Macromolecules

Volume 41, Number 8 April 22, 2008

Communications to the Editor

Polar Nematic Phase in Lyotropic Solutions of Poly(γ-benzyl glutamate) and Its Temperature Instability As Detected by SHG Measurement

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Received January 28, 2008
Revised Manuscript Received March 14, 2008

Rigidity and chirality are topical characteristics of α-helical polypeptides[1] and explain the tendency for polypeptide molecules to form a cholesteric liquid crystal (LC) in concentration solutions.[2,3] The transition behavior from isotropic to LC solution and the resulting superhelicoidal cholesteric structure form the basis of research for clarifying the self-organization of biological macromolecules in living material systems.[4,5] Another feature of polypeptide helices, the polarity, is also important. Since the helical conformation of polypeptides is built up by intramolecular hydrogen bonds between the proton donor N−H group and the proton accepter C═O group, residue dipole components accumulate along the polymer chain, producing an extremely large dipole moment, μ; for example, $\mu = 4000$ D for an α-helix with a degree of polymerization of 1000.[6] Hence, the dipole–dipole interaction will be significant. At this aspect, the theoretical calculations[7–9] and computer simulations[10] have suggested interesting approach to obtain the polar or ferroelectric liquid crystals, which is realized by dipole–dipole interaction. These predict that ferroelectricity appears in the nematic phase if the constituent rodlike molecules have a large dipole moment. However, only a few experimental reports have been concerned with the polar LCs in a polypeptide system.[11–13]

Here, we report a certain second harmonic generation response from lyotropic LC solutions of racemic mixtures of poly(γ-benzyl glutamate) dissolved in benzyl alcohol, showing the spontaneous formation of polar nematic phase and polar-to-nonpolar transition upon increasing the temperature or decreasing the concentration. The decisive evidence of polar nematic liquid crystal will open a new research field on liquid crystals and provide new insights into the biological importance of polar structure in supermolecularly associated materials of living systems composed of fibrous proteins, polysaccharides, and DNA.

A recent second harmonic generation (SHG) study[13] shows that an SHG active packing structure is formed in the solvent-cast films of a typical α-helical polypeptide, poly(γ-benzyl L-glutamate) (PBLG). The formation of an SHG-active structure in cast films depends on the solvents. Solid film from chloroform and dichloroethane solutions show a non-SHG-active structure, whereas an SHG-active structure can be formed from dimethylformamide (DMF) and benzyl alcohol (BA) solutions. This distinct solvent dependence indicates that the SHG response is not artificial but attributable to the polar packing structure. Further, it lets us envisage that the polar structure may be spontaneously formed in the lyotropic LC solutions and then solidified without a loss of the polarity through the solvent evaporation. The decisive evidence for this will be given by a direct SHG observation for the solutions with various concentrations.

We used here a racemic mixture of poly(γ-benzyl glutamate) (PBG) which can form a nematic LC, to avoid the formation of the complex cholesteric helix in the enantiomeric PBLG system.[12] The molecular weights of PBLG and poly(γ-benzyl D-glutamate) (PBDG) are 420 000 and 490 000, respectively. The BA solvent was used since it has a high boiling point of 205 °C, which allows the observation of the SHG response in the solutions over a wide temperature range. The LC solutions of PBG in BA were prepared with various concentrations from 15 to 45 wt %. The resulting solutions form a whitish gel at temperatures lower than 60–65 °C,[14,15] while they form fluid nematic LCs at temperatures above 65 °C. To measure SHG as a means of monitoring the spontaneous polarization in the medium,[16] Q-switched Nd:YAG laser light (1064 nm) was irradiated onto the sample (illumination area: 0.1 mm in diameter) after passing it through a quarter-wave plate and a polarizer. The SH light (532 nm) generated was detected in the direction of transmission after it passed through an IR cut filter, an interference filter, and an analyzer.

