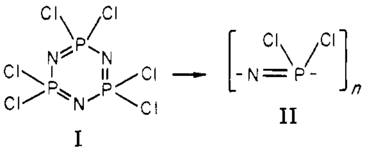
Crystalline Transitions and Related Physical Properties of Poly(dichlorophosphazene)[1,2]

Harry R. Allcock* and Robert A. Arcus

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received May 25, 1979*

ABSTRACT: Highly purified, uncross-linked poly(dichlorophosphazene), $(NPCl_2)_n$ (II), has been examined by X-ray diffraction, optical, differential scanning calorimetry, and dynamic mechanical techniques. The unstressed polymer is amorphous at 25 °C. Crystallization can be induced by cooling the polymer to −7.2 to −12 °C or by stretching of the polymer at 25 °C. Three different crystalline modifications were detected: IIc, crystalline by cooling; IIs, crystalline by stretching; and IIsr, a metastable crystalline form obtained from the stretched and relaxed polymer. The degree of crystallinity of IIs was $\simeq$20% and that of IIsr was calculated to be 11%. The main crystal melting temperature occurred at +33.1 °C (IIc) or +39 °C (IIs), although the crystallization temperature on cooling is near −7.2 °C. However, additional endothermic transitions were detected at +12 and +25.4 °C for IIsr. The values detected by use of the dynamic mechanical method differed from those found from X-ray diffraction or differential scanning calorimetry experiments. This anomaly is almost certainly a consequence of the sensitivity of the crystallization behavior of this polymer to stress effects. The physical properties of $(NPCl_2)_n$ appear to be directly related to the inherent high flexibility of the chain.

Poly(dichlorophosphazene) (II) is an inorganic macromolecule with unusual and unexpected properties. It is a rubbery elastomer at room temperature. In its physical appearance, it shows a superficial resemblance to lightly cross-linked natural rubber or polyisobutylene.



I II

Its main practical importance is as an intermediate for the synthesis of a wide range of poly(organophosphazenes),[3-8] some of which have been developed as technological elastomers[7-11] or biomedical carrier molecules.[12-14] However, poly(dichlorophosphazene) is also of theoretical significance.[4,15-17] Any understanding of the underlying structure–property relationships for poly(organophosphazenes) depends ultimately on a clear comprehension of the behavior of the structurally simpler poly(dichlorophosphazene). Hence, in this paper we explore some of the physical characteristics of the polymer, including the glass transition, melt transitions, and degree of crystallinity, together with the role played by these factors in determining the overall physical properties. The experimental approach has involved the use of differential scanning calorimetry (DSC), torsional braid analysis (TBA), and optical birefringence effects, together with X-ray diffraction experiments. The molecular structure, as deduced from X-ray data, is discussed in a later paper.[18]

A number of earlier studies of the physical properties of poly(dichlorophosphazene) have been reported.[19] It now appears that some of this earlier work was carried out with polymer that had cross-linked, either thermally or following contact with atmospheric moisture, and also contained cyclic oligomers, such as $(NPCl_2)_{3\text{or}4}$, as impurities. Thus, an additional purpose of the present work was to obtain reproducible physical property data for the pure, uncross-linked high polymer. Perhaps the most serious practical problem in this work was to ensure that the polymer was protected from atmospheric moisture at all phases of the purification and storage. The techniques used are described in the Experimental Section.

Experimental Section

Synthesis of Poly(dichlorophosphazene). The high polymer II was prepared from rigorously purified hexachlorocyclotriphosphazene (I)[20] by thermal polymerization. The polymerization took place at 250 °C during 102 h to give a 17% conversion to the high polymer. Unpolymerized I was removed by vacuum sublimation from finely divided chunks of the crude polymerization product. The clear polymeric film remaining in the base of the sublimator was then dissolved in dry benzene, filtered, and precipitated as white, flexible flakes by the addition of dry hexane. These flakes coagulated if the mixture was not stirred. This precipitation was repeated a second time, and the polymer was then redissolved in dry benzene for subsequent fabrication into films and fibers. All the manipulations of I, II, and solutions of II were performed within a dry nitrogen-filled glove bag or in a Schlenk apparatus. The solvents, such as hexane or thiophene-free benzene (Fisher), were distilled twice from lithium aluminum hydride and were then stored over activated 4 Å molecular sieves (Linde).

Considerable care was taken to confirm that the purified polymer was free from residual cyclic oligomers and that extensive chain branching was not present. The ^{31}P NMR spectrum of II in benzene showed only one peak at −17.67 ppm (referenced to phosphoric acid), with a peak half-width of 2.71 Hz. This half-width is actually smaller than the value for the cyclic tetramer, $(NPCl_2)_4$ (3.92 Hz), under the same experimental conditions.

Preparation of Films and Fibers. Polymer films were solution cast from benzene on to glass microscope slides under an atmosphere of dry nitrogen. Fibers were prepared from rolled films or by the solution extrusion of a very viscous solution of II in benzene from a hypodermic syringe into hexane as the nonsolvent. The fibers were annealed in a drying pistol at 78.5 °C under vacuum for 4 h. Both fibers and films were then stored in a vacuum dessicator over Drierite. Under these storage conditions, cross-linking of the polymer was minimized and, if the storage period was less than a few months, the polymer could be redissolved in dry benzene during 24 h.

