# Structure of Poly(1,4-benzamide) Solutions[1b]

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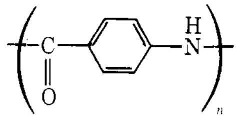
ABSTRACT: Poly(1,4-benzamide) in concentrated solutions forms a nematic anisotropic (liquid crystalline) phase. Amide solvent requirements are very specific; the polymer dissolves in fully substituted amides containing several percent lithium chloride. This specificity is explained by a solvation structure consisting of a polyamide chain negatively charged by association with chloride ion, this negative chain being solvated by a weak lithium ion solvent complex. The overall structure is then soluble in the amide solvent. The concentrated solutions are birefringent and become ordered uniaxially over macroscopic dimensions when sheared or in magnetic fields. Nuclear magnetic resonance spectra exhibit dipolar splittings similar to those of known nematic phases. The differences between these solutions and previously studied anisotropic phases is discussed, along with unusual orientational effects.

Poly(1,4-benzamide) (I) forms unusual anisotropic phases in solvents comprised of fully substituted amides containing several percent of lithium chloride.



I

The first part of this paper represents a discussion of the nature of the solvation and the reasons for the highly specific solvent requirements. The second part is a survey of various aspects of the anistropic phase. It is introduced by a description of a phase diagram which defines the phases discussed below.

The phase diagram (Figure 1) was prepared for the system poly(1,4-benzamide)–*N*,*N*-dimethylacetamide–lithium chloride at room temperature. Below a certain limiting concentration (region A), the solutions are clear and typically isotropic. Above this concentration, approximately 7% for this particular system, an anisotropic phase begins to separate.

The development of such phases has been discussed by Flory.[2] The solutions in region B are emulsions of the isotropic and anisotropic phases. At the lower end of the concentration range the continuous phase is isotropic and at the upper end anisotropic. These mixtures are cloudy, often exhibit pearlescence on stirring, and frequently cannot be distinguished from those in region C without microscopic examination. If the bulk viscosity is not too great, the phases can be separated by centrifugation.

The pure anisotropic phase in region C differs significantly from the translucent nematic thermotropic liquid crystals to which they are related. The appearance of the phase when viewed as a thin layer in polarized light is identical with that of a nematic crystal (Figure 2), being birefringent over small areas but depolarizing when viewed at low or no magnification. However, on standing undisturbed, a vial of the solution will become transparent over a period of hours. The smallest amount of shear will instantly return it to the opalescent, typically anisotropic appearance.

At low lithium chloride concentrations (region E), the concentration in solution remains below the level at which anisotropy can occur. Without magnification, these finely dispersed slurries of crystalline particles are frequently indistinguishable from the emulsions in region B.

Region D consists of undissolved polymer in an anisotropic phase identical with that of region C.

It should be kept in mind that the phase diagram is meant to be illustrative of the type of system and that the details are accurate only for the particular polymer sample. Molecular weight, of course, has a very profound effect. The relationship between inherent viscosity and the concentration at which anisotropy appears is given in Figure 3 for 5% lithium chloride, and this subject is discussed in greater detail in the paper by Kwolek[3] in this series. Details of the diagram are probably also sensitive to molecular-weight distribution.

The position of the line joining regions B and C is only approximate. It is extremely difficult to determine the point at which the last fraction of isotropic material is seen in the bright field produced when the predominately anistropic emulsion is viewed in polarized light. The saturation concentration, represented by the line joining regions C and D, is equally approximate.

For reasons which will be discussed later, these solutions are all prepared with 1% water which is necessary to prevent rapid crystallization of polymer in this particular molecular weight range. This water has little effect on the phase diagram. The concentration at which anisotropy appears, for example, changes by no more than 1%.

The behavior of the phases relative to temperature is very complex because of the multiple equilibria involved. The proportion of anisotropic phase (region B) decreases on going either upward or downward from room temperature. Some reasons for this behavior will be discussed below.

## Experimental Section

Solutions of poly(1,4-benzamide) in amide–lithium chloride solvents were prepared under high shear conditions (3000 to 4000 rpm) at room temperature. Unless specifically stated otherwise, all solutions were prepared with 5% lithium chloride (wt/v) and 1% water (v/v). The solutions were stable with from 0.2 to 2% water. Anhydrous solutions rapidly precipitated and higher water concentrations prevented solution. Higher lithium chloride concentrations yielded unstable solutions which rapidly crystallized. Solvent (Eastman Reagent Grade) was dried over molecular sieve, and lithium chloride (BNA Reagent Grade) was dried in a vacuum oven.

