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Fiber/Film or Tape Forming
Potential of Polyphosphazenes

Final Report

by

Joseph H. Magill

July 27, 1989

MATERIALS SCIENCE AND ENGINEERING

University of Pittsburgh
Pittsburgh, Pennsylvania 15261



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Joseph H. Magill

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U.S. Army Research Office

Contract #DAAL03-86-K-0120

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- i) Couette Spinning form dilute solution
- ii) Spinning for gel (concentrated) solutions
- iii) Solid state extrusion was carried out at different pressures around and above the thermotropic transition temperature

Mixed (blend) spinning of these polyphosphazenes with ultrahigh molecular weight polyethylenes or nylon 6 polymers, using methods (i) and (ii), invariably resulted in phase separation and undesirable fibers that were inhomogeneous in nature.

Rheological properties of selected phosphazenes were studied using capillary rheometry. Melt viscosities were calculated as a function of rate of shear stress and shear rate when all the polymers exhibited shear thinning behavior. A power law model was found to fit the data.

Crystalline (thermotropic transition temperatures) appropriate to each of these polyphosphazenes was measured. Physical and morphological characterization has been made on the fibers/films so produced.

Information appropriate to each orientational technique is summarized and advantages as well as disadvantages, materials-wise, are mentioned.

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ABSTRACT

This report deals with the potential of polyphosphazene homopolymers for their fiber/tape forming ability. Several polymers have been synthesized, characterized** and used for this purpose. Of particular interest here are

- 1) poly[bis(trifluoroethoxy)phosphazene],
- 2) poly[bis(diphenyl)phosphazene],
- 3) poly[bis(phenyl)phosphazene],
- and 4) poly[bis(naphthyl)phosphazene].

Polymers synthesized were polydisperse and had molecular weights of several million Daltons. Fiber forming was attempted using several "state of the art" methods namely

- i) Couette Spinning from dilute solution
- ii) Spinning for gel (concentrated) solutions
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Crystalline (thermotropic transition temperatures) appropriate to each of these polyphosphazenes was measured. Physical and morphological characterization has been made on the fibers/films so produced.

Information appropriate to each orientational technique is summarized and advantages as well as disadvantages, materials-wise, are mentioned.

** Solution NMR, Elemental Analysis; Gel Permeation Chromatography, Differential Scanning Calorimetry, Differential Thermogravimetric Analysis, Optical Microscopy, Wide and Small Angle X-ray Diffraction, Scanning Electron Microscopy and Density measurements were used for polyphosphazenes characterization.

INTRODUCTION

Poly(organo)phosphazenes are inorganic polymers with alternating phosphorous and nitrogen atoms in the backbone, and two organic groups attached to each phosphorous atom. They have some advantages over the conventional C-C backbone polymers. Interest in these polymers has grown for more than a decade, but most of the effort has concentrated on the synthesis, including mechanisms of polymerization. Polymerization of hexachlorocyclotriphosphazene to dichlorocyclotriphosphazene, followed by nucleophilic substitution of the chlorine atoms by the organic groups, is the route usually employed by polymerization. Melt polymerization of hexachlorocyclotriphosphazene is most commonly used, although solution polymerization has some advantages, including shorter residence time and better reaction control.

Some polyphosphazenes including polybis(trifluoroethoxy)phosphazene and polybis(Phenylphenoxy)phosphazene show liquid crystalline properties. They are comprised of long chain rod-like molecules that exhibit an ordered structure in solutions (lyotropic), or in melt (thermotropic). The molecules are found to be associated in an ordered fashion and form elongated chains*. Within each domain, the molecules are parallel to each other. As a result, the basic flow units are not only molecular chains, but also macrostructural units, in which a large number of molecular chains move cooperatively. This gives rise to unusual rheological

* The degree of orientation (fully or partially extended) is still not known since it is not possible to distinguish between fully extended and highly oriented chains with partial chain folding using birefringence or X-ray orientation techniques. Even flow birefringence measurements in solution cannot distinguish clearly between fully and partially chains whenever the greater part of the chain is extended (Dale J. Pearson, private communication).

phenomena, including large relaxation times⁽¹⁾, elasticity and distinct shear thinning effects at low shear rates⁽²⁾. Under application of an external force, this order is increased, and since the relaxation time of liquid crystalline polymers is long, the orientation is preserved whenever solidification of thermotropic polymers occur.

Rheology of liquid crystalline polymers was first reviewed by Porter and Johnson⁽³⁾. Thermotropic polymers are known to show yield stress and plug flow profile in simple shear flow, and high orientation due to elongational flow⁽⁴⁾. Joseph et. al. have used wide angle X-ray scattering, and scanning electron microscopy to study the morphology of extruded liquid crystalline polymers, and the effect of flow history on morphology⁽⁵⁾. Highly oriented skin, and less oriented core morphology was observed in injection molded liquid crystalline polymers. Recently Lin et. al. studied the phase transitions of two liquid crystalline polymers by measurement of linear viscoelastic properties⁽⁶⁾. Orientation studies in liquid crystalline polymers were reported by Kenig⁽⁷⁾ in elongational flow, and by Chung⁽⁸⁾ during extrusion of liquid-crystal polymeric rods⁽⁹⁾.

So far, the rheological properties of polyphosphazenes have received little attention in the indiluted state. We have investigated a few selected polyphosphazenes using capillary rheometry⁽¹⁰⁾. The data were fitted using a power law model to get the fitting constants m and n in the equation. Thermal degradation and stability of the polymers were also studied as a function of residence time in the rheometer barrel. Morphological studies have been carried out on the extrudates to determine the orientation and improvement in alignment of liquid crystalline domains. The morphological results⁽¹¹⁾ will be reported later.

EXPERIMENTAL

Preparation and Characterization of Polyphosphazene

The polyphosphazenes were synthesized in our laboratory using a standard two step solution polymerization procedure*, starting with hexachlorocyclotriphosphazene monomer. The resulting polymer was purified by dissolving it in either THF or cyclohexane, and then precipitating it using methanol and water. The process was repeated three times. From elemental analysis of the polymers, it was determined that the impurities were removed, and negligible amounts of chlorine was found. ^{31}P NMR was carried out to determine if the polymers were free of branches. Thermal characterization was made using the DSC, and molecular weight measurements were performed using GPC, when 0.1 % of $(n\text{-Bu})_4\text{NBr}$ was added to the mobile phase to facilitate analysis.

A Perkin Elmer Differential Scanning Calorimeter (DSC-2) with a scanning autozero was used to measure the transition temperatures, and the corresponding heats of transition for the polyphosphazenes. Measurement of glass transition T_g , mesophase transition $T(1)$ and melting transition T_m were usually made using a dry ice and ethanol bath at a scanning rate of 10K/min. The results of thermal characterization are given in Table I.

Gel Permeation Chromatography: The determination of molecular weight and the molecular weight distribution of the polyphosphazenes were performed on a Walters 150C ALC/GPC. Five microStyragel columns ($500, 10^3, 10^3, 10^5, 10^6$ Å) were used for the analysis. The operating temperature was 35°C and with a flow rate

* modified method of D.P. Sinclair, U.S. Patent #4,242,316 (1980); see reference 10,11.

of 1.0ml/min of tetrahydrofuran. The detector was a refractometer (optical deflection type using fiber optics). The data acquisition and calculations were performed with a Waters 730 Data Module. The polymer samples were dissolved in HPLC grade tetrahydrofuran (.5 wt%) containing 2,6-di-tert-butyl-4-methylphenol as a stabilizer. The solution was filtered through .5 micron stainless steel filters before injection.

The GPC was calibrated with 9 monodispersed polystyrene samples ranging from 1,800 to 1,800,000 molecular weight. The standard error of estimate for the calibration curve was 0.542 and the correlation coefficient using a linear fit was .9984.

Solution ^{31}P Nuclear Magnetic Resonance Analysis: Solution NMR spectra obtained on a Bruker AM500 spectrometer operated at 200 MHz was used to investigate branching in the original polymer and processed fibrous product dissolved in solution. Phosphoric acid was employed as a reference standard (0 ppm). A small amount of D_2 was used as a lock solvent in these measurements.

Differential Scanning Calorimetry: Transition and enthalpy measurements were made using a Perkin Elmer DS-2B with scanning auto zero and computer accessories for data recording and manipulation.

Differential Thermogravimetric Analysis: All polyphosphazenes used in this work were checked for thermal stability using a Perkin Elmer TGS-2 apparatus. Measurements were made mostly in nitrogen and in an air atmosphere was sometimes used.

X-Ray Diffraction Measurements: Wide angle X-ray scattering data was recorded photographically on film. A Cu $\text{K}(\alpha)$ source and a Statton Camera with temperature controls was used for the measurements. Small angle X-ray diffraction patterns were recorded using a Rigaku-Denki Rotating Anode Cu $\text{K}(\alpha)$ source and camera.

Scanning Electron Microscopy: Measurements on fractured fibers and other samples were made using a JOEL JSM-35F scanning electron microscope. Specimens were coated with Pd/Au before examination.

Rheological Measurements: Rheometer: A Monsanto Capillary Rheometer was used to measure the "melt" viscosity of the polymers at different shear rates. The shear stress and shear rate variations were made by changing the pressure on the driving ram rod, and by changing the L/D ratio of the capillary. After applying pressure to the ramrod, the time needed to extrude a particular volume of sample was recorded using a stopwatch. Once the rheometer barrel was filled with polymer, four readings were obtained, and the starting time for each was fixed before the run started. This approach was useful to verify the homogeneity, as well as the thermal stability of the sample.

Couette Fiber Spinning: An apparatus was constructed in the laboratory (following Pennings et. al)⁽¹²⁾. Some modifications such as a premixing container were employed to facilitate the overall process of fiber spinning. The apparatus Figure 1 was tested using a solution of UHMWPE and it functioned well.

Gel Spinning Equipment: Again, an apparatus patterned after Smith and Lemstra⁽¹³⁾ was used for this purpose. The equipment operated well with the conventional UHMWPE (typically 3 to 5 x 10⁶ molecular weight solutions in toluene or paraffin oil at concentrations up to 5% by weight). Polyphosphazene solution concentrations as high as 30 wt% were employed.

Couette Fiber Spinning: The procedure used by Pennings et. al.⁽¹²⁾, Lemstra and others^(13,14) was verified operationally using ultra-high molecular weight polyethylene (UHMWPE) kindly provided by DSM in the Netherlands. Dr. P. J. Lemstra provided us with a recipe for making spinning dopes of 0.5 to 3.0 w/v

UHMWPE in (i) xylene or (ii) light mineral oil. An antioxidant Ionox R30 at the 0.03% w/w was used to protect the polymer when it was being dissolved under reflux conditions. The Couette Spinning technique proved to be successful producing strong thin fibers of the type described in the literature. The orientation was very high (assessed by X-ray diffraction and birefringence measurements).