NMR and Infrared Spectra. ^{31}P NMR spectra were obtained with the use of benzene solutions of highly purified II sealed in 10-mm NMR tubes under dry nitrogen. The reference standard for all spectra was aqueous 85% H_3PO_4. The spectra were obtained with the use of a JEOL 100-MHz Fourier transform NMR spectrometer with the sample at ambient room temperature (25 °C). Typically, 256 scans were used in the FT mode. The infrared spectra were obtained for clear, stretched films (several microns in thickness) with the use of a Perkin-Elmer 267 spectrometer. Calibration was by means of the usual polystyrene film.

Fibers and Equipment for X-ray Diffraction Analysis. Fibers of II for X-ray diffraction work were stretched initially to 6–8 times their original length. Such samples were designated as IIs (crystalline by stretching). Additional annealment or storage of the stretched form for several weeks allowed extensions of up to ten times the original length. The stretched fibers were tensioned in a brass holder that contained a microwinch. This served to eliminate creep of the material from the anchor points and functioned at the same time as a fiber holder within the X-ray camera. Several experiments were carried out with prestretched

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or amorphous fibers in an untensioned mode, and these samples were held in slits cut in wooden splints. Adhesives were not used because of the possibility of reaction with the polymer or the prospect of solvent inhibition by the polymer. Other samples (formerly amorphous) were cooled to −12 °C for 12 h to induce crystallization (designated IIc, crystalline by cooling). Such samples were then stored at low temperatures and were examined at temperatures below 13 °C.

X-ray diffraction photographs were obtained with the use of a Nonius 114.6-mm diameter rotation camera for normal beam and powder-type photographs or a Supper 57.3-mm diameter Weissenberg camera for equi-inclination, flat-cone, and low-temperature photographs. An Enraf-Nonius 601 generator unit was used to power either a copper (Ni filtered) or a molybdenum (Zr filtered) tube at 40 kV and 20 mA. Low-temperature photographs were obtained by the passage of cold, dry nitrogen over the fiber. For this purpose, the Weissenberg camera film holder was insulated in Styrofoam, with the whole camera protected from atmospheric moisture within a large glove bag filled with dry nitrogen. Elevated temperature photographs were obtained by blowing a stream of hot, dry nitrogen over a fiber and by the use of a Nonius Precession camera as a flat-plate camera with both Polaroid and conventional film. An iron–constantan thermocouple referenced to ice water was used for all temperature measurements. Finely powdered NaCl was dusted on to the fibers for camera calibration.

Fiber Birefringence, Shrinkage, and Polymer Depolymerization. A polarizing microscope with a Thomas heating stage was used to observe optical birefringence and to measure film shrinkage and morphology as a function of temperature or solvent absorption. The same equipment was used to examine the crystalline products formed by thermal depolymerization.

Torsional Pendulum Analysis. Samples for torsional braid analysis were prepared by the successive dipping of heat-cleaned multifilament, 20.5-cm long glass braids into viscous solutions of II in benzene under a dry nitrogen atmosphere within a glove bag. The samples were stored vertically in a desiccator before use. Residual solvent was finally removed by exposure of the sample for 4.5 h to a rapid flow of dry nitrogen gas at 150–160 °C within the torsional braid analyzer.

A torsional braid analyzer[21] (Chemical Instruments Corp., with extensively modified electronics) was used to determine the glass transition temperature (T_g) and other transitions by monitoring the components proportional to the in-phase and the out-of-phase shear modulus (rigidity and damping) of the polymer-coated glass filament braid.[22] The temperature change was 2 °C/min. Internal electrical heaters were used to raise the temperature, and evaporating liquid nitrogen was used to lower the temperature of the sample chamber. The transitions were located graphically as inflections or peaks in the rigidity vs. temperature or damping vs. temperature curves.

Differential Scanning Calorimetry (DSC). Samples for DSC measurements were prepared from prestretched fibers that were allowed to relax and were then cut into small segments to fit into the small aluminum sample cups. The total sample weighed $\simeq$10 mg. A Perkin-Elmer differential scanning calorimeter (Model DSC-2) was employed with a scan range from −23 to +77 °C. This temperature range covered the melting and crystallization temperatures reported for II by Connelly and Gillham,[23] using torsional pendulum analysis. The instrument heat sink was cooled by a dry ice–isopropyl alcohol slush bath. The spectra were calibrated for temperature with the use of both distilled water and elemental indium samples. The heat of fusion, ΔH_f, was calculated for the polymer samples by comparison with the response of the instrument to weighed indium samples. The literature value of 6.8 cal/g for indium[24] was used. A separate, weighed sample of IIsr (stretched and relaxed) was used for each of the scanning rates from 2.5 to 40 °C/min. All samples of IIsr used in this study had identical histories.

Density Measurements. The density of II was estimated by flotation in chloroform–bromoform mixtures, with the density of the liquid medium measured by use of a piconometer.