The phase diagram was developed by viewing thin layers of the solutions in polarized light at approximately 60-fold magnification. Figures shown were obtained on a Zeiss Photomicroscope.

Magnetic orientation studies were done with a Varian 4 in. electromagnet equipped with an optical bench and thermostated sample holder. The figures showing the sample tube in a magnet depict an approximately 1000 G permanent magnet.

Electrophoresis experiments were carried out on a Perkin-Elmer Model 38 apparatus.

Solutions used in the model association studies were prepared from well-dried components in a drybox. NMR spectra were taken on a Varian A60 instrument. Infrared spectra were taken in a 0.01-cm cell on a Perkin-Elmer 221 spectrometer used in the absorption mode with 4× frequency expansion. Carbonyl peaks overlapped and unresolved absorbencies are plotted. Quantitative association constants could not be obtained. The complexity of the carbonyl region prevented determination of the effect of water on the $Li^+$–carbonyl association.

The polymer used throughout was of moderate molecular weight.[3] The inherent viscosity was 1.2 and the molecular weight was ap-

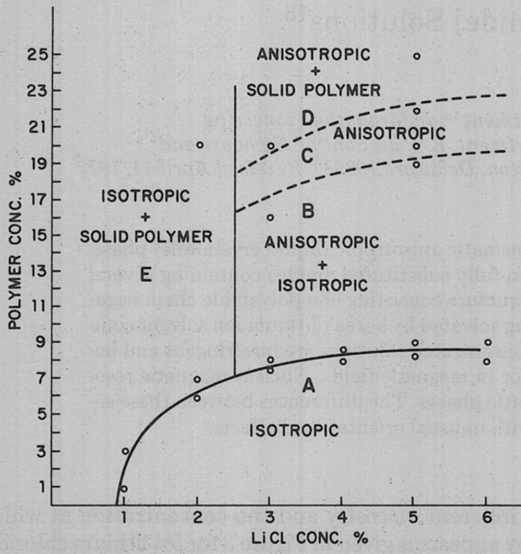


**Figure 1.** Phase diagram prepared for the system I, dimethylacetamide–lithium chloride. All solutions contain 1% water (v/v).

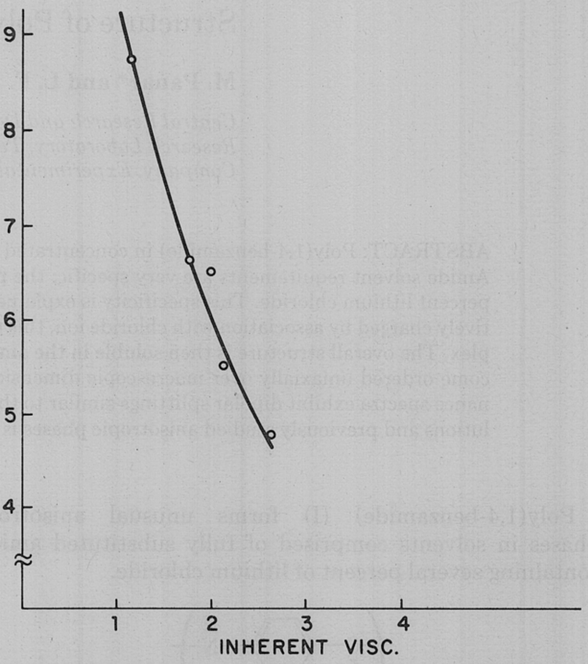


**Figure 3.** Dependence of the concentration at which anisotropy appears relative to molecular weight expressed as inherent viscosity.

**Figure 2.** Thin layer of anisotropic phase of I viewed in polarized light. The appearance is of a typically nematic structure. The bar is 600 μm.

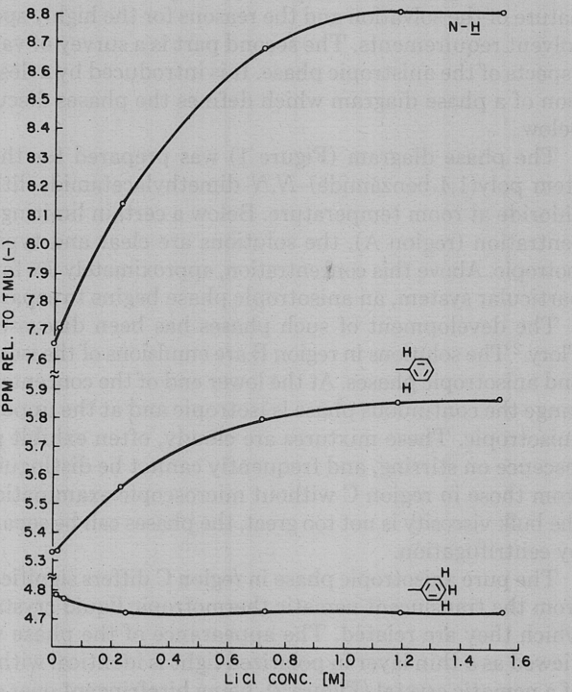


**Figure 4.** Shift in NMR resonances of benzanilide, 1.0 N in tetramethylurea, on titration with LiCl. In the case of the ring protons, the position of a single prominent peak is plotted.

