group in the trans configuration, does not adopt such a conformation.[38–40] Both *N*-acetyl amino acids possess two types of intermolecular hydrogen bonds. The former links the OH to the amide C=O, while the latter the NH to the C=O of the carboxylic acid group. A hydrogen bond between the hydroxyl group and the amide carbonyl has been recently described in the solid state also in the case of *N*-acetyl-L-leucine.[41]

References and Notes

(1) This work is part 32 of the series; for part 31 see E. Benedetti, M. Palumbo, G. M. Bonora, and C. Toniolo, *Macromolecules,* preceding paper in this issue.

(2) (a) Istituto di Chimica Organica; (b) Istituto Chimico.

(3) (a) J. Néel, "Proceedings of the IXth I.U.P.A.C. Macromolecular Microsymposium", B. Sedlacek, Ed., Butterworths, London, 1971, p 201, and references therein; (b) I. L. Karle, "Peptides: Chemistry, Structure, and Biology", R. Walter and J. Meienhofer, Ed., Ann Arbor Science, Ann Arbor, Mich., 1975, p 61, and references therein.

(4) G. Némethy and M. P. Printz, *Macromolecules,* **5,** 755 (1972), and references therein.

(5) B. W. Matthews, *Macromolecules,* **5,** 818 (1972).

(6) H. E. Bleich, R. E. Galardy, and M. E. Printz, *J. Am. Chem. Soc.,* **95,** 2041 (1973), and previous papers in the series.

(7) H. T. Storey, R. C. Thompson, P. M. Hardy, and H. N. Rydon, *Polymer,* **15,** 690 (1974).

(8) V. Madison, M. Atreyi, C. M. Deber, and E. R. Blout, *J. Am. Chem. Soc.,* **96,** 6725 (1974).

(9) D. W. Urry, T. Ohnishi, M. M. Long, and L. W. Mitchell, *Int. J. Pept. Protein Res.,* **7,** 367 (1975).

(10) D. W. Urry, L. W. Mitchell, T. Ohnishi, and M. M. Long, *J. Mol. Biol.,* **96,** 101 (1975).

(11) V. Madison and J. Schellman, *Biopolymers,* **9,** 511 (1970).

(12) V. Madison and J. Schellman, *Biopolymers,* **9,** 569 (1970).

(13) J. T. Gerig, *Biopolymers,* **10,** 2435 (1971).

(14) M. Christl and J. D. Roberts, *J. Am. Chem. Soc.,* **94,** 4565 (1972).

(15) C. A. Evans and D. L. Rabenstein, *J. Am. Chem. Soc.,* **96,** 7312 (1974).

(16) M. Branik and H. Kessler, *Chem. Ber.,* **108,** 2176 (1975), and previous papers in the series.

(17) E. Schnabel, *Justus Liebigs Ann. Chem.,* **702,** 188 (1967).

(18) L. A. Carpino, B. A. Carpino, P. J. Crowley, C. A. Giza, and P. H. Terry, *Org. Synth.,* **44,** 15 (1964).

(19) H. Kaplan, V. B. Symonds, H. Dugas, and D. R. Whitaker, *Can. J. Biochem.,* **48,** 649 (1970).

(20) H. Kessler and M. Molter, *Angew. Chem., Int. Ed. Engl.,* **12,** 1011 (1973).

(21) L. R. Treiber, *Experientia,* **29,** 1335 (1973).

(22) N. Yasuda, T. Yamashita, and Y. Ariyoshi, *Jpn. Kokai,* **74,** 135, 922 (1975); *Chem. Abstr.,* **82,** P171443 (1975).

(23) J. E. Shields, S. T. Mc. Dowell, J. Pavlos, and G. R. Gray, *J. Am. Chem. Soc.,* **90,** 3549 (1968).

(24) A. J. Adler, N. J. Greenfield, and G. D. Fasman, "Methods in Enzymology", Vol. XXVII, Part D, C. H. W. Hirs and S. N. Timasheff, Ed., Academic Press, New York, N.Y., 1975, p 675.

(25) G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A,* **27,** 368 (1971).

(26) E. Benedetti and R. E. Marsh, manuscript in preparation.

(27) R. K. Olsen, *J. Org. Chem.,* **35,** 1912 (1970).

(28) E. Benedetti, M. R. Ciajolo, and A. Maisto, *Acta Crystallogr., Sect. B,* **30,** 1783 (1974).