Following this success spinning solutions of several polyphosphazenes were made. For example the Couette procedure was attempted with

(i) poly[bis(trifluoroethoxy)phosphazene]

(ii) poly[bis(phenoxy)phosphazene]

and (iii) poly[bis(p-phenylphenoxy)phosphazene]

Acetone* and or acetone/water was used as a solvent for (i). Polymers (ii) and (iii) were solubilized in cyclohexanone. Several different spinning conditions were employed usually using solutions <6% w/v polymer solids for polyphosphazenes in the M_w range 1×10^6 to 4×10^6 , this being the highest molecular weight range covered by our solution polymerization methods. The polydispersity index for these samples varied from 2.5 to 12.5 approximately. After much experimentation

(a) varying rotor speed

(b) varying take-off speed

(c) varying the undercooling

and of course polymer concentration, it was discovered that continuous fibers could not be obtained with our samples even under circumstances, because cooling resulted in in situ phase separation of the polymer within the spinning equipment. Although

* This was found to be the most suitable and least noxious solvent for the poly(alkoxyphosphazene).

short lengths of well-oriented polyphosphazenes were obtained sporadically it soon became clear that the molecular weight of the polyphosphazenes was too low for Couette spinning. By comparison with UHMWPE in terms of the degree of polymerization, D.P., not on a molecular basis; it was easily estimated that polyphosphazenes of $15\text{--}20 \times 10^6$ or more, would be required for Couette spinning. Several attempts were made to synthesize these much needed high D.P. polymers with no success. A literature search did not provide any clues or information that they had ever been prepared previously. Yet, it later became clear at the end of this project that synthesis modifications may lead to high D.P. polyphosphazenes of a hybrid type. Unfortunately, the project funding ended before it was possible to pursue this line in any detail, even though several leads became apparent to us.

In tandem with the Couette spinning experiments, other fiber/tape forming operations were attempted. For instance, Gel Spinning (a procedure exploited by Lemstra and Smith⁽¹³⁾ for UHMWPE) was easily duplicated again using this polyolefin in (a) xylene and/or (b) in decalin at concentration upwards of 3% w/v or even above this level. In any case, the polymer could be dissolved by (1) outgassing the PE powder for at least 5-6 hours at 110°C or higher, followed by heating up to solvent reflux temperature, in order to create a solution that had a working (spinning) range of 90°C upwards using the gel process. The equipment was patterned after Figure 2. At one stage a heated mixing tank with a filter was also incorporated in the transfer line just before the PE solution passed/under pressure (nitrogen) into the spinning-tank.

In the case of poly[bis(trifluoroethoxy)phosphazene] solution of concentration as high as 30% w/v in acetone and/or acetone/water were made for polymers in the 1×10^6 to 4×10^6 molecular weight range. Whenever the concentrated solution

was extruded under N_2 pressure (various pressures were used up to several atmospheres (i.e., gauge pressure)). Under these conditions a thread of extrudate about 1 mm diameter was passed into a non-solvent (water), wound around a pulley and then passed along the spin bath before exiting to a wind-up pulley. A later drawing stage was used in which the fiber was stretched on passing through a small oven where further solvent (acetone) was removed and the fiber further oriented. This method proved to be much more successful than the Couette technique mentioned above. However, it was not free of difficulties. Still the orientation produced in PBFP was considerable (about $\times 10$) and the molecular alignment (orientation) well developed (see Figure 3).

At this stage attempts were made to "piggy-back" or coextrude the polyphosphazene on UHMWPE by making a 6% w/v solution of this polyolefin with poly[bis(p-phenoxyphenyl)phosphazene] in 50/50 w/w amounts. At another time decalin was employed, even though the concentration was high enough and the very high DP polyethylene should have provided a useful base for the much lower DP polyphosphazene, the experiment was fraught with difficulties arising from phase separation. Non-uniform heterogeneous fibers could be obtained with difficulty. They were of poor quality.

In independent experiments polyphosphazenes (ii) and (iii) were tested using 20% w/v solution. Poly[bis(phenoxy)phosphazene] was spun at 120°C from cyclohexanone and poly[bis(p-phenoxy)phosphazene] was even tested at a lower temperature range, down to 45°C*. In any case fiber formation was inconsistent,

* This specimen had a lower molecular weight ~ 400,000 for this temperature range.

because of the need to have a high entanglement density in the gel to provide considerable cohesiveness and integrity at the precipitation/drawing stage. In these experiments MeOH, EtOH or naphtha was used as coagulants. Coagulant bath temperatures as low as -20°C were used.

At this stage of experimentation it was essential to change from solvent to pure polymer extrusion procedures using pure polyphosphazenes which should not be DP limited in the same degree or manner. This proved to be true whenever the same polyphosphazenes were used. However, it transpired that other difficulties were encountered based upon the inherent physical characteristics of these polyphosphazenes, i.e., because of their thermotropic characteristics and morphological changes at elevated temperatures. This part of the work will become very clear when physical properties are described shortly.

Rheological Measurements: Capillary rheometry under N_2 pressure was conducted in order to prepare fibers of from different polyphosphazenes --- the preceding three materials listed on page and another one with bulkier side groups, namely poly[bis(β -naphthyl)-phosphazene], was employed. This crystallized less readily than the others for steric and other reasons.

Procedurally each polyphosphazene was ground into a fine powder and then carefully packed into the barrel of the Monsanto capillary rheometer. This procedure was not suitable for PBPP, which was rubbery at room temperature, since its glass transition temperature is 266 K. Care was taken to minimize voids as the sample, was put in the barrel. The rheometer barrel was then heated to the desired temperature, and sample was allowed to equilibrate before the test started. The extrusion time listed in the Tables III to VI is the average extrusion time of four runs made as a function of time at each temperature. Except for PBFP, which was limited in

amount, the readings at a particular processing temperature were made a total of four times. This procedure enabled averaging of results, and an opportunity to check the thermal stability of various polyphosphazenes. The first run was made after a 10 minute interval, following the packing of the capillary and there was a 5 minute interval between runs. The samples did not degrade during this experimentation time span (usually 30 minutes from the start of the experiment), as seen from the consistency of the extrusion times for the four runs. One of the four readings was discarded, if it proved to be in error due to sample heterogeneity. Three dies with L/D ratio of 3.8, 15 and 20 were used for this study. The pressure was usually varied from 1- psi to 65 psi. The observations were made over a wide range of shear rates to include the Newtonian plateau, if it was apparent. Three capillaries were used in the experiments. The capillary dimensions were

die A, Diameter = 0.0826"

Length = 0.315"

L/D = 3.81

die B, Diameter = 0.0409"

Length = 0.820"

L/D = 20

die C, Diameter = 0.0412"

Length = 0.615"

L/D = 15

To ascertain if there was significant shear degradation during extrusion, some samples were ground after the extrusion, and then re-extruded under identical conditions. A decrease in the viscosity would be indicative of shear degradation.

Also the GPC results obtained before and after each run was employed to test if shear degradation occurred during the extrusion.

To determine if the samples degrade as a function of time, for times longer than the normal experimentation time, some experiments were repeated after the polymer was allowed to sit in the rheometer at the processing temperature for an extended period of time. For example, it was noted that PB(4Ph)PP samples showed some degradation after about an hour. The time needed for its extrusion decreased as the residence time of the polymer in the barrel was increased beyond this period. PBNP also showed some deterioration after about 50 minutes. The viscosity was found to decrease. The observations are shown in Tables VII and VIII, and the results are provided in Tables XIII and XIV.

Other Properties of Polyphosphazene Fibers

There was minimal characterization of Couette spun fibers because of their poor quality since they lacked integrity because samples were of relatively low degrees of polymerization.

The more successful gel spun fiber(s)* were examined under the optical microscope and by SEM in many instances. X-ray diffraction results indicated that orientation was well developed in accord with SEM micrograph see Figure 4 and 5 but long phosphazene fiber lengths were not possible to make, even though UHMWPE gave us no difficulty as a test material or model material. Again, it was determined that high molecular weight polyphosphazenes are required for successful fiber/tape

* but still of moderate quality except poly[bis(trifluoroethoxy)phosphazene] but even this was not without blemishes.

processing. This turned out to be so whenever it was discovered that polyphosphazenes, when heat-treated above their respective thermotropic transition temperatures (see Figure 6), the fibers became brittle, fracturing upon bending or flexing. This "deterioration" in properties appears to be associated with morphological changes that occurs within the fibers (or films made elsewhere in these investigations). It occurred whenever fiber or films are heated about $T(1)$ and subsequently cooled to room temperature. Above $T(1)$ the polymers exist in a disordered 2D state, as a mobile "pseudo-hexagonal rotator phase"^{*} which rapidly transform into a 3D orthorhombic phase of much higher crystallinity than the starting material (<50%) that was formed initially from solution below $T(1)$. Indeed, heat treatment rapidly leads to brittle fibers and films since amorphous material is replaced by ordered polymer having little or no ductility. This transformation is disadvantageous in that it restricts fiber applications. Even if very good quality fibers could be prepared from solution or other means, then inherent brittleness that arises when-ever they are heated too high ($>T(1)$), promptly disqualifies them from use in shear load bearing applications^{**}, unless they can be structurally modified.

The same kind of defects are to be found in extruded fibers even though they are usually much thicker in diameter, typically 1mm (+). Figure 7(a) and 7(b) illustrate two different polyphosphazenes prepared by extrusion. The poly[bis(trifluoroethoxy)phosphazene] shown here was extruded from its thermotropic

^{*} The intermolecular interaction are low as recent transformation studies have shown^(15,16).

^{**} Even though they must have high moduli. The nature of the fracture, Figures 3, 4 and 5 support this state.

(disordered state^{*}) at an extrusion pressure of 50 psi. The processing temperature was 163°C, i.e. well above its T(1) temperature of ~80°C approximately. The other specimen poly[bis(β -naphthoxy)phosphazene]^{**} was formed at 45 psi pressure and an extrusion temperature of 124°C which is above or below the T(1) temperature of this polymer. In any case coils of fiber may be formed, (it is compared in size to a quarter dollar). Copious amounts of polymer fibers can be made in the case of all four polyphosphazenes homopolymers. Despite their fiber forming ability under these and other circumstances, it happens that they are subject to inherent brittleness in the transverse (bending or shear mode) even though they must be very strong in the orientation extrusion direction. Unfortunately these materials were too brittle to clamp and carry out ASTM tensile measurements since they failed invariably in the clamps (grips) of the test equipment.^{***}

Anyhow other interesting morphological features of these extruded polyphosphazenes found and these are now documented in several illustrations. The scanning electron microscope proved to be a useful tool (with its considerable depth of field) for examining fibers in their as extruded and fractured states. Figure 8(a) and 8(b) provide a good example of poly[bis(2-naphthoxy) phosphazene]. The surface features of this fiber are induced by the die itself. The distinctly elongated

* This has been referred to as nematic in the literature. This is still some controversy over the precise description of the state of these polymers above their T(1) temperatures, but magic angle spinning solid state NMR is proving very helpful in elucidating polymer conformation^{(16(a))} in our laboratory.