Results and Discussion

Characterization of the Amorphous Polymer. The polymer was soluble at 25 °C in benzene, toluene, xylene, tetrahydrofuran, or chloroform to form clear, viscous solutions. Solutions of II yielded a cross-linked form of the polymer after storage for long periods of time (usually 1 month). Hence the solutions were utilized for the various experiments after minimal storage times. The cast films or unstretched solution-extruded fibers were colorless, adhesive, and elastomeric. They degraded very slowly in contact with atmospheric moisture. They showed no optical birefringence or structural units under the polarizing microscope. Both the unstressed fibers and the bulk polymer, annealed previously at 78.5 °C, showed no evidence of crystallinity at 25 °C when studied by X-ray diffraction. The diffraction pattern consisted of two amorphous halos and a ring, with the *d* spacings corresponding to 9.44 (ring), 5.32, and 2.68 Å separations. Amorphous films that were subjected to stress by scratching with a spatula showed brilliant color streaks along the scratch when viewed under the polarizing microscope. The color disappeared when the polymer was heated above 52 °C. Hence, the effect is apparently not a consequence of changes in the thickness of the sample. The T_g value for the polymer is discussed in a later section.

Crystallization Methods. Two methods were found to bring about crystallization. These were cooling or stretching of the amorphous polymer. Crystallization was induced when the amorphous polymer was cooled to −12 °C and held at that temperature for several hours (material designated as IIc). Stretching of the fiber at 25 °C brought about definite physical changes. The stretched fiber or film (material designated as IIs) was opaque and white, and it was no longer adhesive. The polymer could be stretched to 6–8 times its original length without breaking, or up to ten times by repeated cycles of annealment at 78.5 °C and by the application of tension. The polymer did not undergo the necking deformation normally characteristic of crystalline polymers when stretched.

Detection of Crystallinity by X-ray Diffraction. The highly stretched polymer (IIs) was examined in detail by X-ray diffraction methods. (A later paper in this series[18] deals with the molecular structural interpretation of the fiber diffraction pattern, and only the nonstructural aspects are discussed here). When stretched to ten or more times its original length, the polymer gave an exceptionally well-resolved X-ray fiber diagram that was indicative of high crystallinity. With the use of inclined beam methods,[18] and using Cu radiation, 61 unique reflections were visible on the zero through fourth layer lines (Figure 1a). The smallest *d* spacing of 1.11 Å is indicative of the unusually high resolution obtained for this fiber pattern. In fact, inclined beam methods with the use of Mo radiation clearly showed well-defined layer lines from the zero to the sixth layer lines.

However, although the use of Mo radiation allowed more layer lines to be detected than with Cu radiation, it yielded only a few additional weak reflections on the zero level layer line. Hence, the Cu radiation data were preferred because of the shorter exposure times and the better resolution of the close reflections.

The crystalline-type diffraction arcs appeared only after appreciable elongation of the sample (four times the original length or more). Moreover, the arcs appeared not to be formed by coalescence of regions of the Debye rings, and this suggests that elongation has a more profound effect than simple orientation of existing microcrystalline domains. Reflections on the zero level were the first to be defined, with higher level reflections becoming evident as the degree of stretching was increased. In fact, increased elongation resulted in the appearance of more reflections