proximately 7000. The optical and magnetic phenomenon described are those of material in this molecular weight range. At very low molecular weight the anistropic phase will not form, and at very high molecular weight, solution bulk viscosity makes many of the experiments described impractical or impossible.

## Results and Discussion

**Solvation.** The solvent structure described below explains the specificity for fully substituted amides and the role of salts in mixed solvents of this type.

The structure proposed is, of course, applicable to both isotropic and anisotropic concentration ranges.

Typical amide solvents are tetramethylurea and *N,N*′-dimethylacetamide. Benzanilide was used as a model for poly(1,4-benzamide). As benzanilide (1.0 M) in tetramethylurea is titrated with LiCl, the resonance of the amide hydrogen and of the ortho protons shifts markedly to lower field, while the meta- and para-resonance shifts vary slightly and in the opposite direction (Figure 4). Acetanilide, which has a free N–H group, behaves similarly on titration. However, the aromatic resonance of *N*-methylacetanilide does not shift on addition of LiCl. The conclusion which may be drawn is that the pertinent association requires a free N–H group. Since electrophoresis data show that meta-substituted polyamides are negatively charged in similar solvents, it is reasonable to conclude that it is the chloride which is associating. Thus, this hypothesis can explain why only fully substituted amides are effective solvents; secondary amides would compete with the polymer for chloride ion. Consistent with this postulated absence of any solvent–chloride interactions is the fact that a similar NMR titration of benzanilide in dimethylacetamide yields a titration curve nearly superimposable on that obtained in tetramethylurea.

While these experiments may explain the role of the chloride and why secondary amides are ineffective, they do not explain the requirement for an amide solvent. Insight into this point was obtained from an infrared study of solvent–LiCl

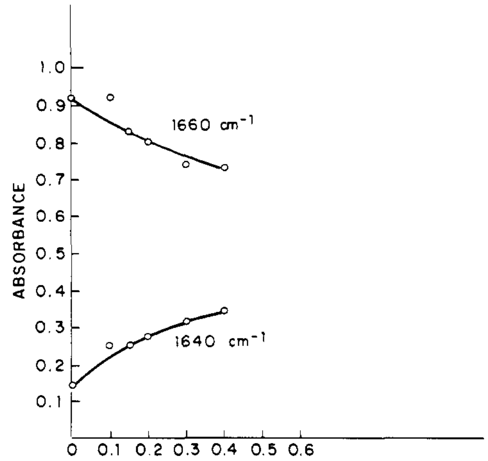


**Figure 5.** Change in the infrared carbonyl absorption of tetramethylurea (0.1 M in tetrahydrofuran) during titration with LiCl.

association. As a 0.1 M solution of tetramethylurea in tetrahydrofuran is titrated with LiCl, the initial carbonyl peak at 1660 cm$^{-1}$ decreases in intensity while a second peak at 1640 cm$^{-1}$ appears (Figure 5). Since two peaks seriously overlap, the data for the 1640-cm$^{-1}$ peak do not start from zero. It should be emphasized that the absorption has not shifted but that a new peak, representing a distinct new species, has appeared. This new species is reasonably considered to have a lithium ion weakly associated with the oxygen of the amide. This formulation is consistent with crystallographic data on the structure of LiCl–amide solid complexes in which case the lithium is located adjacent to the carbonyl oxygen.[4]

If this hypothesis is correct, solvent power, as measured by ease of dissolution and resulting solution viscosity, should depend not so much on the nature of the solvent, but on the concentration of the positive solvating species, i.e., on the association constant for formation of DMA–Li$^+$. Dimethylacetamide is a markedly better solvent than tetramethylurea: the polymer dissolves readily on stirring at room temperature and forms solutions of relatively low viscosity. Consistently, dimethylacetamide associates much more strongly with LiCl than does tetramethylurea. In this case, the solvent is almost totally associated at a fourfold excess of salt. At this level, the shoulder due to the unassociated form has totally dissappeared.