** or bis(2-naphthoxy) as it is often named.

*** Presumably sonic modulus measurements could be made as a means of quantification but this technique was not readily available. Tensile strength would be a much more meaningful engineering parameter if it could be measured.

fibrous/platelet regions of the specimen (Figure 8(a)) are in harmony with these X-ray* diagrams, Figure 9. Figure 9(b) illustrates SEM fracture surfaces of PB(2-Np)P due to (i) internal fracture due to morphology and (ii) is fiber surface features associated with the die surface. The brittle nature of the fiber is analogous to the features shown in Figure 8 for a poly(alkoxyphosphazene). A parallelism exists between extrusion pressure and $T(1)$, and ΔH $T(1)$ and density in most instances where processing takes place close to or above $T(1)$. X-ray diffraction pattern and fiber orientation are dependent upon the type of polyphosphazene die L/D ratio and processing conditions. Although it was not possible to establish detailed correlation between morphology - chemistry and properties, Figure 9 indicates that strong orientation in PBFP extruded from the thermotropic state** just as in gel-spun specimens (see Figure 3). PB(2-Np)P behaves similarly when processes around $T(1)$, but PB(4Ph)PP, surprisingly, exhibits little orientation (although it is crystalline). This aspect of the work is being further investigated. Measurements have not been made on many polyphosphazenes above their melting points because these polymers have relatively high fusion temperatures. The phenoxy substituted specimens especially often undergo degradation before melting can take place.

* It is interesting to note that the small angle X-ray long period found in polyphosphazenes grows as $T(1)$ is traversed and finally disappears as the samples goes above $T(1)$. See references 17 and 18.

** PBFP transforms rapidly^(15,16).
 PB(4Ph)PP transforms relatively fast and possess bulky side groups.
 PB(2-Np)P transforms relatively fast^(15,16) although the kinetics of the transformation have not been measured yet.

Alternatively there exist several changes in physical properties* that may be correlated with extrusion conditions. An analysis of these data is not completed yet, but this will be published in the open literature whenever more data is collected for the evaluation. For instance trends in $T(1)$ and the enthalpy change at $T(1)$ transition, $\Delta H T(1)$ exist. These are shown in Figure 10(a) and 10(b) for poly[bis-(trifluoroethoxy)phosphazene] and for poly[bis(p-phenoxyphenyl)phosphazene] respectively. The changes in $T(1)$ and $\Delta H T(1)$ parallel orientation behavior seen in Figure 9(i)a and 9(i)b for example, which are illustrated at 30 psi and 55 psi extrusion pressure, respectively. Other measurements in the range 20 to 65 psi have been made for all polyphosphazenes in this project. The behavioral trends are similar. Changes in density with processing correlates with pressure and depends upon the L/D of the die (see p. 10) and the processing temperature which needs further evaluation.

DISCUSSION

Viscosity vs shear rate curves are shown in Figure 11 to 14. From these plots, it is clear that all the samples show power law behavior which could be expressed as

$$\eta(\dot{\gamma}) = m(\dot{\gamma})^{n-1} \quad (1)$$

where n = power law index

m = consistency index

Values of m and n for all the samples are given in Table XV. From the nature of the plot and value of n , it is clear that all the samples are shear thinning, i.e., the viscosity decreases as shear rate increases. This is mainly due to the alignment of the chains

* More time and measurement are required to make an in depth analysis of these and other rheological - texture - property correlations outside the time and monetary confines of this report.

in the direction of shear, which decreases the resistance of the chains moving past one another. Inspection of the data shows that the Newtonian plateau is reached at low shear rates only in PB(2Np)P. The value of the zero shear rate viscosity was determined for this sample. The liquid crystalline polymers usually show shear thinning behavior at very low shear rate and also at higher shear rate⁽⁹⁾. The data collected for PBFP and PB(4-Ph)PP was not extensive enough to separate these three regions. However overall shear thinning behavior is observed, but sample quantities were not sufficient to extend experiments further at this stage. Of course, a wider range of shear rates than reported here would be needed before detailed correlations rather than trends could be established.

The PB(4Ph)PP and PBNP samples were subjected to a shear rate of the order of 10^2 - 10^3 sec^{-1} and hence some shear degradation was noted (see Table V). The viscosity of the samples calculated in the second run is given in Table VI and it is found to decrease by a factor of 2, compared to the viscosity at the same shear stress obtained during the first run. Hence shear degradation during extrusion is obvious.

The Table VII and VIII show the results of thermal degradation of PBPPP and PB(2Np)P as a function of time, PB(4Ph)PP was quite stable up to about an hour whereas PB(2Np)P showed a decrease in viscosity earlier. However each sample was stable during the normal experimentation time selected for shorter run (about 30 minutes) and the results were found to be reproducible, whenever the experiment was conducted within this time.

CONCLUSION

Oriented polyphosphazene homopolymers with various side groups are inhibited from forming quality fibers by (a) Couette and to a lesser degree by (b) Gel spinning processes. The main reason for this is due to the limited molecular weight polymer attainable by either melt or solution polymerization processes. The D.P. of polyphosphazenes must be about an order of magnitude higher than is currently achievable. Through pressure extrusion; fibers are readily produced, but they are generally brittle when flexed because of molecular alignment in and from the thermotropic state. Reduced cohesiveness between aligned moieties, is in accord with other data obtained on the crystallization of polyphosphazenes. In any case it seems that, whatever the technique of fiber making, brittleness sets in after the processed materials is heated about $T(1)$ and subsequently cooled. Repeated heating/cooling causes mechanical weakness for morphological reasons without affecting sample molecular weight.

Rheological characterization of selected polyphosphazenes was made as a function of shear rate. All polyphosphazenes show shear thinning behavior over the range of shear rate studied and they could be described satisfactorily by power law model. Extensive work and data would be necessary in order to separate the two shear thinning regions at high and low shear rates for these liquid crystalline polymers. PB(4Np)P showed a Newtonian plateau and some thermal degradation was indicated after exposure to temperature around 125°C for extended periods of time. Shear degradation during extrusion was also evident.

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FIGURE LEGENDS

- Figure 1: Couette spinning apparatus.
- Figure 2: Gel Spinning apparatus schematic.
- Figure 3: X-ray diffraction pattern of gel-spun PBFP fiber.
- Figure 4: Scanning Electron Microscopy of fractured fibers of PBFP.
- Figure 5: Differential Scanning Calorimeter Curve for unoriented PBFP illustrating transitional features.
- Figure 6: Differential Scanning Calorimeter trace of PBFP fiber showing thermotropic transition $T(1) > 93^{\circ}\text{C}$ and melting or isotropic condition of fiber 55 psi, 163°C , die C.
- Figure 7: (a) Extruded PBFP fiber about 1 mm diameter formed at 163°C and 50 psi.
(b) Extruded PB(2Np)P fiber formed at 124°C and 45 psi.
- Figure 8: Scanning Electron micrograph of extruded PBFP fiber
(a) low magnification X40
(b) higher magnification (X3000) of fractured region.
- Figure 9: (a) X-ray diffraction patterns of several polyphosphazene fibers namely:
- (i) Poly[bis(trifluoroethoxy)phosphazene]
(a) 30 psi, die #B, 163°C
(b) 55 psi, die #C, 163°C
 - (ii) Poly[bis(p-phenylphenoxy)phosphazene]
(a) 20 psi, die #A, 196°C
(b) 55 psi, die #B, 196°C
 - (iii) Poly[bis(2 naphthoxy)phosphazene]
(a) 30 psi, die #B, 124°C
(b) 60 psi, die #B, 124°C

Fiber axis (extrusion direction) is vertical in all patterns.

- Figure 9: (b) (i) Initial fracture features of poly[bis(2-Naphthoxy) phosphazene] extruded at 35 psi and 124°C through die #C.
(ii) Surface features of same sample processed at 124°C and 45 psi.
- Figure 10: (a) Trends in $T(1)$ (-●-) and $\Delta H(T(1))$ (-x-) are plotted for PBFP as a function of extrusion pressure.
(b) Trends in $T(1)$ and $\Delta H(T(1))$ (-x-) are plotted for PB(4Ph)PP as a function of pressure, -■- die A; -●- die B
- Figure 11: Plots of viscosity as a function of rate of shear for PB(2Np)P showing fitted lower Newtonian region at 124°C.
- Figure 12: Plots of viscosity vs. rate of shear for PBFP at 163°C. Fitted curve according to power law function, equation (1).
- Figure 13: Plot of viscosity vs. rate of shear for PB(4Ph)PP. Fitted curve according to equation (1).
- Figure 14: Plot of viscosity as a function of shear rate for PBPP. Fitted curve according to equation (1).

Components listed:

PS Power Supply
 TC Temperature Controller
 P Circulating Pump
 H Heater/Dryer
 LC Level Control
 CTC Constant Torque Cylinder
 TV Throttle Valve
 S Polymer Solution (Make up and solution spin bath)
 R Roller Assembly
 AC Electrical Supply
 CSB Couette Spin Bath Assembly
 RC Rotating Cylinder
 F Fiber Take-Off
 CT Constant Tension

