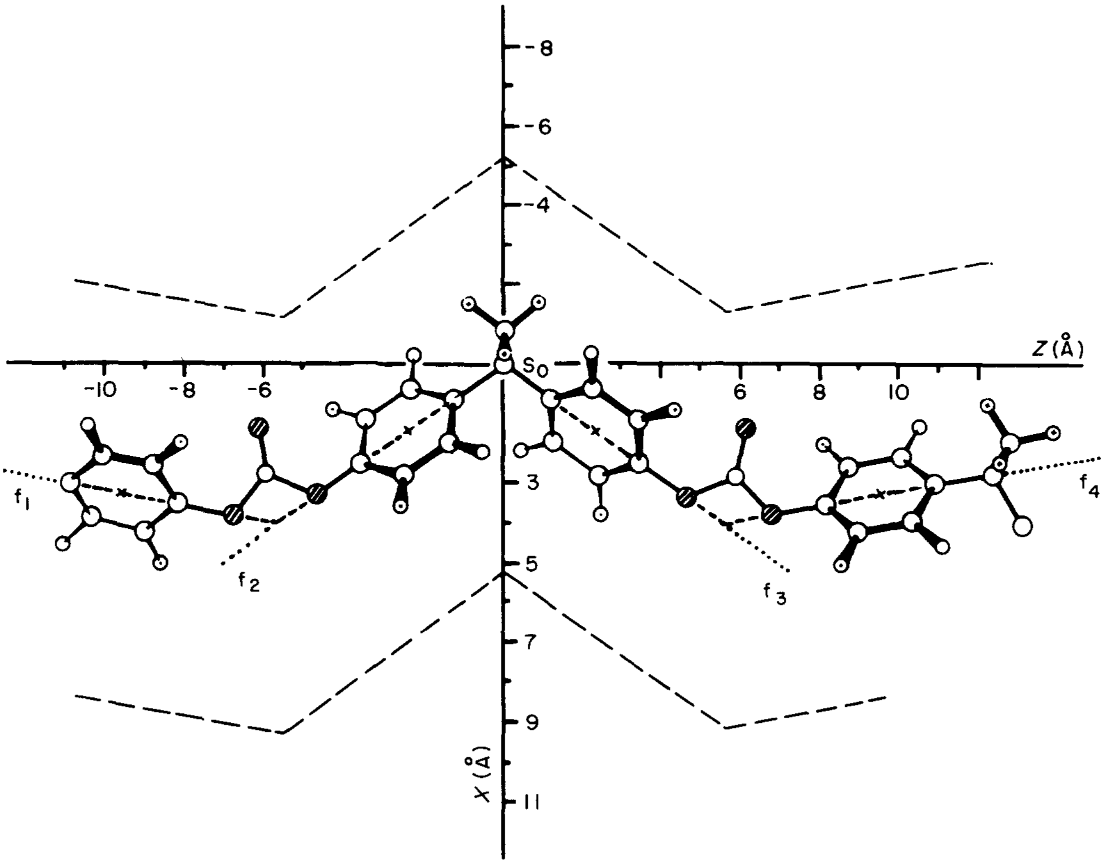

**Figure 3** The *tt* conformation of one PC segment: large open circles, C; small open circles, H; shaded circles, O. Broken lines sketch the positions of two further segments (configuration $(0,H_1,H_2)$, see text)

one. Different theoretical studies[17,19] on the model compound diphenyl carbonate favour the *trans* conformation of the carbonate group by small energy margins over the *cis* conformation. Calculations on diphenyl isopropane[17] and an X-ray study on crystalline diphenyl carbonate[17] both identify tilt angles of $\theta = \pm 45°$ for the phenyl rings as the minima of broad energy wells, the two rings on either side of the isopropyl group being tilted with different sign, i.e. conrotatory tilts. The *tt* conformation shown in *Figure 3* should thus not be overwhelmingly dominant in amorphous PC, but it should be the most probable one.