To summarize this hypothesis of solution structure, the positively charged species solvates the negatively charged polymer molecule (Figure 6), and it is this neutral entity which is soluble in dimethylacetamide and probably in other solvents. This conclusion would explain the fact that as much as 30% of nonhydrogen-bonding solvents, such as toluene, may be added to a polymer solution without causing precipitation.

The polymer model, benzanilide, associates with Li$^+$ (Figure 7) as would be expected. However, competition of polymer for lithium ion is not critical because (a) this association is considerably weaker than that for Cl$^-$ (benzanilide is fully associated with chloride ion at an equimolar ratio) and (b) the solvent is present in about a 10 M excess.

Solutions of low molecular weight poly(1,4-benzamide) in dimethylacetamide–LiCl can tolerate up to 2% water. Over 2% water will prevent dissolution of the polymer. One can explain this effect by reversal of the carbonyl–Li$^+$ association by water. Although attempts to detect this effect in IR titrations are complicated by superfluous H-bonding absorption bands, the effect of adding water to an equimolar solution of benzanilide and LiCl in dimethylacetamide can be followed by a reversal of the NMR shift caused by LiCl titration (Figure 4). Titrations of an equimolar solution of benzanilide and LiCl with water demonstrate a reversal of the amide–Cl$^-$ association. This result is probably a secondary effect resulting from the effect of water on the positive complex and the hydration of the ions in solution.

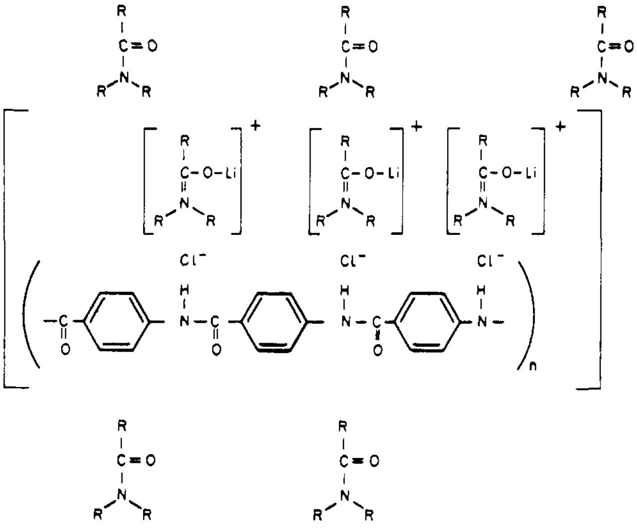


**Figure 6.** Proposed solvation structure for aromatic polyamide in amide solvent.

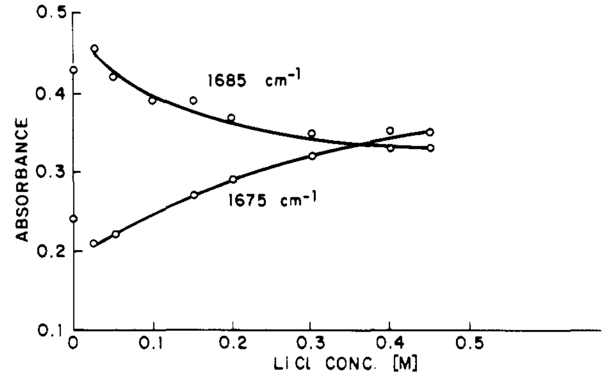


**Figure 7.** Change in the infrared carbonyl absorption of benzanilide (0.1 M in tetrahydrofuran) during titration with LiCl.

The 1% added water greatly stabilizes the solutions to precipitation. Anhydrous solutions in this molecular-weight range frequently precipitate within hours. The water presumably functions by inserting itself between chains and preventing chain–chain contact. Consistent with this interpretation, the quantity of water which is effective is roughly up to, but no more than, one water molecule per polymer amide.

**The Anisotropic Phase.** The molecules in the anisotropic state are highly associated. Figure 8 shows the aromatic proton magnetic resonance intensity of a series of molecular-weight samples of poly(1,4-benzamide). The concentrations of the solutions are the same in each case. The high-resolution spectrum will be seen at full intensity only to the extent that individual molecules are free to tumble in solution. This series shows significant intensity only for molecules having an inherent viscosity under 0.6. At this molecular weight, the molecules are too short to form an anisotropic phase, while those molecules which are sufficiently long to form a nematic state are too highly associated to yield an intense spectrum.

Solutions of poly(1,4-benzamide) are nematic as will be seen from the following discussion.