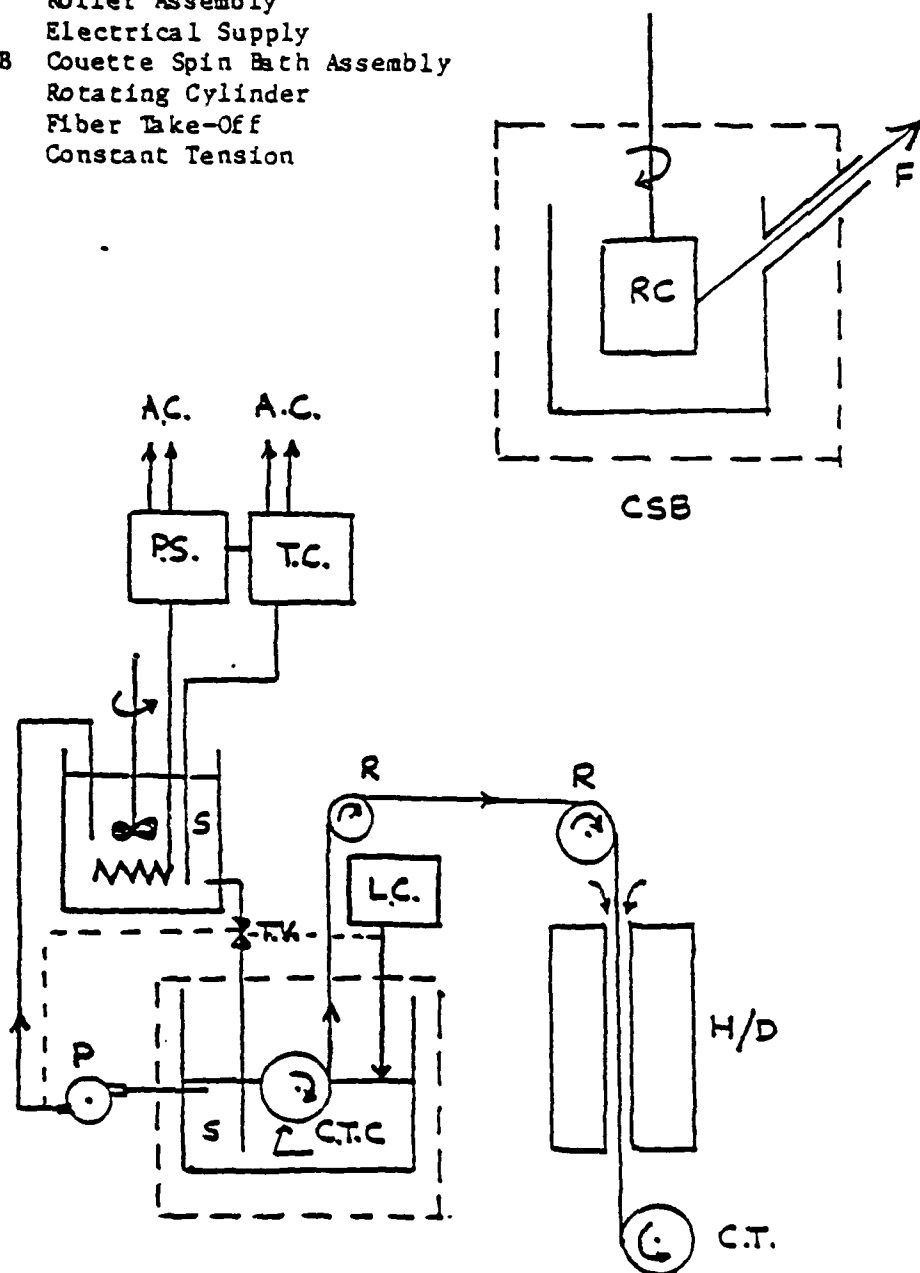


Figure 1: Couette spinning apparatus.

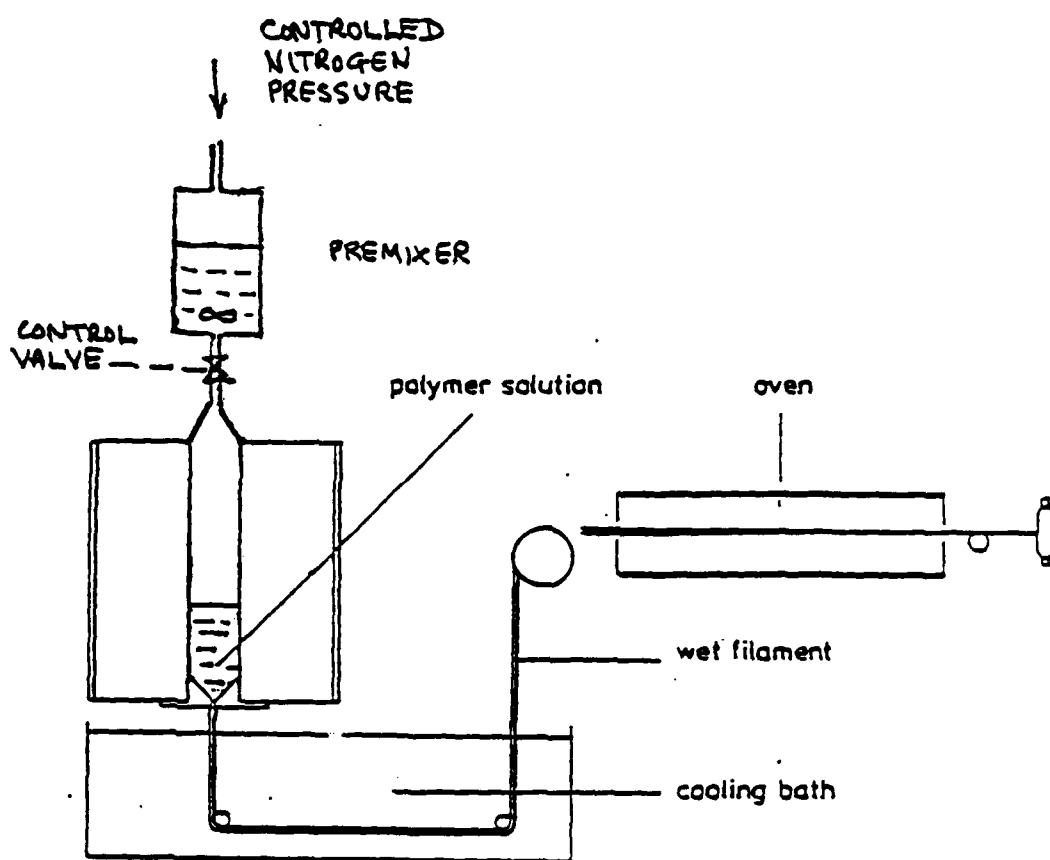


Figure 2: Gel Spinning apparatus schematic.

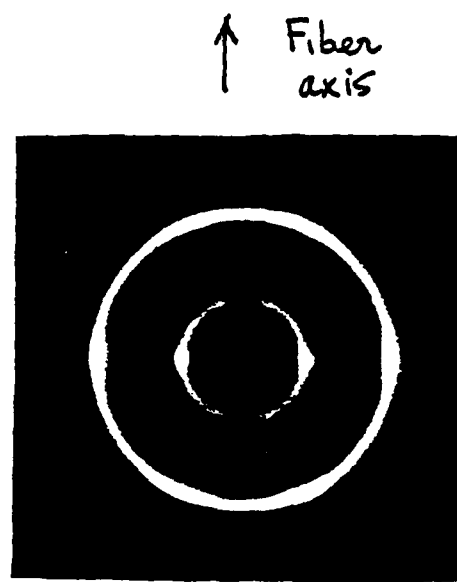


Figure 3: X-ray diffraction pattern (Cu K (α) radiation) for poly (bis-trifluoroethoxy) phosphazene fiber prepared by the gel spinning technique; solvent was acetone, non-solvent water.

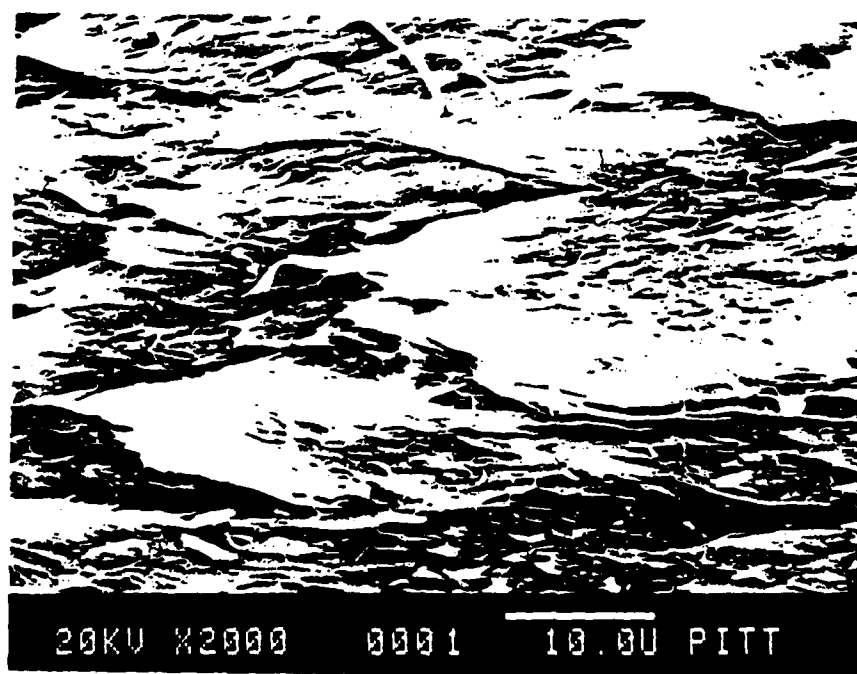
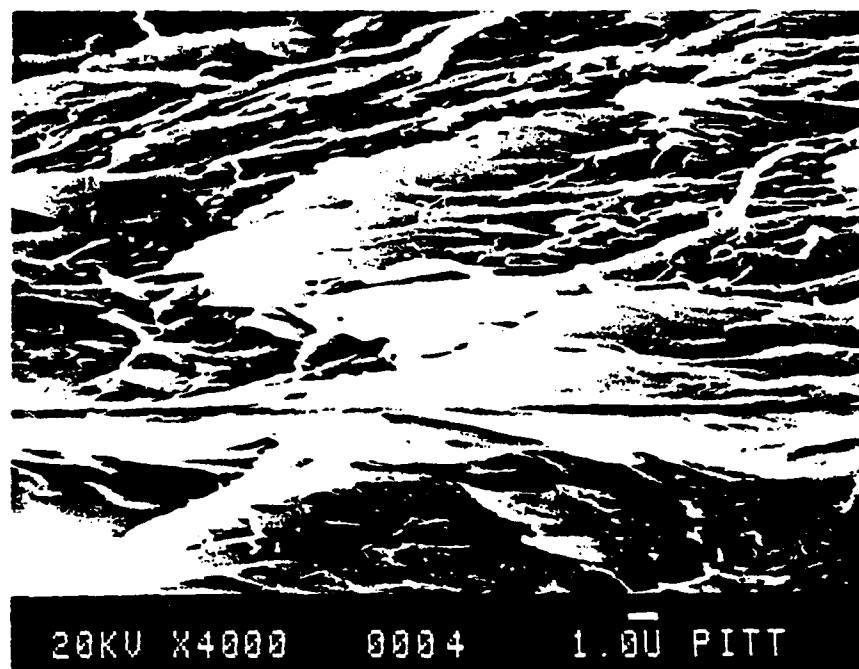


Figure 4: Scanning Electron Microscopy of fractured fibers of PBFP.

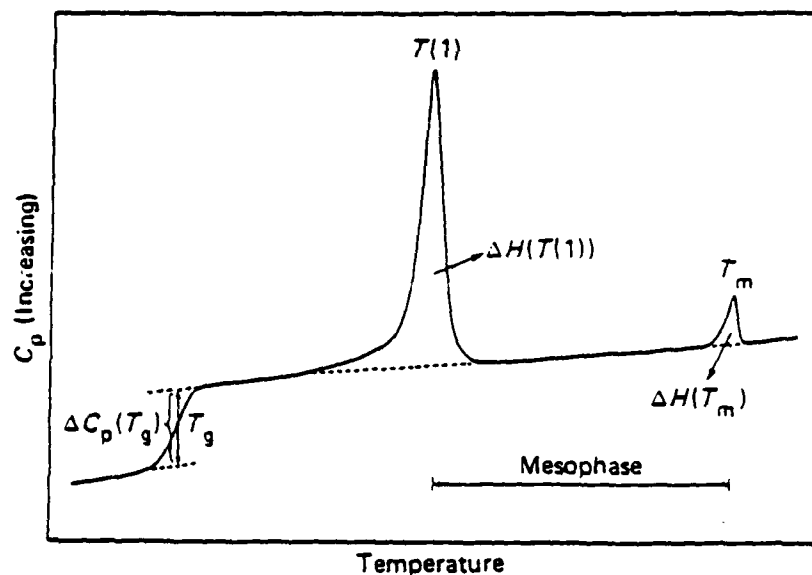


Figure 5 General schematic of thermal behaviour for polyphosphazene homopolymers. In this figure, T_g^* is the glass transition temperature (taken as the mid-point of the slope of the C_p - T curve: $\Delta C_p(T_g)$ =specific heat change at T_g ; $T(1)$ =thermotropic transition temperature; $\Delta H(T(1))$ =enthalpy change at $T(1)$; T_m =melting point; $\Delta H(T_m)$ =enthalpy change at T_m (*Richardson's method of T_g determination based upon enthalpy change (ref. 25) was also employed for some determinations. The results obtained by both methods were self consistent (within ± 2 K) for polyphosphazenes. Consequently, the simpler mid-point technique once it was substantiated, was adopted for these polymers) Reference 19.

