Infrared Spectra and Crystallinity. Part III. Poly(ethylene Glycol).*

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Infrared spectra of poly(ethylene glycol) in the molten and the crystalline state are reported; crystalline samples oriented by rolling were examined with polarised radiation. The spectra indicate an essentially *gauche* configuration of the $O{\cdot}[CH_2]_2{\cdot}O$ portion of the polymer chain and all the main absorptions are assigned by comparison with *gauche* ethylene dichloride. The observed dichroisms support the assignments and also show that the chain is oriented obliquely to the direction of stretch. This orientation is consistent with the highly crumpled helical structure suggested by *X*-ray measurement.

On melting, there is a loss of sharpness of some bands, but the $O{\cdot}[CH_2]_2{\cdot}O$ grouping largely retains its *gauche* configuration; the main rotation is probably about the CO bonds.

No previous spectroscopic studies of poly(ethylene glycol) are known, but *X*-ray diffraction measurements (Barnes and Ross, *J. Amer. Chem. Soc.*, 1936, **58**, 1129) have shown that it has the same crystal structure as poly(ethylene oxide) (Sauter, *Z. phys. Chem.*, 1933, *B*, **21**, 161; Fuller, *Rubber Chem. and Tech.*, 1941, **14**, 323). The repeating unit is $[(CH_2)_2O]_p$ and the dimensions of the unit cell show that the chain has a very crumpled configuration.

In this paper infrared spectra of the polymer in the amorphous and the crystalline state are used to study the configuration of the chain. In the absence of a complete *X*-ray analysis, we attempt to establish the configuration and arrangement of the polymer in the crystal lattice, using oriented samples and polarised radiation.

EXPERIMENTAL

Samples of poly(ethylene glycol) of different origins and molecular weights were examined; they differed mainly in the degree of crystallinity shown at room temperature. A sample of $M = 6000$ showed the maximum crystallinity and this was used for the spectra in Figs. 1 and 2. It was examined several times under each of the following conditions: (*a*) melted and allowed to recrystallise between rock-salt plates; (*b*) dispersed in potassium chloride by the pressed-disc technique (Ford and Wilkinson, *J. Sci. Instr.*, 1954, **31**, 338); (*c*) rolled between sheets of silver chloride during solidification to obtain oriented, crystalline samples. Samples (*a*) and (*b*) were examined crystalline, amorphous (at 80°), and after being recrystallised.

The spectra of the polymer which had been allowed to crystallise between rock-salt plates (shown as a dot-dash line in Fig. 1) showed considerable differences from those measured in potassium chloride (full line in Fig. 1) or between silver chloride plates. The crystalline spectra between rock-salt plates showed only weak shoulders at 1345 and 960 cm.$^{-1}$, in contrast to the strong bands observed at these frequencies in other spectra.

Spectra measured with the rock-salt plates at an angle to the beam showed these absorptions more intensely; it follows that they had been weakened by orientation normal to the plane of the sample. Similar orientation also occurred with samples rolled between silver chloride plates; in favourable cases, however, a high degree of orientation was achieved along the direction of rolling.

No difficulty was experienced when heating the potassium chloride discs to melt the polymer (Fig. 1); recrystallisation was slower than normal but showed the same degree of crystallinity as the original discs (Part II, *loc. cit.*). The potassium chloride pressed discs were made in a die designed by Ford and Wilkinson (*loc. cit.*).

Polarised measurements were made with a five-plate silver chloride transmission polariser placed immediately before the entrance slit, double-beam operation being used. The efficiency of polarisation was such that a pair of identical crossed polarisers transmitted only 5% of the radiation transmitted by the same polarisers when parallel to each other.

All measurements were made with a Grubb-Parsons S.3/DB1 double-beam spectrometer

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* Part II, *J.*, 1955, 2431.

with sodium chloride prism. Re-examination of the 2900-cm.$^{-1}$ region with a lithium fluoride prism failed to resolve the CH stretching region.

