D. *J. Appl. Phys.* **1959**, *30*, 1479. Norton, D. R.; Keller, A. *Polymer* **1985**, *26*, 704.
(14) Clark, E. J.; Hoffman, J. D. *Macromolecules* **1984**, *17*, 878.
(15) Parker, R. L. *Solid State Phys.* **1970**, *25*, 152.
(16) Cahn, J. W. *Crystal Growth*; Peiser, H. S., Ed.; Pergamon: New York, 1967; p 681.

Registry No. iPP, 25085-53-4.

Communications to the Editor

Comment on a Paper by Hurung-Rern Lee, Tsai-An Yu, and Yu-Der Lee

The recently published paper "Characterization and Dissolution Studies of a Benzophenone-Containing Organic-Soluble Polyimide", by H. R. Lee et al. (*Macromolecules* **1990**, *23* (2), 502), contains numerous paragraphs and a mathematical model previously published in our contribution (Parsonage et al. "Properties of positive resists. II. Dissolution characteristics of irradiated poly(methyl methacrylate) and poly(methyl methacrylate-*co*-maleic anhydride)", *J. Vac. Sci. Technol.* **1987**, *B5*, 538). Their mathematical model uses virtually the same definitions, the same words, the same equations, and the same parameter evaluation as our previous work—albeit with an error in one of the boundary conditions—without any statement acknowledging that their model is in fact our 1987 model.

Ping I. Lee
Faculty of Pharmacy, University of Toronto
Toronto, Ontario, Canada M5S 2S2

Edward Parsonage
Department of Chemical Engineering
University of Minnesota, Minneapolis, Minnesota 55455

Nicholas A. Peppas*
School of Chemical Engineering, Purdue University
West Lafayette, Indiana 47907

Received May 3, 1990

Liquid-Crystalline Polymer Gels. 2. Anisotropic Swelling of Poly(γ-benzyl L-glutamate) Gel Cross-Linked under a Magnetic Field

Polymer gels are usually isotropic and swell and shrink equally in all directions.[1-6] If gels of anisotropic molecular structure were prepared, anisotropic mechanical behavior will be expected.

Liquid crystals are typical anisotropic materials in which molecules are arranged along a specific direction. Polymer gels with liquid-crystalline order have been prepared by cross-linking lyotropic cholesteric liquid crystals (CLC) of poly(γ-benzyl L-glutamate) (PBLG) with several diamino compounds as cross-linkers.[7] The gel retained original CLC order when the PBLG molecules take helix conformation, but it became isotropic when it was immersed in a random-coil solvent. The CLC–isotropic change was reversible and could be repeated many times.[7]

However, since the PBLG CLC gels had a multidomain structure (texture), the CLC–isotropic change induced a volume change with a very small anisotropy. In this study, a concentrated solution of PBLG in dioxane (DOX) was cross-linked under a magnetic field to prepare polymer gels with a nematic liquid-crystalline (NLC) order. In the NLC state the polypeptide helices are known to be oriented along the magnetic field.[8-10] The NLC gel showed an anisotropic volume change when the solvent was changed from a helix-supporting one to a random-coil one. Preparation of PBLG films oriented under a magnetic field has been reported.[10] The non-cross-linked *film* showed an anisotropic swelling in benzene. The anisotropic change of cross-linked PBLG *gels* that are oriented under a magnetic field is first reported in this paper.

PBLG (a gift from Ajinomoto Co., Ltd., $M_w = 170\,000$) was dissolved in DOX (17–25 wt %) containing triethylenetetramine (TETA) or diethylene glycol bis(3-aminopropyl) ether (DGBA) as a cross-linker. The concentration of the cross-linker was 10 mol % with respect to the monomer unit of PBLG. The solution was placed in a glass tube of 2–5-mm diameter. The tube was allowed to stand under a magnetic field (21 kG) at 25 °C. The magnetic field was applied perpendicular to the glass tube. After the orientation of PBLG was equilibrated (24 h), the mixture was heated to 55–70 °C and maintained at this temperature for 7–10 days under the magnetic field. Under this condition, the helix axis of the polypeptide chain has been reported to orient along the magnetic field.[8-10] The cylindrical gels prepared were sliced into disks in which PBLG helices are aligned along the disk surface and oriented to the direction of the magnetic field. Macroscopic dimensions of the gel were measured for the disk-like gel (2–5-mm diameter).

