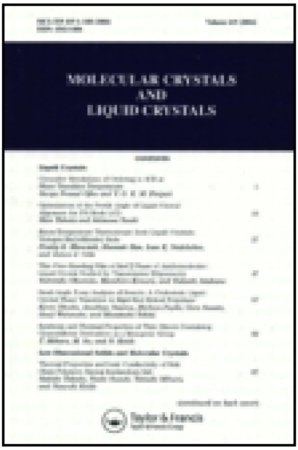

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Poly-γ-Benzyl-L-Glutamate: Order Parameter, Oriented Gel, and Novel Derivatives

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POLY-γ-BENZYL-L-GLUTAMATE: ORDER PARAMETER, ORIENTED GEL, AND NOVEL DERIVATIVES

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Abstract Deuterium NMR is used to indicate the degree of ordering of the PBLG helix axis in lyotropic phases. Sources of difficulty when comparisons are made with theory are emphasized. The preparation of magnetically oriented gels of PBLG in benzyl alcohol is described. Delineation of the phase boundaries with NMR probes is a convenient way to monitor the gelation process. The synthesis and properties of PBLG having the benzyl ester exchanged for oligomers of ethylene glycol is presented.

INTRODUCTION

Synthesized almost 50 years ago at the Courtaulds Ltd. Research Laboratory in Maidenhead, England, in an effort to develop a man-made polymer fiber that would be competitive with natural fibers such as wool, poly-γ-benzyl-L-glutamate (PBLG) was the first synthetic polymer to exhibit a liquid crystalline phase.[1] In spite of its age, PBLG contiunes to serve as the prototypical example when new aspects of liquid crystallinity in polymers are demonstrated. Its versatility and relative ease of utilization are due in part to the inherent stability of the α-helical conformation that the polypeptide backbone adopts. PBLG's solubility in a large number of common organic solvents also facilitates investigations. It forms a lyotropic mesophase when its concentration Φ exceeds a critical value Φ_A.[2,4] (Φ_A is dependent on the degree of polymerization, i.e., it depends on the aspect ratio of the rod-like macromolecule.)[3] Solutions exhibit a two-phase regime $\Phi_A < \Phi < \Phi_B$

and above Φ_B the equilibrium texture in the homogeneous mesophase is cholesteric: the α-helix is a chiral molecule.[4]

Herein we consider three aspects of PBLG liquid crystals: 1. The order parameter of the helix axis in the (induced nematic) mesophase of PBLG in a magnetic field; 2. The nature of the gel phase exhibited by PBLG in benzyl alcohol when gelation occurs in a magnetic field; 3. New derivatives of PBLG produced by exchanging the benzyl ester terminus of its sidechain with oligomers of mono-methoxy ethylene glycols: Poly-(ethylene glycol)$_n$-L-glutamate (P-nEGLG), where n = 1, 2, 3, and 4.

RESULTS AND DISCUSSION

1. HELIX ORDER PARAMETER

Deuterium NMR in oriented uniaxial liquid crystals is a powerful and direct method for investigating molecular ordering. The deuterium NMR spectrum of a labelled molecule exhibits a doublet for each type of deuteron. This quadrupolar splitting is a result of the anisotropic molecular motion in the liquid crystal. In contrast with isotropic liquids wherein a single resonance would be observed, the electric field gradient (efg) at the deuterium nulceus is not averaged to zero in liquid crystalline fluids and the deuterium quadrupole moment couples with this residual field gradient lifting the degeneracy of the two Zeeman transtions ($m = -1 \rightarrow 0$; $m = 0 \rightarrow +1$) of this spin $I = 1$ nucleus. The frequency difference between the resulting doublet resonances, i.e., the quadrupolar splitting $\Delta\nu$, is a direct measure of the motional anisotropy of the vector along the principal component of the efg tensor. To a good approximation this vector is coincident with the covalent bond to the deuterium atom, e.g., the C-D, N-D, etc. bonds in organic molecules. (Reference[5] gives a review of the deuterium NMR techniques.)

The assumption of an axially symmetric efg tensor with the principal value of the quadrupolar interaction directed along the bond yields a simple relationship between the observed quadrupolar splitting and the bond orientational order parameter:

$$\Delta\nu = \frac{3}{2}\frac{e^2qQ}{h} S_{bond} \tag{1}$$

The quadrupolar interaction constant $q_{bond} = e^2qQ/h$; $S_{bond} = \; < P_2(\cos\beta) >$, where β is the angle between the optic axis of the sample (the nematic director) and the bond. The brackets < > signify an average over molecular reorientational diffusion.

Deuterium Labelled PBLG

In the current study, we have exchanged the amide hydrogen in the PBLG helix backbone with deuterium using trifluoroacetic acid-d_1 . As we are interested in determining the order parameter of the helix axis, the quadrupolar interaction tensor must be transformed from the N-D bond to the helix axis. However, as η, the asymmetry parameter of the N-D efg tensor in the amide is not negligible, the following transformation is required:

$$q_{hh} = q_{11}\left(\cos^2\theta - \frac{1}{2}(1-\eta)\sin^2\theta\cos^2\varphi - \frac{1}{2}(1+\eta)\sin^2\theta\sin^2\varphi\right) \tag{2}$$