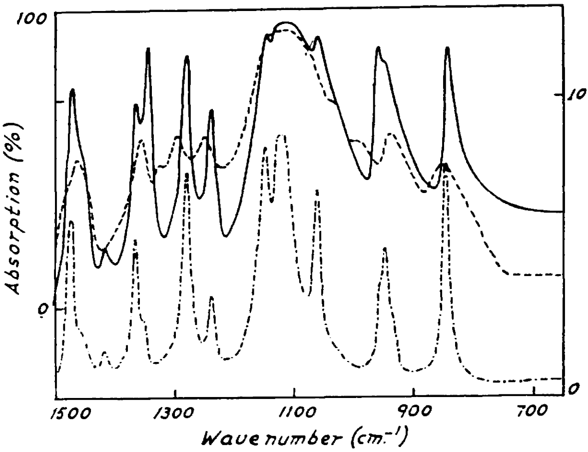

FIG. 1.

Poly(ethylene glycol) :

———— *Crystalline in* KCl *disc.*

– – – – – – *Molten in* KCl *disc.*

—·—·— *Crystalline between* NaCl *plates (displaced downward).*

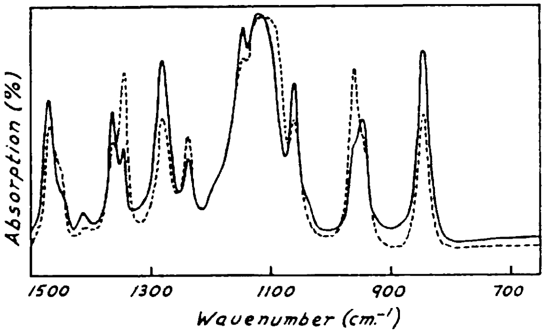

FIG. 2.

Oriented, crystalline poly(ethylene glycol) :

———— *With perpendicularly polarised radiation.*

– – – – – *With parallel polarised radiation.*

DISCUSSION

X-Ray studies (Sauter, *loc. cit.*; Fuller, *loc. cit.*) show that crystalline poly(ethylene glycol) has a very crumpled chain in which nine repeating units occur in a fibre period of 19·5 Å. Although this suggests a helical structure, it is insufficient to decide the configuration and we will try to establish this from the infrared spectrum of the crystalline polymer. Since the CH_2 rocking modes in the 700—1000-cm.$^{-1}$ region are particularly sensitive to configuration (Brown and Sheppard, *Trans. Faraday Soc.*, 1952, **48**, 128; Brown, Sheppard, and Simpson, *Phil. Trans.*, 1954, *A*, **247**, 35) we use these to decide the configuration of the $O{\cdot}[CH_2]_2{\cdot}O$ portion of the chain.

Although it is not strictly permissible to apply the selection rules for an $X{\cdot}[CH_2]_2{\cdot}X$ molecule to a polymer, vibrations which are formally forbidden in the smaller molecule should still be relatively weak in the less symmetrical polymer. If the configuration of this group were *trans* (symmetry C_{2h}) there should be one strong rocking absorption (A_u) at about 773 cm.$^{-1}$ and a weak absorption at about 992 cm.$^{-1}$ (B_g, formally forbidden). A *gauche* configuration (C_2) should show two strong bands at about 880 cm.$^{-1}$ (B) and 944 cm.$^{-1}$ (A). The frequencies quoted are those of ethylene dichloride (Brown and Sheppard, *loc. cit.*); this molecule is the closest model which has been analysed in sufficient detail. Some frequency shifts would be expected between the dihalide and the poly(ethylene glycol), but these cannot be predicted; mass effects alone should raise the frequencies somewhat (cf. ethylene dibromide frequencies).

The two strong absorptions observed in the crystalline polymer at 844 and 947, 960 cm.$^{-1}$ (the origin of the doublet will be discussed later) are in better agreement with a *gauche*- than with a *trans*-configuration. We therefore provisionally assign the remainder of the bands of the polymer on the basis of the frequencies of *gauche* ethylene dichloride (see Table) and check the consistency of these assignments by the relative intensities and dichroic behaviour of the absorption bands.

