Examination of the Electrotropic Cholesteric to Nematic Phase Transition of Liquid Crystal Poly(γ-benzyl-L-glutamate) by Laser Light Beating Spectroscopy

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ABSTRACT: Reported are the results of our study of the electric field induced cholesteric to nematic phase transition of liquid crystal poly(γ-benzyl-L-glutamate) by the techniques of laser light beating spectroscopy. The transition was evident as a narrowing of the line width of scattered radiation as the lyotropic liquid crystal passed through the transition point at 350 V/cm. Transient studies suggest that two reorientation processes with different time constants may be involved.

Above a critical concentration in certain solvents that support the α-helical conformation of the polypeptide, poly(γ-benzyl-L-glutamate) (PBLG) forms a lyotropic liquid crystal of the cholesteric structure.[1] In the presence of sufficiently strong electric or magnetic fields liquid crystalline PBLG is known to undergo a mesomorphic phase transition from the natural cholesteric structure to one that resembles an aligned nematic. Presumably the applied field unwinds the helicoidal superstructure of the cholesteric phase and forms an oriented nematic with the director (a unit vector pointing along the direction of liquid crystal alignment) of the rod like PBLG molecules more or less parallel to the field axis (Figure 1). The nematic phase has, indeed, been defined as a special case of the cholesteric, one in which the pitch of the helix is infinite. Electric or magnetic fields interacting with the respective anisotropic susceptibilities of the macromolecule induce a pitch dilation in the liquid crystal and, at some critical field strength, the mesophase looses the high optical rotatory power and optical retardation properties associated with the cholesteric phase.[2] The phenomenon of field induced phase transition may be termed electro- or magnetotropism, in analogy to the more usual lyotropic or thermotropic mesomorphic transitions which occur with changes in solvent concentration or temperature. The critical magnetic field strength for the event has been shown by deGennes[3] to be inversely proportional to the pitch of the undisturbed cholesteric structure through the relation

$$H_c = (\pi^2/2)(\kappa/\chi_a)^{1/2}(1/p_0)$$

where H_c is the critical field, κ the "twist" elastic constant[4] of the medium, χ_a the diamagnetic anisotropy of constituent molecules, and p_0 the undisturbed cholesteric pitch (π divided by the undisturbed spiral wave vector, q_0). χ_a must be positive for helical distortion to occur. For most cholesterics of moderate periodicity, the critical field H_c can be as high as 100 kG and the effect is not observable. The analogous critical electric field for the electrotropic cholesteric–nematic transition would be

$$E_c = (\pi^2/2)(4\pi\kappa/\epsilon_a)^{1/2}(1/p_0)$$

where ϵ_a is the dielectric anisotropy, also a positive number. E_c for a typical cholesteric liquid crystal is also large. Field-induced helical unwinding has been observed visually in thermotropic liquid crystals prepared so as to be of larger than normal pitch.[5-7] In PBLG solutions, p_0 is already beyond the wavelength of light, considerably reducing the field requirements for this transition.[8]

Reported here are the results of our study of the electrotropic cholesteric–nematic transition of liquid crystal PBLG as followed by the techniques of quasielastic, or light beating, spectroscopy.[9,10] This relatively new spectroscopic method provides an effective resolving power in excess of 10^{13} and is therefore capable of determining the actual line width of a laser beam broadened in frequency by molecular interactions. In our studies the cholesteric to nematic transition was clearly evident as a narrowing of the line width of scattered laser radiation as the liquid crystal passed through the transition point. Alignment of the macromolecules as well as the untwisting of the helicoidal superstructure is shown to be time dependent even after the critical electric field potential is surpassed. Transient studies suggest that two reorientation processes may be involved.

Experimental Section

PBLG of mol wt 310,000 was obtained from Pilot Chemicals, Inc., and used without further purification. Liquid crystal solutions ranging from 14.8 to 15% (w/v) were prepared in Millipore-filtered chloroform which had been distilled from NaOH solution to remove traces of water that could result in electrolytic hydrolysis of the polypeptide. The samples were matured for several weeks in order to obtain uniform lyotropic solutions. A standard 1-cm path-length spectrophotometric cell was internally fitted with two thin strips of transparent conductive glass on opposite cell walls and acted as our light scattering cell. The separation of the electrodes was 0.8 cm and with our regulated dc power supply applied field strengths as high as 2500 V/cm were possible.