The 1,2,3-axis system is defined in reference 6. The helix order parameter can be determined with

$$S_{helix} = \Delta\nu/\frac{3}{2}q_{hh} \tag{3}$$

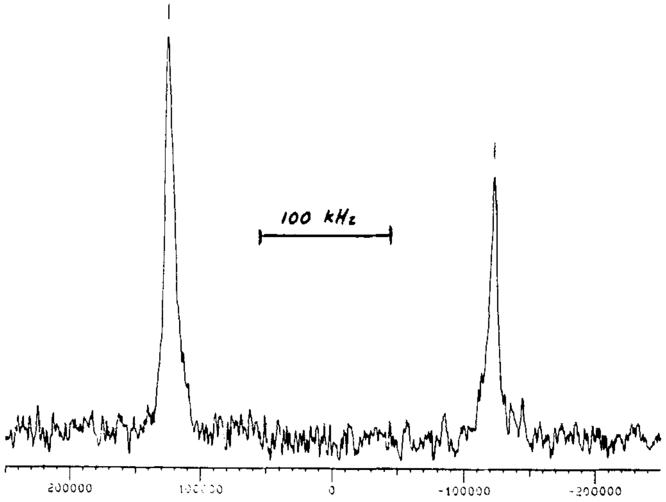


Fig. 1 Deuterium NMR spectrum of PBLG-d_1 in solution

Figure 1 shows the deuterium NMR spectrum of PBLG-d_1 (MW = 190,000) dissolved (Φ = 0.2) in chloroform at 300 K. The observed quadrupolar splitting is 248.0 kHz. In order to extract S_{helix} values for q_{hh} and η are required. In 1970 Chapman, Campbell and McLauchlan[6] suggested a value of q_{hh} = 192.9 kHz on the basis of single crystal studies of deuteriated urea: (q_{11} = 210.8 and η = 0.139 with eqn (2)). These values in conjunction with θ = 14.1°, φ = 0° were recently used by Yamazaki and Abe[7] to obtain S_{helix} in PBLG-d_1 liquid crystals. Moreover, these researchers contrasted their observations with various theoretical predictions of the φ-dependence of the helix order parameter. In all instances, the experimental S_{helix} is significantly smaller than predicted values. There is always the usual disclaimer: a polydisperse MW distribution for PBLG (i.e., a mixture containing a variety of axial ratios) prevents rigorous comparisons of experiment with theory. However, even though this is valid concern there are other considerations that could influence the prescription for deriving S_{helix}.

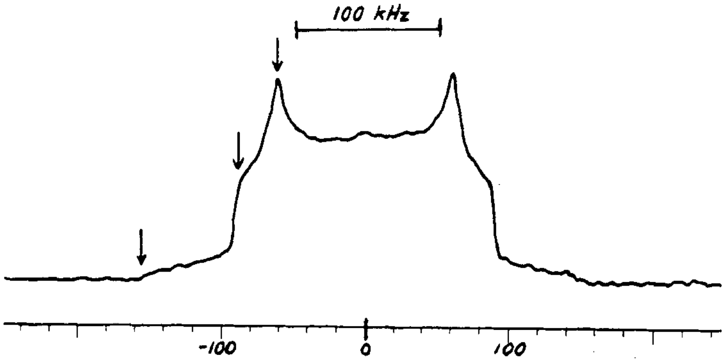


Fig. 2 Solid state deuterium NMR spectrum of PBLG-d_1

Is it appropriate to use the urea single crystal data to compute q_{hh} ? This question can be addressed directly. Figure 2 shows the solid state deuterium NMR spectrum for a random fibrous sample of PBLG-d_1 . The discontinuities in the intensity directly yield the diagonal elements of the quadrupolar interaction tensor and the asymmetry parameter: We observe from the spectrum values of 201.9, -81.3 and -120.4 kHz for q_{11}, q_{22} and q_{33} respectively; η = 0.194. This translates with eqn (2) into q_{hh} = 185.1 kHz. In other words, we may anticipate a 4 - 5% increase in in the observed values for S_{helix} over that reported by Yamazaki and Abe with our experimental efg tensor of PBLG-d_1. From the data in Figure 1 we find S_{helix} = 0.89 for the q_{hh} value above. It is also possible to check the transformation (θ, φ) by observing uniaxial solid films of labelled PBLG with the magnetic field parallel to the helix axis. This work is in progress.

Concluding Remarks

Is it conceivable, for example, that dynamic helix flexing could be averaging q_{hh} further and, if properly accounted for, would lead to larger values of S_{helix} ? Such motion would necessitate a modification of the transformation of the efg tensor from the N-D bond to the helix axis:

$$q_{hh} = q_{11} \left[< \cos^2\theta > - \frac{1}{2}(1 - \eta) < \sin^2\theta \cos^2\varphi > - \frac{1}{2}(1 + \eta) < \sin^2\theta \sin^2\varphi > \right] \tag{4}$$

Here the brackets symbolize an average over hypothetical undulations of the helix. How might such averaging be confirmed experimentally? Clearly such motion would be damped to insignificance in a solid state consisting of close-packed helices, and the experiment on uniaxial solids suggested above would not detect a reduced q_{hh}. Nevertheless, it would be desirable to examine highly oriented, isolated PBLG helices in a solvent to resolve this and remove the uncertainties in S_{helix} determined by deuterium NMR. Perhaps the oriented gel phase described in the next section is a reasonable starting point to experimentally quantify the extent of any helix flexing in PBLG.