The texture of the gel was observed for a sample prepared in a flat cell with a thickness of 0.2 mm under the magnetic field applied perpendicular to the cell. An optical microscope equipped with a cross-polarizer was used for the observation of the texture.

Microscopic pictures of the LC gels prepared from a mixture of PBLG (20 wt %) in DOX containing TETA were taken under crossed polarizer. The gel prepared

0024-9297/90/2223-3868$02.50/0

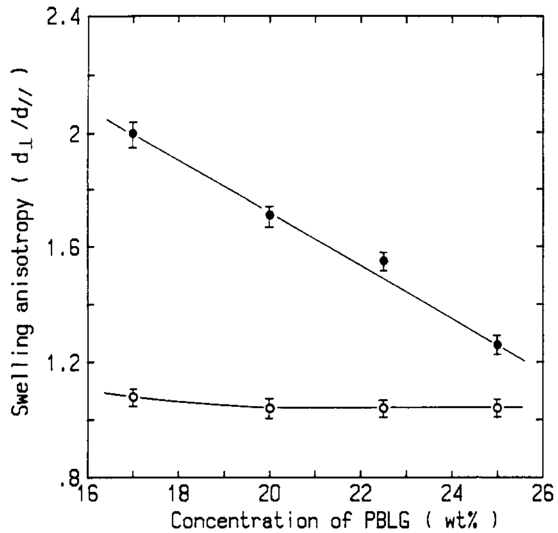

Figure 1. Swelling anisotropy ($d_\perp/d_\parallel$) in DOX (○) and in DCA (●) plotted against the PBLG concentration in the gel preparation mixture, at room temperature. $d_\perp$ and $d_\parallel$ are the diameters perpendicular and parallel to the magnetic field, respectively. The error bars were calculated from the minimum scale of the microscope.

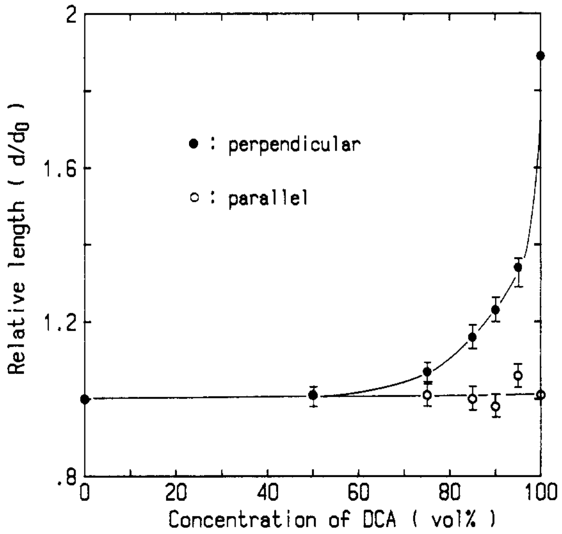

Figure 2. Swelling anisotropy of NLC gel in a DCA/DOX mixture at room temperature. The ordinate shows the ratios of dimensions in the mixed solvent and in DOX, for parallel (○) and perpendicular (●) directions to the magnetic field. The NLC gel was prepared from 20 wt % PBLG in DOX with 10 mol % TETA.

under no magnetic field shows a typical fingerprint texture of the CLC phase.[7] The gel prepared under a magnetic field of 21 kG indicated a pattern of nematic phase when observed under microscope. Both the CLC and NLC gels were macroscopically homogeneous.

The NLC gels were prepared from PBLG solutions of different concentrations (17–25 wt %) in cylindrical tubes. No significant volume change was observed in the cross-linking process. The cylindrical gels were sliced into disks, and the disk were immersed in DOX or dichloroacetic acid (DCA). The dimensions of the disks parallel and perpendicular to the magnetic field were measured. The disks were swollen to ovals, with larger diameters perpendicular to the magnetic field ($d_\perp$) and shorter diameters parallel to the magnetic field ($d_\parallel$). The $d_\perp/d_\parallel$ ratios as the measure of swelling anisotropy are plotted against the PBLG concentration in Figure 1. In both solvents, $d_\perp$ is larger than $d_\parallel$. Larger swelling in the perpendicular direction indicates that the swelling is more marked perpendicular to the PBLG helix. Therefore, a major mechanism of the swelling in the NLC gel is an insertion of solvent molecules between the helices of PBLG that are aligned parallel to the magnetic field. The anisotropy became marked when the initial concentration of PBLG is smaller. The concentration dependence can be interpreted in terms of the degree of molecular orientation of PBLG that is retarded at high concentrations of PBLG. For example, the CLC mixture of 17 and 20 wt % PBLG became NLC under the magnetic field after 24 h, but the molecular orientation did not reach the completion within 24 h for 22.5 and 25 wt % PBLG solutions.

