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PRECURSOR STRUCTURE – FIBER PROPERTY RELATIONSHIPS IN POLYACRYLONITRILE BASED CARBON FIBERS

By

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INTERIM TECHNICAL REPORT for the period June 1, 1979 – May 31, 1980

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GEORGIA INSTITUTE OF TECHNOLOGY
SCHOOL OF TEXTILE ENGINEERING
ATLANTA, GEORGIA 30332

Annual Report

June 1, 1979 - May 31, 1980

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A complete facility has been designed and constructed to prepare carbon fiber under carefully controlled conditions from selected monomer and polymers. The facility includes laboratory polymerization equipment for preparing and characterizing acrylonitrile copolymers; a spinning dope preparation unit for preparing polymer solutions for extrusion; fiber wet-spinning equipment for conversion of polymer to fiber form; two linear ovens for programmed heat treatment of fiber to produce a stabilized yarn; and

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two high temperature furnaces for conversion of stabilized fiber to carbon fiber. All processing steps can be carried out under carefully controlled conditions of time, temperature and tension. All units of the facility have been tested and several minor problems have been identified and corrected. All components are now fully operational.

Initial studies have concentrated on preparation and characterization of polyacrylonitrile polymers and copolymers of known composition and properties. One series of polyacrylonitrile samples with viscosity average molecular weights between 45,000 and 2,000,000 have been prepared to investigate the effects of end-groups on stabilization behavior. Preliminary analysis of a differential scanning calorimetric (DSC) study on these samples suggest that two distinct mechanisms are involved in stabilization, at least one of which is molecular weight dependent. A more detailed analysis of the DSC data is underway.

Samples of PAN copolymer fibers have been prepared with different levels of stretch in the gel state and in the plasticised state. X-ray diffraction and sonic modulus are being employed to characterize the molecular orientation in these samples.

PRECURSOR STRUCTURE-FIBER PROPERTY RELATIONSHIPS
IN POLYACRYLONITRILE BASED CARBON FIBERS

I. INTRODUCTION

Recent projections suggest that carbon fibers will become an important structural material by the mid-1980's (1,2). Military applications alone are expected to require one million pounds of fiber by 1985 and applications in the transportation industry are estimated to require twenty million pounds. Air frames for the F-18 fighter plane are 10% composites by weight and the air frame of the next generation plane is predicted to be 70% by weight fiber reinforced composites.

Carbon fibers are produced from precursor fibers (acrylic, pitch or rayon) by a series of thermal treatments, usually in the presence of an oxidizing atmosphere. The "stabilized" fibers that result from these thermal treatments are subjected to temperatures in the range of 1000 - 3000°C to produce carbon or graphite fibers. Typical carbon fibers have tensile strengths of the order of 200 to 400 x 10^3 psi and moduli of 30 to 90 x 10^6 psi. These properties combined with the low density of carbon fibers give very high strength and modulus-to-weight ratios for carbon fiber composites.

As is generally the case with new developments of significant commercial interest, most research on carbon fibers has been empirical, directed toward increased production speeds and circumvention of specific problems (e.g., fiber-resin adhesion) that arise. There have been only a few published, systematic studies of the relationships between precursor structure, thermal treatment conditions (time, temperature, tension) and final carbon properties. The mechanisms and kinetics of chemical reactions involved in the thermal treatment of acrylic fibers have received some attention (3-5) and several studies have attempted to relate carbon fiber solid state structure with properties (6,7). Little information is available on the structures of precursor fibers and their relationship to carbon fiber properties. Properties such as precursor composition, orientation and morphology have not been carefully studied and the effects of these parameters on carbon fiber modulus, tensile strength, thermal and electrical properties are essentially unknown. Studies in this area are needed since the structure established in the precursor fiber coagulation bath and the degree of orientation of the precursor fiber are believed to have major effects on carbon fiber properties.

II. OBJECTIVE

The objective of the project is to develop fundamental relationships between precursor structure and properties of derived carbon fibers. Carbon fibers produced from polyacrylonitrile based precursors is the primary focus of the investigation. Comonomer type, copolymer composition, fine structure developed in fiber extrusion, and precursor orientation will be related to carbon fiber structure, morphology, modulus, tensile strength and electrical conductivity.

A major part of the effort during the first year of the project has been directed toward development, installation and testing of equipment necessary to convert monomers into carbon fiber under precisely controlled conditions during each step of the process. The various components of this carbon fiber facility are described in Section III.

Initial studies have been directed toward investigation of the effects of precursor chemical structure on properties of the derived carbon fiber. These studies are described in Section IV.

Proposed work during the second year of the contract are outlined in Section V.

III. CARBON FIBER PREPARATION FACILITIES

A. Polymerization Equipment

Both bench-scale and large-scale equipment have been set-up to conduct polymerization of polyacrylonitrile homopolymer and copolymers under carefully controlled conditions. For screening tests on the bench-scale apparatus, acrylonitrile can be distilled directly into the reaction flask and the polymerization carried out under precise temperature and atmospheric control. Comonomer can be added at a controlled rate to ensure that copolymer composition does not vary during the course of polymerization reaction.

Large scale polymerizations are carried out in a two-liter Parr jacketed and stirred autoclave. This autoclave is also equipped for good temperature and atmospheric control and permits addition of selected comonomers during the course of the polymerization. Approximately 250 grams per batch of polymer samples can be prepared in the Parr autoclave.

B. Fiber Spinning Equipment

A schematic diagram of wet spinning line is shown in Figure 1. The polymer solution (dope) to be spun, is placed in the pressure vessel which is connected both to a vacuum and a high pressure nitrogen line. By repeated evacuation and pressurization the spinning solution is degassed. The spinning solution is forced from the pressure vessel to the metering pump by nitrogen gas pressure. The spinning solution is filtered through several layers of felt fabric prior to extrusion through a spinneret. A variety of spinnerets is available with 15 to 360 holes, 3 mils in diameter. The viscosity of the spinning solution can be monitored with a Brookfield Viscometer.