The different angles $\alpha = 134.0°$ and 109.5° cause a banana-like bend in the long axis of the segment, so that it is unlikely that this bent conformation is also encountered in crystalline PC. Still, a somewhat distorted version of the *tt* conformation should be the basis of the crystal as well. A distorted *tt* conformation was indeed proposed in one[20] of the two X-ray studies on crystalline PC[20,21] in the literature. Thus, in summary, the *tt* conformation of *Figure 3* is frequent in amorphous PC, and a probably somewhat distorted version of it is most likely the basis of crystalline PC.

### *Scattering curves of one-, two- and three-segment units*

As a first approach, scattering curves were calculated for one segment and for units of two and three segments in intermolecular arrangements to be specified below. *Figure 4* shows results for the cases PC-H and PC-MeD.

At small $q$ values, all curves are inevitably dominated by a large form factor peak centred at $q = 0$, which is, irrespective of any internal structure, common to all particles of the size and overall shape of the PC units considered here. As the unit grows in size, this peak narrows and eventually turns into a $\delta$ peak at $q = 0$. (The narrowing is already noticeable in the curves for the two- and three-segment units.)

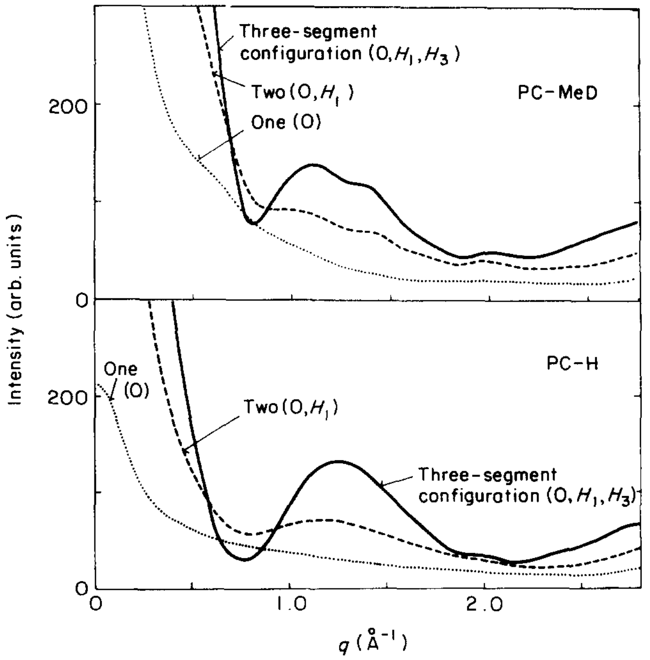

**Figure 4** Model scattering curves for one-, two- and three-segment units (configurations (0), $(0,H_1)$, $(0,H_1H_3)$ according to *Figure 5*), calculated for the cases of PC-H and PC-MeD

Apart from the form factor peaks, the two scattering curves for the single segment are almost featureless; peaks reflecting the internal structure of the segment are hardly noticeable.

The picture changes considerably as soon as intermolecular correlations come into play. Structural features become apparent and are already quite developed in the case of the three-segment unit. The scattering curves thus indicate almost exclusively intermolecular order effects.

A comparison of *Figures 4* and *2* shows that the two scattering curves for the three-segment model unit are even quite similar to the respective experimental curves of PC-H and PC-MeD. Hence, a highly ordered model unit gives reasonable results. Similar units were, therefore, chosen as the objects of all further model calculations.

### *Three-segment configurations*

Highly ordered three-segment units were constructed as follows. All units consist of the segment in the origin ($S_0$) in *Figure 3* and of further segments generated by parallel translational displacements of $S_0$ in directions within the vertical *xy* plane (e.g. to the positions $H_1$ and $H_2$ generating the two segments sketched in *Figure 3*). The displacements shift $S_0$ only sideways; rotations and shifts along its main axis are not involved.