Having just hypothesized a possible problem with the deuterium NMR experiment, we are very doubtful that such significant corrections to the experimental q_{ii} and thus to the derivation of S_{helix} will be found. And, it is also doubtful that the large discrepancy between theory and experiment reported by Yamazaki and Abe[7] can be attributed to polydispersity. Either there are fundamental problems with theory or the observed $\Delta\nu$ is being further averaged by another mode of motion intrinsic to the PBLG mesophase. Theoretical values of S_{helix}[8,9] are derived from a thermodynamic analysis of the hard rod system. They do not include possible dynamical effects such as director fluctuations (which lead via averaging similar to that expressed in eqn. (4) to lowering of the observed S_{helix}). Warner[10] has emphasized that this contribution to the apparent order parameter accounts for the discrepancy between experiment and theory in thermotropic mesogens. In all probability these modes are operative in the PBLG liquid crystal lowering measured S_{helix} and preventing a quantitative comparison with thermodynamic predictions. Director fluctuactions will always influence observations on bulk samples and must be properly accounted for when interpretating order parameters.

2. ORIENTED PBLG GELS

Gelation in macromolecular systems continues to challenge theorists and experimentalists. One central problem in non-covalently crosslinked gels is the nature of the cohesion between polymer chains that leads to a 3-dimensional gel network. A striking characteristic of many of these networks is that they can be reversably transformed (via temperature and/or solvent) from a gel to a solution consisting of isolated macromolecules. Frequently micro-crystalline "crosslinks" are invoked to explain this revesible phase transformation. Herein we describe a procedure for forming an equilibrium uniaxial gel. The high symmetry during the course of the phase transition may make uniaxial gels more amenable to detailed experimental investigation aimed at elucidating the gelation mechanism.

PBLG gels have been studied for a number of years; Reference 11 gives a recent entry to the literature. Early on in the course of studying PBLG liquid crystals it was found that the cholesteric twist (helicoidal supramolecular structure) could be unwound in an external magnetic field[12] and that oriented uniaxial films could be fabricating by evaporating PBLG solutions in a field.[13,14] The magnetic orientation mechanism has been briefly reviewed recently by Samulski.[15] Prompted by work on PBLG-benzyl alcohol (BA) gels by Hill and Donald,[16] we decided to explore the feasibility of preparing a uniaxial gel by cooling the magnetically aligned liquid crystal phase of PBLG into the gel state.

Deuterium NMR Probes

In this study, perdeuteriated benzene (C_6D_6) is dissovled in the PBLG-BA solutions (1%/wt.), and it average orientational order is monitored with deuterium NMR. The C_6 symmetry of the probe along with the assumption of an axially symmetric electric field gradient (tensor with principal values along the $C - D$ bond), modifies the simple relationship given in eqn. (1) for the observed quadrupolar splitting by a factor of 1/2:

$$\Delta\nu = \frac{3}{2}\frac{e^2qQ}{h}\frac{1}{2}S \tag{5}$$

S is orientational order parameter of the C_6D_6 symmetry axis. As indicated in the previous section the brackets < > signify an average over probe molecular reorientational diffusion. (The factor $\frac{1}{2}$ indicates that the symmetry axis of the quadrupolar interaction, i.e., the $C - D$ bond vector, is perpendicular to the C_6 -axis.) The quadrupolar coupling constant e^2qQ/h = 196 kHz.[17] Hence a measure of $\Delta\nu$ is a measure of the probe order parameter, which in turn, is proportional to the average orientational order the probe samples in the anisotropic fluid.

In the PBLG phases $\Delta\nu$ is an indirect indicator or the orientational order of the PBLG helices. The probe gets its net anisotropic orientation via collisions with the aligned PBLG helices. (The major component of the solution, the solvent BA, is similarly oriented.[18,19]) Relating the observed $\Delta\nu$ of the probe to a quantitative measure of the PBLG orientational order itself is not really feasible. The former involves a complex average over sites with very different degrees of orientational order. That is, one is faced with a chemical exchange of the probe between essentially isotropic environments removed from the PBLG and anisotropic sites proximate to the polymer. This serious difficulty does not invalidate the probe technique, however. In general, the behavior

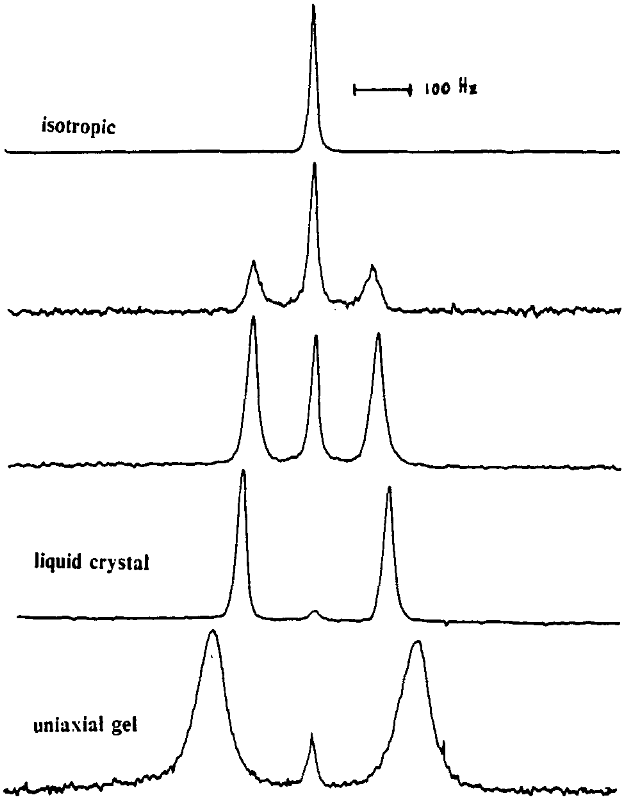


Fig. 3 Deuterium NMR spectrum of benzene-d_6 probe (1%)

of Δν observed with guest probes reflects the average environment of the host[5] and we exploit this finding to monitor the PBLG-BA system via the benzene probe.