The fiber is coagulated in a stainless steel spinbath approximately 30 inches long. The spin bath can be heated and is provided with a circulation pump and nonsolvent makeup system. Spin bath composition is monitored with an Abbe refractometer. Washing of the coagulated fiber is carried out on the first godet. Both a spray and a dip wash are used at this point. In the spray wash, a spray bar is positioned above the upper godet and water is allowed to cascade over and down the filaments. As the filaments pass around the lower godet, they pass through a standing rinse bath. The speed of the first godet is adjusted to give the desired fiber stretch in the spin bath. The level of stretch here, known as jet stretch, is defined as the ratio of the linear velocity of the first godet to the average velocity of the polymer solution exiting from the

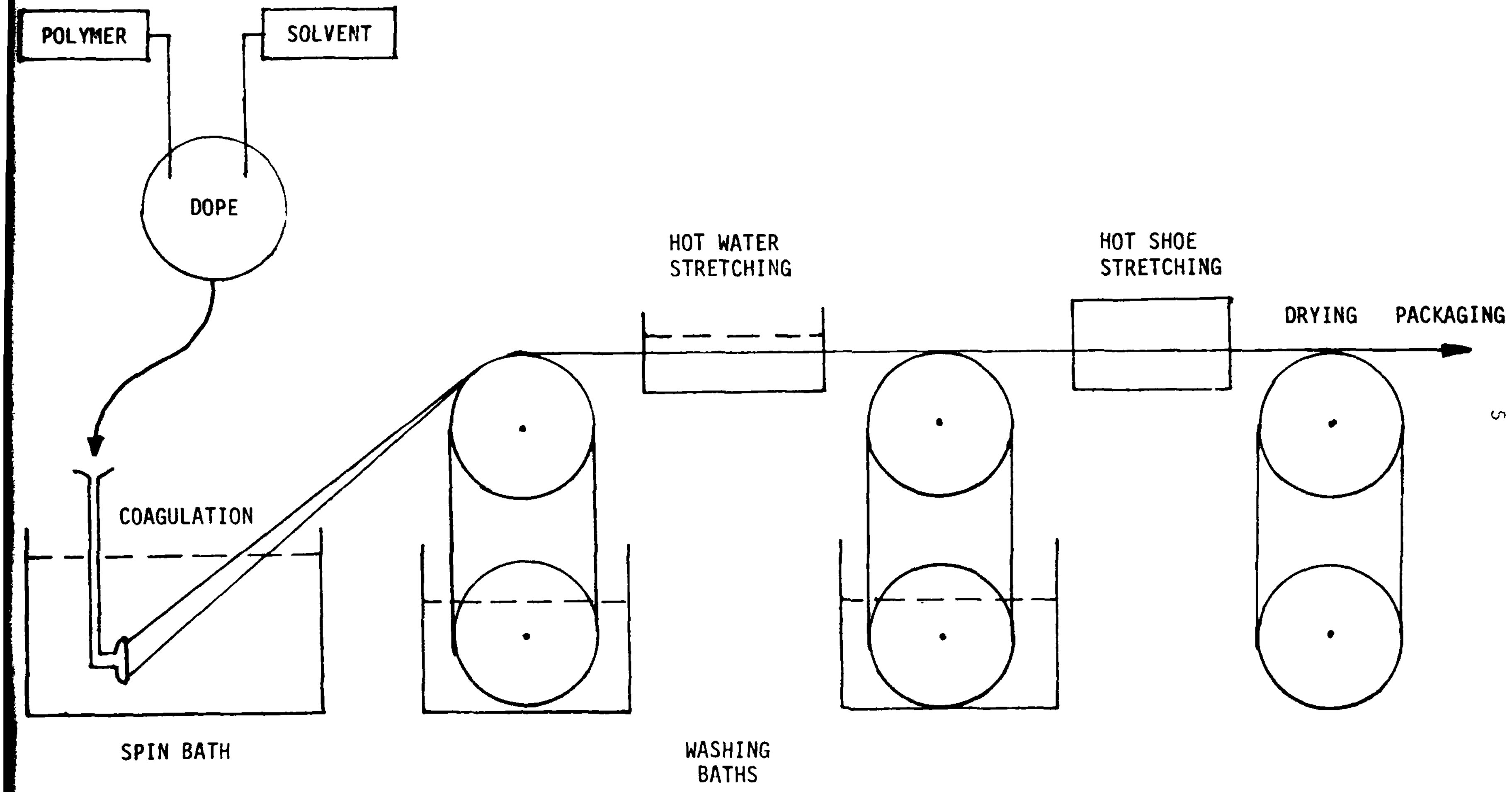

FIGURE 1

SCHEMATIC OF WET SPINNING PROCESS

spinneret hole.

The fiber can be stretched further by varying the relative speeds of godets 1 and 2. Additional washing can be carried out also by both spray and dip on godet 2.

Fiber collapse is accomplished on godet 3 which is equipped with an internal heater and temperature control system. Either stretch or relaxation can occur between godets 2 and 3 depending on the relative speeds. To aid in stretching or relaxing the filaments in the zone, they can be passed over a hot pin or through a hot shoe. These devices may be used (as well as a steam tube) for post stretching of the collapsed fiber.

Fiber is taken up on a Leesona 959 winder. Overall capacity of the system is approximately 250 gram of fiber per spinning run.

It became apparent in early spinning trials that the spinning solution preparation techniques were not satisfactory. A high incidence of gel in the polymer solutions resulted in blocking of the filter or plugging of holes in the spinnerets. A Ross Model LDM double planetary mixer has been requested to solve this problem. This mixer will handle the very viscous spinning solutions and can be heated or cooled to promote uniform polymer solution preparations. Uniformity of filaments is ensured by frequent microscopical examination and testing of mechanical properties at several places along the length of the filaments produced in every spinning trial.

C. Stabilization Equipment

Two linear ovens have been constructed to convert PAN based fibers to a stabilized form suitable for carbonization. The initial linear oven is shown in Figure 2. This oven is constructed in three sections which can be operated and controlled independently. Each section consists of two coaxial pyrex glass