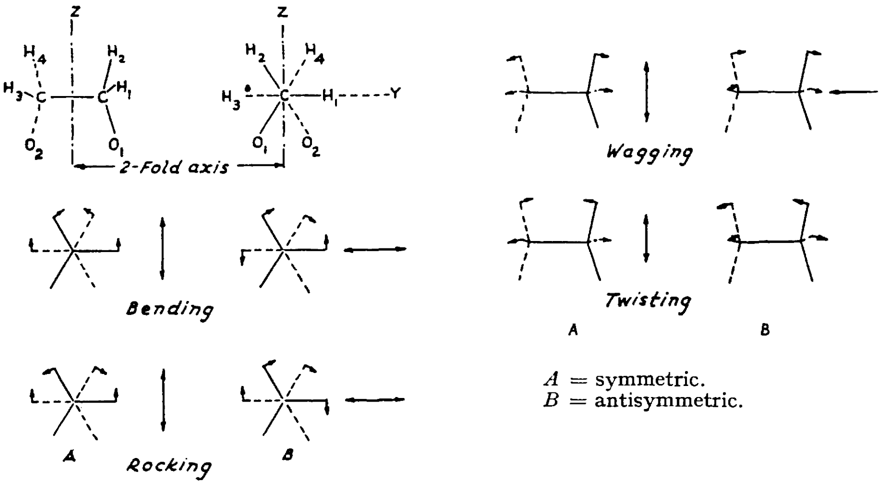

FIG. 3. *Hydrogen deformation modes of gauche* O·[CH$_2$]$_2$·O *group*; ↔ *indicates direction of change of dipoles.*

A = symmetric.
B = antisymmetric.

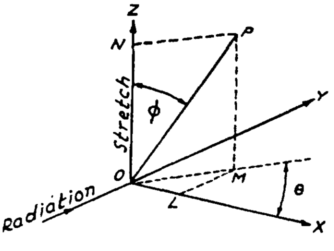

FIG. 4. *Orientation of absorber in singly-oriented specimen.*

The relative intensities of the bands are in good agreement with those of ethylene dichloride except that the twisting modes are stronger. From the movement of the hydrogen atoms only (Fig. 3) we would expect the twisting modes to be inactive; in the dihalide the A mode is only observed as a Raman shift and the B mode as a weak infrared absorption. However, this is an over-simplified picture and the twisting modes also involve skeletal movement and interaction with skeletal vibrations. Any skeletal interactions or relaxation of symmetry in the polymer would therefore increase the intensities of these bands.

All vibrations of species A must have dipole changes parallel to the two-fold axis, from symmetry considerations (see Table 55, Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand Co., N.Y., 1945). Vibrations of species B must have dipole changes in the plane perpendicular to the axis, but it is not possible to decide the direction by symmetry.

Considering the movements of the hydrogen atoms alone, the probable directions of dipole changes of the B vibrations are as shown by double-headed arrows in Fig. 3; the dipole vectors for the A and B twisting modes will be particularly sensitive to interaction with other modes. The assignments can therefore be tested by checking whether vibrations which have the same dipole vector have the same dichroic behaviour. All A deformation modes have parallel dichroism and all B modes have perpendicular dichroism; this is consistent with the provisional assignments.

Each of the doublets at 947, 960, and at 1344, 1362 cm.$^{-1}$ consists of two components of strong, but opposite dichroism; the dichroisms of the components are markedly higher than of the single bands. The splitting of these *A* fundamentals is attributed to coupling between vibrations in the crystalline state. A similar explanation has been advanced for the 720-cm.$^{-1}$ doublet of crystalline polyethylene (Stein and Sutherland, *J. Chem. Phys.*, 1954, **22**, 1993; Krimm, *ibid.*, p. 567). From the model of the helix which we propose later, the coupling is probably between repeating units in the helix (Higgs, *Proc. Roy. Soc.*, 1953, *A*, **220**, 472) rather than between helices in the crystal lattice. Either explanation would result in strictly orthogonal vibrations and explain why these components show higher dichroisms than those of the other absorption bands.