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10.1021/ma800208y CCC: $40.75

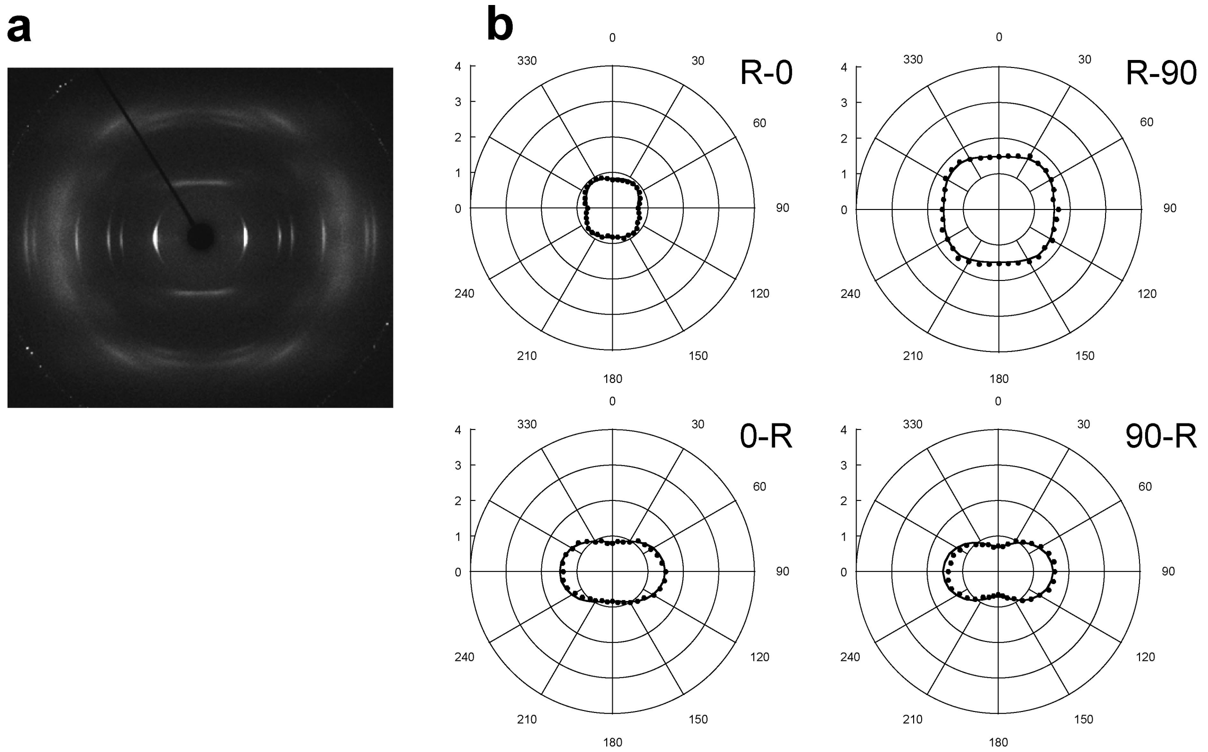

Figure 1. Characterization of magnetically aligned PBG film cast from BA solution. (a) X-ray diffraction photograph. (b) Intensity profiles of SH light. The molecular long axis of PBG corresponding to the field direction is set in the vertical direction for the X-ray pattern. The SHG profiles are measured as functions of the polarizer rotation angle (φ_p) for fundamental beam and the analyzer rotation angle (φ_a) for SHG light. The clockwise rotation is defined as being viewed along the beam and the molecular polar axis is set to 0°. Intensities are plotted as polar coordinates for four configurations (R-90, R-0, 0-R, and 90-R). The combinations of R-0 and R-90 represent that the polarization direction of fundamental light is rotated about the beam direction (i.e., R: φ_p variation from 0° to 360°) while the analyzer angle, φ_a, is fixed at 0° and 90°, respectively. In the combinations of 0-R and 90-R, φ_a is rotated with φ_p fixed at 0° and 90°, respectively. The solid curves show the theoretical calculations based on C_s symmetry where the angle between the experimental and the sample coordinates was averaged. The determined second-order nonlinear optical susceptibilities are $\chi_{11} + \chi_{12} = 1.38$, $\chi_{13} = 1.89$, $\chi_{26} = 1.24$, $\chi_{15} + \chi_{24} = 0.95$, $\chi_{31} + \chi_{32} = 1.86$, $\chi_{33} = 1.00$, and $\chi_{35} = 0.57$.