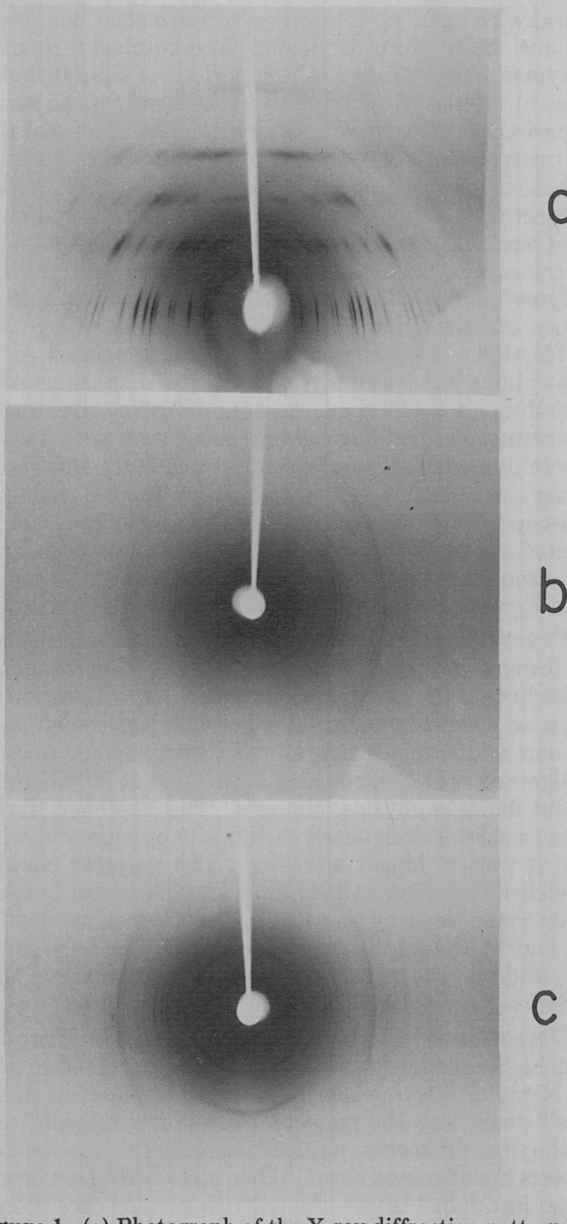

Figure 1. (a) Photograph of the X-ray diffraction pattern of a highly stressed fiber of poly(dichlorophosphazene). The photograph was obtained with the use of a Weissenberg camera in the flat-diffraction cone geometry for the second layer line. A copper X-ray tube with a nickel filter was used. The exposure time was 12 h. (b) Photograph of the X-ray diffraction pattern of a cooled fiber of poly(dichlorophoshazene). The amorphous fiber was crystallized by cooling it to around −18 °C for 12 h. A Weissenberg camera was used in a normal beam geometry with the use of nickel-filtered copper radiation. The exposure time was 4 h. (c) Photograph of the X-ray diffraction pattern of a stretched, and then relaxed, fiber of poly(dichlorophosphazene). The experimental conditions were as described for 1b. The fiber was maintained under tension for several days before release of the tension and recording of the X-ray pattern.

(especially on the upper levels of the photograph), in shorter reflection arc lengths, and in a greater breadth of all the reflection arcs.[25] These changes paralleled the development of more vivid optical birefringent colors and sharper optical extinctions at 90° intervals. No significant over-all intensity differences were detected between the different layer lines.

The effects of temperature changes on the X-ray diffraction pattern of elongated IIs were also examined. The same basic pattern was observed from −108 ± 2 °C to +39 ± 0.5 °C. At 39 °C, the diffraction arcs were short and thick as would be expected from the increased thermal vibrations of the polymer chains and from the increased fiber tension due to fiber shrinkage at the higher temperatures. However, the crystalline-type pattern was completely lost when the sample was heated to 58 °C, and at this temperature, no arcs, halos, or rings were visible.

X-ray photographs were also obtained of polymer IIc (cooled but not stretched). The diffraction pattern consisted of Debye rings that were similar in disposition and intensities to the reflections on the zero level fiber diagram of the stretched polymer but which showed no evidence of crystallite orientation (Figure 1b). With one exception only, those reflections that corresponded to the *d* spacings given by the upper level layer lines of the stretched polymer were not detected, nor was the meridional reflection. Moreover, the first and the ninth reflections of the zero level were of greatly reduced intensity in the patterns obtained from IIc. The one reflection that arose from a nonzero layer was the first reflection from the l = 1 layer of IIs. This reflection had approximately the same breadth as that in the fiber diagrams from IIs. It corresponded to a *d* spacing of 3.716 Å. This is close to the van der Waals separation of 3.6 Å for the two chlorine atoms. The other rings from IIc were of slightly narrower breadth, and this might indicate the presence of larger crystallites than those in IIs. Amorphous polymer was still present in IIc, as indicated by the presence in the diffraction photographs of the halos that were characteristic of the amorphous material.

Thus, the X-ray diffraction results provide strong evidence for the existence of a microcrystalline modification of II. Further evidence for crystalline domains was obtained by the use of differential scanning calorimetry, torsional braid analysis, and fiber shrinkage measurements. They will be discussed in later sections.

Optical Birefringence. Another property that changed as the degree of stretch increased was the optical birefringence. The optical birefringence of IIs increased with the degree of extension. The fully stretched polymer was highly birefringent, with striations visible along the stress direction. The birefringence was extinguished at 90° intervals as the polymer was rotated perpendicular to its axis under crossed polarizers. No definitive substructures, such as spherulites, were observed. The amorphous polymer shows no birefringence. We interpret the birefringence as a preferential ordering of the chains but not as a criterion of crystallinity.

Relaxation of IIs with Retention of Crystallinity. Amorphous fibers of II that had been oriented and crystallized by a five-times elongation and a maintainance of the tension for several minutes did not relax totally on release of the stress but remained extended by roughly 2.5-times the original length. Moreover, after relaxation, the fibers remained birefringent for several days at 25 °C, although the optical extinctions at 90° rotation intervals were less distinct than were those for the fully stretched material. Short segments could be cut from the relaxed fibers and, except for minor end effects, these also showed birefringence. A loss of birefringence and crystallinity occurred when the material was heated to above 36 °C. This form of the polymer was designated as IIsr (stretched and relaxed).

Segments of IIsr yielded X-ray diffraction patterns that resembled that of the stretched crystalline polymer, IIs, except that the arc lengths were now longer (Figure 1c). Calculations based on the length of the arcs suggested that the crystallites in IIsr were randomly tilted 15 to 20° from the fiber axis. Upper level X-ray reflections were also evident for IIsr, as was the tail of the meridional reflection of the second layer line. These data suggest that IIsr has a microcrystalline structure with some preferred orientations of the crystallites. Furthermore, the existence of IIsr allowed the use of characterization techniques that could be applied only with great difficulty to a polymer that required constant tension to remain crystalline.