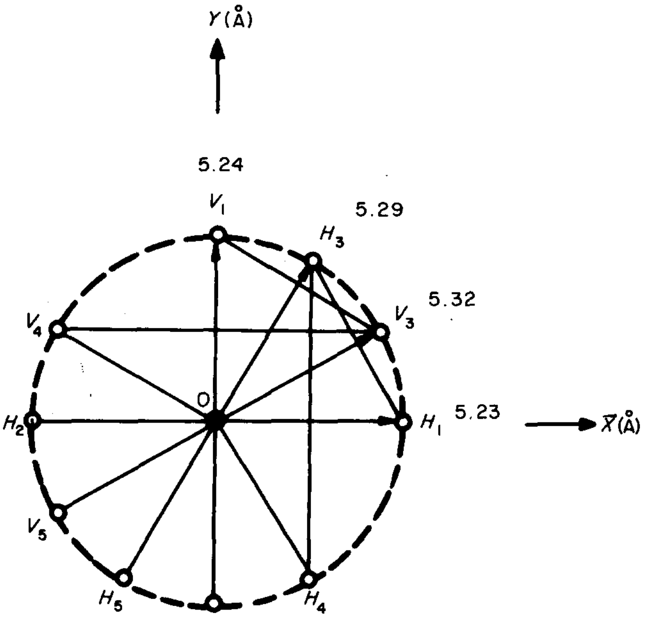

**Figure 5** Segment positions for all model configurations. The points $X_i$ ($X = H, V, i = 1$–$5$) indicate the position of the central isopropyl C atom of each segment in the *xy* plane of *Figure 3* (see also *Table 1*)

*Figure 5* summarizes the configurations studied. The respective positions of the central isopropyl C atom of each segment are now indicated in the *xy* plane of *Figure 3*, the segment $S_0$ being at the origin.

Two subsets of configurations were designed with segments centred in positions $X_i (X = H, V, i = 1$–$5)$ in the *xy* plane (see *Table 1* and *Figure 5*). Only the vectors $X_1$ and $X_3$ of each subset were adjustable; $X_2$, $X_4$ and $X_5$ are images. To arrive at the coordinates described in the legend of *Figure 5*, $X_1$ and $X_3$ were optimized so that the calculated scattering curves of the configurations $(0, X_1, X_2)$ and $(0, X_1, X_3)$ had their main peak maximum at $q = 1.25\,Å^{-1}$, which is the experimental value for PC-H. In this manner, first $X_1$ was adjusted using $(0, X_1, X_2)$, then $X_3$ was adjusted using $(0, X_1, X_3)$, thereby keeping the triangle $0, X_1, X_3$ symmetrical. *Figure 6* shows steps in the optimization of the vectors $\boldsymbol{H}_1$ and $\boldsymbol{H}_3$ and also gives an impression of the sensitivity of the peak maximum positions.

## RESULTS

*Figure 7* shows the scattering curves for all eight three-segment configurations calculated for PC-H in