The SHG response was first examined for an oriented PBG film that was cast from the BA solution at 80 °C under a magnetic field (5 T). Nematic liquid crystal formed during the solvent evaporation process promises the perfect alignment of PBG molecules as found in the X-ray pattern of Figure 1a. The same sample shows the well-established SHG profiles in Figure 1b, which are detected with different combinations of rotation angles of the polarizer and analyzer. The noncentrosymmetry of molecular packing is obvious; the intensity profiles are fitted with the solid curves calculated by C_s symmetry, attributed to the polar monoclinic lattice with the same "up" or "down" directionality.[13] Such a clear SHG response is also observed for the film cast from DMF, but not for the film cast from chloroform, showing the same solvent dependence of the polar structure formation as in the enantiomeric PBLG system.[12,13]

In the present PBG−BA system, the nematic LCs are formed in solutions with concentrations above 15 wt %. The nematic solutions were kept inside a capillary tube with a diameter of 1 mm and placed under the magnetic filed. The perfect orientation of nematic LCs can be detected in the X-ray pattern as shown in the inset of Figure 2. The SHG measurement was then performed for this highly aligned monodomain solutions to eliminate the artificial SHG effect from the domain surface.[16] Figure 2 shows the temperature dependence of SHG intensity, which is typically observed for the solution of 28.2 wt % concentration. As envisaged above, the SHG response is clearly detected at low temperatures around 80 °C. However, SHG intensity decreases upon heating and disappears at temperatures higher than 140 °C. Upon cooling, the SHG intensity recovers to its initial value at 80 °C. A hysteresis effect can be seen upon heating and cooling. This may be partly because the annealing time of 30 min for each data point is not sufficient for the thermodynamic equilibrium. In the nematic phase with simple packing symmetry of $D_{\infty h}$, SHG activity is expected from

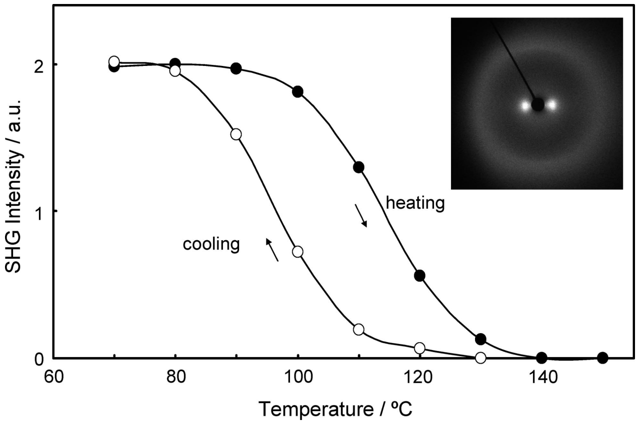

Figure 2. SHG response from nematic PBG solution in BA on heating and cooling cycle. The solution with concentration of 28.2 wt % was kept inside a capillary tube with a diameter of 1 mm, and the SHG response was then observed for the monodomain nematic solution aligned uniaxially under the magnetic field. The polarization direction of irradiated light is set parallel to the n-director, and the SHG light is detected without analyzer. To achieve equilibrium, the sample was annealed for 30 min at each temperature. The closed and open circles represent data collected during heating and cooling, respectively. The inset shows the X-ray pattern taken for the magnetically aligned nematic solution at 140 °C. As found here, the high orientation in the nematic solution is maintained during the SHG observation.

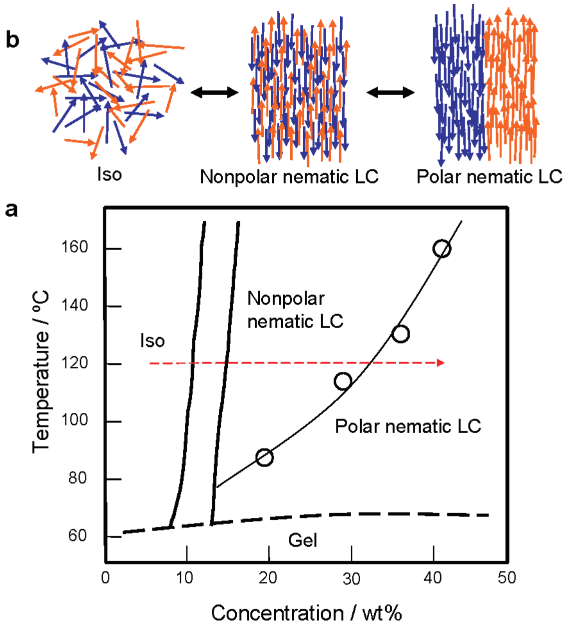

Figure 3. Polar-to-nonpolar transition in lyotropic PBG solution in BA. (a) The temperature–concentration phase diagram, including the polar-to-nonpolar transition temperature (T_c) as plotted by open circles. The isotropic–nematic coexisting region of 10–13 wt %, as given by the solid curves, was determined by a conventional optical observation of the birefringent nematic phase and dark isotropic phase between the cross-polarizers. At temperatures lower than 60 °C, solutions form the whitish gel. (b) Schematic illustration of nonpolar-to-polar transition taking place when the concentration of solution increases along the arrow in part a.