(29) M. Cesari, L. D'Ilario, E. Giglio, and G. Perego, *Acta Crystallogr., Sect. B,* **31,** 49 (1975).

(30) Y. Sasada, K. Tanaka, Y. Ogawa, and M. Kakudo, *Acta Crystallogr.,* **14,** 326 (1961).

(31) J. L. Dimicoli and M. Ptak, *Tetrahedron Lett.,* 2013 (1970).

(32) C. M. Deber, F. A. Bovey, J. P. Carver, and E. R. Blout, *J. Am. Chem. Soc.,* **92,** 6191 (1970).

(33) O. Oster, E. Breitmaier, and W. Voelter, "NMR Spectroscopy of Nuclei Other Than Protons", T. Axenrod and G. A. Webb, Ed., Wiley, New York, N.Y., 1974, p 233, and previous papers in the series.

(34) L. E. Webb and C. F. Lin, *J. Am. Chem. Soc.,* **93,** 3818 (1971).

(35) F. A. Bovey, "Peptides, Polypeptides, and Proteins", E. R. Blout, F. A. Bovey, M. Goodman, and N. Lotan, Ed., Wiley, New York, N.Y., 1974, p 248.

(36) R. Deslauriers, Z. Grzonka, K. Schaumburg, T. Shiba, and R. Walter, *J. Am. Chem. Soc.,* **97,** 5093 (1975).

(37) Gy. Lovas, A. Kalman, and Gy. Argay, *Acta Crystallogr., Sect. B,* **30,** 2882 (1974).

(38) G. B. Carpenter and J. Donohue, *J. Am. Chem. Soc.,* **72,** 2315 (1950).

(39) J. Donohue and R. E. Marsh, *Acta Crystallogr.,* **15,** 941 (1962).

(40) M. F. Mckay, *Cryst. Struct. Commun.,* **4,** 225 (1975).

(41) A. Waskowska, K. Lukaszewicz, L. G. Kuzmina, and Yu. T. Struchkov, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.,* **23,** 149 (1975); *Chem. Abstr.,* **83,** 89101t (1975).

Mesomorphic Structure at Elevated Temperature in Meta and Para Forms of Poly[bis(chlorophenoxy)phosphazene]

C. R. Desper* and N. S. Schneider

Army Materials and Mechanics Research Center, Watertown, Massachusetts.

Received February 17, 1976

ABSTRACT: Two polymers, the meta (I) and para (II) isomers of poly[bis(chlorophenoxy)phosphazene], have been studied in their high-temperature mesomorphic state by x-ray diffraction. Previous studies revealed two first-order thermal transitions: a lower transition at $T(\mathrm{l})$ involving a large enthalpy change, and an upper transition at $T(\mathrm{m})$ involving very little enthalpy change. In the intervening temperatures, a span of 300 °C for I and 200 °C for II, a mesomorphic phase is known to be stable. Stretched films of I and II heated to 180 °C (between $T(\mathrm{l})$ and $T(\mathrm{m})$ for both) retain molecular orientation but transform from orthorhombic to pseudohexagonal structure. The observed sharp equatorial lines have been indexed (100), (110), and (210) for I, (100) and (110) for II. In both I and II the same spacing of 14.2 Å is observed between chain axes in the two-dimensional lattice. The question of order or disorder with respect to chain directionality is discussed. The $T(\mathrm{l})$ transition involves a 30% expansion in the *ab* plane which is much larger than the previously estimated volume change suggesting a longitudinal contraction of the chains. Analogies are drawn with liquid crystal and plastic crystal structures of small molecules.

A variety of polyphosphazene polymers can be synthesized with a phosphorus–nitrogen backbone and various organic side groups. Allen, Lewis, and Todd[1] and later Singler and co-workers[2–4] reported unusual thermal transition behavior observed by calorimetry and other techniques in several polyphosphazenes. A common feature of many polymers of this class is the existence of two first-order transitions, the lower one denoted $T(\mathrm{l})$ and the upper $T(\mathrm{m})$. The $T(\mathrm{l})$ transition appears to be a transformation between two ordered phases, while the $T(\mathrm{m})$ transition, which occurs just below the decomposition temperature $T(\mathrm{d})$, is the true melting temperature. Spherulitic morphology and birefringence present at room temperature persist above $T(\mathrm{l})$, disappearing only when $T(\mathrm{m})$ is reached, although a change in the magnitude of the birefringence is observed at $T(\mathrm{l})$. On the other hand, the polymer shows fluid properties between $T(\mathrm{l})$ and $T(\mathrm{m})$ and can be molded in this temperature range, which can extend for 150 to 300 °C (see Table I).