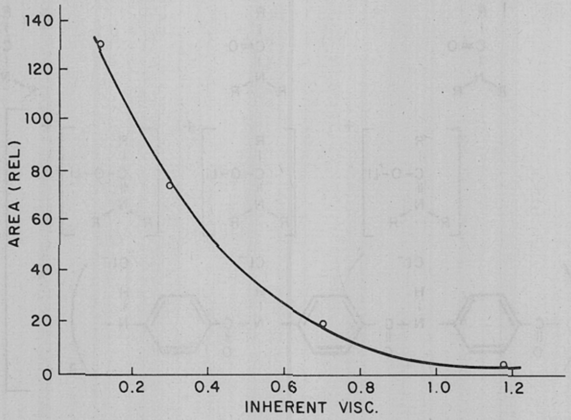


**Figure 8.** NMR proton intensity of a series of isotropic solutions of I of low molecular weight plotted against the inherent viscosity. The intensity has been corrected to equal concentration and is expressed in relative units.

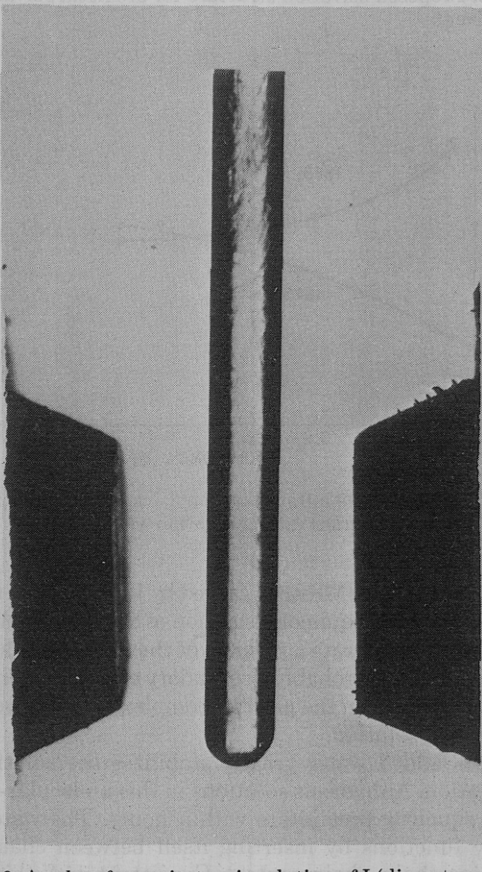


**Figure 9.** A tube of an anisotropic solution of I (diameter = 4 mm). The lower part of the tube, between the pole faces of a 1000-G magnet, is oriented uniaxially. The nematic lines can be seen in the tube above the magnet.

Figure 9 illustrates the response of the anisotropic state to a magnetic field.[5] In the 4-mm NMR tube above the pole pieces, we see the threadlike lines from which the nematic state derives its name. Between the pole faces, the nematic lines have oriented with the field and the solution has become a uniaxial crystal with the axis along the lines of force. (When not oriented, the material is depolarizing.) The degree of light scattering through the tube at various angles relative to the magnetic orientation is shown in Figure 10. The transparency of the sample is twice as great along the magnetic lines of force as across, consistent with less scattering when looking along the long axis of the molecules. The visible spectrum of the sample is identical except for intensity in the two directions.

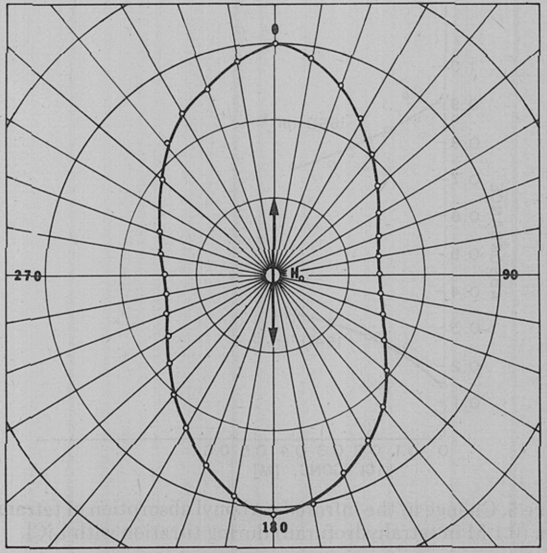


**Figure 10.** Transparency of a magnetically oriented anisotropic solution I relative to the direction of the orienting field ($H_0$). The transparency is in relative units.