Fibers of IIsr showed other unusual properties. Compression of a fiber between glass microscope slides caused a loss of the optical birefringence. Release of the pressure was accompanied by regeneration of the original vivid birefringence effect. However, the repeated application and release of pressure at 29 °C resulted in a contraction of the fiber by roughly 30% of its original length. Relaxation of IIsr could also be induced by treatment with solvents such as benzene. Immediate swelling occurred, coupled with contraction of the fiber length. Slow evaporation of the solvent yielded thicker but shorter fibers ($\simeq$60%) than the original amorphous starting material. This product showed no microcrystalline birefringence. Heating of IIsr resulted in a reversion to the dimensions of the original amorphous polymer with loss of optical birefringence. Excessive heating of II, for example, to 230 °C, caused depolymerization to $(NPCl_2)_n$ cyclic oligomers. The cyclic tetramer, $(NPCl_2)_4$, was specifically identified as a product from its crystal morphology (square platelets) and the melting point (122 °C).

Degree of Crystallinity. The degree of crystallinity of an annealed and well-stretched sample of IIs was estimated to be around 20%, based on the X-ray intensity distribution between the amorphous and crystalline reflections. This is the highest crystalline value observed in this study.

A second estimate of the degree of crystallinity was based on a comparison of the densities of the amorphous polymer and polymer IIsr, with the use of the equation: degree of crystallinity = $(V_a - V)/(V_a - V_c)$, where V_a, V, and V_c are respectively the specific volumes of the amorphous sample, a well-oriented fiber sample, and the value required for perfect crystallinity as defined by the crystallographic unit cell.[26] Experimental values of 0.5050, 0.5005, and 0.4632 cm^3/g respectively were obtained for V_a, V, and V_c, and the degree of crystallinity of IIsr was then calculated to be 11%.

Crystalline Melting Temperature. The crystallization and melting phenomena of II are complex. A characteristic of II is its ability to exist in either the totally amorphous form or the partially crystalline state at 25 °C. This behavior is a consequence of the fact that the crystalline melting point of IIs or IIsr is above room temperature, but the temperature at which the unstressed polymer crystallizes is below room temperature. In view of this phenomenon, the crystalline melting characteristics of II were examined with the use of X-ray diffraction, differential scanning calorimetry, and dynamic mechanical techniques.

As discussed earlier, a loss of the crystalline X-ray fiber pattern occurred when polymer IIs was heated in the range between 39 and 58 °C. However, this melting temperature is undoubtedly higher than the unperturbed crystalline melting point because of the tension-induced stress. Differential scanning calorimetry (DSC) techniques were employed to obtain a more accurate estimate. Figure 2 shows DSC plots for IIc and IIsr. First, it should be noted that cooling of the amorphous polymer to form IIc (Figure 2a) showed a broad exotherm that corresponds to a crystallization temperature near -7.2 °C.[27] Second, melting of the crystallites formed in IIc took place in one broad endotherm with a peak at +26.3 °C. Third, the heating cycle for polymer IIsr showed three main endothermic melting transitions at $\simeq$+12 °C (possibly a composite of two closely spaced transitions), at +25.4 °C, and at +33.1 °C. Of these, the transition at +25.4 °C probably corresponds to the one at +26.3 °C detected for the melting of IIc and may be generated by the same mechanism, i.e., by the formation of IIc from the amorphous domains in IIsr as the sample is cooled to -23 °C before the onset of the heating cycle. However, the transitions at +12 and +33.1 °C appear to be unique to the oriented polymer and could reflect additional different modes of crystallization in the material. As will be discussed below, the +12 °C transition is the only transition detectable by torsional pendulum techniques. The DSC transition at +33.1 °C almost certainly corresponds to the crystalline melting point detected at +39 °C by X-ray diffraction analysis of IIs. This appears to be the main crystal-amorphous transition for the ordered polymer.

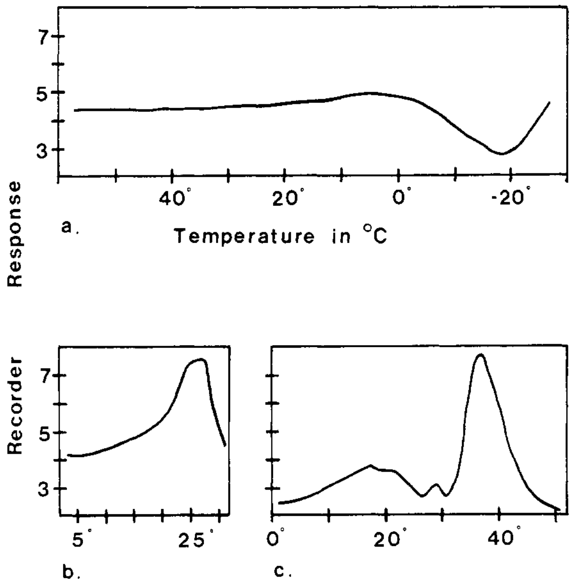

Figure 2. Differential scanning calorimetry (DSC) curves for poly(dichlorophosphazene). All the plots were obtained at a scan rate of 40 °C per minute with the use of a DSC-2 Perkin-Elmer instrument: (a) the cooling curve for polymer IIa; (b) the heating curve for polymer IIa; (c) the heating curve for polymer IIsr.