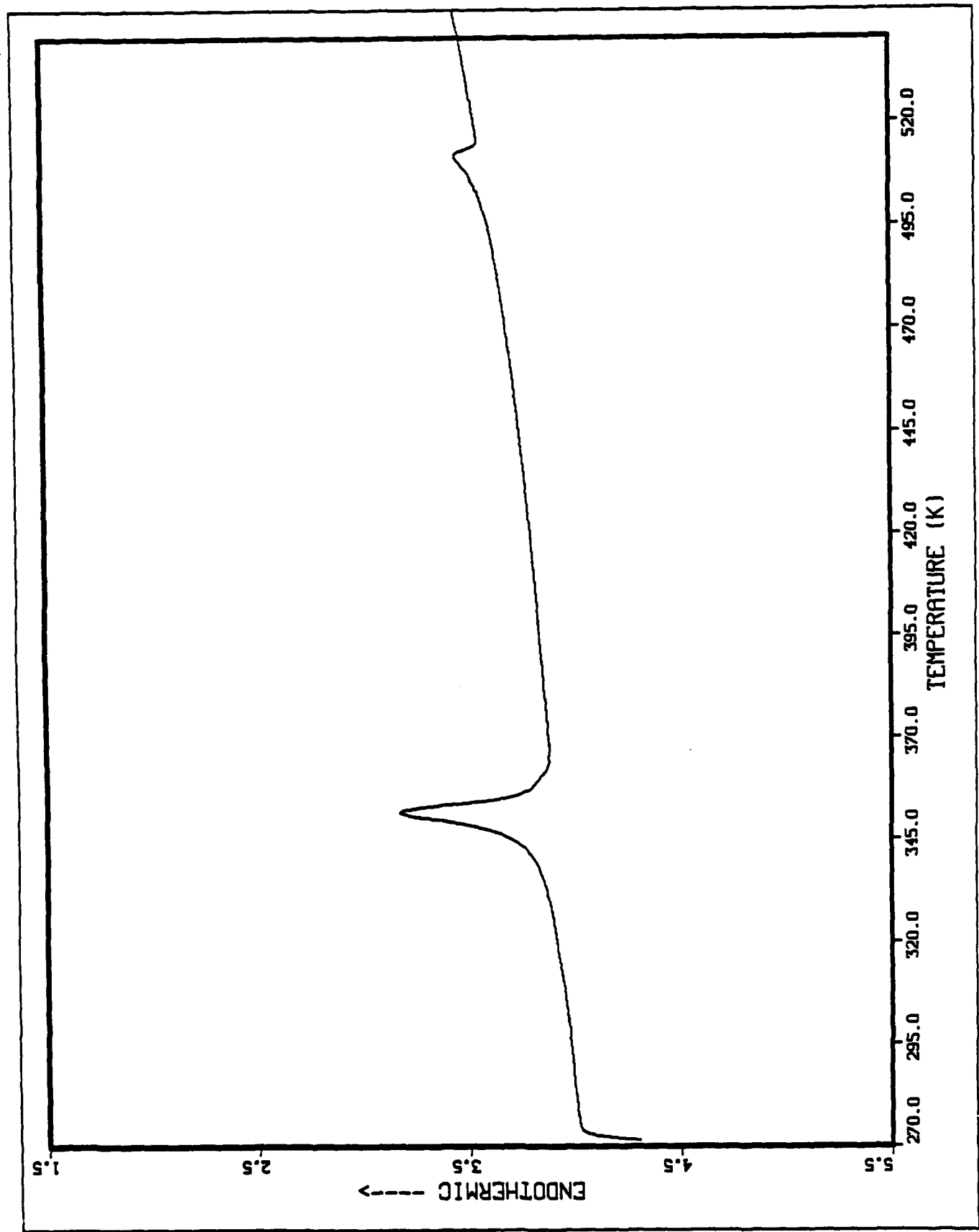
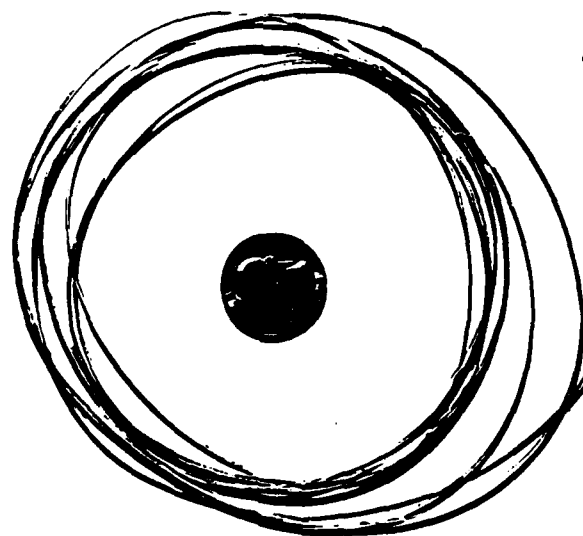
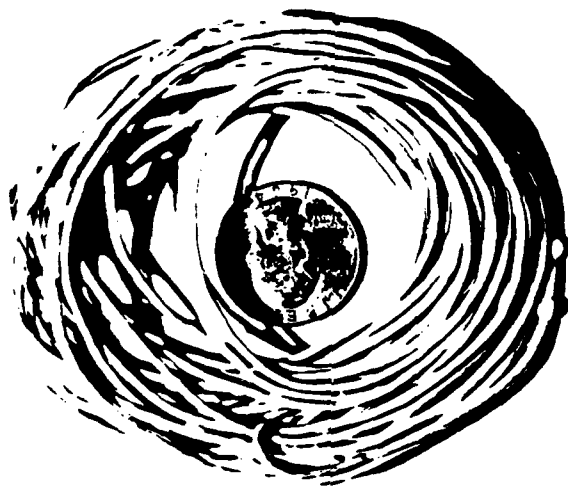


Figure 6: Differential Scanning Calorimeter trace of PBFP fiber showing thermotropic transition $T(1) > 93^{\circ}\text{C}$ and melting or isotropic condition of fiber 55 psi, 163°C , die C.



(a) PBFP 50 psi 325°F die #3



(b) PBNP 45 psi 295°F die #4

Figure 7: (a) Extruded PBFP fiber about 1 mm diameter formed at 163°C and 50 psi.

(b) Extruded PB(2Np)P fiber formed at 124°C and 45 psi.

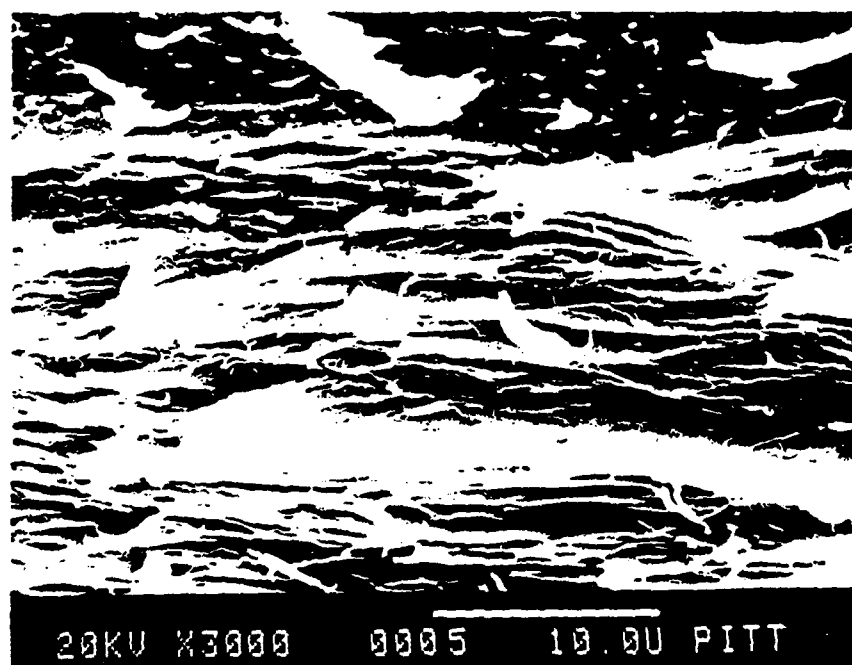
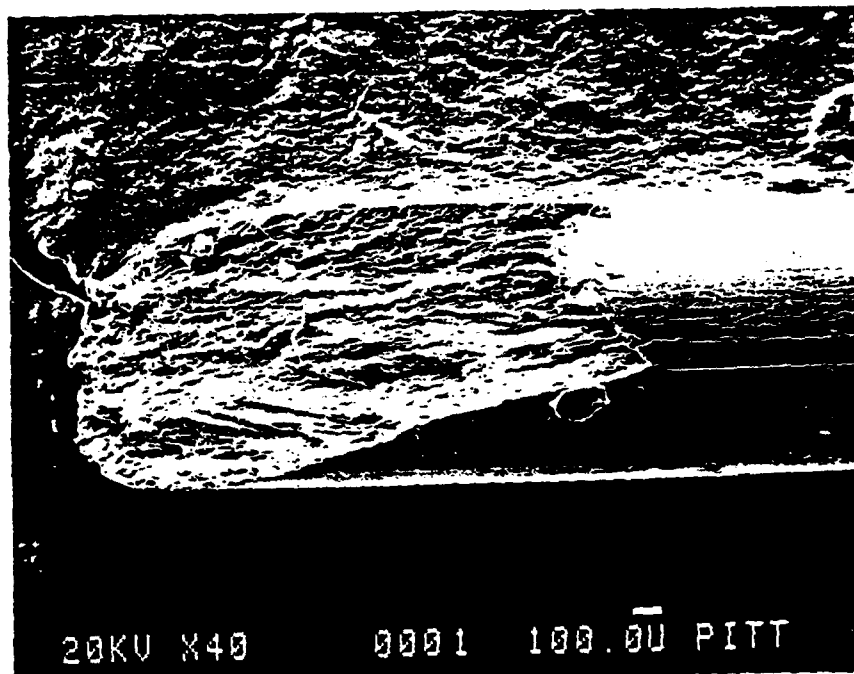
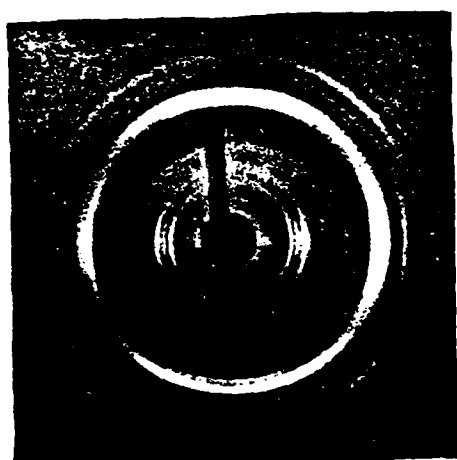
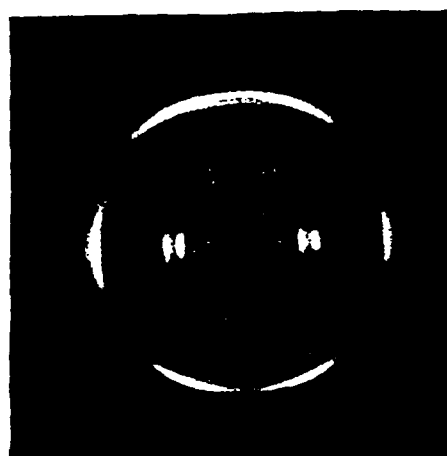