Table I
Thermal Transition Temperatures for Poly[bis(chlorophenoxy)phosphazenes][a]

	m-Chloro isomer I	*p*-Chloro isomer II
T(l), °C	81	167
T(m), °C	370	365
T(d), °C	380	410

[a] Data from Singler and co-workers.[2–4]

Table II
Poly[bis(chlorophenoxy)phosphazene]'s X-Ray Diffraction Lines at 180 °C

Chloro position	Spacing	Position	Intensity	Indices
Meta	12.13	Equator	Strong	(100)
Meta	7.05	Equator	Weak	(110)
Meta	4.58	Equator	Weak	(210)
Meta	4.12	Meridion	Diffuse	(*hkl*)
Para	12.07	Equator	Strong	(100)
Para	7.14	Equator	Weak	(110)
Para	4.51	Meridion	Diffuse	(*hkl*)

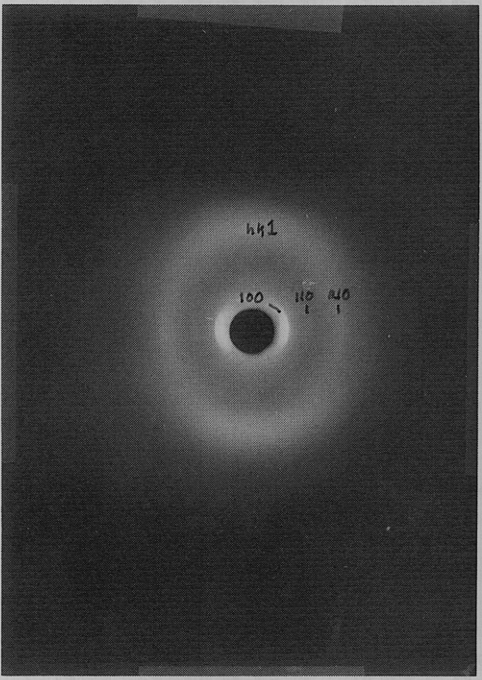
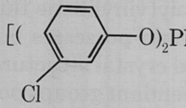


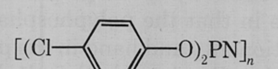
Figure 1. X-ray Diffraction Pattern at 180 °C for I.

Allen, Lewis, and Todd[1] observed a single sharp x-ray diffraction line at 11 Å at the equatorial position for oriented poly[bis(trifluoroethoxy)phosphazene] between *T*(l) and *T*(m). They concluded that lateral order is retained in this temperature range, although the three-dimensional order of the crystalline phase below *T*(l) is lost. Preliminary data have been reported by Schneider, Desper, and Singler,[4] indicating a similar state of intermediate order occurring above *T*(l) for poly[bis(*p*-chlorophenoxy)phosphazene]. In this case, two sharp lines were observed at 12.1 and 7.4 Å in the range 199–246 °C for the mesomorphic material. Since there was evidence for the presence of oligomeric species including cyclic trimer in this sample and the amount of cyclic trimer was undoubtedly increased by the prolonged heating of the sample in this earlier work,[4] the experiment has been repeated under carefully controlled conditions, and has been extended to a closely related polymer, poly[bis(*m*-chlorophenoxy)phosphazene].

Experimental Section

The present work is a continuation of previously reported synthesis and characterization efforts.[3] Two polymers, the meta (I) and para (II) isomeric forms of poly[bis(chlorophenoxy)phosphazene], were selected for further investigation by x-ray diffraction. Details of the synthesis procedure and characterization have been reported, and the thermal transition behavior is summarized in Table I.