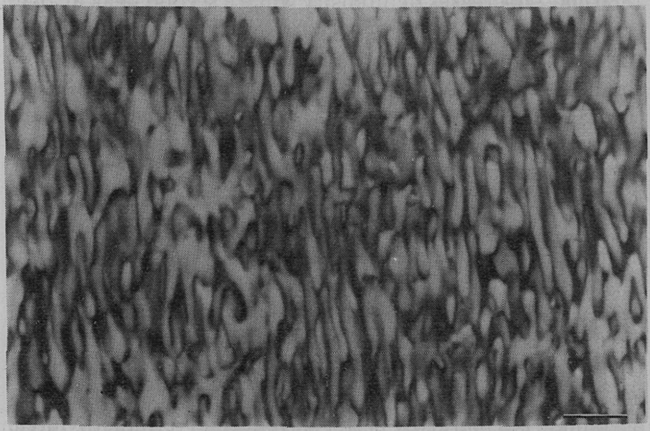


**Figure 11.** Micrograph of a thin layer of anisotropic I sheared by sliding the cover slip in a direction parallel to the visible striations. The bar represents five micrometers.

The polymer seen in Figure 9 is very transparent and aside from the nematic lines would look isotropic when seen in ordinary light. This characteristic of relaxing to a transparent state in which the oriented correlation volume has grown to macroscopic dimensions too large to scatter light is typical of this polymer in the low molecular-weight range. The slightest shear, however, as in stirring or pouring, will cause the solution to break up into small ordered light-scattering volumes in the micrometer range.[6]

Figure 11 illustrates a thin layer of the pure nematic phase which has been sheared by sliding the cover slip in a direction which is vertical relative to the photograph. By observation with a full-wave retardation plate it can be seen that in the bands of about 1-$\mu$m width the molecules are arranged alternately in the two directions at 45° to the shear direction.

Figure 12 of an emulsion of isotropic phase in anistropic phase shows characteristic football-shaped droplets. This shape results from the anisotropy of the surface tension caused by the ordering. The long axis of the molecules surrounding the isotropic droplet is parallel to the long axis of the football. Figure 13a shows a thin layer of such a solution in polarized light. The football droplets are randomly oriented and the background is disordered as can be seen more clearly in the interference colors which obtain in the microscope. The slide shown in Figure 13b is the same one which has been placed

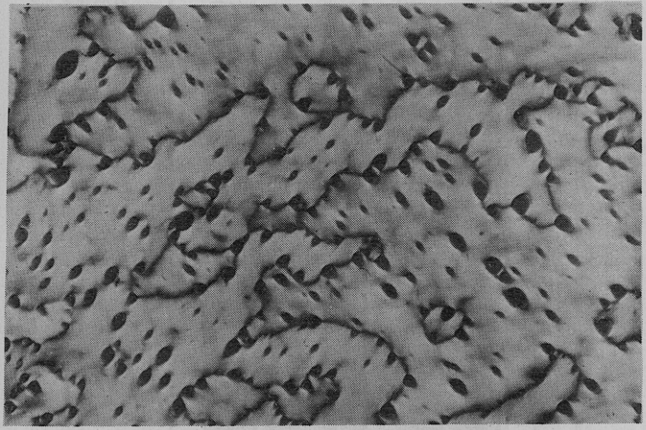


**Figure 12.** Micrograph of a thin layer of largely anisotropic I which has spontaneously separated into zones of differing orientation. Observation in polarized light demonstrates that the molecules in the anisotropic phase are parallel to the orientation of the isotropic droplets.

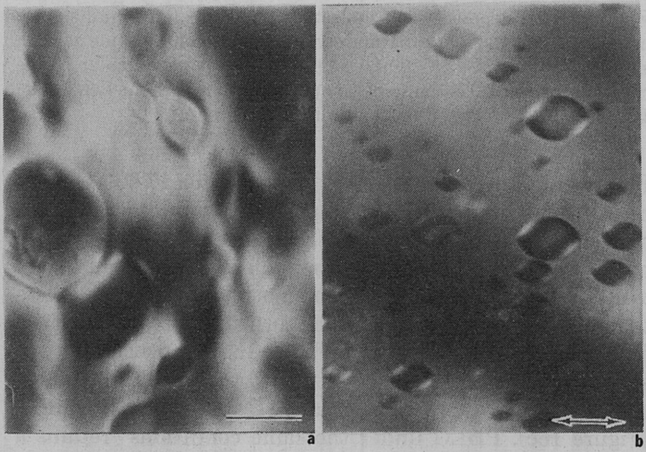


**Figure 13.** (a) Micrograph of thin layer of emulsion of the isotropic phase in anisotropic phase. The bar represents 10 $\mu$m. (b) The same slide as in (a) after having been placed overnight in a 10 000-G magnetic field in the direction represented by the arrow.

overnight in a 10 000 G magnetic field which is horizontal relative to the photograph. The anisotropic phase has oriented smoothly and become uniaxial and the footballs have lined up with the field. Droplets of anisotropic phase also form similar shapes. Observation in polarized light using a full-wave retardation plate demonstrates that the molecules align parallel to the sides of the droplet as a very deformed spherulite.