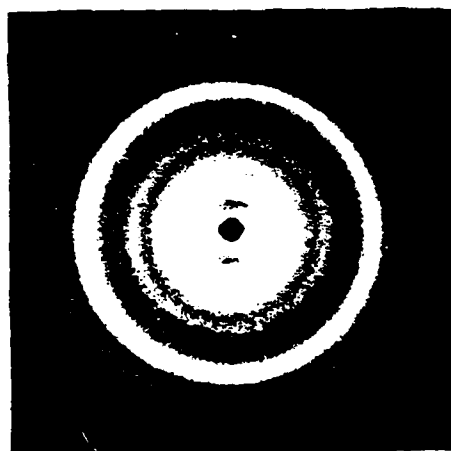
Figure 8: Scanning Electron micrograph of extruded PBFP fiber
(a) low magnification X40
(b) higher magnification (X3000) of fractured region.



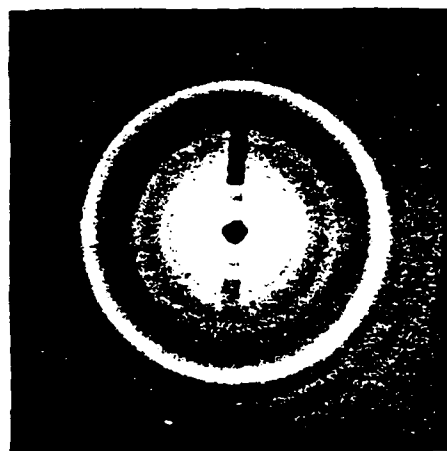
(i) (a)



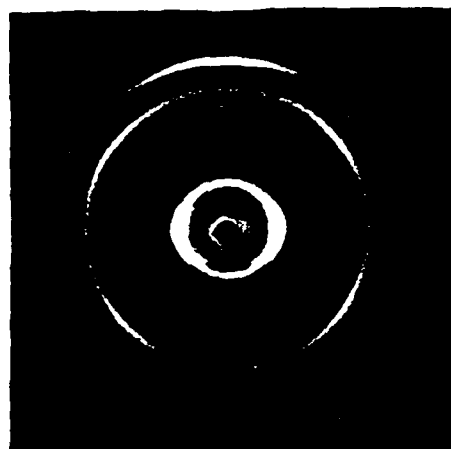
(i) (b)



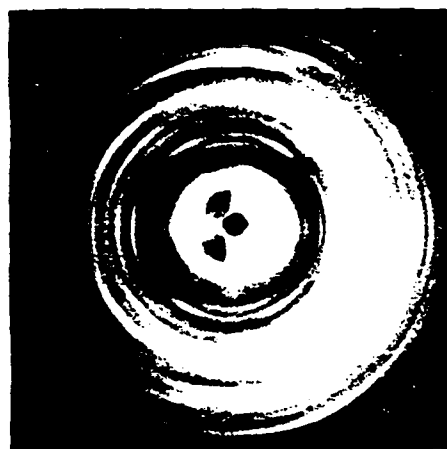
(ii) (a)



(ii) (b)



(iii) (a)



(iii) (b)

Figure 9: (A) X-ray diffraction patterns of several polyphosphazene fibers namely:

- (i) Poly[bis(trifluoroethoxy)phosphazene]
 - (a) 30 psi, die #B, 163°C
 - (b) 55 psi, die #C, 163°C
- (ii) Poly[bis(p-phenylphenoxy)phosphazene]
 - (a) 20 psi, die #A, 196°C
 - (b) 55 psi, die #B, 196°C
- (iii) Poly[bis(2 naphthoxy)phosphazene]
 - (a) 30 psi, die #B, 124°C
 - (b) 60 psi, die #B, 124°C

Fiber axis (extrusion direction) is vertical in all patterns.



Figure 9: (b) (i) Initial fracture features of poly[bis(2-Naphthoxy)phosphazene] extruded at 35 psi and 124°C through die #C.
(ii) Surface features of same sample processed at 124°C and 45 psi.

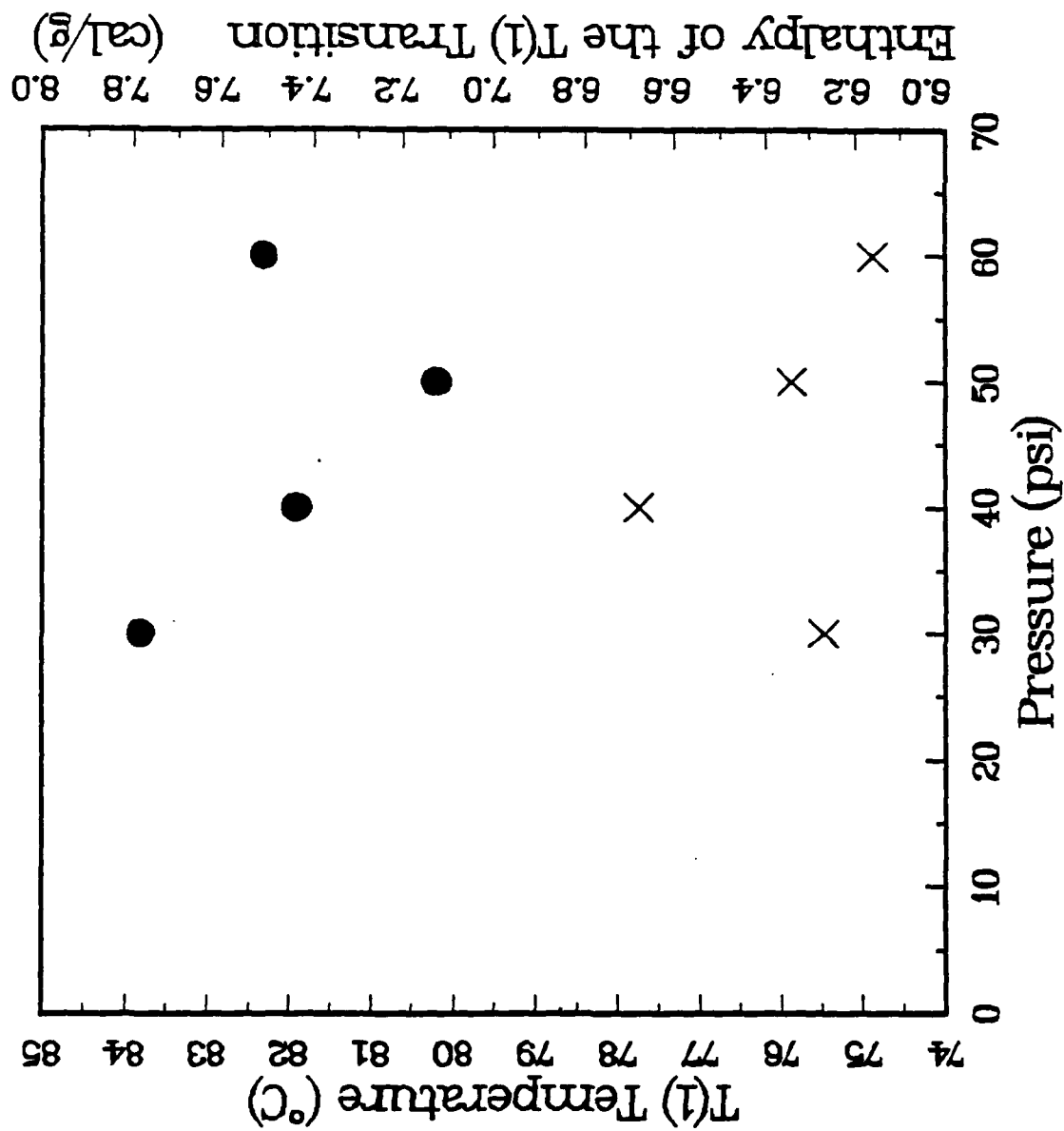
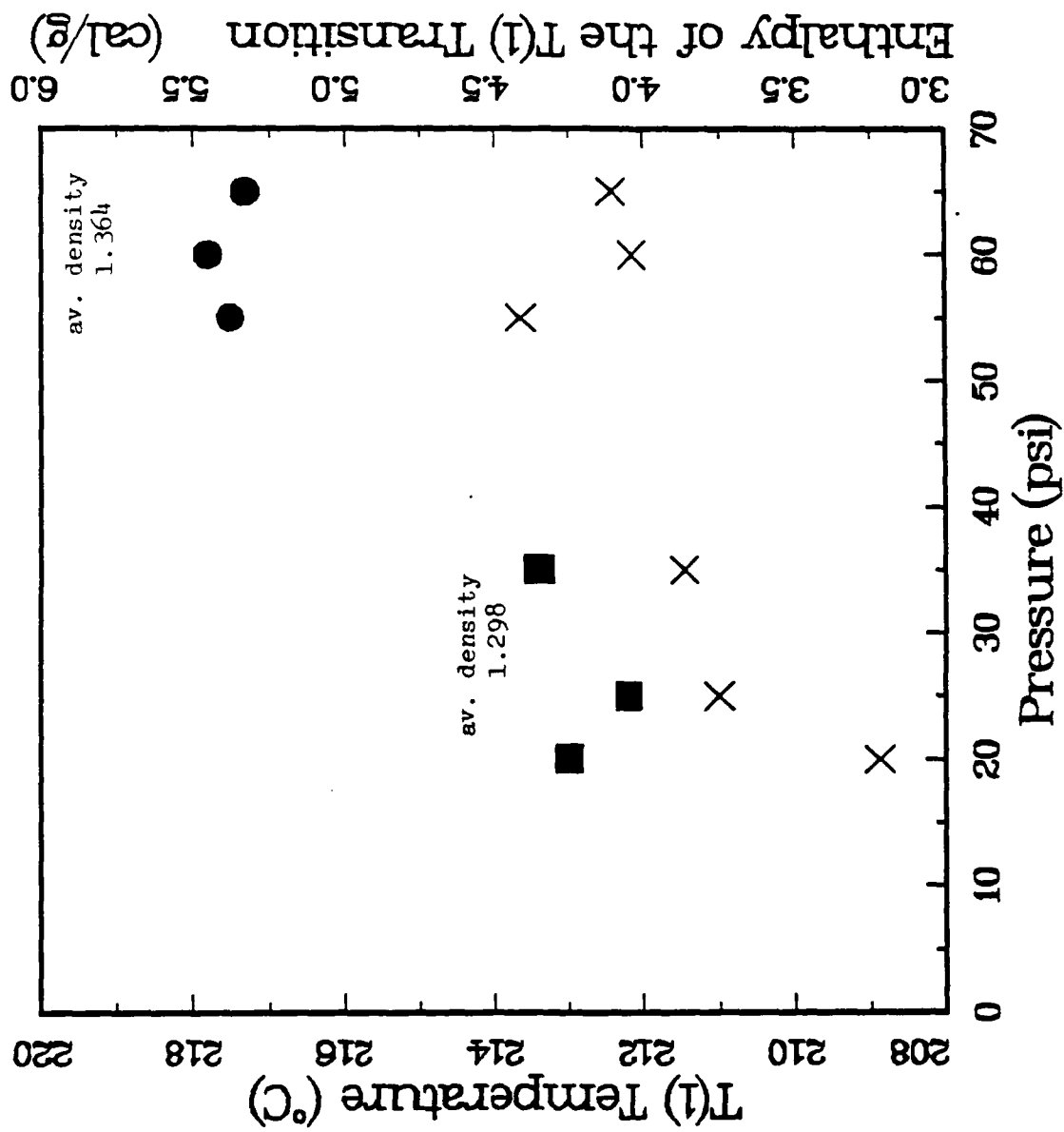