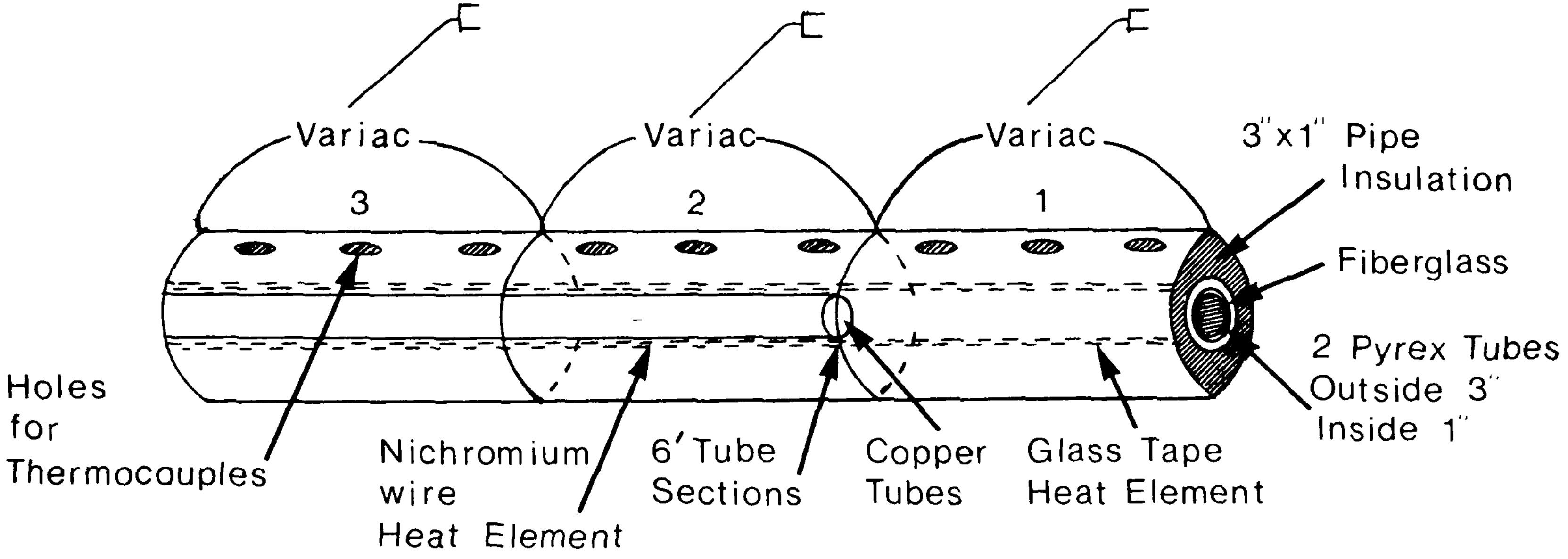

FIGURE 2

Linear Stabilization Oven Number 1

sections which can be operated and controlled independently. Each section consists of two coaxial pyrex glass tubes with Fiberglas covered heating tape wrapped around the inner tube. The outer tube is covered with Fiberglas tape insulation. Each section has three thermocouple wells for monitoring the temperature. The heating tape in Section 2 and 3 is wrapped to provide a flat temperature profile. To prevent hot spots, and to insure a flat profile, these sections have two concentric heavy copper pipes in the inner tube. Section 1 has a different profile. The temperature profile increases from the inlet to the center of the oven (36") and is flat from the center to the exit end. The linear ovens can be separated into three sections so that the fiber being stabilized can be stretched at certain points in the stabilization process and relaxed at other points.

Typical temperature profile for the number 1 linear oven is shown in Figure 3. These are actual profiles obtained by passing a thermocouple down the length of the oven and recording the temperature. Different profiles were used to stabilize commercially-available precursor fibers as shown in Figure 3.

A second more versatile stabilization oven has been constructed and is undergoing preliminary testing (Figure 4). It consists of 12 eighteen-inch ceramic jacketed tube ovens surrounding a pyrex glass liner tube. The power to each of the 12 sections is individually controlled to give a very versatile temperature profile. Desired temperature differences can be obtained with this oven over short distances, and "tailing" near the tube exit (see Figure 3) can be minimized. The heating coils are uniformily wrapped inside the ceramic jacketed ovens, giving an even point-to-point temperature distribution than that obtained with the heating tape-wrapped oven. This oven can also be separated into three sections for independent tension control during various phases of stabilization.