The spontaneous ordering which causes the solution to go transparent is also seen in thin layers (Figure 12) in which the sample is ordered over dimensions of millimeters. (The boundaries of the ordered zones are the optical discontinuities which form the characteristic nematic lines.) This uniform ordering, which occurs both spontaneously and in magnetic fields, is considered to be analogous to the result of extensional forces in fiber spinning. Shear forces, in contrast, have a markedly different effect. The disorder evident in Figure 11 can also be seen in solutions flowing in capillary tubes on the microscope stage. In this case, the order in the shear direction is less well developed. The size of the oriented zones, which can be seen to "tumble" during very slow flow, is in the micrometer range. High shear disrupts this orientation.

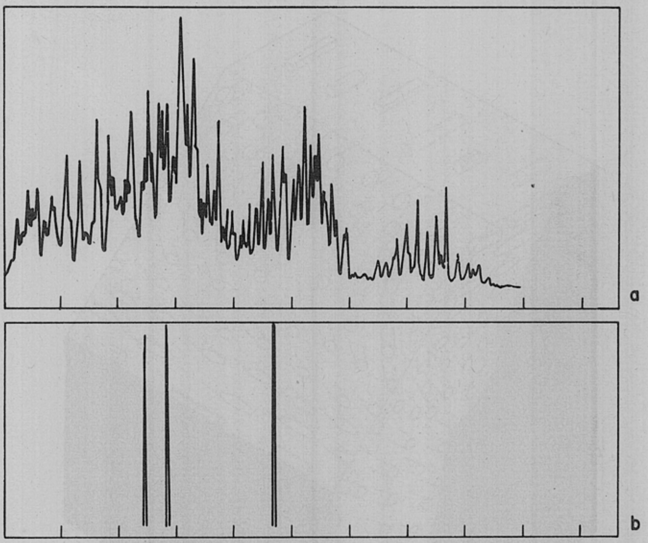


**Figure 14.** Comparison of the proton magnetic resonance spectra of *N,N*-dimethylacetamide (b) and the same solvent in the anisotropic phase of I (a). The dipolar splitting of the solvent covers a range of 900 Hz (220 MHz instrument).

Some further insight into the ordering in these phases can be obtained by NMR.[7–9] In ordered fluid systems, the intermolecular dipole–dipole interactions which are averaged to zero in isotropic liquids by rapid tumbling, and which result in broad-line spectra in solids, can be readily detected in high resolution. The spectrum of dimethylacetamide in an anisotropic solution of poly(1,4-benzamide) is compared in Figure 14 with that of dimethylacetamide itself.

The complexity of the spectrum cannot be directly compared to spectra taken in other anisotropic systems such as poly($\gamma$-benzyl L-glutamate) because the observed spectrum represents an average of solvent molecules which are free, those which are adsorbed to the polymer–solvent complex, and those tightly solvating the polymer and as a result is very characteristic of the polymer structure.

The dipolar splitting for a spinning sample is one fourth that for a stationary sample when the axis of sample spin and $H_0$ are perpendicular as they are in conventional spectrometers. This result is explainable if, in the stationary sample, the time-averaged solvent dipole–dipole vector and $H_0$ are parallel. This would be the case if the solvent can exchange rapidly with the polymer and the only fixed direction is that parallel to the field, i.e., the molecules align with their long axes in the field direction.

The high-resolution aromatic resonance of the polymer is not seen in the anisotropic phase because of the intramolecular nuclear dipolar interactions of the highly oriented polymer molecule. The spectrum can be detected but is extremely broad.

The behavior of mixtures of the two phases to temperature is very complex. As the temperature increases, optical experiments demonstrate that the mixture goes isotropic. While this behavior, which is confirmed by NMR, is to be expected for a nematic–isotropic transition, the situation in this complex system is much more involved. The $Cl^-$–polymer association appears to be reversed by increasing temperature. The NMR shift of the NH proton of benzanilide which results from titration with lithium chloride (Figure 4) is reversed on heating. At 150 °C the shift has returned to a point identical with that in the absence of lithium chloride. The complexity which results from the several equilibria present makes it difficult to calculate an activation energy for the transition.