Figure 10: (a) Trends in $T(a)$ (●) and $\Delta H(T(l))$ (x) are plotted for PBFP as a function of extrusion pressure.



(b) Trends in $T(l)$ and $\Delta H(T(l))$ (-x-) are plotted for PB(4Ph)PP as a function of pressure, $\blacksquare$ die A; $\bullet$ die B

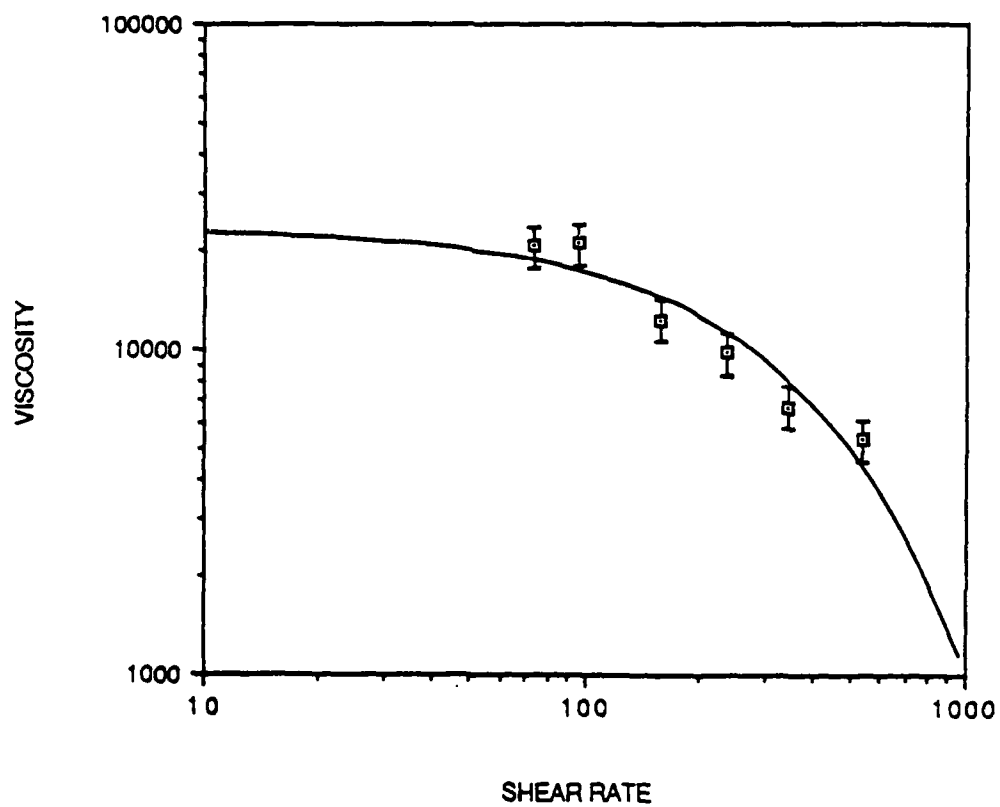


Figure 11: Plots of viscosity as a function of rate of shear for PB(2Np)P showing fitted lower Newtonian region at 124°C.

MELT VISCOSITY OF PBFP

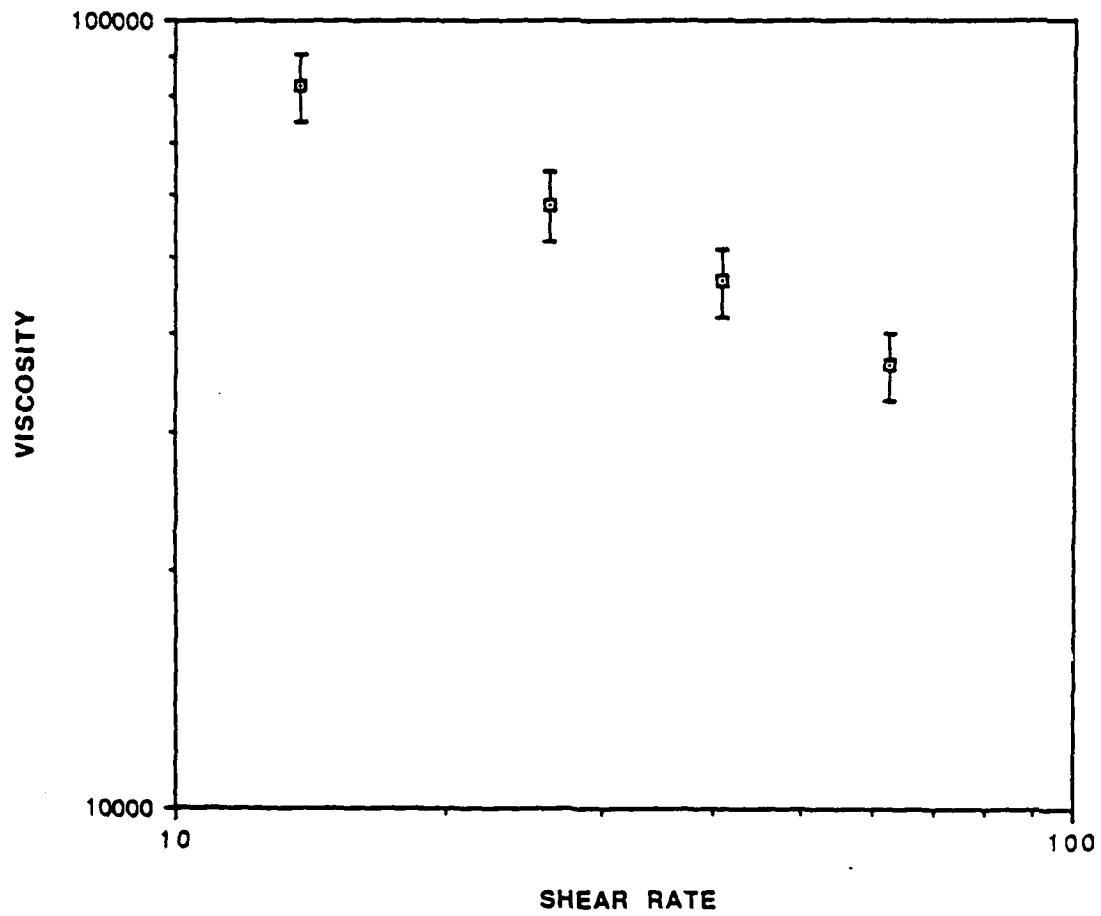


Figure 12: Plots of viscosity vs. rate of shear for PBFP at 163°C. Fitted curve according to power law function, equation (1).

MELT VISCOSITY OF DPP

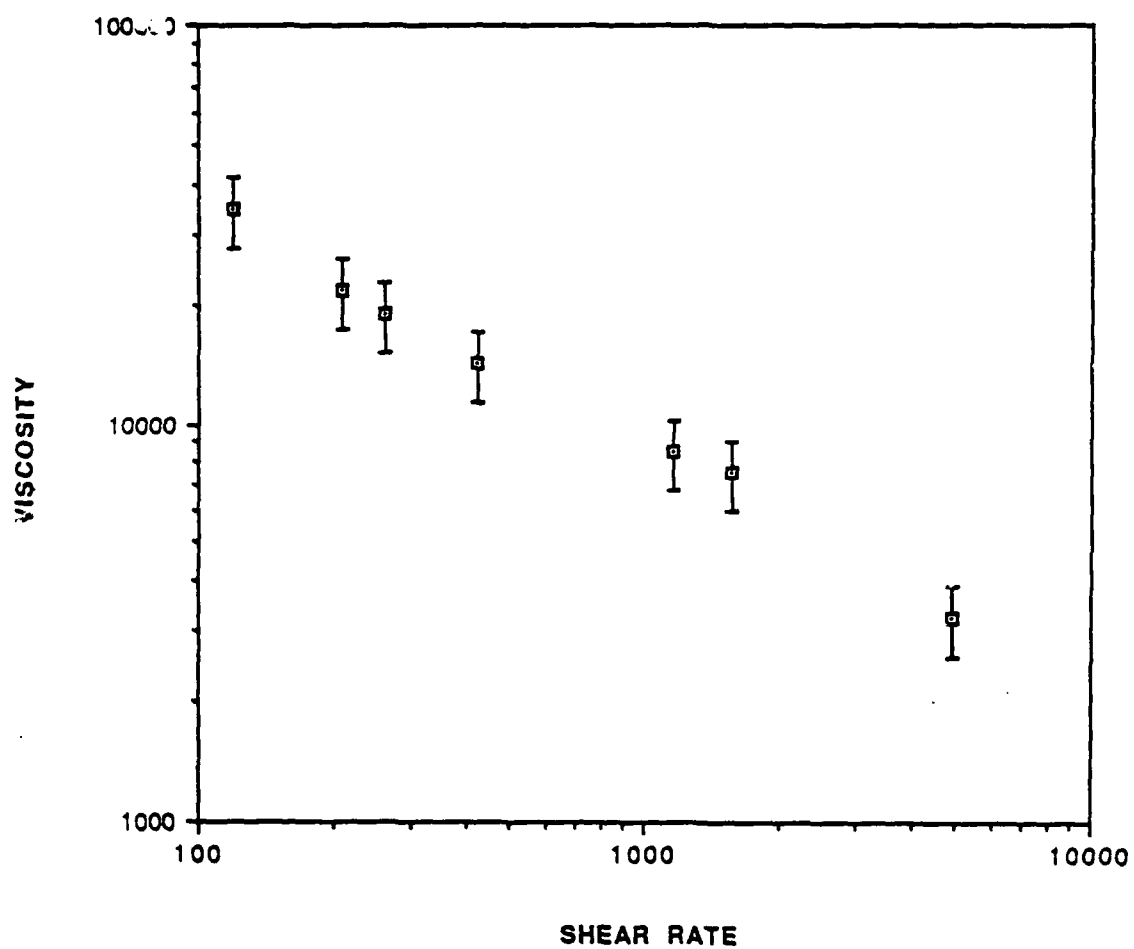


Figure 13: Plot of viscosity vs. rate of shear for PB(4Ph)PP. Fitted curve according to equation (1).