Figure 3 shows representative deuterium NMR spectra of C_6D_6 (1%) dissolved in PBLG-BA solutions. At elevated temperature ($T > 350K$), a single resonance is observed: the sample is isotropic. The existence of the isotropic phase was confirmed by optical polarizied light microscopy at this temperature. On lowering the temperature, a quadrupolar splitting appears, increasing in intensity (at the expense of the isotropic resonance). At 320K the entire sample is essentially a homogeneous, uniformly aligned liquid crystal. (The small residual isotropic resonance only accounts for 1% of the probe and is attributed to the fact that the concentration of PBLG in the solution is not quite above the critical concentration (Φ_B) for liquid crystal formation.) If the temperature is further decreased $\Delta\nu$ increases reflecting improved PBLG orientational ordering. At 308K the gel forms (on cooling), and there is an abrupt change in the character of the probe NMR spectrum. The linewidth of the resonance increases and there is a discontinuous increase in $\Delta\nu$ at the mesophase-gel transition.

The gel spectrum exhibits the $(\frac{3}{2}\cos^2\Omega - \frac{1}{2})$ dependence expected for a dynamically averaged uniaxial system. This is also consonant with the line width of the C_6D_6 probe found in an isotropic gel (formed in the absence of a field). These observations suggest that the increased line width in the gel is indicative of a superposition of (uniaxial) environments with rapid averaging of probe interactions within each but encumbered probe communication between environments.

The probe NMR observations are sumarized in Figure 4 where $\Delta\nu$ and the linewidths are ploted versus the temperature. A marked hysteresis is observed for the mesophase-gel transition. This appears to reflect previously reported observations: there is evidence that more than one gel phase may be induced in the PBLG-BA system depending on the thermal history of the sample.[20] In Figure 5 the relative amounts of isotropic (singlet) and anisotropic (quadrupolar doublet) signal is shown versus the temperature. This is a convenient, quantitative indicator of the wide biphasic regime known to occur in the PBLG-BA solutions. The hysteresis between heating and cooling is evident in the figure and the temperature range of the homogeneous mesophase ($\Phi > \Phi_B$ with no isotropic singlet) between the biphase ($\Phi_A < \Phi < \Phi_B$) and the gel is indicated on the figure.

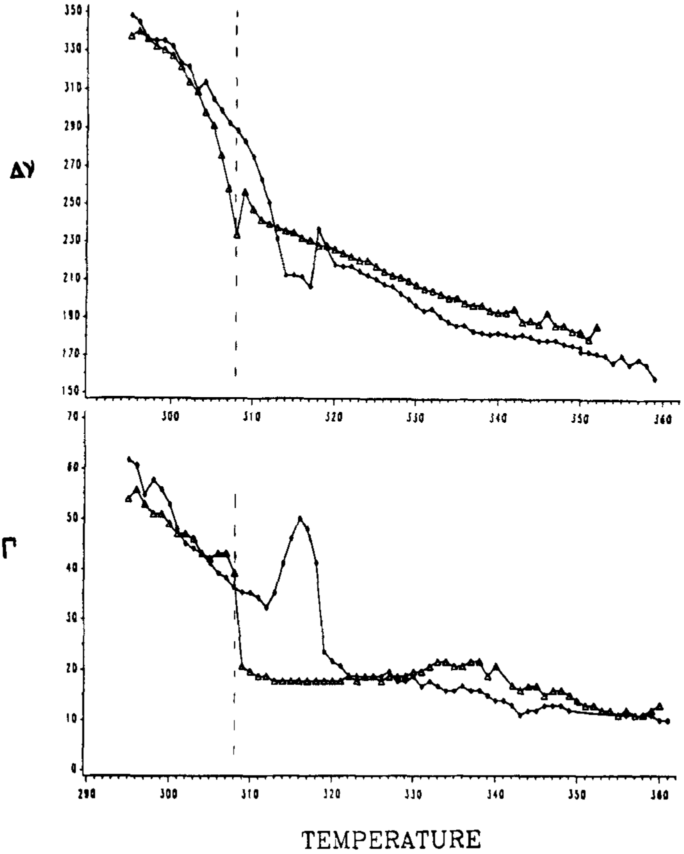


Fig. 4 Quadrupolar splittings and linewidths versus temperature

X-ray Diffraction

The NMR data is indicative of an oriented uniaxial phase in both the liquid crystal and the gel states. Previous work with the PBLG liquid crystal shows that the diamagnetic anisotropy of PBLG is positive (the helices align parallel to the field) and hence we anticipate a gel phase wherein the PBLG helices are aligned approximately parallel to one