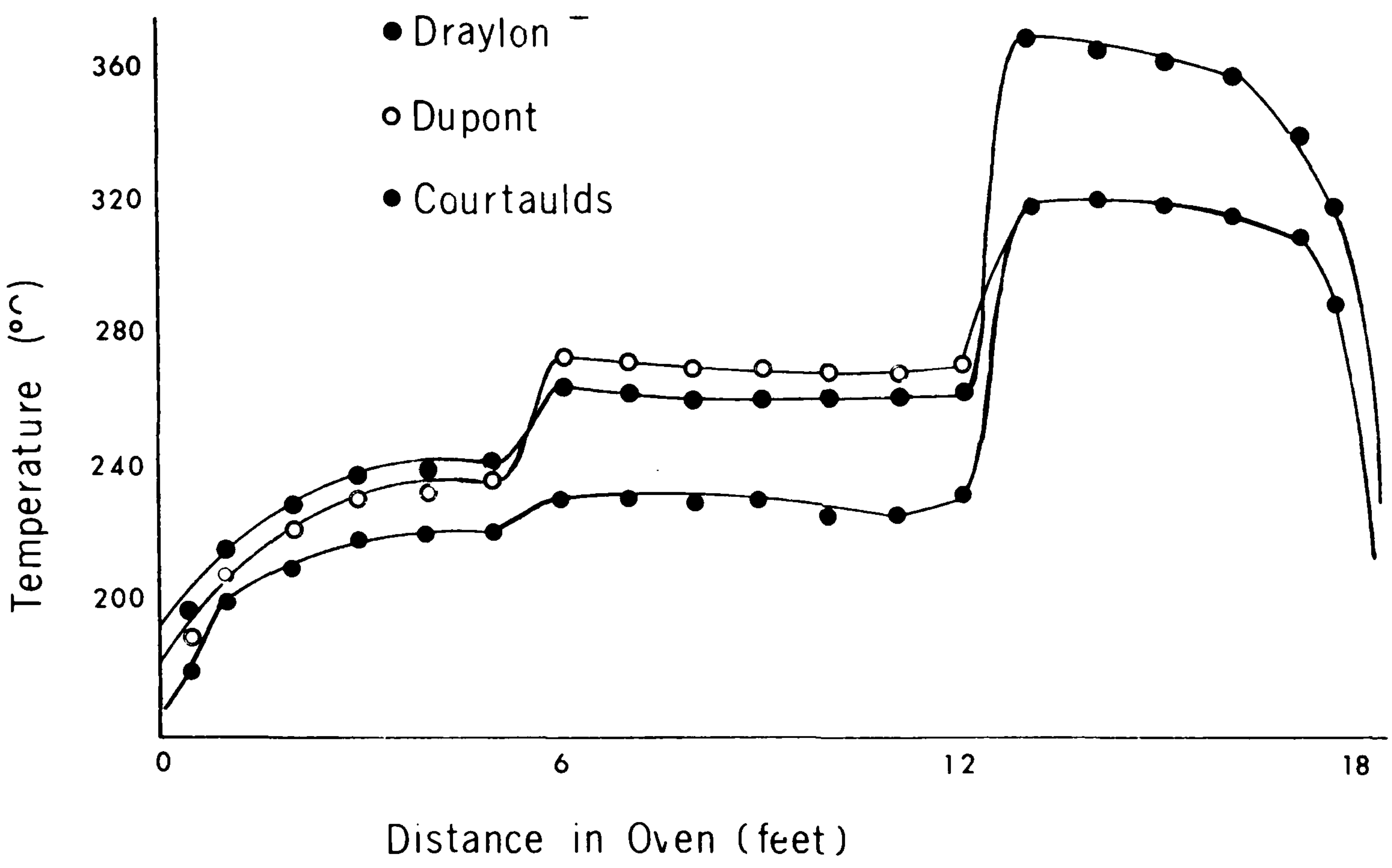

FIGURE 3

Optimized Temperature Profile for Stabilization of Known Precursors

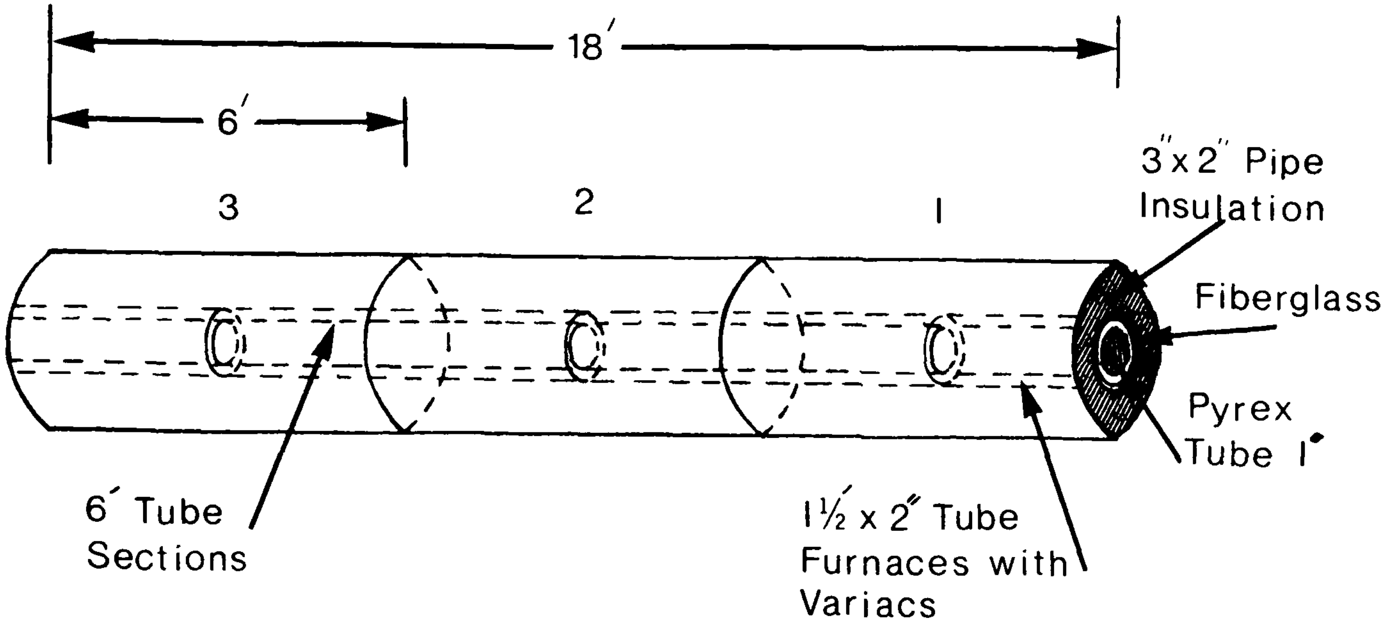

FIGURE 4

Linear Stabilization Oven Number 2

Several pieces of auxiliary equipment have also been developed to optimize the stabilization process. A programmable microprocessor Lindberg tube furnace is used in conjunction with an Instron Testor to determine strain or stress as a function of time and temperature. This information will be useful in establishing temperature profiles and tensions in the the stabilization process.

D. Carbonization Equipment

Two carbonization furnaces have been obtained and installed to produce fiber from stabilized precursors. Power sources for the furnaces are TOCCO 15 KW motor driven generators. The 10 kilowatt output of the generator is coupled through a control system to a copper coil surrounding a high quality carbon tube inductor. The heated length of the carbon tube is approximately 6 inches in one of the furnaces, and approximately 12 inches in the second furnace. Temperatures approaching 3000°C can be achieved in the furnace. Both furnaces are equipped for inert gas blanketing.

IV. INITIAL STUDIES

Initial efforts have been directed toward investigation of the effects of chemical composition of PAN copolymer on the properties of carbon fibers. Polymers were first synthesized with controlled molecular weight and known composition. End groups present in the polymer as a result of the initiator used or of chain transfer reactions with solvents complicates the study of comonomer effects. Thus precursor presumably prepared from 100% PAN has a number of impurity groups present which can effect the stabilization of precursor and thereby the final carbon fiber properties.

A. Polymerization Procedures

Polymer has been prepared by both solution and emulsion polymerizations so that end-group effects and chain transfer effects can be investigated. The procedures for the bench scale polymerizations (which were eventually scaled up for the autoclave) are detailed in Table 1 (Solution) and Table 2 (Emulsion). Variables such as initiator concentrations were altered as needed to obtain a spectrum of molecular weights. When the emulsion procedure was scaled up to the Parr autoclave, the emulsifier was omitted from the procedure to give better $\overline{M_v}$ control. The scaled-up procedure was thus a modified suspension polymerization rather than a true emulsion. The viscosity average molecular weight of all samples was measured.

B. Effect of Polymerization Impurities on Pyrolysis Behavior

Both solution and emulsion polymerizations were conducted with pure AN to determine the effects of different end groups on pyrolysis behavior. In the AIBN-initiated solution polymerization in DMF, expected end groups would be the isobutyronitrile radical and a fragment of DMF from chain transfer reactions. The persulfate initiator in the emulsion polymerization would give a sulfate or bisulfite end group on the initiation side. On the termination side of the polymer, a variety of end groups dictated by the various termination modes (coupling, hydrogen abstraction, back-biting, disproportionation, etc.) would be present. Since these latter end groups are alkane or alkene end groups with no nucleophilic heteroatoms, initiation effects on nitrile polymerization during pyrolysis would be expected to be minimal.

Solution polymerizations were conducted under various AIBN concentrations to give a range of molecular weights, and the emulsion polymerizations were similarly modified in initiator and surfactant concentrations. Ideally, a viscosity average molecular weight of ≈150,000 was sought for spinning, as this corresponded to commercial samples of PAN powder supplied by Monsanto. Celanese, Hercules and duPont personnel confirmed that a 150,000 corresponded well with

TABLE 1

Bench-Scale Solution Polymerization Procedure

A. Acrylonitrile (AN)/Dimethylformamide (DMF) Purification

1. Aldrich-grade AN was fractionated by distillation at 1 atm. using a Vigieux column, and then redistilled under vacuum via an acetone/dry ice cold trap.
2. DMF was distilled at 1 atm. from barium oxide.