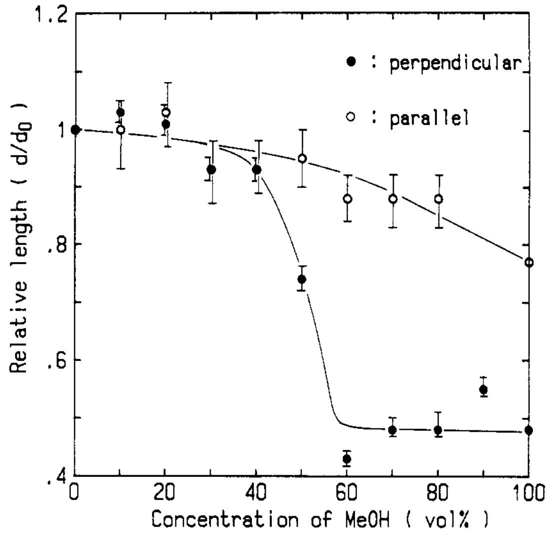

Figure 3. Shrinking anisotropy of NLC gel in MeOH/DOX mixture at room temperature. The ordinate shows the ratios of dimensions in the mixed solvent and in DOX, for parallel (○) and perpendicular (●) directions to the magnetic field. The NLC gel was prepared from 25 wt % PBLG in DOX with 10 mol % DGBA.

Figure 2 shows anisotropic behavior when the disk samples were swollen in mixtures of DCA/DOX. The ordinate of Figure 2 is the ratio of dimensions in the mixed solvent and in DOX, for parallel and perpendicular directions, respectively. The helix–coil transition of PBLG has been known to occur when the DCA volume percent is about 0.90.[7] Figure 2 shows that the anisotropic change of dimensions occurs at the helix–coil region and the degree of anisotropy reaches about 2. Interestingly, no additive swelling was observed parallel to the magnetic field when the gel was transferred from DOX to DCA. This suggests that the helix–coil transition does not influence the molecular dimension of PBLG. It may be possible that some extent of helical structure is still remaining in the gel even after the gel was immersed in DCA. However, at present, the evaluation of the extent of helix content is difficult and no quantitative discussion can be made.

The NLC gel prepared from 25 wt % PBLG in DOX with 10 mol % of DGBA showed a $d_\perp/d_\parallel$ ratio of 2.3 in DOX. The high swelling anisotropy of this gel may be attributed to a low degree of cross-linking due to the low reactivity of DGBA.[7] The swelling and shrinking behavior of this sample was studied in a DOX/methanol mixture. The ratio of the dimensions in the mixed solvent and in DOX was plotted against the methanol content in Figure 3. The dimension along the magnetic field shrank gradually with an increase in the methanol content, but no drastic change was observed. On the other hand, the dimension perpendicular to the magnetic field or perpendicular to the helix decreased suddenly when the methanol content exceeded about 50%. The anisotropic behavior suggests that the shrinkage occurs by the solvent exclusion from the intervening regions between helical polypeptide chains.

The anisotropic change of dimensions presented in this paper was reversible when the solvent composition was changed alternatively.

In conclusion, PBLG gels having nematic liquid-crystalline order were prepared. The NLC gel showed reversible anisotropic swelling and shrinking by a change of solvent compositions. This is the first observation of anisotropic dimensional change in polymer gels.

References and Notes

(1) Irie, M.; Kunwatchakun, D. *Macromolecules* **1986**, *19*, 2476.
(2) DeRossi, D. E.; Chiarell, P.; Buzzigoli, G.; Domenci, C. *Trans.-Am. Soc. Artif. Intern. Organs* **1986**, *32*, 157.
(3) Kishi, R.; Osada, Y. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 655.
(4) Suzuki, M. *Kobunshi Ronbunshu* **1989**, *46*, 603.
(5) Hirasa, O.; Morishita, Y.; Onomura, R.; Ichijo, H.; Yamauchi, A. *Kobunshi Ronbunshu* **1989**, *46*, 661.
(6) Shiga, T.; Hirose, Y.; Okada, A.; Kurauchi, T. *Kobunshi Ronbunshu* **1989**, *46*, 709.
(7) Kishi, R.; Sisido, M.; Tazuke, S. *Macromolecules*, in press.
(8) Sobajima, S. *J. Phys. Soc. Jpn.* **1967**, *23*, 1070.
(9) Panar, M.; Phillips, W. D. *J. Am. Chem. Soc.* **1968**, *90*, 3880.
(10) Samulski, E. T.; Tobolsky, A. V. *Macromolecules* **1968**, *1*, 555.
(11) To whom correspondence should be addressed.
(12) Deceased July 11, 1989.