The crystalline transitions were also examined by the torsional pendulum technique,[22] and Figure 3 shows typical plots of the polymer rigidity and damping coefficients as a function of temperature. The slight changes in the rigidity curves were attributed to a T_m (melting transition) at 15 °C and a T_c (crystallization temperature) at -10 °C. These results are similar to those reported by Connelly and Gillham[23] for the torsional braid analysis of II. Our results differ from those of these authors in that the heating and cooling damping curves do not superimpose as well. The main anomaly is the presence of a large damping peak at $\simeq$-10 to 0 °C and the absence of a complementary melting peak in the heating cycle. This pattern was not changed when the sample was heated at 150 °C for 4.5 h in a stream of dry nitrogen. Hence, the effect is probably not due to the presence of residual solvent. The broadness of the peak suggests that it might reflect the formation of partially ordered domains that do not have the three-dimensional structure of the microcrystallites of IIs.

Polymer II, cast on a glass braid at 25 °C, is deposited as IIa (the amorphous modification). Thus, the crystallization transition detected at -10 °C almost certainly corresponds to the one detected at -7.2 °C by DSC analysis. However, the melting transition at 26 °C that

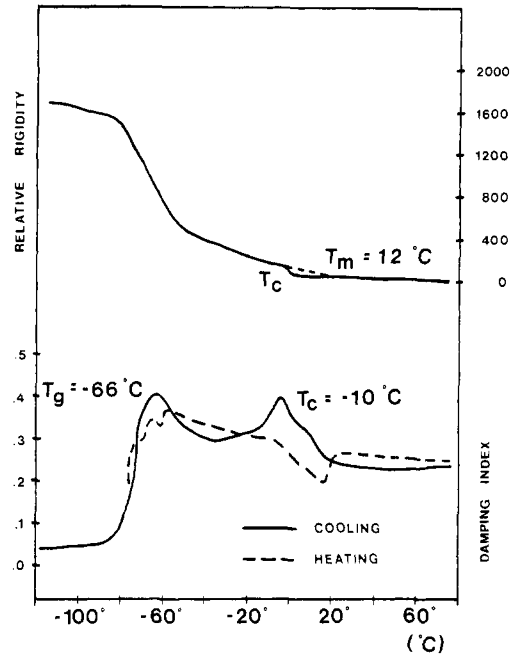

Figure 3. The thermomechanical spectra of poly(dichlorophosphazene) obtained with the use of a torsional braid analyzer. The upper curve shows the variation of relative rigidity with temperature, and the lower curve shows the damping index.

was evident in the DSC analysis was not detected from the dynamic mechanical changes. Instead, surprisingly, the melting transition detected (at +15 °C) in the dynamic mechanical results corresponds closely to one of the melting transitions detected by DSC analysis for the stretched–relaxed polymer (IIsr). We speculate that the dynamic stresses caused by the twisting glass braid in the TBA technique facilitate the formation of crystallites that are similar to the low-melting phase of type IIsr. For polymer II, the DSC method appears to be more sensitive than the dynamic mechanical technique for the detection of crystalline transitions. The constant torsional motion in the latter method appears to affect the crystallization and melting behavior for highly flexible polymers in which the crystallite formation is sensitive to mechanical stress.

Enthalpy and Entropy of Crystallite Melting. An analysis of the DSC peak area of the main 33.1 °C melting transition was used to estimate the enthalpy (ΔH_f) and the entropy (ΔS_f) of melting. The ΔH_f value calculated for this transition was 2000 cal/mol of $NPCl_2$ units.[28] If melting is assumed to be an equilibrium process such that the expression $\Delta S_f = \Delta H_f / T_m$, is valid, then the corresponding ΔS_f value is 6.5 cal/(mol K). This value is appreciably higher than that for the 4.3–4.8 and 2.3 cal/(mol K) values reported, respectively, for polyethylene and polypropylene.[29] For the purposes of comparison, the ΔH_f value for the peak at +12 °C was calculated to be $\simeq$500 cal/mol of $NPCl_2$ units.

Crystallite Size. The breadth of the X-ray reflections from the highly oriented polymer, IIs, at 25 °C was analyzed to estimate the crystallite size. Half-widths, determined from densitometer tracings of the zero level arcs, were defined as the arc breadths. The arc breadths remained virtually constant and were well-defined even at high 2θ values. Extra cycles of annealment and stretching did not cause the arc lengths to decrease significantly below the 4° value. By approximating the arc breadth as a powder diffraction line, and with the use of Scherrer's treatment as described by Bunn,[30] a crystallite thickness of 260 Å perpendicular to the orientation direction was estimated. This would correspond to 40 to 45 chain segments packed together.[31] An analysis of the arc lengths and the spread of the meridional reflection suggested that the chains were randomly tilted 4–6° from the orientation direction. An alternative treatment of the half-width data by use of the paracrystalline theory of Hoseman, as described by Alexander,[32] yielded a crystallite size of 180–200 Å, together with a very low paracrystalline g value of 0.07%. These estimates of crystallite width give values that are comparable to those in other microcrystalline polymers.

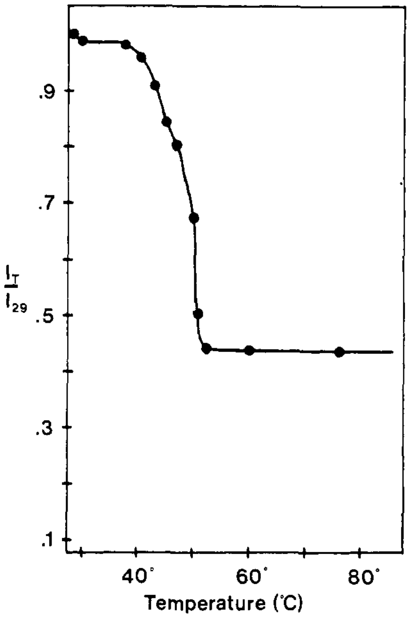

Figure 4. A plot of the fiber shrinkage ratio, l_T/l_{29}, vs. temperature for an oriented fiber of poly(dichlorophosphazene) (IIsr).

