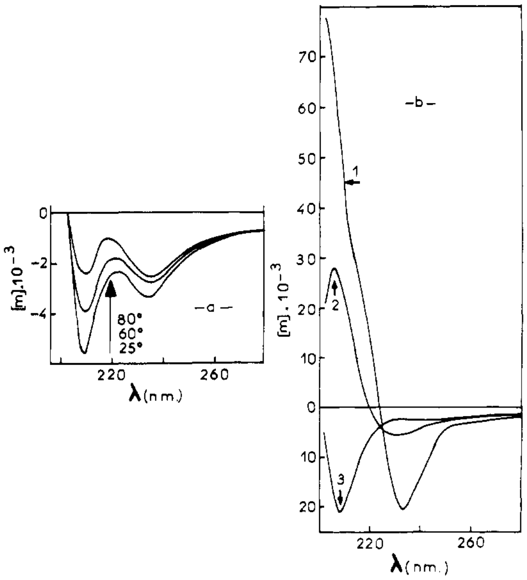

Figure 1. (a) Temperature dependance on ORD spectra for DP = 12 ($C = 10^{-3}$ equiv L^{-1}; $\alpha' = 0.4$). (b) Characteristic ORD spectra[5] for: (1) α helix; (2) β form; (3) extended structure.

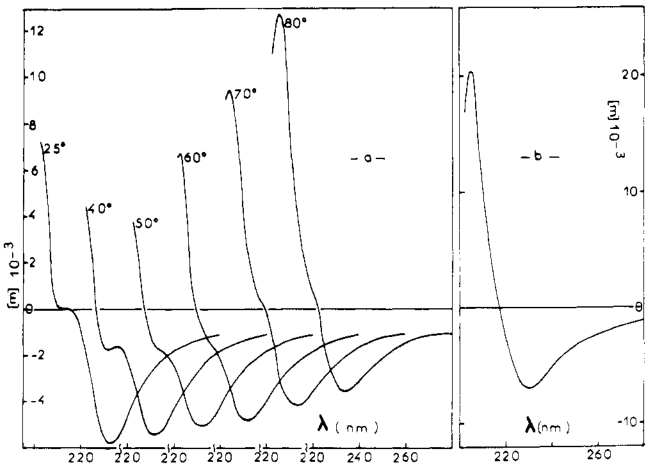

Figure 2. (a) Temperature dependance on ORD spectra for DP = 12 ($C = 10^{-3}$ equiv L^{-1}; $\alpha' = 0$). (b) ORD spectra for the same solution after a decrease of the temperature from 80 to 25 °C.

tation is almost instantaneous at 40 °C, showing the important effect of temperature on this kinetic process.

The interpretation of the ORD spectra is made possible by using the characteristics of the different peaks reproduced in Figure 1b and by resorting to the same process of combination as for CD on the four limiting spectra.[4] For the polymer of DP = 12, under acidic conditions, the ORD spectra given in Figure 2a for various temperatures clearly demonstrate that the $\alpha \rightarrow \beta$ transition proceeds through an unordered form with maximum yield at 50 °C. This process is fully reversible up to 60 °C.

At 80 °C, the spectrum corresponds to a perfectly stable equilibrium between β and unordered structures. When the temperature decreases to 25 °C (Figure 2b), the spectrum becomes characteristic of the pure β form followed by precipitation.

For a DP greater than 12 it is impossible to induce a complete β-structure formation at 10^{-3} equiv L^{-1}, whatever the time, pH, and ionic strength may be. Thus for $DP_n = 16$, the process starts in the same way as for DP = 12, but only a small amount of β form is obtained at 80 °C (Figure 3a). Therefore, the equilibrium is entirely reversible when the temperature is lowered to 25 °C. Nevertheless, as one increases the concentration to 1.84×10^{-3} equiv L^{-1} an irreversible β structure can be observed at ambient temperature (Figure 3b) with apparent precipitation after 6 h. When the DP is larger than 16 no experimental conditions allow us to separate β-structure formation from precipitation.