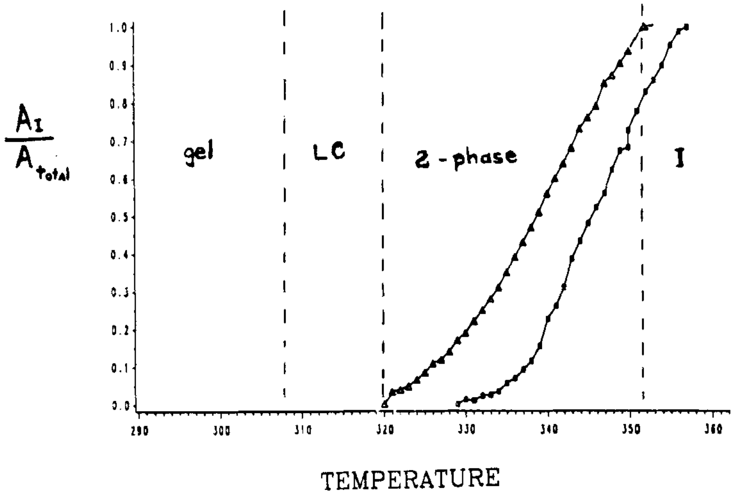


Fig. 5 Relative amounts of isotropic and anisotropic signal

another and the magnetic field. This was confirmed experimentally with x-ray diffraction. The equatorial scattering could be indexed on an approximate hexagonal lattice. The diffraction pattern taken from this oriented gel was essentially the same as that reported in 1967 by Parry and Elliott for swollen fibers.[21] Their interpretation of the diffraction data centered about specific sidechain interactions between neighboring helices -- stacks of the planar phenyl rings terminating the sidechains were thought to exist on the periphery of the helical backbone. Evidence of comparable unit cell dimensions have been obtained by Sasaki in unoriented gels.[20]

Concluding Remarks

We have demonstrated that a uniaxial gel will form in the PBLG-BA solution if it is cooled in a magnetic field. This differs from other (mechanically) oriented gels in that it is an equilibrium uniaxial phase and will retain its orientation when removed from the field. The PBLG concentration Φ must be in excess of the critical concentration for liquid crystal formation, however. We failed to get oriented gels for $\Phi < \Phi_A$. The probe NMR linewidth in the gel could be indicative of a heterogeneous phase (on the scale of microns). The scale is inferred by assuming a probe diffusion constant of 10^{-6} cm^{2}sec^{-1} and a diffusion time on the order of the inverse (average) quadrupolar interaction ($\Delta\nu^{-1} \propto 10^{-2}$ sec), yielding the rms diffusion distance 10^{-4} cm. A crystal-solvate with heterogeneity (inter-crystallite separations) of these dimensions could account for the observations.

In the PBLG system liquid crystal formation is a prerequisite for orientation. We hypothesize, however, that this does not have to be a limiting prerequisite. It is conceivable, for example, that if gelation occurs via micro-crystallite formation, such crystallites may be very mobile in the early stages of gelation in conventional (flexible) polymers. Concommitantly, suppose that the micro-crystallites are sufficiently diamagnetically anisotropic to orient in a magnetic field re-organizing the otherwise random pendant polymer chains. In such cases magnetically oriented gels could form in systems which do not exhibit a liquid crystalline phase. This hypothesis is worth further investigation.

In fact, Hartmann[22] has shown that the Durham precursor to polyacetylene may be a good candidate for testing this hypothesis. He showed that solutions of the precusrsor polymer will gel during the transformation reaction that yields polyacetylene. And moreover, if this transformation is carried out slowly in a magnetic field, there is x-ray evidence for a partially oriented, solid polyacetylene film wherein the chains are aligned parallel to the field direction. This coupling of a polymer conformational transition with orientation was reported over a decade ago for a poly-l-lysine HBr solutions in a magnetic field.[23]

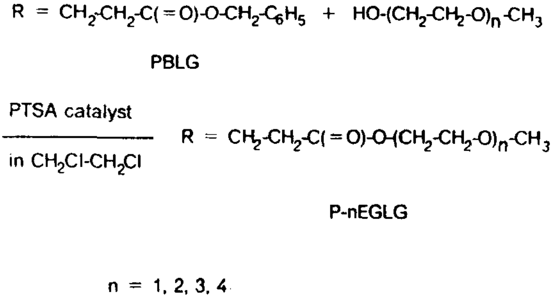
In general, the possibility of forming equilibrium uniaxial gels should facilitate a detailed investigation of the gelation mechanism. One may also anticipate such gels to exhibit anisotropic physical properties (e.g., elastic moduli[11,16]). In the PBLG gels considered here, the very high degree of polpeptide orientation in the gel state indicates that these uniaxial gels could yield ideal limiting values of α-helix orientation dependent molecular attributes (dichroic ratios, second rank tensorial NMR interactions, etc.). As indicated in Section 1, such attributes are essential for quantitative helix orientational order parameter determinations in polymer liquid crystals.

3. ETHYLENE GLYCOL DERIVATIVES OF PBLG

The long range molecular order in polymeric liquid crystals makes it possible to study subtle aspects of the polymer itself. In particular, the role of the sidechain on the exterior of the helical polypeptides can be examined.[18,19] New derivatives of PBLG produced by exchanging the benzyl ester terminus of its sidechain with oligomers of mono-methoxy ethylene glycols were prepared. The effect of the sidechain length on thermal properties and molecular packing in the solid state, and cholesteric pitch and secondary structure in lyotropic liquid crystals was examined.