B. Solution Polymerization

1. Nitrogen flow was maintained for 10 minutes over the entire polymerization apparatus.
2. The purified DMF (50 g., 54 ml.) was added to the apparatus under N_2 flow, followed by the required quantity of AIBN initiator[a], the latter either added as a solid or in 1 ml. DMF solution.
3. The purified AN (10 g., 13 ml.) was added to the vessel under N_2, and stirring was begun.
4. The temperature was slowly raised to 55°C, and controlled at that temperature for 22 hours.
5. To precipitate the polymer, the reaction mixture was poured into 300 ml. of methanol contained in a stainless steel blender.
6. The solid PAN was filtered ans washed with additional alcohol, and dried at RT for two days, or under vacuum at 40°C for six hours.

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[a] The initiator concentration was systematically altered to increase the $\overline{M}v$.

TABLE 2

Bench-Scale Redox Procedure

1. The reaction flask was charged with 120 ml. of freshly-distilled water.
2. The temperature was raised to 35°C, and the water was stirred under N_2 for 10 minutes.
3. The N_2 flow was reduced, and 2 gm.[a] of lauryl sulfate surfactant added.
4. Purified AN (see Table 1 for AN purification scheme) was then added in an 80 gm. quantity.
5. Quickly, 0.1 gm. of $K_2S_2O_8$ and 0.0333 gm. of $Na_2S_2O_5$ were added in the solid form. No pH control was utilized.
6. The system was closed under a blanket of N_2, and the reaction continued for three hours.
7. The reaction mixture was poured into 500 ml. of water and the polymer coagulated with NaCl while stirring.
8. The polymer was filtered, washed in succession with water and methanol, and dried at RT.

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[a] The quantities given for initiator and emulsifier were systematically altered to increase the $\overline{M}v$.

the $\overline{M}_v$'s of the three known precursors (Draylon T, Courtaulds and duPont) utilized in the initial stabilization studies. As with the synthesized polymers, $\overline{M}_v$'s were calculated from the Mark-Houwink relationships:

$$[\eta] = K\,m^{a}$$

$[\eta]$ = intrinsic viscosity

K = constant = 24.3×10^{-5}

$M = \overline{M}_v$

a = constant = 0.75

The intrinsic viscosity was derived from polymer solution flow times using standard viscometery techniques with a Cannon-Fiske viscometer. The constants, K and a, for PAN were reported by Cleland and Stockmayer (DMF solvent, 25°C) and were utilized directly in the reported research. Calculations were first conducted using literature equations for prediction of molecular weight as a function of "effective" initiator concentrations in solution polymerization and the experiments were run based on the calculations.

The $\overline{M}_v$'s of the synthesized polymers are detailed in Table 3. The emulsion polymers compared favorably with the commercial 100% PAN precursor, Draylon T. As expected, however, the solution polymerization gave a lower $\overline{M}_v$ than the emulsion route due to the ease of chain transfer to the DMF solvent, even at extremely low AIBN concentrations ($< 9.8 \times 10^{-4}$ M). Yields ranged from > 90% on bench polymerizations to as low as 40% on the scaled-up autoclave polymerizations.

Infrared analyses were conducted on the synthesized PAN polymers in an

TABLE 3

$\overline{Mv}$ of Synthsized Polymers[a]

METHOD	$\overline{Mv}$
Solution	120,000
"	90,000
"	68,000
"	45,000
Emulsion	2,000,000
"	400,000
"	300,000
"	250,000
Draylon T [b]	270,000
duPont [c]	150,000
Courtaulds [c]	150,000

---

[a] Cleland-Stockmayer constants for Mark-Houwink equation used: $K = 24.3 \times 10^{-5}$, $a = 0.75$ (DMF, 25°C).

[b] By viscosity measurements conducted on fiber at Georgia Tech.

[c]

attempt to detect intrachain impurities as well as end groups. Ketonitrile intrachain units were not detectable on the IR in either the solution or emulsion polymers. Residues of DMF and/or AIBN, or end groups fragments of the same, were picked up in the spectra. Spectra of the emulsion polymers were the closest to that expected for pure PAN, with the sulfate or bisulfite end groups detected.

DSC scans were conducted under air atmosphere and over the available range of molecular weights for both solution and emulsion polymers. The scans are reproduced in Figures 5-8. DSC conditions and sample weights were kept as nearly identical as possible. The most pronounced change in the solution polymers in progressing from an $\overline{M_v}$ of 120,000 to 45,000 was the marked reduction in the intensity of the exotherm peak in the 285°C to 306°C peak range, and the increase in relative size of the exothermic peak occurring in the 252°-255°C peak range (Figure 5). Sample weight was not an initial factor, as the DSC scan of the $\overline{M_v}$ = 120,000 polymer (Figure 6) conducted at a 48% lower weight than the initial scan (Figure 5) gave essentially the same shape pattern with slight sharpening of the exotherm peak at 306°C. The area under the curve for the lower weight sample was less, as expected. Similar results were obtained with the emulsion polymers (Figure 7). In the 250,000 $\overline{M_v}$ sample, the lower temperature exotherm became large enough to merge with the higher temperature exotherm.

DSC scans were also conducted on the three commercial acrylic precursors for comparison purposes (Figure 8). As expected, the Draylon T had a much sharper main exotherm than the comonomer-containing duPont and Courtaulds precursors. The comparative broadness of the DSC peaks was due to the selection