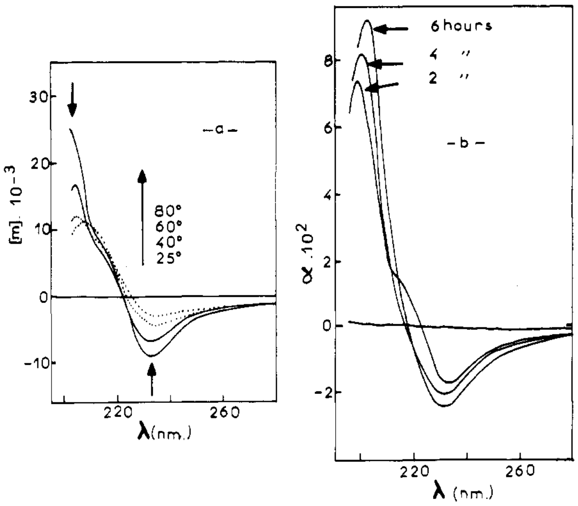

Figure 3. (a) Temperature dependance on ORD spectra for $\overline{DP_n} = 16$ ($C = 10^{-3}$ equiv L^{-1}; $\alpha' = 0$). (b) Time dependance on ORD spectra for $\overline{DP_n} = 16$ at 25 °C ($C = 1.84 \times 10^{-3}$ equiv L^{-1}; $\alpha' = 0$).

Conclusion. In this work we demonstrate that the β-structure formation induced by an increase of temperature necessarily passes through an unordered form and that the $\alpha \rightarrow \beta$ transition is reversible when the proportion of β form is lower than a critical value.

Finally, the different steps of the mechanism proposed by Zimmerman et al. are proved.

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Nuclear Magnetic Resonance and X-Ray Study of the Mesomorphic Transition in Poly[bis(2,2,2-trifluoroethoxy)phosphazene]

A number of polyphosphazene polymers, which have the general formula $[(RO)_2PN]_n$, exhibit two first-order transition temperatures. The lower temperature, denoted $T(1)$, appears to involve transformation from a crystalline to a mesomorphic phase, while the upper temperature, T_m, involves transformation to the true melt.[1,2] In poly[bis(2,2,2-trifluoroethoxy)-phosphazene], for which RO = CF_3CH_2O, $T(1) \approx 80$ °C, and $T_m = 240$ °C.[1] The transition temperatures appear to be reproducible on samples from several different preparations, though $T(1)$ depends on thermal history.[2]

X-ray diffraction work by Allen, Lewis, and Todd[3] showed the $T(1)$ transition in $[(CF_3CH_2O)_2PN]_n$ involves loss of order along the direction of the polymer backbone. The presence at 90 °C of a single equatorial diffraction line corresponding to an 11 Å spacing was taken to indicate that order in the lateral plane, perpendicular to the backbone, is retained. Subsequently, Desper and Schneider observed as many as three sharp lines in the mesomorphic phase of the meta and para isomers of poly[bis(chlorophenoxy)phosphazene] and proposed a disordered pseudohexagonal structure for the mesomorphic state.[4] Studies of two more aryloxy-substituted polymers, as well as the present trifluoroethoxy-substituted polymer, suggest that the pseudohexagonal structure is a general phenomonon for polyphosphazenes in the mesomorphic state.[5]

The pseudohexagonal structure could arise from either static or dynamic disorder. The polyphosphazene chain in the cis-trans conformation possesses directionality since all the ligand bonds are inclined in the same direction with respect to the chain axis. In the fully ordered form of the structure proposed for poly[bis(*p*-chlorophenoxy)phosphazene], each "up" chain is surrounded by four "down" chains, and vice versa. If the arrangement of the "up" and "down" chains is randomized, a static disorder along the *c*-axis direction results,[4] and it is possible that the transformation to the mesomorphic state is associated with such a loss of directional order. This loss would not affect the sharp ($hk0$) reflections in x-ray measurements, but it would affect layer lines.