The light beating spectrometer was only a slight modification of those reported elsewhere.[11,12] The light source was a 3-mW He-Ne laser. The output of a Tektronix 3L5 spectrum analyzer was amplified and interfaced with a Wang Series 600 calculator for signal averaging purposes. The calculator was programed to accumulate the signal intensity across 50 channels, allowing many sweeps of the spectrum to be recorded and averaged. Considerable noise reduction was thereby obtained. Linear regression (least-squares) analysis of the data provided an accurate measurement of the half-width at half-height, Γ, of the spectra which were always Lorentzian. Spectra were recorded at a 90° scattering angle in the scattering plane defined by the optic axis of the laser and the applied electric field. The cell stood normal to the scattering plane with its flat walls perpendicular to the laser beam and electric field. Light scattering spectra were recorded in observations taken both perpendicular and parallel to the field direction.

Results and Discussion

Light scattering in cholesteric liquid crystals has been shown[13,14] to arise from modes of interplanar molecular twisting and untwisting (twistons) and viscous splay (splayons). These modes, being overdamped, result in a spectral broadening of scattered radiation without any overall shift of the central frequency of the laser.

Figure 2 shows the variation in the spectral half-width at 90° scattering angle as the liquid crystal passes through the electric field induced cholesteric to nematic transition. As the cholesteric supramolecular structure unwinds in the presence of the field a distinctive narrowing of the

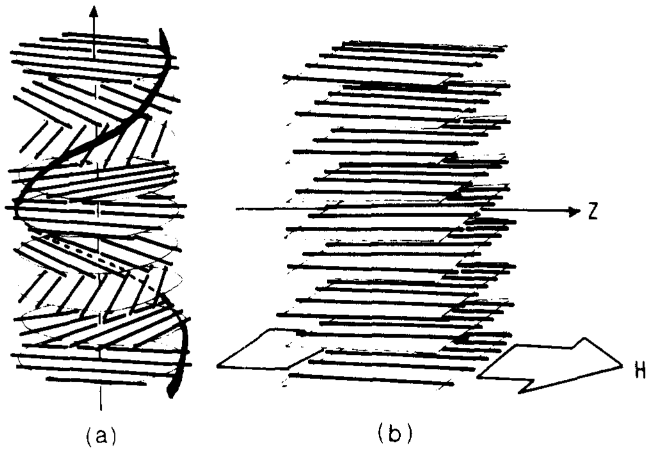

Figure 1. Supramolecular structures present in PBLG liquid crystal: (a) cholesteric structure; (b) nematic structure with H the direction of the magnetic field. Polypeptide molecules are represented by thick, straight lines, the optic axes by Z.

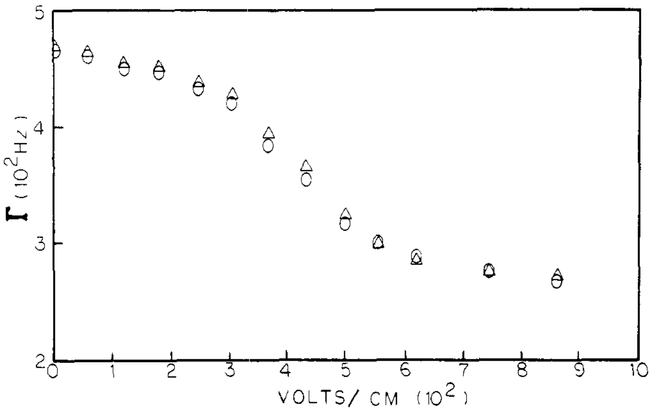

Figure 2. Spectral half-width (Γ) of a 14.8% PBLG sample *vs.* electric field potential. The triangles are the data points for scattering parallel to the electric field; the open circles for scattering perpendicular.