MELT VISCOSITY OF PBPP

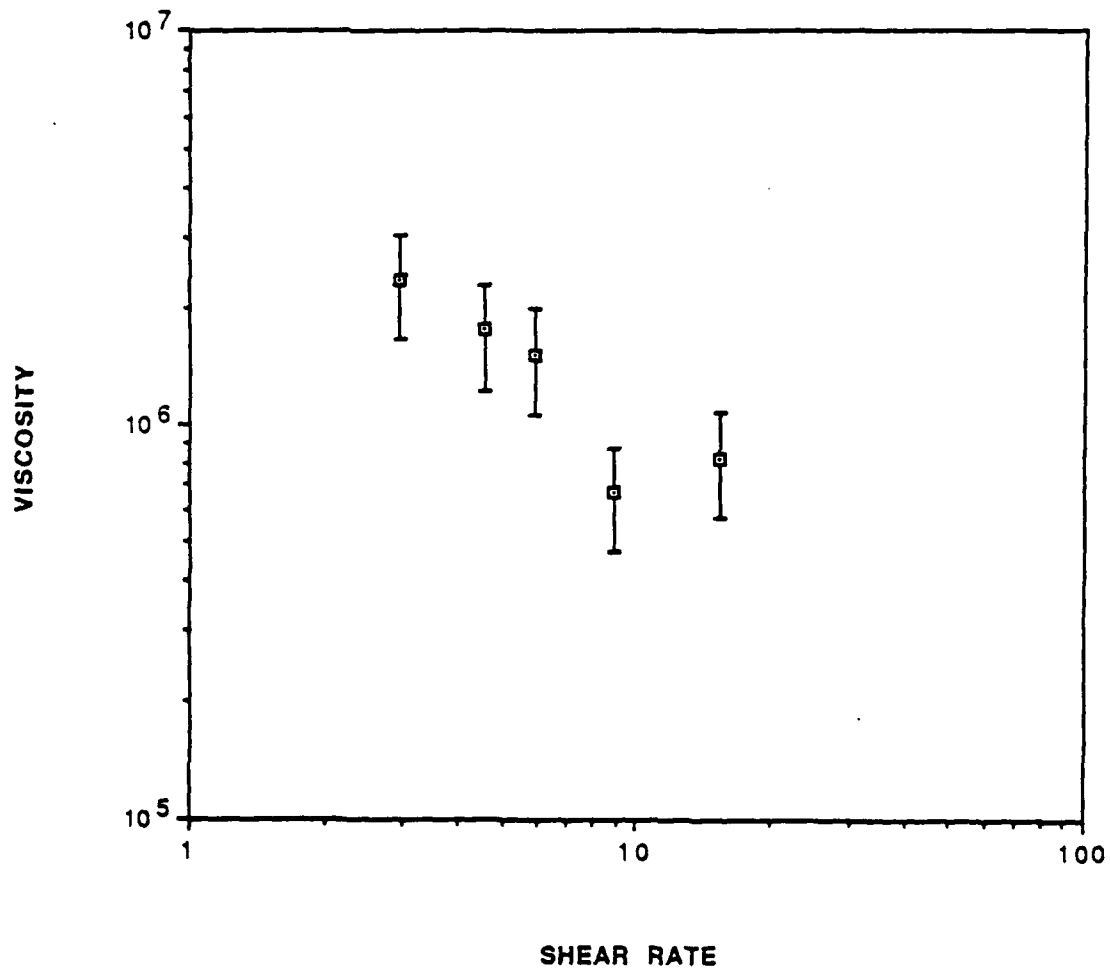


Figure 14: Plot of viscosity as a function of shear rate for PBPP. Fitted curve according to equation (1).

TABLE I*
THERMAL TRANSITIONS OF SAMPLES USED

SAMPLE	T _g ,(K)	T(1),K	T _m ,K
PBPP	276	432	---
PBFP	216	347	498
PB(2Np)P	307	433	---
PB(4Ph)PP	317	490	482

*In the interest of brevity, symbols are used to represent the polyphosphazenes in this work. They are:

<u>Symbol</u>	<u>Polymer</u>
PBPP	Poly[bis(phenoxyphosphazene)]
PBFP	Poly[bis(trifluoroethoxyphosphazene)]
PBNP	Poly[bis(naphthoxyphosphazene)]
PBPPP	Poly[bis(p-phenylphenoxyphosphazene)]

TABLE II
MOLECULAR WEIGHT DATA OF THE SAMPLES USE

SAMPLE	M _w	M _n	POLYDISPERSITY
PBPP	2.8 E 6	3.7 E 5	7.7
PBFP	1.6 E 6	1.6 E 5	12.3
PFNP	2.2 E 6	1.8 E 5	12.5
PB(4Ph)PP	---	---	---

EXPERIMENTAL OBSERVATIONS:

TABLE III

EXTRUSION TIME FOR PBPPP AT DIFFERENT PRESSURES

SAMPLE PBPPP TEMPERATURE 196 °C

S.N.	DIE	PRESSURE(psig)	EXTRUSION TIME(sec)
1	A	15	20.7
2	A	25	7.8
3	A	30	6.9
4	A	40	0.3
5	B	55	292.2
6	B	60	75.0
7	B	65	53.7
RUN 2			
8	A	25	4.05

TABLE IV

EXTRUSION TIME FOR PBNP AT DIFFERENT PRESSURES

SAMPLE: PBNP TEMPERATURE 124 °C

S.N.	DIE	PRESSURE(psig)	EXTRUSION TIME(sec)
1	B	40	96.63
2	B	50	71.56
3	B	60	36.30
4	C	35	83.40
5	C	45	49.05
6	C	55	22.40

TABLE V

EXTRUSION TIME FOR PBFP AT DIFFERENT PRESSURES

SAMPLE: PBFP

TEMPERATURE 148 °C

S.N.	DIE	PRESSURE(psi)	EXTRUSION TIME(sec)
1	B	30	717.0
2	B	40	388.8
3	B	50	255.0
4	B	60	166.2

TABLE VI

EXTRUSION TIME FOR PBPP AT DIFFERENT PRESSURES

SAMPLE: PBPP

TEMPERATURE 121 °C

S.N.	DIE	PRESSURE(psig)	EXTRUSION TIME(sec)
1	A	35	564.0
2	A	40	325.2
3	A	45	243.6
4	A	50	147.9
5	A	65	82.0

TABLE XIII

MELT VISCOSITY AT DIFFERENT RESIDENCE TIMES IN THE BARREL

SAMPLE PBPPP

TEMPERATURE 121 °C

TIME (min)	SHEAR STRESS (gm/cm.sec ²)	SHEAR RATE sec ⁻¹	VISCOSITY poise
45.00	4.073×10^5	15.90	4.114×10^4
55.19	4.073×10^5	15.98	4.135×10^4
67.39	4.073×10^5	16.79	3.231×10^4
79.11	4.073×10^5	24.03	1.112×10^4

TABLE XIV

SAMPLE PBNP

TEMPERATURE 124 °C

TIME (min)	SHEAR STRESS (gm/cm.sec ²)	SHEAR RATE sec ⁻¹	VISCOSITY poise
35.00	2.713×10^5	38.92	8.272×10^3
50.36	2.713×10^5	38.92	6.910×10^4
64.95	2.713×10^5	47.38	5.720×10^4
78.37	2.713×10^5	52.23	5.190×10^4

TABLE XV
THE RESULTS OF POWER LAW FIT TO MELT VISCOSITIES OF
POLYPHOSPHAZENES

Sample	Power law index	Consistency Index
PBPP	0.2580	5.09×10^5
PBFP	0.4633	3.37×10^4
PBNP	0.2527	5.60×10^4
PBPPP	0.3990	5.67×10^4

APPENDIX

CALCULATIONS

The shear stress is given by

$$\tau = \Delta P r / 2L \text{ gm/cm.sec}^2$$

where ΔP = pressure difference driving force

= gauge pressure applied to the ram (gm/cm.sec²)

r = orifice radius (cm)

L = orifice length (cm)

For die A

$$\text{shear stress } \tau = \Delta P r / 2L$$

$$\begin{aligned} \tau_w &= \Delta P r(\text{die A}) / 2 L(\text{die A}) \\ &= 2.011 \times 10^5 \end{aligned}$$

where P is the load on the barrel in pounds.

Similarly for the die B and C, it can be shown that

$$\text{shear stress(die B)} = 3.83 \times 10^4 P \text{ gm/cm.sec}^2$$

$$\text{shear stress(die C)} = 5.137 \times 10^4 P \text{ gm/cm.sec}^2$$

The shear rate is given by

$$\begin{aligned} \Gamma &= 4Q/\pi r^3 \text{ sec}^{-1} \\ &= 4V/\pi r^3 t \text{ sec}^{-1} \end{aligned}$$

where Q = flow rate

$$V = \text{volume of the material extruded.} = 0.4645 \text{ cm}^3$$

r = orifice radius (cm)

t = extrusion time (sec)

This expression of shear rate is valid only for Newtonian liquids, and Rabinowitch correction is made to account the non-Newtonian nature of the polymers. According to Rabinowitch, the shear rate at the wall is given by

$$\gamma_w = [3Q + \Delta P (dQ/d\Delta P)]/\pi r^3$$

The flow rate Q was plotted against driving pressure difference, ΔP . The slopes of

tangents to these curves at different values of ΔP gives $dQ/d\Delta P$, and which was used in the equation to calculate the true shear rate. The γ_w is usually greater than the Newtonian shear rate Γ for polymeric liquids, hence the true viscosity is usually less than the apparent viscosity. The difference becomes more and more prominent at higher shear rates.

The melt viscosity is then obtained as the ratio of shear stress and shear rate,

$$\text{Viscosity} = \text{shear stress} / \text{shear rate (gm/cm. sec)}$$

These results are given in Tables IX to XIV