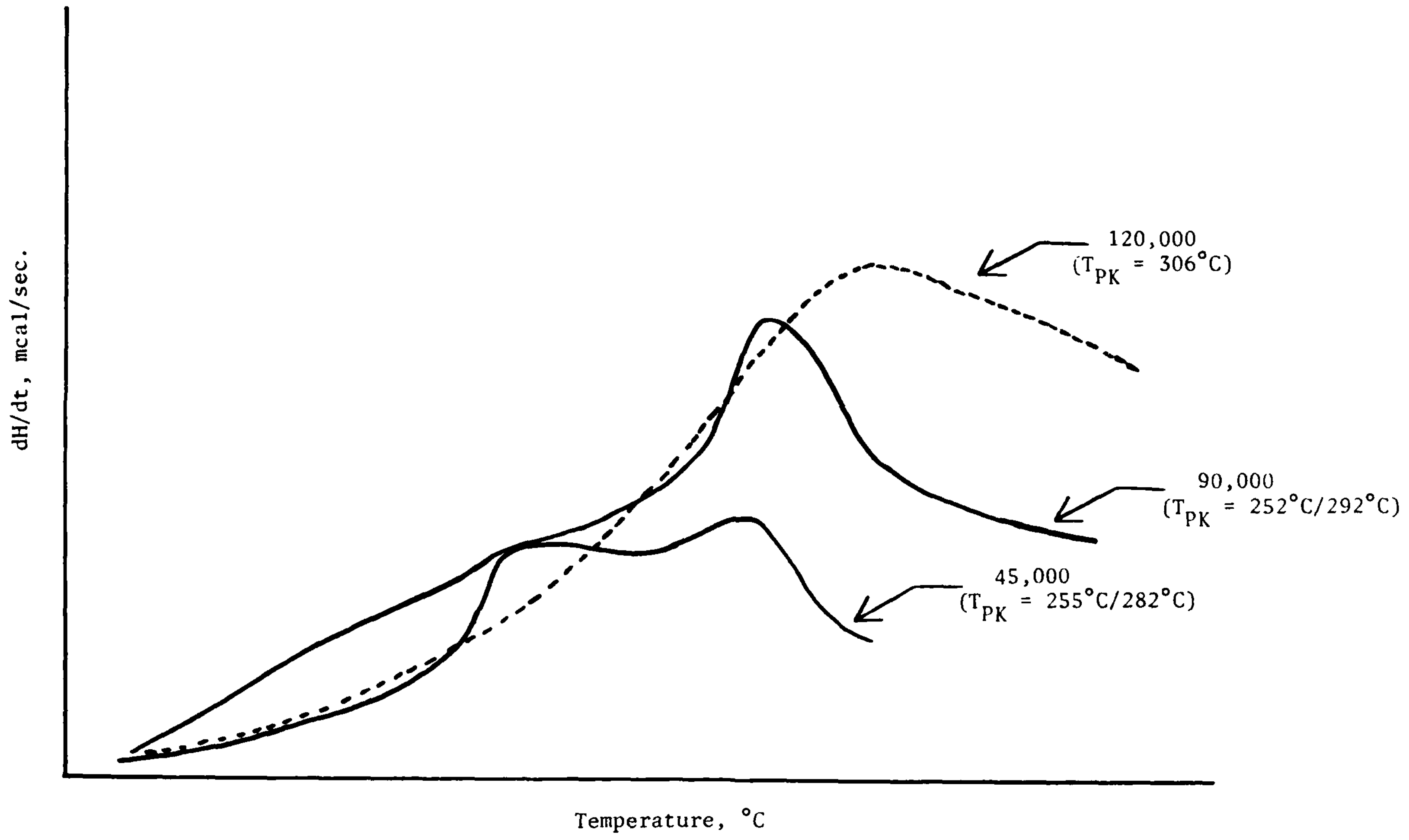


FIGURE 5. DSC Plots of Solution PAN Polymers of Different $\overline{M}_v$.

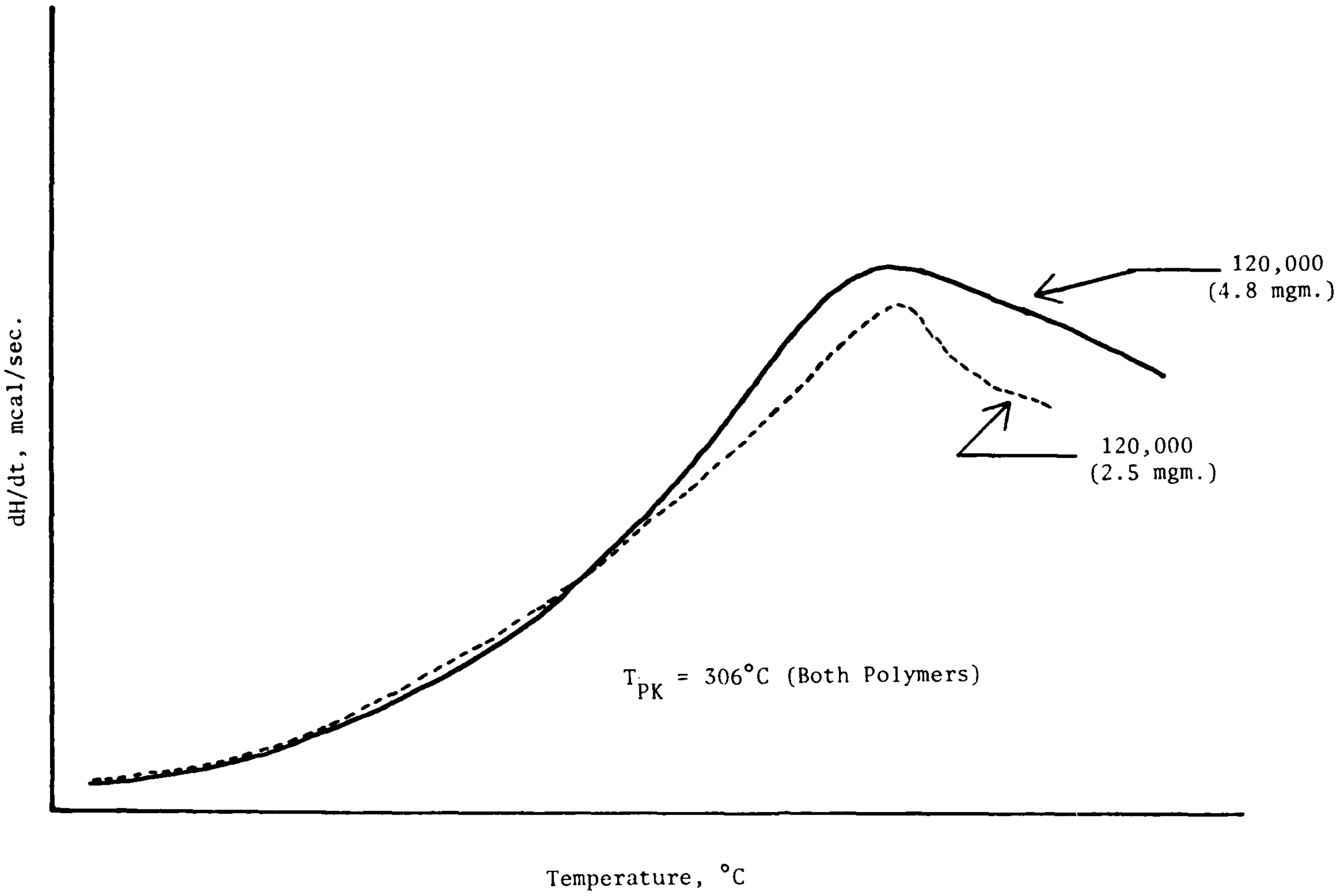


FIGURE 6. DSC Plots of the Same $\overline{M}_V$ Solution PAN at Different Sample Weights.