only the polar structure with a symmetry of $C_{\infty v}$.[17] Further, the optical microscopic and X-ray observations show that the nematic LC is stable in the experimental temperature region. Thus, Figure 2 represents not only the formation of the polar nematic structure in the lyotropic LC solutions but also the temperature-induced transformation from polar to nonpolar LC.

All the nematic solutions prepared with various concentrations from 20 to 45 wt % show the similar temperature dependence of SHG response, clarifying a clear trend that the polar-to-nonpolar transition (instability) temperature is increased from 85 to 160 °C with an increase in concentration. The instability temperatures, together with the well-known chimney type of coexisting region of isotropic and nematic phases,[2] are given in the temperature–concentration phase diagram of Figure 3a. At relatively high temperatures, the nonpolar nematic LC initially appears from the isotropic solution and the nonpolar-to-polar transition takes place with increasing concentration (shown by the arrow in Figure 3a). Since the present PBG molecules with a large axial ratio of 200 cannot easily rotate around their short axis to change the head–tail direction, the nonpolar-to-polar transformation proceeds by a simple migration of polypeptides in such a way that those with the same directionality gather together to form the polar domain (refer to Figure 3b). The time required for the nonpolar-to-polar transformation in the solution of 28.2 wt % concentration was estimated as ~12 min from the time dependence of the SHG intensity recovering upon the temperature jump from 150 to 80 °C. Figure 3 also shows that in the limited temperature region of 60–75 °C the system goes directly from the isotropic to the polar nematic phase. The three phases then coexist at a triple point of ~13 wt % and 75 °C.[8–10]

Terentjev and Osipov[7] predicted that in conventional nematics, polar-to-nonpolar temperature, T_c, can be estimated as

$$T_c \sim (d/l)\rho m^2/k_B$$

Here, d is the diameter of the molecule, l is the length of the molecule, ρ is the number density, and m is the longitudinal dipole moment of the rodlike molecule. For typical low-molecular-weight nematic molecules, $m \sim 1$ D and $\rho \sim 2 \times 10^{21}$ cm^{-3}, and it gives $T_c \sim 1$ K. The transition temperature is appreciably low; thus, the ferroelectric polar ordering may be destroyed by thermal molecular motion. On the same basis, ferroelectric ordering would be possible if molecules have a dipole moment m as large as 10 D.[7,9] Such large values of m are possible only in polar polymers like α-helical polypeptides[13] and aromatic polyesters.[17,18] The degree of polymerization in the present PBG is ~2000; thus, m is roughly 8000 D, d/l is 5×10^{-3}, and ρ is $\sim 3 \times 10^{17}$ cm^{-3} for the solution of 30 wt % concentration. Using these values, we arrive at the estimate $T_c \sim 10^2$ K. This is a sufficiently high temperature that can explain the present results, i.e., the formation of the polar structure in a realistic temperature region and the polar-to-nonpolar transition with the temperature variation. The increase in T_c with concentration can be attributed to the increase in ρ.

This is a first report on the polar nematic phase and its temperature-induced instability. The large dipole moment of α-helical PBG resulting from the accumulation of residue dipole components is attributable to the unusual formation of the polar nematic phase. Similar principles may apply to the self-ordering of biological macromolecules in living material systems, including polysaccharides such as cellulose and chitin, fibrous proteins such as keratin and collagen, and DNA, all of which are rigid in certain environments and simultaneously possess the head–tail characteristic. These macromolecules in aqueous solutions are known to self-organize with a uniaxial alignment in the LC field during the drying process to solid state, producing the materials with excellent properties which function particularly well as skeletal materials.[19] The present results remind us of another topical feature in the self-organization of biological macromolecules in the LC field; polar ordering that may induce piezoelectricity and pyroelectricity of materials in living systems.

Supporting Information Available: Figure S1 showing temperature dependence of SHG intensity for nematic PBG solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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