Polymer Synthesis

Poly (L-glutamates) with ethylene glycol oligomer side chains were prepared by transesterification of poly- γ -benzyl L-glutamate with monomethoxy (and monomethoxy-d_3) terminated ethylene glycol oligomers in 1,2-dichloroethane with p-toluene sulfonic acid as a catalyst (Scheme 1). The monomethoxy terminated ethylene glycol oligomer were prepared by etherification of ethylene glycol oligomer sodium salts with iodomethane. The synthetic details will be published separately.



Scheme 1 Synthesis of poly (methoxy n-ethylene glycol L-glutamate)s

Characterization of Solid P-nEGLGs

The structures of α-helical P-nEGLG with various sidechain lengths (n = 1-4) were confirmed by proton NMR. Figure 6 shows the differential scanning calorimetry of the P-nEGLGs with PBLG as a reference.

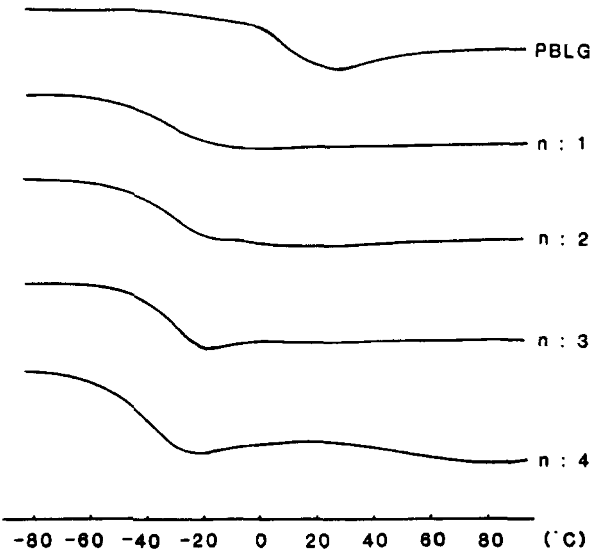


Fig. 6 DSC diagram of P-nEGLG in the region of T_g

In contrast with PBLG which shows a T_g near room temperature, the flexible ethylene glycol sidechains melt at about $-30°C$; the transition is more exaggerated the longer n is.

Oriented fibers of P-nEGLG show characteristic X-ray diffraction[13,14] and allow determination of the d_{100} spacing of the nearly hexagonally packed polypeptides. Of particular interest is the behavior of d_{100} with increasing n. Earlier work by Watanabe *et al.*[24] on poly(-n-alkyl-L-glutamates) showed a strong dependence on the number of atoms a in the sidechain in the range $4 \leq a \leq 12$. Figure 7 illustrates that the P-nEGLGs exhibit only a small increase in d_{100} in the same range of a. These findings suggest that the effective radius of the polypeptide does not increase with a as rapidly in the ethylene oxide sidechain as in the case of the alkyl sidechain. Qualitatively these two sidechains differ in

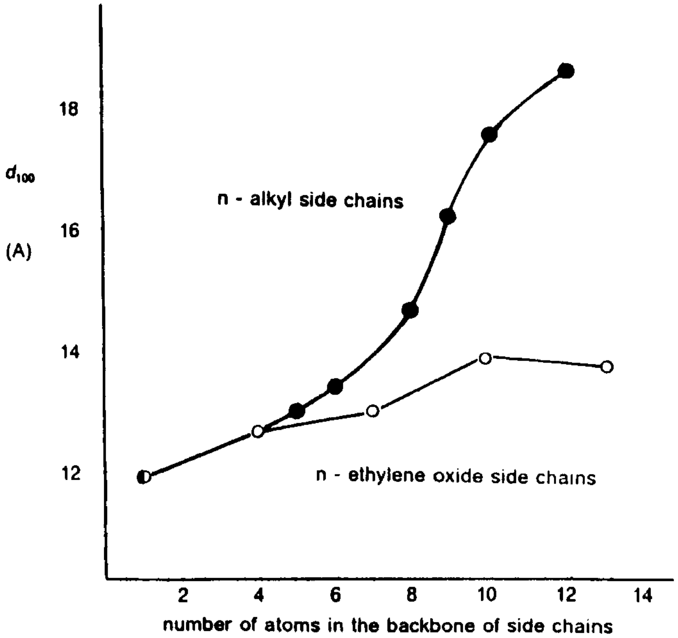


Fig. 7 d_{100} versus the number of atoms in the backbone of sidechain terms of their secondary structures. *Gauche* states are preferred at the C-C bonds in the ethylene oxide chain while *trans* states are preferred at all bonds in the alkyl chain. These differences could account for a contracted sidechain secondary structure in P-nEGLG versus an expanded one in the alkyl glutamates.

Characterization of Fluid P-nEGLGs

Figure 8 shows the cholesteric pitch of CH_2Cl_2 solutions of the P-nEGLGs at constant mole fraction of monomer units (0.001 mol monomer/cc solvent). The n = 4 polymer shows an anomalously high pitch compared to the n = 1,2,3 P-nEGLCs. It would appear that the effective chirality of the n = 4 derivative was decreased relative to the others in this series. Figure 9 and 10 show respectively, the temperature