Very unexpectedly, the proportion of isotropic phase in an emulsion also increases on cooling from room temperature to 0 °C. The change can be seen both optically and by NMR. On cooling, a striated texture, which appears to be the result of a nucleation process, develops in the nematic phase. If the sample is returned directly to room temperature, the striations

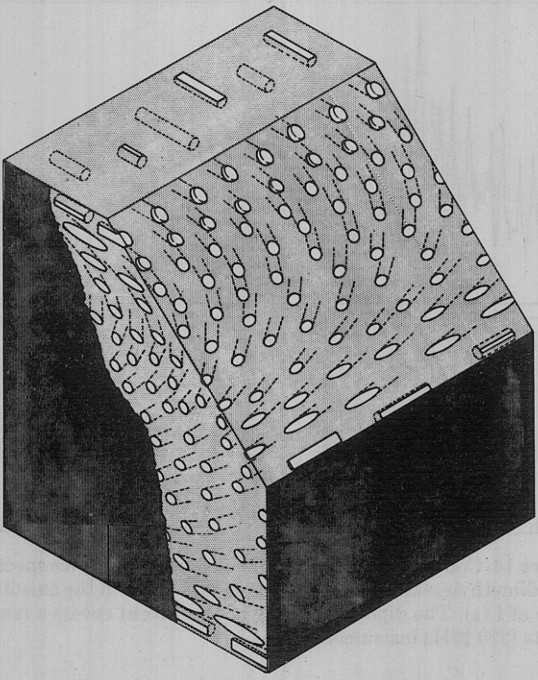


**Figure 15.** Schematic representation of a polymeric cholesteric structure. The distance between the top and bottom of the figure represents the spacing between the visible cholesteric lines. The rodlike molecules of varying length (which represents the distribution of molecular weight) are tilted slightly relative to their neighbors and develop a helical orientation.

disappear, and the normal nematic appearance is regained. However, if the sample is held overnight at 0 °C, the process becomes irreversible and the polymer remains precipitated. The development of this precrystalline structure is analogous to the phenomenon of shear induced crystallization, with the significant difference that the nucleation derives from the inherent anistropy rather than from flow orientation. A related phenomenon is the tendency for mixtures of nematic and isotropic phases of poly(1,4-benzamide) to precipitate at nematic–isotropic interfaces, where surface forces assist nucleation.

Small molecules added to the nematic solutions associate with the polymer and take on the orientation of the ordered phase. This association can be seen in the proton magnetic resonance dipolar splittings of the additive. It also leads to a novel structural effect which is similar to the previously described cholesteric phase formed by poly($\gamma$-benzyl L-glutamate) (PBLG), although it results from a completely different molecular structure. In the cholesteric phase of PBLG, each optically active molecule is tilted slightly relative to its neighbor and a helical structure develops.[10,12] This structure is shown schematically in Figure 15. In viewing such a solution, one is looking alternately along and across the long axis of the molecule. This alternation of refractive index results in a series of parallel lines approximately 0.1 mm apart. When several percent of an optically active additive, such as (+)2-methyl cyclohexanone is added to a nematic (20%) poly(1,4-benzamide) solution, the additive associates sufficiently with the chain to make it act as though the monomers were optically active, and the solution forms the cholesteric state seen in Figure 16a. When this solution is placed in a 17 000-G magnetic field, horizontal with respect to the photograph, the molecules attempt to line up with the field but, because of the helix, only a resultant 50% of the molecules can align at one time. The structure, therefore, breaks up into volumes of less than millimeter dimensions which turn alternately toward the field to form a zig-zag pattern (Figure 16b). Concurrently, but at a slower rate, the helix is untwisted to form a uniaxial ordered solution exactly as is obtained from the nematic phase (Figure 16c). PBLG under the same conditions[7] retains a larger coherent volume so that the "wavelength" of the zig-zag is greater.

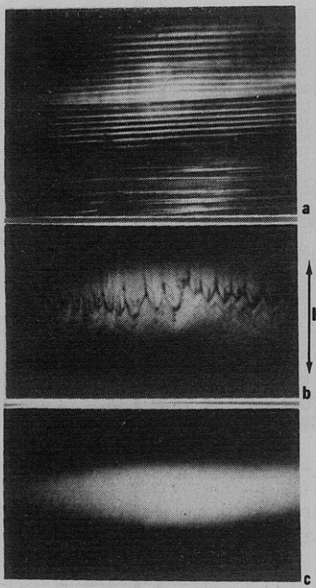


**Figure 16.** (a) Micrograph of cholesteric phase of I. The parallel lines have the spacings of approximately 0.1 mm. (b) is the same sample as (a) after 20 s in a 17 000-G magnetic field perpendicular to the cholesteric lines. (c) is the same sample after 40 min in the field. (The sample is photographed in a cylindrical container.)

**Acknowledgments.** The schematic of the cholesteric structure was drawn by Mr. Ames Schuck.

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