I


II

The earlier x-ray results[4] were obtained with a sample of II synthesized by Horizons Corp. and compression molded in this laboratory. In the present work new samples of I and II were used which were synthesized in-house. These samples were subjected to prolonged extraction with a boiling methanol/water mixture to remove low molecular weight species. Gel permeation chromatograms in tetrahydrofuran confirmed the absence of cyclic trimer, cyclic tetramer, and other oligomers in these two samples. Films of the two extracted polymers were solution cast from tetrahydrofuran, then stretched six times at room temperature. The film relaxed to a draw ratio of five times upon removal from the stretching rack for placement in the x-ray camera. A heated flat-film x-ray camera was used with monochromatic Cu Kα radiation at a sample-to-film distance of 30.08 mm. The diffraction patterns for the two polymers were recorded at 180 °C, chosen to lie between *T*(l) and *T*(m) for both polymers. The *T*(l) value of these polyphosphazenes can vary somewhat with thermal history or polymerization conditions, particularly for I. The 180 °C temperature is well above the range of variation of *T*(l) for both I and II. The samples were heated only for the 22-h period required to obtain a diffraction pattern, and no trimer or tetramer lines were found after cooling. The sample temperature was controlled by a thermocouple to better than 1 °C accuracy.

Results

At room temperature, both polymers showed a fiber pattern consistent with the unit cell proposed by Bishop and Hall[5] for the para-substituted polymer. Diffuse scattering indicated the possibility of a second noncrystalline phase at room temperature. At 180 °C an oriented pattern was recorded for both polymers, with two or three sharp equatorial lines, and a diffuse scattering maximum at the meridion position. The data obtained are summarized in Table II, and a representative diffraction pattern is shown in Figure 1. Both polymers exhibited a strong equatorial reflection at 12.1 Å, and a weaker reflection at 7.1 Å; the meta-substituted polymer also exhibited a third weak, but sharp, line at 4.58 Å. The three observed equatorial lines are close to the ratios $1{:}1/\sqrt{3}{:}1/\sqrt{7}$, suggesting a pseudohexagonal structure, and may be indexed (100), (110), and (210), respectively, indicating a lattice parameter of a = 14.2 Å.

The temperature dependence was examined for I only, and the data are summarized in Table III. The same two equatorial lines appear at 180, 199, and 238 °C. These lines are not present at 146 or 22 °C [below *T*(l)], where lines indexed with the Bishop and Hall[5] unit cell appear. Within experimental error, there is no expansion of the pseudohexagonal structure in the equatorial plane with temperature, and the spacings of the first two sharp lines are approximately in the ratio $1/\sqrt{3}$. The transformation from the Bishop and Hall orthorhombic structure to the proposed pseudohexagonal structure involves an expansion of 30% in the *ab* plane area (see Table IV). If the preliminary experiments[4] which indicate that the volume expansion is much less than 30% are correct, then a contrac-

Table III
Poly[bis(chlorophenoxy)phosphazene]'s Ratio $D(100)/D(110)^a$ for Pseudohexagonal Structure

Chloro position	T, °C	$D(100)^b$	$D(110)^a$	Ratio
Para	180	12.07	7.14	1.69
Para	199	12.10	7.04	1.72
Para	238	12.18	7.12	1.71
Meta	180	12.13	7.05	1.72
Estimated error, %		1.9	1.0	2.9

[a] The ratio $D(100)/D(110)$ for the pseudohexagonal lattice is identical with the ratio b_0/a_0 for the alternate orthorhombic lattice of Figure 2A. [b] Unit cell of Figure 2B used for indexing.

Table IV
Poly[bis(chlorophenoxy)phosphazene]'s Pseudohexagonal Structure. Lateral Expansion from Orthorhombic Crystal^a

Chloro position	T, °C	a_0/a_{BH}	b_0/b_{BH}	$a_0b_0/a_{BH}b_{BH}$
Para	180	1.09	1.19	1.30
Para	199	1.08	1.20	1.29
Para	238	1.09	1.20	1.31
Meta	180	1.08	1.20	1.29

[a] a_{BH} = 13.08, b_{BH} = 20.23 for room temperature crystal structure of Bishop and Hall.[5]

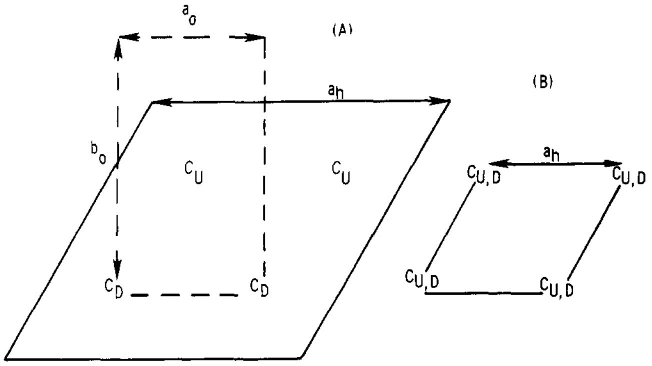


Figure 2. Two alternate (001) projections of the pseudohexagonal structure for I and II: (A) structure in which up and down directions of chains are correlated; (B) structure with randomization of the chain directions.

tion in the polymer chain direction must occur on transformation from the crystalline to mesomorphic state.