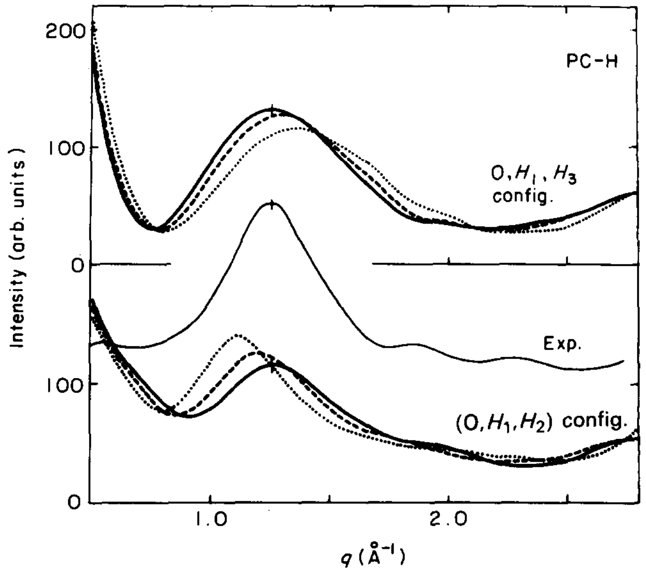

**Figure 6** Optimization of the vectors $\boldsymbol{H}_1$ using configuration $(0, H_1, H_2)$ and $\boldsymbol{H}_3$ using configuration $(0, H_1, H_3)$. $|\boldsymbol{H}_1|$: 5.23 (———), 5.52 (– – –), 6.02 Å (·····). $|\boldsymbol{H}_3|$: 5.29 (———), 5.12 (– – –), 4.78 Å (·····). The peak maxima of the full curves match the experimental peak position at $q = 1.25\,Å^{-1}$ for PC-H

**Table 1** Configurations of PC three-segment units (see also *Figure 5*). $X_i$ is the intersegmental distance $0$–$X_i$

| Configurations | Type | Specification | $X_i$ coordinates (Å) | $\lvert X_i\rvert$(Å) |
|---|---|---|---|---|
| 'Horizontal' (H) set | $(0, H_1, H_2)$ | Planar, $\boldsymbol{H}_2 = -\boldsymbol{H}_1$ | $H_1$ (−5.23; 0; 0) | 5.23 |
| | $(0, H_1, H_3)$ | Triangular | $H_2$ (5.23; 0; 0) | 5.23 |
| | $(0, H_3, H_4)$ | Triangular, $\boldsymbol{H}_4 = \boldsymbol{H}_1 - \boldsymbol{H}_3$ | $H_3$ (−2.616; 4.60; 0) | 5.29 |
| | $(0, H_3, H_5)$ | 'Diagonal' planar, $\boldsymbol{H}_5 = -\boldsymbol{H}_3$ | $H_4$ (−2.626; −4.60; 0) | 5.29 |
| | | | $H_5$ (2.616; −4.60; 0) | 5.29 |
| 'Vertical' (V) set | $(0, V_1, V_2)$ | Planar, $\boldsymbol{V}_2 = -\boldsymbol{V}_1$ | $V_1$ (0; 5.24; 0) | 5.24 |
| | $(0, V_1, V_3)$ | Triangular | $V_2$ (0; −5.24; 0) | 5.24 |
| | $(0, V_3, V_4)$ | Triangular, $\boldsymbol{V}_4 = \boldsymbol{V}_1 - \boldsymbol{V}_3$ | $V_3$ (−4.627; 2.62; 0) | 5.32 |
| | $(0, V_3, V_5)$ | 'Diagonal' planar, $\boldsymbol{V}_5 = -\boldsymbol{V}_3$ | $V_4$ (4.627; 2.62; 0) | 5.32 |
| | | | $V_5$ (4.6270; −2.62; 0) | 5.32 |