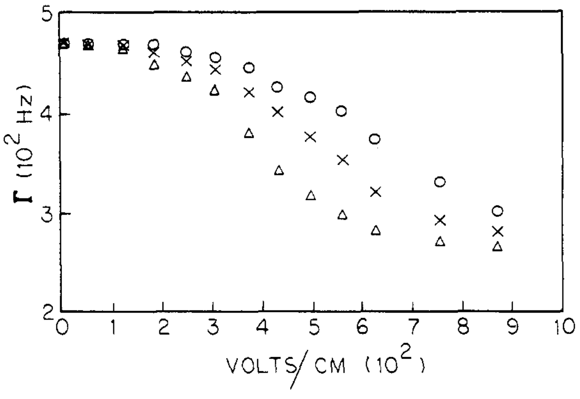

Figure 3. Spectral half-width (Γ) of a 14.8% PBLG sample versus electric field potential with various intervals between data points. Open circles represent a 10-min residence time at each voltage before data acquisition, crosses represent a 20-min interval, and the triangles, 30 min.

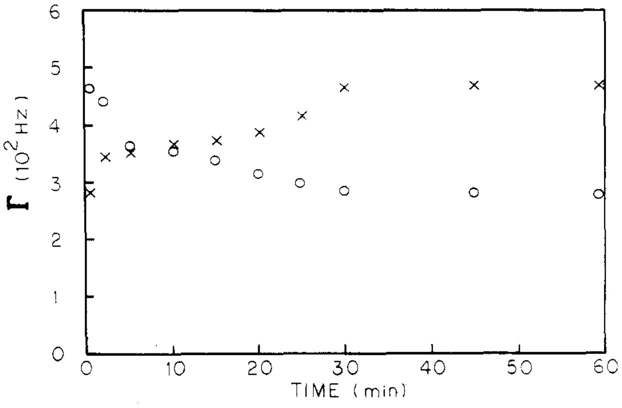

Figure 4. Transient behavior of a 14.8% PBLG solution subjected to a field in excess of E_c. Open circles represent the time dependence of the change in the spectral half-width after a sudden application of a 500-V/cm potential. Crosses are the data points for the reverse procedure where the aligned sample experiences a 500–0-V/cm potential decrease in a single step.

line width occurs. At some critical field (~350 V/cm) the transition is accomplished. This value is somewhat larger than the 300 V/cm reported by Toth and Tobolsky[15] who studied the transition of a similar PBLG solution optically. The difference may be a result of differing sample cell thickness (0.013 *vs.* 0.8 cm) and solution preparation. Narrowing of the line width of the scattered laser radiation can be understood as a tightening-up of the diffusive modes as a result of a reduction in the mean-square oscillation amplitude of molecules under the influence of the field. It should be noted that results are essentially identical for both scattering geometries, which are themselves a reverse of one another.

A time lag which is undoubtably of a viscous origin was noticed in our data collection. Figure 3 demonstrates the effect of different time intervals between the recording of spectra at each voltage level. When the spectra were recorded with only a 10-min residence time at each voltage, the transition was very difficult to follow. A 20-min separation between data points improved the resolution of the transition. A separation of at least 30 min between points however was required for utmost accuracy. Waiting longer did not result in any significant divergence.

Transient studies were performed with a sudden application or termination of an electric field in excess of the critical field (Figure 4). In one experiment the voltage across the cell was increased from 0 to 500 V per cm in a single step and the spectral half-width recorded as a function of time (open circles). The procedure was carried out in reverse with a sudden voltage decrease from 500 to 0 V per cm (crosses). The liquid crystal is seen to exhibit a rapid structural change within a 2- to 5-min time span and a longer term change which requires 30 min to stabilize. It is interesting to note that the time dependence of the half-width is identical whether or not the voltage is suddenly increased or decreased. These results suggest two liquid crystal reorientation processes that occur perhaps simultaneously, but with different rates. A possible explanation is one of an initial reorientation of cholesteric microregions whose axes are not perpendicular to the suddenly imposed electric field, followed by a more sluggish unwinding of the helical superstructure. Shorting of the field would result in the reverse process with a rapid randomization of aligned nematic directors and a slower rewinding of the cholesteric structure. It is curious that the rate of initial reorientation of the cholesteric axes and the rate of randomization of nematic directors are comparable.