The source of the diffuse meridional scattering maxima which are observed at angles corresponding to d = 4.12 Å (I) and d = 4.51 Å (II) is not clear at present. Lack of any sharp off-equator scattering indicates that the pseudohexagonal material is less highly ordered along c than in the ab plane. The diffuse scattering could be attributed to overlapping, poorly defined (hkl) reflections from a pseudohexagonal structure since the Bishop and Hall structure has strong (101), (021), and (031) reflections in this range. Alternately, the diffuse scattering could originate in polymer in a greater state of disorder than the pseudohexagonal state, i.e., from an amorphous phase.

Upon cooling to room temperature, the diffraction patterns of the polymers showed normal three-dimensional crystalline order with retention of preferred orientation as in the previously reported work.[4] For the para-substituted polymer (II), the lines of the Bishop and Hall structure[5] reappeared upon cooling from 180 °C. However, the meta-substituted polymer (I), which showed the same lines as (II) before heating, showed a notably different pattern of three-dimensional order upon cooling from 180 °C.

Since depolymerization to cyclic trimer or tetramer is known[6] to occur in these polymers with prolonged heating, the possibility of spurious diffraction lines arising from their crystals was considered. For this purpose, the cyclic trimers and tetramers corresponding to the two polymers under study, hexa-*m*- or *p*-chlorophenoxycyclotriphosphazene and octa-*m*- or *p*-chlorophenoxycyclotetraphosphazene, were synthesized and purified. The diffraction patterns obtained from these compounds rule out the assignment of any lines in the present polymer work to trimer or tetramer, and confirm the formation of trimer under much more severe heating conditions in the previous work.[4] The properties of the trimers and tetramers will be discussed more fully in a later publication.

The molecular orientation is preserved throughout the heating and cooling cycle, despite the known fluid properties of these polymers above $T(1)$. In fact, an extruded monofilament gave an oriented pattern quite similar to the stretched film indicating that the flow process in this temperature range involves plastic deformation rather than ordinary viscous flow.

Discussion

A pseudohexagonal type of structure is indicated between $T(1)$ and $T(m)$ by the ratios of the ($hk0$) spacings. The absence of all but the first few ($hk0$) reflections may be explained by the presence of a certain degree of disorder in the (001) projection of the structure. The presence of a pseudohexagonal structure suggests that interactions between side groups of approximately spherical shape (i.e., the freely rotating chlorophenoxy groups) have become the controlling factor determining the lattice, while intrachain potentials have become less controlling. A good example of such a pseudohexagonal structure is phase I of poly(vinylidene fluoride), studied by Lando, Olf, and Peterlin,[7] in which the spherical hydrogen and fluorine atoms become controlling. The present case is somewhat more complex than the poly(vinylidene fluoride) case in that the polyphosphazene chain possesses both directionality and hand in the proposed crystal structure.[5] Directionality, i.e., whether the bulky pendant groups point up or down from the backbone of the chain, is expected to exert a stronger influence on interchain packing than hand. Thus correlation in chain directionality must be considered as a possible source of disorder.

Two alternate pseudohexagonal structures are shown in Figure 2. In the Figure 2A structure, the "up" and "down" chains are correlated, so that layers of chains will be alternately all "up" or all "down". An orthorhombic unit cell, shown in dashed lines in Figure 2A, may be drawn between equivalent sites. This cell contains two chains, one "up" and one "down", and in terms of symmetry is of the same plane group *pgg* as the (001) projection of the Bishop and Hall[5] low-temperature crystal structure. Thus the Figure 2A structure may be obtained from the Bishop and Hall structure by merely allowing unequal expansion along a and b to change the b:a ratio (see Tables III and IV) and allowing disorder in the c direction. A slight departure from a metrically hexagonal pattern is possible, in the Figure 2A structure, due to the fact that lattice planes containing all "up" or all "down" chains (such as the horizontal planes in Figure 2A) may not be equivalent in packing characteristics to planes containing alternating "up" and "down" chains, such as those planes approximately 60° above and below horizontal in Figure 2A. In a well-developed structure of this type, the orthorhombic nature of the cell could be detected by splitting of the pseudohexagonal lines, as in the polyacrylonitrile case,[8] but this is not possible in the present disordered structures.