Ryoichi Kishi, Masahiko Sisido,*[11] and Shigeo Tazuke[12]

Research Laboratory of Resources Utilization
Tokyo Institute of Technology, 4259 Nagatsuta
Midori-ku, Yokohama 227, Japan

Received May 3, 1990
Revised Manuscript Received June 11, 1990

Spectroscopic Characterization of Piezochromism in Poly(alkylsilanes): Poly(di-*n*-hexylsilane)

Although the conformational and crystal structures of poly(di-*n*-hexylsilane) (PDHS) have been well-known for some time,[1-3] a complete understanding of its thermochromic behavior has not yet been obtained. Initial results[1] indicate that, at the transition temperature, gauche bonds are introduced into the *n*-hexyl side chains, thus relieving the steric constraints that had locked the silicon (Si) backbone into a planar zigzag conformation. This disordering of the backbone results in a change in the overlap of the electronic wave functions, giving rise to the change in UV absorption from 370 to 315 nm. Information about the exact structure of the *n*-hexyl side chain is as yet unknown, but conformational energy calculations[4] have revealed that some rotations about the C–Si bond to alleviate the interaction of side chains along the main chain are likely. Furthermore, little is known about the intermolecular packing of the *n*-hexyl side chains on adjacent Si backbones, but band splittings observed in the Raman spectra of PDHS suggest that the side chains organize into an orthorhombic subcell arrangement similar to that of the odd *n*-alkanes.

It is the purpose of this paper to report the effect of elevated pressure on the spectroscopic properties of PDHS. This work is a continuation of that reported[5] earlier in which piezochromism was first observed in PDHS by Raman scattering. In this case Raman measurements were made on PDHS as it underwent a transition from an ordered state to a disordered state when submitted to elevated pressures (1–44 kbar) in a diamond anvil cell.[6] Recently, Schilling et al.[7] have used pressure (<2.5 kbar) and temperature to explore the nature of the piezochromic effect in poly(di-*n*-alkysilanes) in the low-pressure regime. In this case X-ray diffraction, solid-state NMR, and UV spectroscopy were used to characterize structural changes with pressure and temperature.

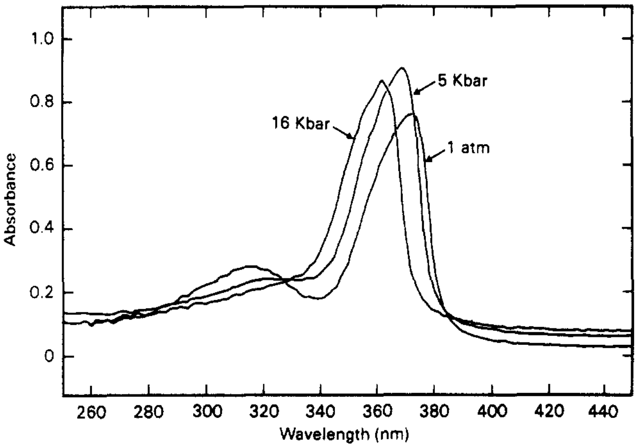

Figure 1. UV–vis spectrum of poly(di-*n*-hexylsilane) as a function of pressure.

As shown in Figure 1 the UV absorption spectra of PDHS change as a function of pressure. At 1 atm two bands are observed at 370 nm (ordered phase) and 315 nm (disordered phase). However, as the pressure is increased there is a shift of the 370-nm peak to lower wavelength while that at 315 nm appears to decrease in intensity, possibly shifting slightly to higher wavelength. This latter observation was also observed by Schilling et al.[7] and may reflect the conversion of disordered PDHS to the trans planar structure at low pressure. Interestingly, changes in the Raman spectra shown in Figure 2 are minimal until the pressure exceeds 12 kbar with the exception of a continuous shift of most of the bands to higher frequency with pressure and small changes of the Si–Si stretching bands found in the 400–500-cm^{-1} region. As the pressure increases further, however, the decrease of scattering

0024-9297/90/2223-3870$02.50/0