Conclusion

We have followed the electrotropic mesomorphic cholesteric to nematic phase transition of liquid crystal PBLG by the methods of laser light beating spectroscopy. The transition is evident as a change of the line width of laser radiation scattered from fluctuations in refractive index caused by interplanar twiston and splayon modes. These diffusive modes apparently tighten up upon the application of an applied field narrowing the laser line width. The critical electric field for our samples in chloroform solution occurs at 350 V/cm. The untwisting process is relatively slow (~30 min) and apparently involves two reorientation mechanisms with different time constants.

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Pyrolysis Gas Chromatographic Evaluation on Sequence Distribution of Dyads in Vinyl-Type Copolymers: Acrylonitrile–*m*-Chlorostyrene and Acrylonitrile–*p*-Chlorostyrene Copolymers

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ABSTRACT: Thermal degradation of vinyl-type copolymers which yield dimers was studied theoretically and experimentally by means of pyrolysis gas chromatography (pgc). New parameters, dimer formation probability constant, were proposed to account for the influence of boundary effects on the formation of dimers during pyrolysis of copolymers. The proposed method was successfully applied for characterizing dyad sequence distribution in acrylonitrile-*m*-chlorostyrene and acrylonitrile-*p*-chlorostyrene copolymers.

Although thermal decomposition is probably one of the oldest techniques for the chemist, it has played an important role in the development of our present knowledge of the nature and structure of high polymers. Especially, pyrolysis gas chromatography (pgc) has become an increasingly useful tool for the elucidation of the detailed structure, thermal stability and degradation kinetics of polymers. However, studies on copolymer microstructure have been relatively few, mainly because of our incomplete knowledge about the detailed processes of copolymer decomposition.

One general feature of the degradation results is that the yield of monomers, dimers, etc., from copolymer changes as a function of many factors, such as the nature of the constituent monomers, the arrangement and the distribution of the monomer units in the copolymer chain, pyrolysis temperature and atmosphere, etc. Wall[1-3] has developed a theory to relate the monomer yield from vinyl-type copolymer to the arrangement of monomer units in the polymer, introducing a concept of the boundary effect caused by the neighboring monomer units. Shibasaki[4-6] has modified Wall's concept and estimated that the boundary effect is mainly due to the influence of penultimate units on the stability of depropagating copolymer chain radicals. He applied it to acrylonitrile–styrene and methyl methacrylate–styrene copolymers. In the studies, he defined that the value of the boundary effect parameter, β, should be constant for a copolymer system at a given pyrolysis temperature. However when the penultimate effect is to be strictly applied for the degradation of copolymer, the formation of different types of depropagating polymer chain radicals should also be affected by the original neighboring monomer units. Accordingly the value of β might not always be constant, but could change as a function of monomer distribution in the polymer chain. Reported relations between the boundary effect and copolymer composition also suggest that the value of β is not necessarily constant.

In recent reports,[7-9] dyad distributions in some vinyl-type copolymers such as acrylonitrile–methyl acrylate, acrylonitrile–styrene, styrene–*m*-chlorostyrene, and styrene–*p*-chlorostyrene copolymers have been discussed on the basis of the dimer yield by means of pgc. In this work, a new theory was developed for the evaluation of dyad sequence distribution in vinyl-type copolymers applying the both-side boundary effect on the dimer yield from copolymer through pyrolysis. This theory was successfully applied for acrylonitrile-*m*-chlorostyrene (AN-*m*-CSt) and acrylonitrile-*p*-chlorostyrene (AN-*p*-CSt) copolymers.

Theory for the Formation of Dimers from Copolymers During Degradation

On thermal decomposition a copolymer composed of A and B monomer units, breaking bonds through various processes, would produce monomers (A and B), dimers (AA, AB, and BB), etc. Provided that these degradation products are free from recombination and other complicated secondary reactions, they should reflect the original microstructures to some extent.

As was discussed in earlier papers,[7-9] there should be some functionality between dyad concentration and observed relative dimer yield