Alternatively, the transition to the mesomorphic state could be associated with dynamic disorder along the *c* axis which results from side chain and/or backbone motion. This dynamic process might be visualized as involving simple rotations of chain segments, and if hand reversal defects move freely along the polymer backbone helices the notion of "up" and "down" chains would no longer apply. The result would be a disorder along the *c*-axis direction which would lead to the same x-ray reflections as obtained in the case of the static disorder described above, but the disorder would be due to motions of chain segments rather than a random arrangement of chains having well-defined "up" and "down" directions.

Nuclear magnetic resonance (NMR) has been used to study the onset of rapid reorientation in a number of solid polymers. In poly(tetrafluoroethylene)[6,7] and in *trans*-1,4-poly(butadiene),[8] reorientations were shown to be associated with the freeing of rotation about the polymer chain axis and with transformation to a pseudohexagonal structure. A particular advantage of the choice of $[(CF_3CH_2O)_2PN]_n$ for NMR studies is the presence of three nuclei, ^{1}H, ^{19}F, and ^{31}P, which can readily be studied. ^{1}H and ^{19}F provide information about the side group, and ^{31}P provides information about the chain backbone. The results reported here, although preliminary, provide evidence that the transition to the mesomorphic state is accompanied by rapid reorientational motion.

The $[(CF_3CH_2O)_2PN]_n$ was synthesized from poly(dichlorophosphazene) by the well-known substitution route.[1,9] The material was dissolved in tetrahydrofuran, precipitated with methanol, and compacted by centrifugation. The chlorine content of the resulting polymer was 0.07%, indicating practically complete substitution. The sample had an intrinsic viscosity of 1.06 dL/g (THF, 25 °C). Gel permeation chromatograms of samples, both before and after the x-ray and NMR experiments, verified that the trimer and tetramer, and low molecular weight oligomers, were absent.

X-ray diffraction patterns obtained on unoriented bulk specimens at 100 and 120 °C showed a strong line at 10.1–10.2 Å and a diffuse halo at 4.4–4.5 Å. The same lines appear in the 90 °C pattern reported by Allen, Lewis, and Todd.[3] Upon cooling to room temperature the sample exhibits the pattern of sharp crystalline lines reported previously.[10] The x-ray data thus confirm the crystalline-to-mesomorphic nature of the $T(1)$ transition for this sample.

The ≈10 Å line observed at 100 and 120 °C was found to be about twice as broad as the corresponding line at room temperature. The other sharp reflections arising from the crystalline regions at room temperature are absent above $T(1)$. It is possible that a static disordered structure could be compatible with these observations. However, the observations are generally consistent with the hypothesis of rotation of the polymer backbone, and the hypothesis is supported further by the fact that the diffuse halo near 4.5 Å could be due to rotational smearing of the ($hk1$) lines.

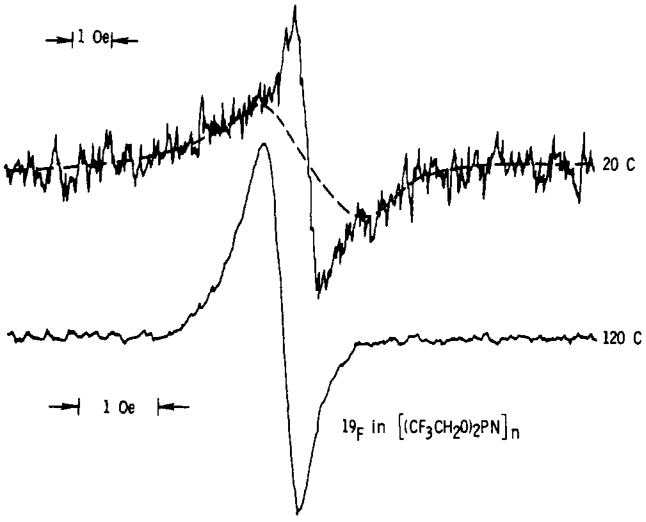

Figure 1. ^{19}F lock-in absorption spectra (first derivative presentation) in poly[bis(2,2,2-trifluoroethoxy)phosphazene], at 20 and 120 °C. The magnetic field scale is given for each spectrum (magnetic field inhomogeneity is ≈0.1 Oe), and the line corresponding to the crystalline state is sketched on the recorder trace for 20 °C.