Assignment	C_2	Dipole change (Fig. 3)	Ethylene dichloride	Poly(ethylene glycol)	Dichroism	
$(CH_2)_2$ Bending	*A*	*Z*	1433 (s)	1455 (sh)	∥	
	B	*Y*	1429 (R)	1470 (s)	⊥	
$(CH_2)_2$ Rocking	*A*	*Z*	944 (s)	947 (sh)	⊥	} ∥
				960 (s)	∥	
	B	*Y*	880 (s)	844 (s)	⊥	
$(CH_2)_2$ Wagging	*A*	*Z*	1312 (s)	1362 (w)	⊥	} ∥
				1344 (s)	∥	
	B	*X*	1286 (s)	1280 (s)	⊥	
$(CH_2)_2$ Twisting	*A*	(*Z*)	1207 (R)	1237 (m)	∥	
	B	?	1143 (w)	1145 (s)	⊥	
C–C Stretching	*A*	(*Z*)	1032 (m)	*ca.* 1100 (sh)	∥	
C–O–C Stretching	Antisym.	—	—	1120 (vs)	⊥	
	Sym.	—	—	*ca.* 1061 (m)	⊥	

[Intensities are shown as very strong (vs), strong (s), medium (m), or weak (w); shoulders are shown as (sh). R indicates that the vibration is only observed in the Raman effect.]

Although some interaction of skeletal stretching vibrations will occur, the crumpled or helical configuration will make such coupling less extensive than in planar long-chain compounds (Brown, Sheppard, and Simpson, *loc. cit.*) and we consider it possible to neglect long-range coupling. The main coupling will probably occur between the CO stretching vibrations. In dimethyl ether (Herzberg, *op. cit.*, p. 353) there is an anti-symmetric mode at about 1120 cm.$^{-1}$ and a stronger symmetric mode at about 940 cm.$^{-1}$. The former band has been observed in a large number of ethers at about this frequency (Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 1954, p. 101), but the symmetric mode has not generally been characterised. The extent of coupling will be very dependent upon the COC angle and should be reduced by the greater effective mass of the polymer chain.

The type and dichroism of the 950-cm.$^{-1}$ doublet, together with the general consistency of the deformation assignments, prevent our re-assigning this doublet to a CO stretching mode. We tentatively assign the sharp perpendicular 1061-cm.$^{-1}$ absorption of poly-(ethylene glycol) to a symmetric COC stretching mode, and the parallel shoulder at about 1100 cm.$^{-1}$ to a CC stretching mode (cf. 1032 cm.$^{-1}$ for *gauche* ethylene dichloride); the parallel dichroism of the latter is consistent with its assignment to an *A* symmetry species.

Highly oriented samples of the crystalline polymer between silver chloride plates showed no signs of double orientation (by measurement of the spectrum of samples inclined to the beam); this would be expected even if the crystals were doubly-oriented since the chain appears to have an odd-number screw-axis. We will therefore assume, at least as an approximation, single orientation, *i.e.*, the various absorbing groups are oriented with respect to the fibre axis (direction of rolling) but randomly distributed about this axis.

Consider the vector of dipole change associated with a given vibrational mode OP in the orthogonal reference system shown in Fig. 4. The direction of radiation is OY, normal to the fibre axis. Radiation polarised with the electric vector parallel to the fibre axis OZ will be absorbed to the same extent whatever the angle θ; the absorption will be proportional to $(OP \cos \phi)^2$. However, perpendicularly polarised radiation will be absorbed by an amount proportional to $(OP . \sin \phi . \cos \theta)^2$. As the vectors are randomly distributed with respect to θ, the ratio of the total components absorbing parallel and perpendicular radiation (the dichroic ratio) is obtained by integrating with respect to θ within the limits 0 and $\pi/2$.

The dichroic ratio is therefore given by:

$$\frac{A_{\parallel}}{A_{\perp}} = \frac{\int_0^{\pi/2} (OP \, . \cos \phi)^2 \, . \, d\theta}{\int_0^{\pi/2} (OP \, . \sin \phi \, . \cos \theta)^2 \, . \, d\theta} = \frac{2}{\tan^2 \phi}$$

The same result is obtained, but by a different method, for a helical molecule (Eqn. 10, Higgs, *loc. cit.*). Qualitatively, this means that the observed dichroic ratio must exceed 2·0 before we can deduce that the vibration has a change of dipole inclined at less than 45° to the direction of orientation, *i.e.*, mainly parallel.