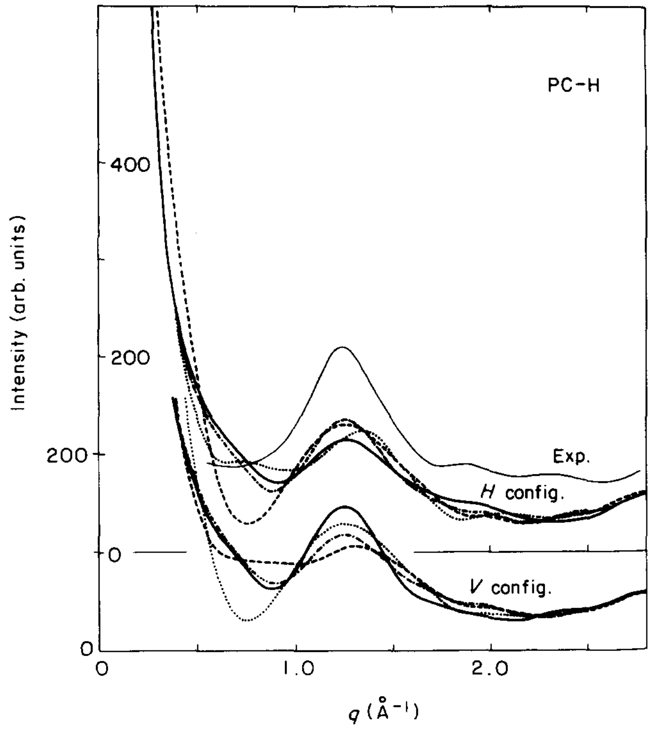

**Figure 7** Model scattering curves for all eight three-segment units in comparison with the experimental curve of PC-H

comparison with the experimental curve. There are interesting differences between the curves of different configurations. It seems, however, more realistic to study not the single configurations but the (equally weighted) average of all eight. This models an amorphous structure, where PC segments are arranged parallel without any directional preference. In *Figure 8*, these averaged scattering curves are seen in comparison with the experimental curves for all cases, PC-H, PC-PhD, PC-MeD and PC-D.

### *Corrections for the form factor peaks*

The form factor peaks obscure all structure information at $q < 1$ Å$^{-1}$, as is seen in *Figure 7*. In *Figure 8* they were, therefore, largely removed via subtraction of a form factor intensity approximated by an exponential form to arrive at a corrected intensity $I_c(q)$:

$$I_c(q) = I(q) - I_0(q)$$

$$I_0(q) = I(q=0)\exp(-q^2R^2/5)$$

where $R$ was adjusted so that $I_c(q)$ touches zero in the range $0.3 < q(\text{Å}^{-1}) < 0.5$. Procedures to correct for the form factors more carefully will be described in a later paper.

The calculated scattering intensities in *Figure 8* are the corrected intensities $I_c(q)$. These $I_c(q)$ give a good qualitative picture of the structural features also in the range $0.5 < q(\text{Å}^{-1}) < 1$.

### *Comparison of experimental and model scattering curves*

The agreement between the corrected model scattering curves and the experimental ones in *Figure 8* is quite satisfactory in the major points: the positions and shapes of the main peaks ($q = 1.25$ Å$^{-1}$ for PC-H) are matched well, with PC-PhD being a minor exception. The peak splitting in the curves of PC-MeD and PC-D is nicely recovered in both model curves. There is also some agreement as far as the smaller peaks are concerned, e.g. the fairly large peak in the curve of PC-PhD at 0.63 Å$^{-1}$ is also large in the model curve. Other features, however, are missing, most noticeably the large broad peak at 1.87 Å$^{-1}$ in the curve of PC-D. A detailed discussion of these minor points is not yet possible.

As a quantitative result, the average intersegmental distance in amorphous PC is found to be 5.27 Å$^{-1}$ (see *Figure 5*). In summary, the coincidence of experimental and model curves in *Figure 8* seems remarkable considering the parallel arrangement of these model units. The procedure used to construct the geometry of these units should have prevented the danger that the coincidence is forced and thus artificial: only four vectors were adjusted, and only the peak maximum position of the experimental curve of PC-H was used to adjust them.

*Figure 4* shows clearly that the scattering curves respond mainly to intermolecular order. The tendency to form parallel arrangements of segments could even spread over larger units than units of only three segments: the main peak in the curves for PC-H comes out broader in the calculated curve than in the experimental one (see *Figure 8*). The experimental peak form could be