The second possibility for a pseudohexagonal structure is one in which the chains pack without regard to their directionality as depicted in Figure 2B. In this case, all the chain sites are equivalent and are occupied by an equal number of "up" or "down" chains. It should be mentioned that the motion of a hand-reversal defect offers a possible mechanism for changing the directionality of a given chain segment.

There is no evidence to distinguish whether the actual structure conforms to either the Figure 2A or the Figure 2B structure, which differ only in the ordering or the randomness of the chain directionality. Indeed, the difference need not be clearcut; a continuous variation between the two alternatives is possible, as proposed by Hikosaka and Seto[9] to explain variations in the diffraction pattern of monoclinic crystalline polypropylene caused by ordering and disordering in chain directionality. In this regard, it is noteworthy that the degree of organization in the mesomorphic state of the present polymers is influenced by the thermal history of annealing between $T(\mathrm{l})$ and $T(\mathrm{m})$ as indicated by the improved crystal structure which results when the treated sample is cooled below $T(\mathrm{l})$.[4] It is possible that the transformation from the less ordered Figure 2B structure to that of 2A may be involved in these thermal history effects, although no definite conclusion is possible at this time, particularly since recent experiments indicate that the presence of oligomers may play a role.

In the light of the information on the properties and structure of these two polymers in the mesomorphic state and the related behavior of a large number of other organophosphazene polymers, the question arises as to what name should be used to describe the structure present between $T(\mathrm{l})$ and $T(\mathrm{m})$. The term "mesomorphic" indicates an intermediate level of order between the classical crystal and the liquid state. In this sense, there is no doubt that the structure is mesomorphic, but the term is not very specific.

"Paracrystalline" is a term pertaining which relates the diffraction characteristics of structures intermediate between the crystalline and the liquid states to lattice distortions. There is every reason to believe that paracrystalline theory could be used to develop a quantitative evaluation of the nature of the lattice distortions in the mesomorphic state of these two polymers. Because of the sharpness of the equatorial lines and the diffuse character of the meridion reflection, we may anticipate that distortions would be greater in the c direction than in the ab plane. However, paracrystalline theory, because of its general nature and because it is not model dependent, does not address itself to the origin of these distortions.

The term "liquid crystal" carries with it an even wider range of implications. The various liquid crystal models are constructed to explain calorimetric and diffraction properties, but also carry further implications with regard to persistence of morphology, or flow properties. Thus, the more descriptive term "liquid crystal" may be useful in the present case, in view of the marked softening and susceptibility to flow observed above $T(\mathrm{l})$.

However, problems arise in fitting the present structure into the liquid crystal classification schemes.[10-12] Before the present x-ray data were available, the structure was tentatively described as "nematic".[2] Sharp diffraction peaks of the type observed here are not characteristic of nematic type liquid crystals,[10] however, but the smectic category of liquid crystals can give sharp lines. In particular, lines of the ratios $1{:}1/\sqrt{3}{:}1/\sqrt{7}$, such as the three sharp lines of polymer I in Table II, are characteristic of smectic structures possessing pseudohexagonal packing.[11,12] In polymers, such a structure, stable over a range of 150 °C for poly(p-xylylene), was termed "smectic" by Niegisch.[13]

Using the term "smectic" to describe polymer structure presents difficulties. In the liquid crystal sense, "smectic" also involves layering in the third dimension as well as ordered packing in two dimensions, i.e., there is correlation of the ends of the small liquid crystal molecules which is connected with the flow behavior. In the polymer case, the chain ends would be much further apart than the intermolecular spacings, and there is no evidence that they are correlated. Instead, equivalent positions of the repeating structure along the chains might be correlated, but even if this proved to be the case this does not provide a relation between the structure and flow behavior. In particular, a crystal-type slip process in response to shear stress is restricted to the chain direction in the polymer case, but not for a liquid crystal.