An attempt was made to estimate the average number of monomer units per crystallite length by use of the thermal fiber shrinkage technique described by Tobolsky.[33] Cylindrical fibers of IIsr underwent a gradual, irreversible shrinkage in length (with proportional increases in diameter) as the temperature was raised from 29 °C to 39–42 °C. Within this latter temperature region, the fiber shrinkage became rapid, and this temperature was designated as the shrinkage temperature, T_s. By 52 °C, the fiber shrinkage was complete, and the optical birefringence had disappeared completely. Use was then made by Tobolsky's equation:[34,35] $\bar{h} = ((D_s^3 - 1)(1 - Q)/2Q) - {}^1/_2$, where $\bar{h}$ is the average number of monomer units per crystallite length and Q is the percent crystallinity. D_s is the ratio of the initial length (l_0) over the length at temperature T_s (l_{T_s}). A plot of $1/D$ vs. temperature is shown in Figure 4.[36] The average value of $1/D_s$ due to thermal shrinkage was found to be 2.4. Since the percent crystallinity of IIsr by density measurements was 11% and by the X-ray analysis of IIs was 20%, the number of monomer units per crystallite length was calculated to be 50 and 25, respectively. The value of 50 monomer repeats is considered to represent an upper limit because the density value quoted is the lowest value compatible with the experimental measurement.

Glass-Transition Temperature. The T_g value of polymer II was found to be −66 °C[37] by torsional braid analysis and $\simeq$−58 °C by dilatometry experiments in absolute ethanol.

Conclusions. Poly(dichlorophosphazene) (II) gives similar X-ray diffraction fiber patterns when stretched and heated or cooled, when stretched and allowed to relax, or when cooled without tension. The cross-linked form of II behaves similarly, although the X-ray diffraction pattern intensity for the upper layer lines is reduced, presumably because the cross-links decrease the ability of the material to undergo orientation. However, the X-ray photographs of polymers IIs and IIc are sufficiently different with respect to relative *intensities* of the zero level reflections that the possibility exists that the chains occupy slightly different conformations or different packing arrangements in the two forms. The cooled polymer, IIc, certainly possesses considerably less order than IIs as indicated by the absence of most of the upper level reflections, including the meridional arcs.

Uncross-linked poly(dichlorophosphazene) is viscoelastic in the true sense of that word. Polymer samples that have been stretched and tensioned for a week contract less on release of the stress than do polymer samples stressed for only a few hours. Moreover, polymer samples stretched for a week shrink less when they are allowed to relax and are then subsequently heated. Thus, it appears that polymer chain entanglements and the microcrystalline domains prevent chain slippage under the prolonged tension. Moreover, the microcrystallites themselves are easily disrupted by heating, by contact with solvents, such as benzene, or by mechanical compression applied perpendicular to the direction of tension. On the other hand, the crystallites appear to retain their integrity when compressed along the direction of original stretch because the contraction that accompanies the release of tension does not lead to disruption of the crystalline domains. This contrasts with the behavior of natural rubber, where the stretch-induced crystallites are destroyed by shearing forces as the tension is released and the amorphous domains contract.[38] Polymer II more closely resembles polyethylene and gutta-percha in this respect.[38] Polymer II differs from poly(difluorophosphazene), $(NPF_2)_n$, in the absence of a low-temperature phase transition in the −40 to −60 °C region. In $(NPF_2)_n$, that transition has been attributed to a change in chain conformation.[39] It appears that IIs is already close or actually at the most favored chain conformation at room temperature.

Finally, it should be noted that both II[23] and $(NPF_2)_n$ are anomalous in their failure to conform to the T_g/T_m rule postulated by Boyer.[40-42] Poly(dimethylsiloxane) is also anomalous in this respect. All three of these polymers possess small substituent groups attached to every other chain atom. Hence, intramolecular steric hindrance effects are much lower than those for most organic macromolecules.[43] Thus, the prospect exists that these highly flexible chain systems yield microcrystallites that melt at lower temperatures than would be expected. If the T_g/T_m rule did apply to polymer II, a crystalline melting temperature near 140 °C would be expected rather than the experimentally measured value of 33.1 °C. It is of interest that the cyclic tetramer, $(NPCl_2)_4$, melts at 123.5 °C, whereas the short-chain linear oligomer, $S{=}P(Cl_2)NP(Cl_2)NP(Cl_2)NPCl_3$, melts at 34–35 °C.[44] Moreover, successively higher chlorophosphazene oligomers show a trend of decreasing melting temperatures, a result that adds additional support to the influence of skeletal mobility in lowering the T_m in this system. Significantly, poly(organophosphazenes) that possess bulky organic groups do follow the T_g/T_m rule. As noted by Connelly and Gillham,[45] $[NP(OCH_2CF_3)_2]_n$ yields a T_g/T_m ratio of 0.43. Poly(dibromophosphazene), $(NPBr_2)_n$, which has a T_m of 270 °C,[46] shows a T_g/T_m ratio of 0.48. These values are similar to those found in many organic macromolecular systems.