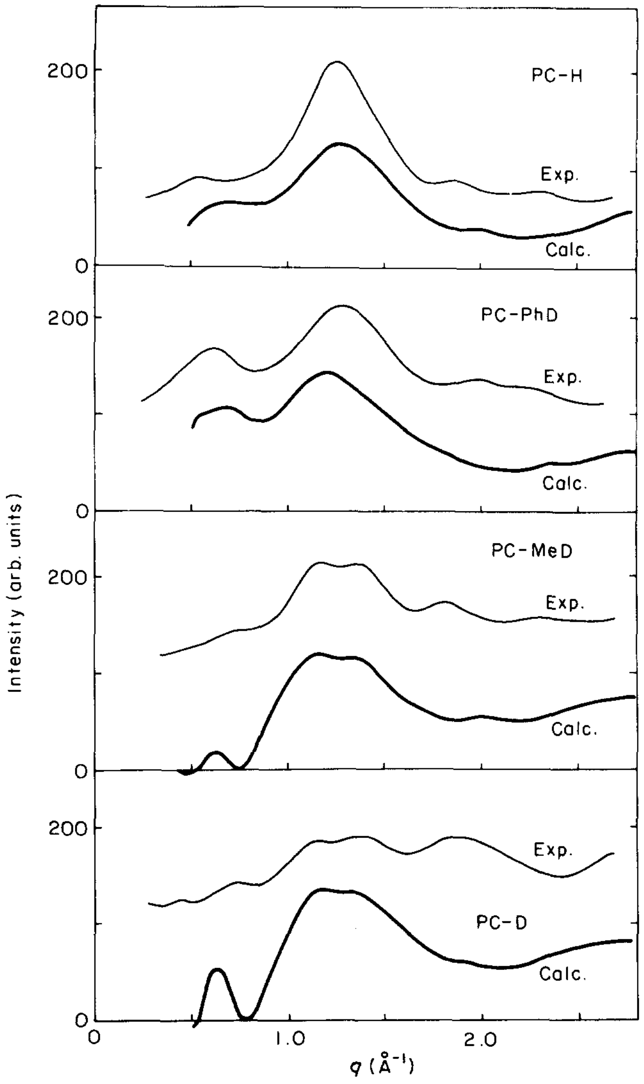

**Figure 8** Averaged and corrected model scattering curves for all isotopic isomers of PC in comparison with the experimental neutron scattering curves

reproduced if units of four or even more segments were taken as models. To test whether such units would actually have been better models was beyond our computer capacity. There is certainly an upper limit to the size of these ordered units, otherwise PC would show large fluctuations of the optical anisotropy, which is not the case[22].

We would like to emphasize that banana-like chains in *trans–trans* conformation were put into a parallel arrangement and that it is certainly impossible to build a crystalline structure with this type of a nonlinear chain.

At the same time our preliminary results of an extension of the present study indicate that with linear chains we cannot obtain the observed experimental curves of neutron scattering and that calculations of neutron scattering for chains that mutually cross each other at appropriate distances do not present scattering curves comparable with the experimental ones, mainly in the PC-D case. Therefore one may conclude that a large portion of roughly parallel short sequences exists in the bulk amorphous state, although the structure factor of the whole single chain reveals unperturbed dimensions[10].

The idea behind studies of this kind is to find eventually explanations for the different mechanical behaviour especially of glassy polymers. In the case of PC, it is important to know if this ductile polymer owes its outstanding mechanical properties to a special short-range order. The results reported above point in this direction: a tendency towards local parallelization of segments may be helpful in the unravelling processes during a shear yielding deformation. Definite conclusions, however, seem premature.

## CONCLUSIONS

The study yields the result that the main features of the low wide-angle neutron scattering curves of amorphous polycarbonate are reproduced by curves calculated from highly ordered units represented by different configurations of three parallel-ordered polycarbonate segments—each segment consisting of two monomer units. With a definite set of configurational coordinates characterizing the intermolecular ordering we obtained for differently deuterated polycarbonates the main features of the neutron scattering curves (the splitting of the maximum at 1.25 $Å^{-1}$ for PC-D and DC-MeD) by changing only the appropriate scattering factors.

The intra- and intermolecular segment configurations in these units, however, differ from those in crystalline polycarbonate: nonlinear (banana-like) segments in *trans–trans* conformation were used and the intermolecular distances are different from those in the crystalline state, where the chains have to be stretched out. The analysis of the scattering curves of partially crystallized PC is on the way.

## ACKNOWLEDGEMENT

The neutron scattering experiments were carried out at the Institut Laue–Langevin, Grenoble, France.

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