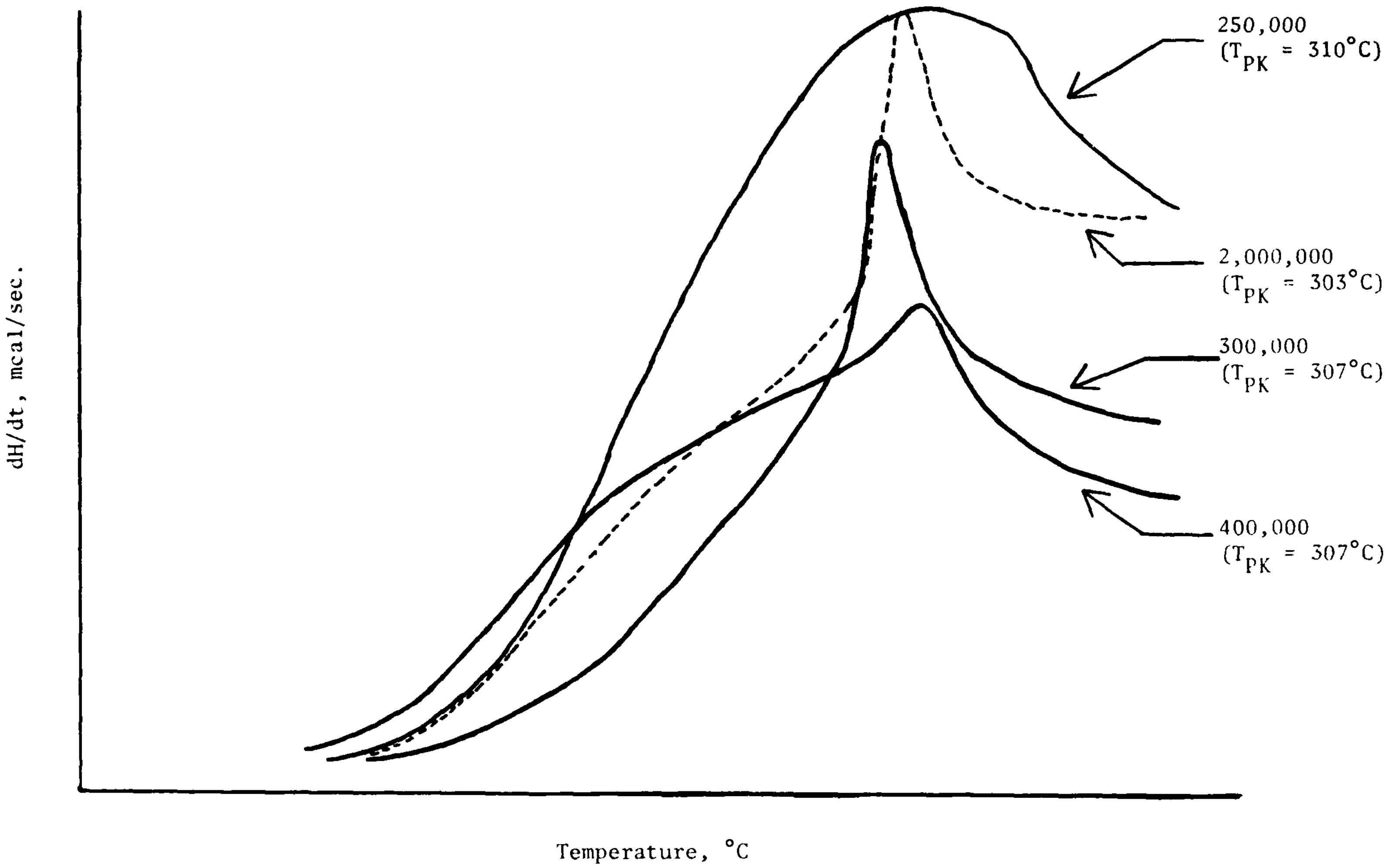


FIGURE 7. DSC Plots of Emulsion PAN Polymers of Different $\overline{M}_V$.

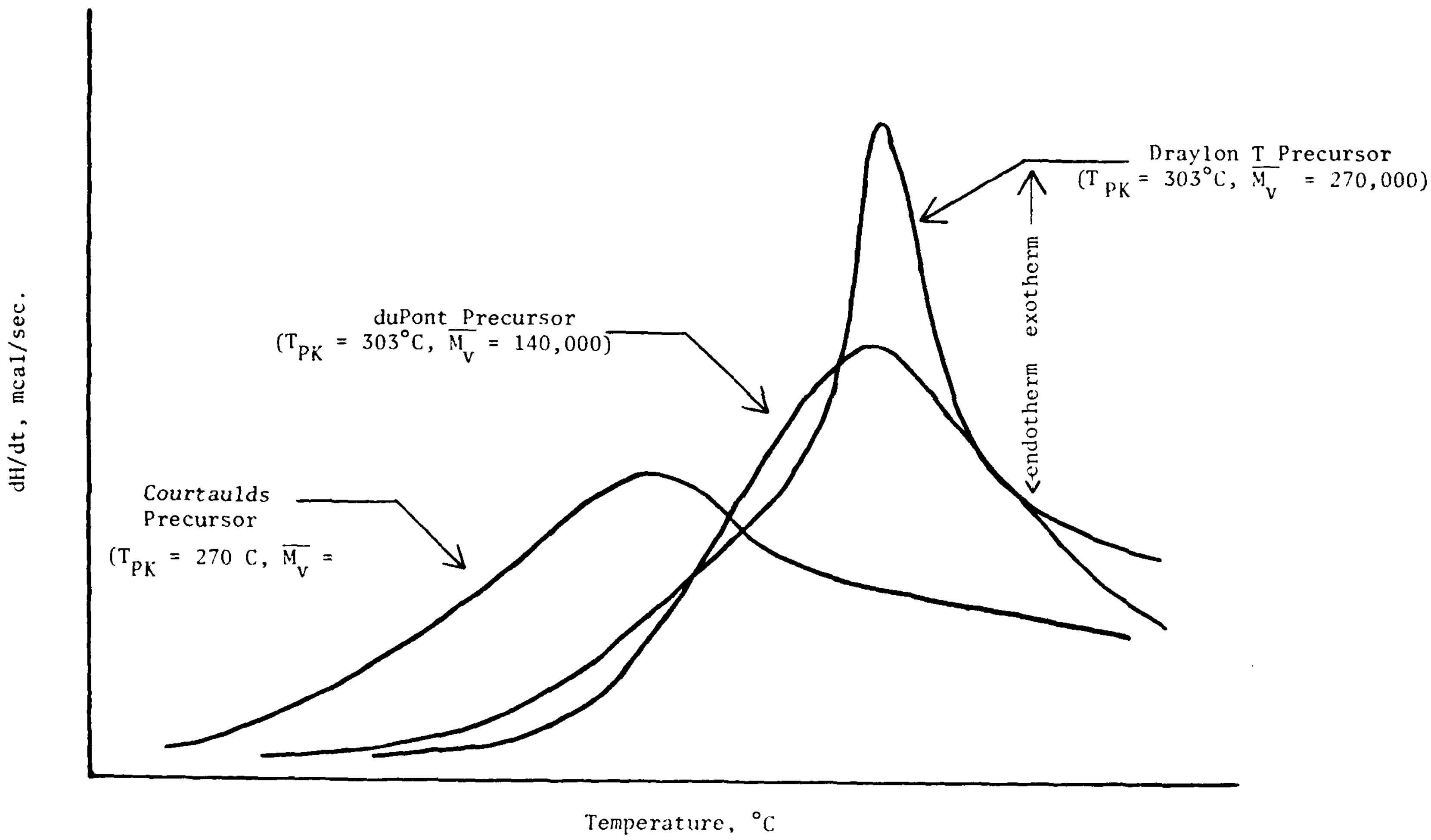
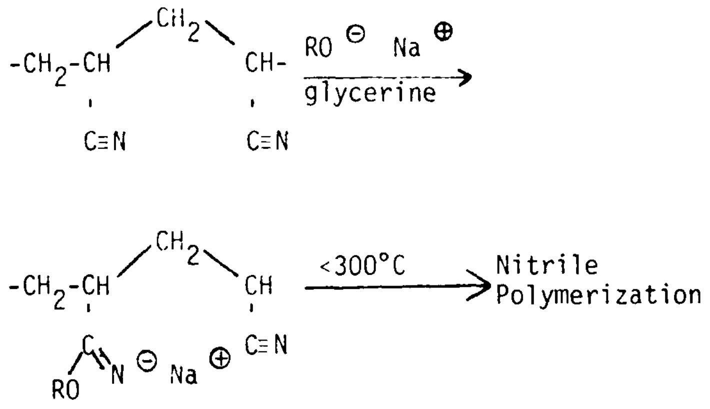