NMR measurements at 20 MHz were performed on each of the three nuclei, at 20 and 120 °C. The apparatus has been described elsewhere.[11] Figure 1, which shows the ^{19}F first derivative lock-in absorption spectra of the solid polymer at 20 and 120 °C, is typical of the continuous-wave data. At 20 °C the spectrum consists of two lines which have the same center. The broad line has a width $\delta H \approx 2.3$ Oe (all line widths will be given as the distance between derivative extrema), and the narrow line has a width $\delta H = 0.7$ Oe. A similar broad-line–narrow-line ^{1}H spectrum was observed, with line widths ≈6 and 0.8 Oe. By noting that the broad ^{1}H line disappears but the narrow ^{1}H line is essentially unaffected when the pulse rate is increased in a pulse NMR spectrometer, we explicitly demonstrated the two lines originate from nuclei in different portions of the sample. Presumably the broad line originates in crystalline regions and the narrow line in amorphous regions.

At 120 °C this structure is gone. A single narrow line, of width ≈0.4 Oe for ^{19}F and ≈0.6 Oe for ^{1}H, remains. Since the NMR lines at 120 °C are narrower even than the lines ascribed to the amorphous region at 20 °C, passage through the $T(1)$ transition appears to enhance the mobility of side chains in both the crystalline and amorphous regions. The 120 °C lines are too narrow to be explained on the basis of side group motions alone, and thus suggest there is motion of the polymer backbone as well. Since it was difficult to prevent saturation of the NMR lines at 120 °C, we do not attach great precision to the line widths.[12,13] The magnetic field inhomogeneity was 0.1 Oe. Thus we could not have resolved high-temperature structure of the sort recently reported for poly(diethylsiloxane).[14]

The ^{31}P measurement at 20 °C shows a single unstructured line having a 2.4 Oe width. Virtually the entire 2.4 Oe width can be accounted for by ^{11}P–^{31}P and ^{31}P–^{14}N dipolar interactions on the same polymer backbone if a Gaussian line shape is assumed, so that half the width between derivative extrema equals the square root of the second moment. The backbone parameters determined[15] for the crystal structure of $[F_2PN]_n$ are used in this calculation. When ^{31}P–^{1}H and ^{31}P–^{19}F interactions are added, using a molecular model to estimate internuclear distances, the predicted line width becomes ≈ 4 Oe. We tentatively conclude, therefore, that at 20 °C we were able to observe only the ^{31}P nuclei in amorphous regions of the sample, in which a partially narrowed line would be expected. The ^{31}P line was very easily saturated, so a poor signal-to-noise ratio precluded observation of the broader, crystalline line predicted by the calculation.

The ^{31}P line narrows to 1.1 Oe when the temperature is raised to 120 °C, indicating the presence of rapid motion. One of the simplest models for such motion is rotation about the backbone axis. If γ_i is the angle between the axis of rotation and the line which links the ^{31}P nucleus under consideration and the nucleus i, the second moment in the presence of rotation, $M_{\rm Rot}$, may be written[16]

$$M_{\rm Rot} = \sum_i M_{{\rm RL},i}[\tfrac{1}{2}(3\cos^2\gamma_i - 1)]^2 \tag{1}$$

where $M_{{\rm RL},i}$ is the contribution of nucleus i to the "rigid lattice" second moment. Equation 1 presumes the axes of rotation have random orientations relative to the external magnetic field, as in a polycrystalline sample.