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Spin Relaxation and Local Motion in Dissolved Polycarbonate

Alan Anthony Jones* and Michael Bisceglia

Department of Chemistry, Jeppson Laboratory, Clark University,
Worcester, Massachusetts 01610. Received June 28, 1979

ABSTRACT: Carbon-13 and field-dependent proton spin-lattice relaxation times were measured as a function of temperature and molecular weight for 10 wt % solutions of polycarbonate in $CDCl_3$. The spin-lattice relaxation times are interpreted in terms of segmental motion characterized by the sharp cutoff model of Jones and Stockmayer, phenyl group rotation, and methyl group rotation. Correlation times for all of the three local motions are very similar, from −10 to +60 °C, leading to the conclusion that these three local motions are coupled or synchronous. Correlation times range from about 0.35 ns at −10 °C to 0.05 ns at +60 °C. The temperature dependences of the motions differ slightly with phenyl group rotation, having the lowest apparent activation energy of 13 kJ. This low value is reasonable in view of a semiempirical calculation by Tonelli, and the apparent activation energies of segmental motion and methyl group rotation have more typical values of 19 and 22 kJ, respectively. Facile phenyl group rotation occurs in another engineering plastic, poly(2,6-dimethyl-1,4-phenylene oxide), but in this latter polymer the phenyl group rotation is not close in time scale to the other motions.

The polycarbonate of bisphenol A is the object of considerable interest because of the technologically important properties of the bulk material and the apparent relationship of these properties to local chain dynamics. While many informative dynamic studies of polycarbonates have been presented,[1-10] a nuclear spin relaxation investigation of dissolved polycarbonate is undertaken now to capitalize on the detailed information available on local motions at several positions within a repeat unit. To obtain a fairly complete dynamic description, an extensive series of carbon-13 and proton spin-lattice relaxation time experiments, the latter at two field strengths, is conducted. In addition, an interpretation based on a mathematical model for motions likely in this polymer is employed, since in the judgment of the authors this best serves the goal of elucidating local motions. The current work on dissolved polycarbonate is compared with a number of dynamic studies on solid polycarbonates, and there is a strong similarity between the interpretation in the bulk[1,5-9] and in solution. Also the bisphenol A polycarbonate is one of a number[11] of engineering plastics with aromatic groups in the backbone scheduled for comparative dynamic characterization based on nuclear spin relaxation and already considered in a series of semiempirical calculations.[12,13]

Experimental Section

A 20-g sample of Lexan 145 ($[\eta] \simeq 0.5$) was fractionated from a methylene chloride solution, using methanol. A total of 12 fractions was collected, and viscosity average molecular weights were calculated from the intrinsic viscosity of each fraction, according to the equation[14]

$$[\eta] = 1.2 \times 10^{-4} M_v^{0.82} \tag{1}$$

Fractions range in viscosity average molecular weight, M_v, from 4.5×10^4 to 3.7×10^3.

For the spin relaxation measurements, 10 wt % solutions of some of the fractions in $CDCl_3$ were prepared in 10 mm NMR tubes. These samples were then subjected to five freeze–pump–thaw cycles and sealed.

The spectrometer used was a variable field multinuclear pulse Fourier transform Bruker SXP 20-100. Carbon-13 spin–lattice relaxation times were measured at 22.63 MHz with simultaneous proton noise decoupling, and field stability was maintained by an internal deuterium lock. Pulse Fourier transform proton measurements were made at 20 and 90 MHz. Both carbon and proton spin–lattice relaxation times were observed with a standard 180–τ–90 pulse sequence. The temperature was regulated to ±1 °C with a Bruker B-ST 100/700, which was calibrated against a thermocouple placed in a sample tube as well as the usual chemical NMR temperature standards.

Results

The methyl carbon and the two protonated phenyl carbon magnetizations all display a simple exponential dependence on delay time, τ, in the 180–τ–90 experiment. Therefore, T_1, the spin–lattice relaxation time, was calculated from a linear least-squares fit of the data in the form

$$\ln (A_\infty - A_\tau) = \ln 2A_\infty - \tau/T_1 \tag{2}$$

The two protonated phenyl carbon magnetizations always had the same T_1 value within experimental error so that henceforth only one phenyl carbon magnetization, which is the average of the two observed values, will be discussed.

The methyl proton magnetization and one phenyl proton magnetization resulting from all eight phenyl protons produced the only two resolvable proton signals at 20 and 90 MHz. Again the data appear to follow eq 2 quite well with no indication of a nonexponential character to the return to equilibrium. This simple behavior is quite different from the strongly nonexponential behavior observed for the return of the proton magnetizations to equilibrium in solutions of poly(2,6-dimethyl-1,4-phenylene oxide).[11,15] In the present case, the exponential return to equilibrium is taken to indicate an absence of significant cross-relaxation and cross-correlation. Cross-relaxation is likely to be negligible since dipolar interactions among phenyl protons and dipolar interactions among methyl protons are much larger than dipolar interactions between phenyl

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