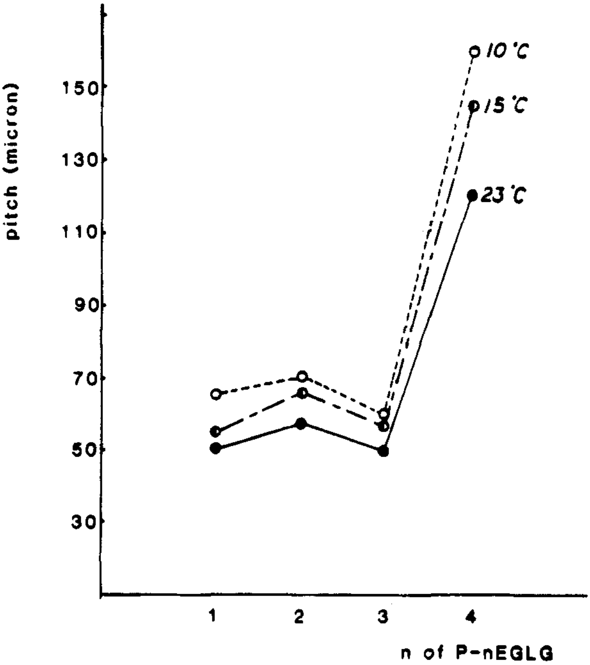


Fig. 8 Cholesteric pitch versus *n* of P-nEGLG

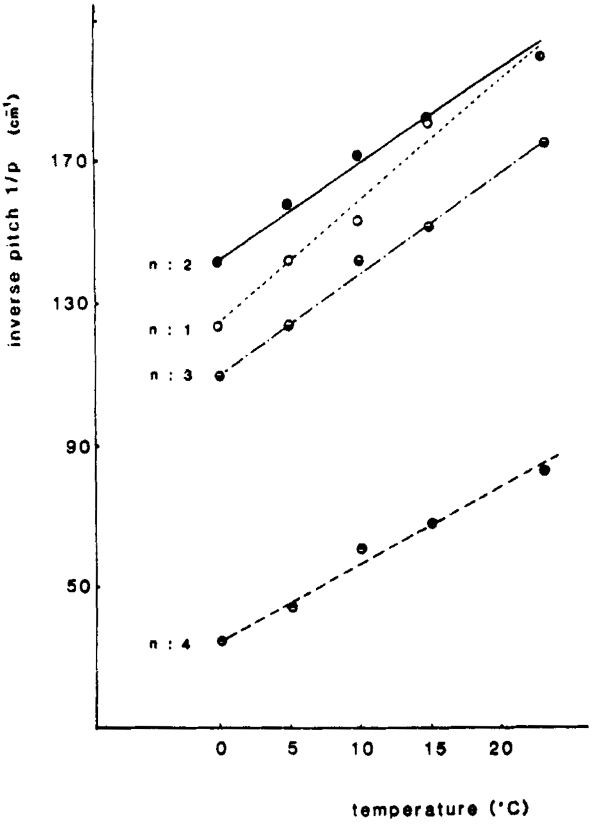


Fig. 9 Temperature dependence of inverse optical pitch

dependence of the cholesteric pitch in the P-nEGLG (constant mole fraction given above) and the rate of change of the pitch with temperature. The values of $d(1/p)/dT$ are contrasted with observations on PBLG in the same solvent. A steady decrease in the temperature dependence of the cholesteric pitch is observed as the sidechain length is increased (Figure 10).

The sidechain secondary structure of the P-nEGLGs has been directly probed by examining the quadrupolar splittings exhibited by the

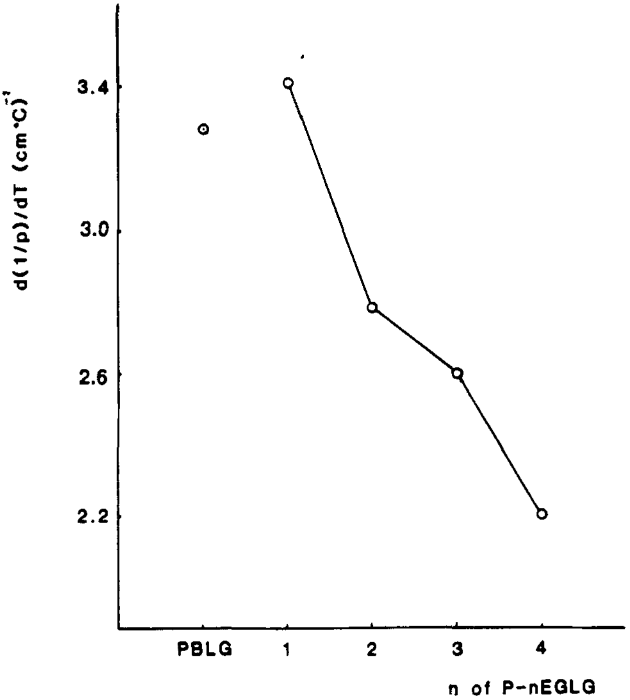


Fig. 10 Variation of the temperature dependence of optical pitch

deuterium labelled sidechains. The methyl terminus of each (n = 1-4) P-nEGLG has been synthesized with a $-CD_3$ group. In the liquid crystalline phases of the P-nEGLGs in CH_2Cl_2, a distinct deuterium NMR spectrum is observed (Figure 11). The n = 0 polymer corresponds to PBLG partially exchanged ($\approx$ 10%) with methanol-d_3. The quadrupolar splitting for n = 0 is related to the average orientation of the $O\text{-}CD_3$ bond in the ester; this bond may be considered as the "first" bond of the series of n-EG ester sidechains and our NMR findings will be discussed relative to the n = 0 result.