Iwayanagi and Miura[14] have used the term "plastic crystal" for an analogous pseudohexagonal high-temperature phase of *trans*-1,4-polybutadiene, while Beatty et al.[15] have described the mesomorphic phase of poly(diethylsiloxane) as a "viscous crystalline phase". Both papers draw an analogy with the structures classically denoted as "plastic crystals" in the realm of low molecular weight compounds. In this regard, Westrum and McCullough[16] list four distinguishing characteristics common to "plastic crystals" of low molecular weight compounds: (a) low entropy of fusion, (b) high triple-point temperature and pressure, (c) crystals usually of cubic or hexagonal symmetry, and (d) one or more quite energetic transitions in the solid state. With the exception of (b), which is not applicable to polymers, the present polymeric compounds satisfy the criteria for plastic crystals. The same criteria, however, are also fulfilled by substances forming smectic liquid crystals. Thus, while many analogies can be drawn between the present mesomorphic structures and the "liquid crystal" and "plastic crystal" categories, an unambiguous assignment is not possible at present.

Evidence is also lacking at present regarding the details of the underlying molecular conformations and dynamic processes giving rise to the properties of the mesomorphic state in these polyphosphazenes. An analogous pseudohexagonal state in poly(tetrafluoroethylene) above 30 °C is the subject of intensive study by Clark and Muus.[17,18] X-ray diffraction and nuclear magnetic resonance data indicate that the 30 °C transition involves increasing angular disorder about the chain axes resulting from torsional oscillations, with gradually developing translational displacements of chain segments parallel to the chain axes. Similar processes may occur in the polyphosphazene. On the other hand, Allcock has shown that in the case of poly(difluorophosphazene) a complete change in conformation occurs between low-temperature and high-temperature crystal forms.[19] The structure below −56 °C shows a fiber (c) axis repeat of 4.86 Å suggesting a cis, trans planar conformation, a special case of the 2_1 helix. The higher temperature form shows a fiber (c) repeat of 6.49 Å with at least three monomer units per repeating segment. We consider such a change in conformation unlikely in the present case.

Conclusion

For two isomeric forms of poly[bis(chlorophenoxy)phosphazenes] a pseudohexagonal structure has been observed by x-ray diffraction which is stable over a wide range of elevated temperatures. The structure possesses ordered packing of parallel chains in two dimensions, leading to sharp equatorial reflections. Diffuse meridion scattering indicates disorder in the third dimension. This evidence, in conjunction with previous evidence of flow properties and persistence of structure, suggests a close kinship with the liquid crystal structures observed in certain small molecules. The structure most closely resembles the smectic category of liquid crystals, although the analogy with small molecule liquid crystals is somewhat imperfect. Striking analogies are also observed between the present structure and the so-called plastic crystal.

The question of possible ordering of the chain directionality is also discussed, but no conclusion is possible at present. Further research in the structure and morphology of poly(aryloxyphosphazenes) is a subject of continuing investigation at this laboratory, with the goal of affording a more complete description of the molecular processes associated with the thermal transitions.

Acknowledgment. The authors wish to express their gratitude to Dr. J. B. Lando for helpful discussion, and to Dr. R. E. Singler and Mr. B. R. LaLiberte for their contributions in terms of polymer synthesis and characterization.

References and Notes

(1) G. Allen, C. J. Lewis, and S. M. Todd, *Polymer*, **11**, 44 (1970).
(2) R. E. Singler, N. S. Schneider, and G. L. Hagnauer, *Polym. Eng. Sci.*, **15**, 321 (1975).
(3) R. E. Singler, G. L. Hagnauer, N. S. Schneider, B. R. LaLiberte, R. E. Sacher, and R. W. Matton, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 433 (1974).
(4) N. S. Schneider, C. R. Desper, and R. E. Singler, *J. Appl. Polym. Sci.*, in press.
(5) S. M. Bishop and I. J. Hall, *Br. Polym. J.*, **6**, 193 (1974).
(6) H. R. Allcock, G. Y. Moore, and W. J. Cook, *Macromolecules*, **7**, 571 (1974).
(7) J. B. Lando, H. G. Olf, and A. Peterlin, *J. Polym. Sci., Part A-1*, **4**, 941 (1966).
(8) P. H. Lindenmeyer and R. Hosemann, *J. Appl. Phys.*, **34**, 42 (1963).
(9) M. Hikosaka and T. Seto, *Polym. J.*, **5**, 111 (1973).
(10) A. deVries, Proceedings of the International Conference on Liquid Crystals, Bangalore, Dec. 1973.
(11) G. H. Brown, *J. Electron. Mater.*, **2**, 403 (1973).
(12) G. H. Brown and J. W. Doane, *Appl. Phys.*, **4**, 1 (1974).
(13) W. D. Niegisch, *J. Appl. Phys.*, **37**, 4041 (1966).
(14) S. Iwayanagi and I. Miura, *Rep. Prog. Polym. Phys. Jpn.*, **8**, 303 (1965).
(15) C. L. Beatty, J. M. Pochan, M. F. Froix, and D. D. Hinman, *Macromolecules*, **8**, 547 (1975).
(16) E. F. Westrum and J. P. McCullough, "Physics and Chemistry of the Organic Solid State", Vol. I., D. Fox, M. N. Labes, and A. Weissberger, Ed., Interscience, New York, N.Y., 1963, p 90.
(17) E. S. Clark and L. T. Muus, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **117**, 119 (1962).
(18) L. T. Muus and E. S. Clark, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **5**, 17 (1964).
(19) H. R. Allcock, R. L. Kugel, and E. G. Stroh, *Inorg. Chem.*, **11**, 1120 (1972).