Now the mean dichroic ratio of the symmetrical (*A*) wagging, twisting, and rocking CH_2 modes is about 1·6; this means that the two-fold symmetry axis of the $O{\cdot}[CH_2]_2{\cdot}O$ group is inclined at about 48° to the fibre axis. From the dichroic ratios of the *B* rocking mode (about 0·4) and of the *B* wagging mode (about 0·5) the *X* and *Y* axes of this group must be inclined at about 65° to the fibre axis. While these figures can only be regarded as approximate, they provide a consistent picture of the $O{\cdot}[CH_2]_2{\cdot}O$ group lying obliquely with the two-fold axis at about 48° and the CC bond at about 65° to the fibre axis. The two COC vibrations have perpendicular dichroisms, from which it follows that both the CC direction and the bisectrix are at about 70° to the fibre axis. The oblique orientation of the methylene and COC groups is consistent with a helical configuration. The unit cell (Sauter, *loc. cit.*) contains four chains within a unit cell of 12 × 9·5 Å, and nine polymer repeating units within a fibre period of 19·5 Å.

The inclination of the C_2 axis with respect to the direction of stretch, combined with the odd number of repeating units in the fibre period, means that the chains have an " up " or " down " sense. The unit cell will therefore probably contain two chains which are upside down with respect to the other two (Bunn, " Chemical Crystallography," Oxford Univ. Press, 1946, p. 321).

By use of Stuart-type atomic models (*Z. phys. Chem.*, 1934, *B*, **27**, 350) and the configuration and orientations deduced above, the best model of the chain which we can construct is a helix with a three-fold screw axis (Fig. 5). Nine polymer repeating units of this model occupy the fibre period of 19·5 Å found by *X*-ray diffraction measurements.

Molten poly(ethylene glycol) has a rather different spectrum from that of the crystalline material (Fig. 1) but the differences are not as marked as for the polyesters (Part I, *J.*, 1955, 2428) or dicarboxylic acids (Part II, *loc. cit.*). There is considerable broadening (and consequent reduction of apparent intensity) of most of the absorptions, but none of the strong bands completely disappears as in the polyesters or dicarboxylic acids. On the other hand, no new strong bands appear as in the *n*-paraffins (Brown, Sheppard, and Simpson, *loc. cit.*) or in ethylene dihalides (Brown and Sheppard, *loc. cit.*).

The configuration of the $O{\cdot}[CH_2]_2{\cdot}O$ group is therefore substantially the same in the molten state as in the crystalline, *i.e.*, a *gauche* form; in this it is similar to crystalline ethylene chlorohydrin (Mizushima, Shimanouchi, Miyazawa, Abe, and Yasumi, *J. Chem. Phys.*, 1951, **19**, 1477) and a number of other ethylene glycol derivatives (Davison and Corish, unpublished work). Since some rotation must occur on melting it is suggested that this occurs mainly at the CO bonds which have lower barriers to rotation than the CC bonds. The second-order effect of such rotation would account for some of the broadening of the methylene deformation absorptions, which is rather more than would be expected from a a change of state alone.

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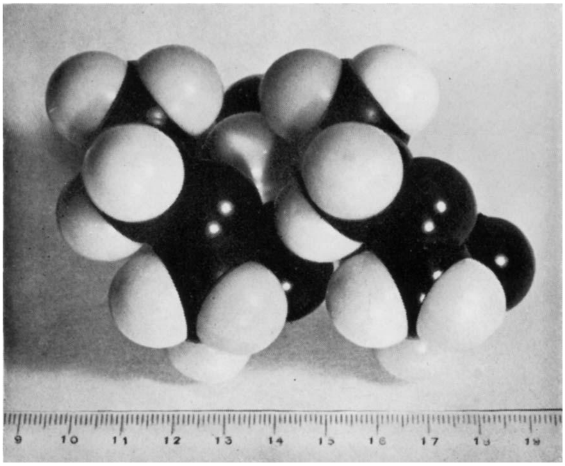
FIG. 5. *Poly*(*ethylene glycol*).



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