The quadrupolar splittings for the methyls in the series n = 1-4 are shown in Figure 12; measurements at constant mole fraction of

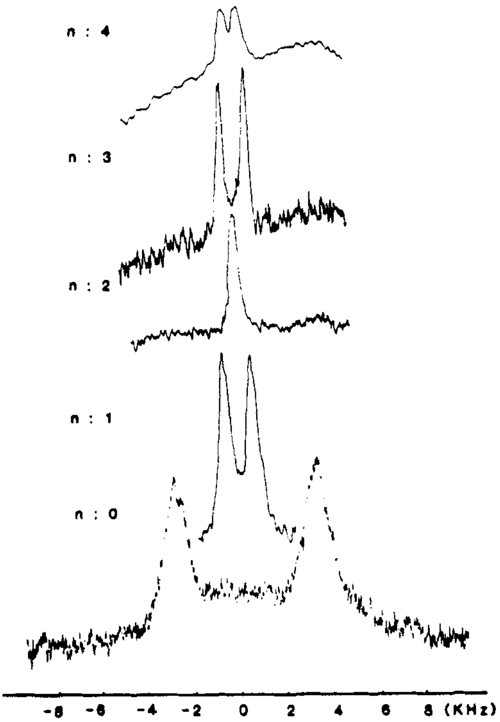


Fig. 11 Deuterium NMR spectrum of P-nEGLGs-d_3

monomer (open circles) and constant volume fraction of polymer (closed circles) are the same within experimental error. Also within this error, the quadrupolar splitting of the n = 2 polymer would have to be less than 100 Hz. At some sidechain length, we anticipate that the sidechain becomes decoupled from the helical backbone of the polypeptide and the measured average orientation of the *O-CD*$_3$ bond would merely reflect the general uniaxial constraints of the polypeptide liquid crystal not unlike those orientational constraints that a solvent molecule experiences. We have attempted to determine at which point (n-value) the secondary structure of the sidechain no longer influences the orientation of the *O-CD*$_3$ bond by considering the bond correlation function $\frac{1}{2} < 3(b_1 \cdot b_j)^2 - 1 >$. Here, b_1 is the "first" bond of the ester

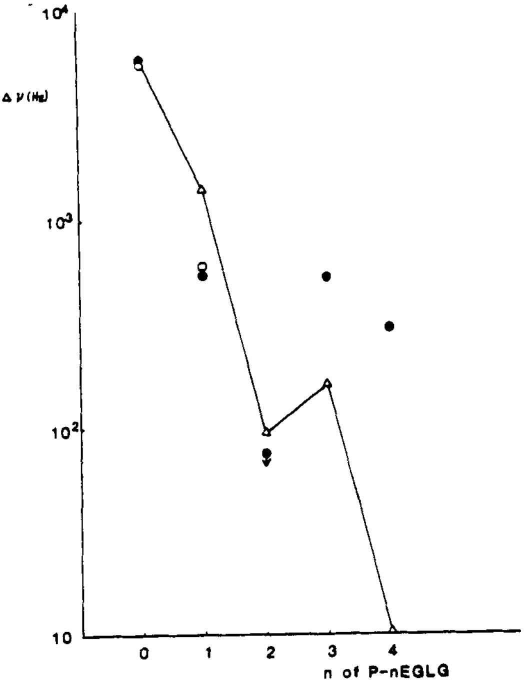


Fig. 12 Quadrupolar splittings of P-nEGLG-d_3

sidechain (the $O\text{-}CD_3$ bond in the partially exchanged PBLG). For the P-nEGLG series $j = 4,7,10$ and 13 for the $O\text{-}CD_3$ bonds terminating respectively the $n = 1,2,3$ and 4 EG sidechains. The angular brackets indicate an average over the rotational isomeric states (RIS) accesible to the sidechains. The recent RIS parameters of Abe *et al*[25] were employed to perform the average and the results have been scaled to yield the observed quadrupolar splitting of the $n = 0$ reference polypeptide.

The calculated quadrupolar splittings,

$$\Delta\nu\,(n > 0) = \Delta\nu\,(n = 0) \times \frac{1}{2} < 3(b_1 \cdot b_j)^2 - 1 >$$

are shown as the open triangles in Figure 12. The agreement between calculated and experimental Δν is reasonable up to $n=2$; the correct trend is suggested for $n=3$ (an increase relative to $n=2$), but calculations suggest that for $n=4$, the terminal bond is completely uncorrelated with the "first" bond of the ester. Hence the observed $\Delta\nu(n=4)$ indicates that the orienational anisotropy is due to the mean field in the polypeptide liquid crystal and not to intramolecular RIS constraints.

Concluding Remarks

The series of P-nEGLG polymers graphically illustrate a deterioration of sidechain secondary structure with increasing sidechain length. This increasingly isotropic fluid-like exterior on the helical backbone manifests itself in the solid state and the liquid crystal phase. Insofar as the source of chirality in these materials is the helical backbone, the chiral element is increasingly shielded by increasing n; there is an associated decrease in the inverse cholesteric pitch and its temperature dependence at large n. The crossover from a sidechain that is influenced by intramolecular energetics (dihedral angle constraints coupling it to the polymer backbone) to one that is free to aquiesce to the constraints in the liquid crystal is clearly shown with deuterium NMR. This is perhaps the most graphic illustration of "decoupling" of a sidechain from the mainchain to date.

Finally, The P-nEGLG molecules may act as stable, monomolecular "aggregates" in water-based lyotropic mesophases giving particles whose dimensions would be independent of concentration and temperature. The P-nEGLGs also could provide the basis of a new class of (anisotropic) superionic conducting polymers.

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