The Effect of Temperature on the Cellulose/Water Interaction from NMR Relaxation Times

Michael F. Froix* and Andreas O. Goedde

Xerox Corporation, Webster, New York 14580. *Received January 2, 1976*

ABSTRACT: An earlier investigation of the interaction between cellulose and sorbed water has revealed dramatic changes in molecular mobility at the point of plasticization. This transition region is associated with the satisfaction of primary adsorption sites and the resultant swelling of the system accompanying this condition. Many drastic changes in physical properties are predicted on the basis of this phenomenon. On lowering the temperature, the cellulose/water system continues to permit the determination of spin–spin relaxation times for a cellulose phase, bound water, and free water phases. The cellulose and bound water phases also exhibit plasticization which seems to require smaller amounts of moisture to attain this condition at lower temperatures. The freezing point of free water is lowered from 273 K for bulk water to between 221 and 252 K while freezing of bound water occurs at 196 K. Above room temperature the exchange prorcess, involving water molecules between the various phases, makes a large contribution to the T_2's observed. As a result a bound water phase can no longer be distinguished from the others. Increasing the temperature also probably opens the structure up making previously inaccessible sites available with the result that primary adsorbed water does not impart additional motion to the system above room temperature.

In a recent NMR study on the interaction of water with cellulose the molecular motion of the cellulose chains, bound water, and free water were monitored as a function of the amount of sorbed water in cotton linters.[1] In that study both the cellulose and bound water exhibited an increase in molecular motion at the point of plasticization. This plasticization point is associated with the transition between the primary bound and secondary bound water and results from the swelling of the structure allowing increased mobility of the cellulose chains.[1] Even though free water was found to exist at very low moisture contents the quantity increased dramatically above the point of plasticization where multilayer buildup is expected.[1] This is consistent with the upturn in the adsorption isotherm for the system.[1]

Following the dramatic effects which were observed at constant temperature, this study was undertaken to determine what added perturbations a temperature variable would impose on the cellulose/water system. As a result, the spin–lattice (T_1) and spin–spin (T_2) relaxation times of cellulose containing varying amounts of water were measured as a function of temperature.

Experimental Section

The cotton linters used and the method of treatment have been described previously.[1] The pulsed NMR apparatus and the techniques for measuring T_1 and T_2 are also described in an earlier publication.[1]

Results and Discussion

The relaxation times of cellulose/water systems were measured as a function of moisture content and temperature in the range 196 to 360 K. At temperatures below room temperature the T_2 behavior is similar to that reported previously where the free induction decays (FIDs) are observed to consist of a cellulose component (T_{2c}), a bound water component (T_{2b}), and free water (T_{2f}).[1] These features are found even at temperatures as low as 221 K, except that the free water phase disappears between 252 and 221 K. This is in agreement with previous observations where sorbed water was found to freeze within the same temperature range.[2] As pointed out earlier the freezing process is not indicative of ice formation but reflects only the reduction in molecular mobility which produces icelike behavior[2] in the free water component. At temperatures below the freezing of free water T_{2c} and T_{2b} are still observed. Figure 1 contains plots of T_{2c} and T_{2b} as a function of moisture content at 221 K. The plots are typical of T_{2c} and T_{2b} for temperatures below room temperature. T_{2b} is still larger than T_{2c} reflecting the greater motional freedom available to bound water as compared to the cellulose chains.