We assume the side groups make a negligible contribution to $M_{\rm Rot}$ because of their high degree of motion. The ^{31}P–^{31}P and ^{31}P–^{14}N distances used in the $M_{{\rm RL},i}$, and the cos γ_i, are determined from the data for $[F_2PN]_n$.[15] We let the sum in eq 1 run over the two nitrogen and two phosphorous nuclei which are nearest the ^{31}P nucleus under consideration, and which are on the same backbone. The result is $M_{\rm Rot} = 0.50$ Oe^2, which corresponds to a Gaussian line width of 1.4 Oe.

This estimate is in reasonable agreement with the experimentally determined 1.1 Oe, suggesting strongly that segments of the polymer backbone go into rapid motion at temperatures above $T(1)$. By "rapid" we mean that the correlation frequency of the motion exceeds 5 kHz. Such rotational motion in the mesomorphic state will appear as loss of static order in the chain axis direction but will not affect order in the plane perpendicular to the axis. Thus the NMR results provide a convenient interpretation for the x-ray results for the mesomorphic state. A dynamically disordered pseudohexagonal structure might be expected from the essentially cylindrical volume which molecules with rotating segments would occupy, similar to that found[4] for the meta and para isomers of poly[bis(chlorophenoxy)phosphazene].

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A Large Single Crystal of Poly(γ-benzyl L-glutamate)

The study of synthetic high polymers by x-ray methods encounters special difficulties, which arise mainly because these substances cannot be obtained in the form of well-developed single crystals large enough to be investigated by usual x-ray diffraction techniques.[1,2]

In spite of extensive efforts for preparation of large single crystals of synthetic polymers for polymer crystallography, by a number of investigators, such crystals have been reported only for poly(ethylene oxide) complexes with urea[3] and mercuric chloride.[4]

The crystal and molecular structures of synthetic polypeptides have been studied by x-ray,[5,6] electron diffraction,[7] and infrared (IR) absorption spectroscopy.[8] Poly(γ-benzyl L-glutamate) (PBLG) +CHR–NH–CO+_n (in which R = $CH_2CH_2COOCH_2C_6H_5$) was the first synthetic polypeptide to be obtained in a highly oriented form, giving a striking x-ray diffraction pattern and polarized infrared spectrum. These results indicated that the PBLG fiber took the α-helical conformation with an identity period of 27 Å, and that the packing of the molecules was shown to be nearly, but not exactly, hexagonal with a repeat length of 15 Å.[9,10]

In most of the polypeptides examined, however, only the conformation of the backbone has been determined, the precise arrangement of the atoms in the side chain being unknown.

In this communication, we should like to report some preliminary results on a large single crystal of PBLG.

The sample, PBLG, used in this study was prepared by polymerizing highly purified γ-benzyl L-glutamate N-carboxyanhydride in dichloroethane with triethylamine as initiator.[11] The intrinsic viscosity of the resultant polymer was $[\eta] = 1.336$ dL/g in dichloroacetic acid at 25 °C, corresponding to a weight-average molecular weight $\overline{M}_{\rm w}$ = ca. 2.41×10^5 (degree of polymerization $\overline{\rm DP}_{\rm n}$ = ca. 1100), estimated from eq 1 by Doty et al.,[12]

$$[\eta] = 2.78 \times 10^{-5}\overline{M}_{\rm w}^{0.87} \tag{1}$$

The large single crystals of PBLG were successfully prepared from a chloroform solution of PBLG by concentrating very gradually at room temperature. These crystals were grown from the viscous residue of this polymer.

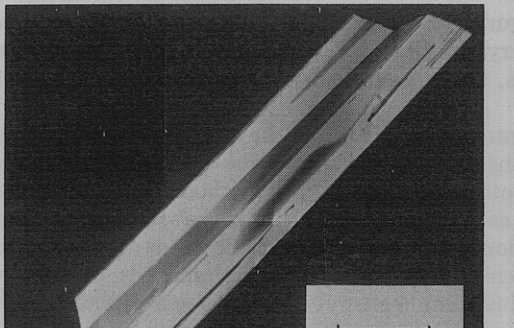

Figure 1. Polarized optical micrograph of the single crystal of poly(γ-benzyl L-glutamate).