FIGURE 8. DSC Plots of Commercially-Available Carbon Fiber Precursors.

of machine variables (sample weight, speed, rate of cooling, etc.).

Explanation for the molecular weight effect is uncertain at this point, as is the derivation of the lower exothermic peak. Speculation is tempting, however, to attribute the peak at ≈250°C to initial short-chain link up of nitriles through end-group initiation. The lower the $\overline{M}_v$, i.e., the higher the concentration of end groups in the solid-state structure per unit volume, the more low-temperature initiation occurs. The high temperature exothermic DSC peak is attributed to massive, thermally-assisted nitrile polymerization and oxygen incorporation by Hay (8). Hay also found a weaker endothermic peak masked by the strong exotherm, the former progressively increasing with temperature. By heating the sample at 290°C for several minutes, Hay was able to completely remove the exotherm, clearly unmasking the endotherm. The endotherm was associated with the cleavage and volatilization of low molecular weight fragments (H_2, HCN, NH_3, monomer, and larger chain nitriles.). No lower-temperature exotherm was observed by Hay, however, on his commercially-available, high $\overline{M}_v$ acrylic samples. If more of the nitriles are "zipped up" in short lengths during the end group initiation phase, then fewer would be available for massive intra and inter-nitrile polymerization during the higher temperature exotherm phase. The theory of initial ring closure and formation of active sites at lower temperatures than required for massive nitrile polymerization is not without precendent, as referenced by the work of V.S. Menickheim (9). In the latter research, glyceroxide in glycerin pretreatment of the PAN at 195°C was claimed to form stable imine anion initiation sites in the PAN which would not initiate further nitrile polymerization without benefit of a thermal environment in the 300°C range:



Imine Anion
Initiator Site

To the author's knowledge, no one has previously investigated DSC behavior as a function of molecular weight, which would account for the absence of the 250°C exotherm peak in literature DSC curves. E. V. Thompson, however, observed similar dual-exotherm peak behavior in DTA studies of PAN samples over a variety of molecular weights (10).

The conclusion drawn from Figures 5 and 9 was that the broadened exotherm of the highest $\overline{M}_v$ solution polymer compared to the emulsion polymer indicated a higher end group initiator activity in the former. Again, however, the difference in $\overline{M}_v$ (120,000 solution vs. 2,000,000 emulsion) and therefore end group concentration may have played a role in the shape of the exotherm.

B. Effect of Comonomers

As shown in the DSC curves of the commercial precursor, comonomers have a broadening and reducing effect on the exotherm in the 280°-305°C range associated with massive nitrile polymerization. Often, more than one comonomer is present in the commercial precursors, which complicates delineation of the effects of a single comonomer on the pyrolysis behavior and solid state structure of the precursor. For example, the Courtaulds precursor used by Hercules in its carbon fiber production is reported to be a terpolymer of AN, methylmethacrylate and itaconic acid. The Menikheim research at Monsanto was conducted on the Acrilan formulation, which is reported to contain AN and vinyl acetate.

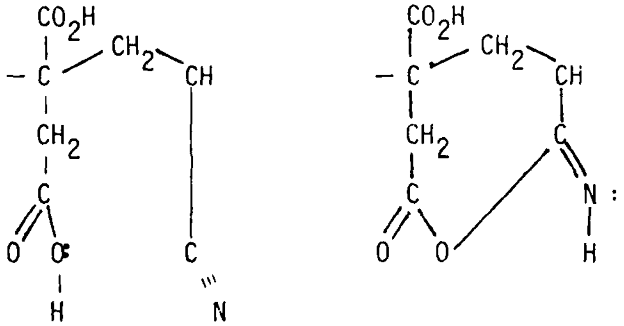
To assess the effects of single comonomers on the spinnability, solid state structure, and pyrolysis behavior of PAN-based precursors, several copolymers are being synthesized and evaluated:

a. Poly(acrylonitrile-co-styrene)

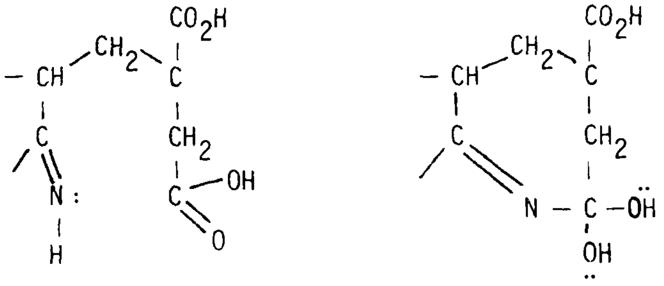
Styrene has been reported by Grassie to be a blocking comonomer to the polymerization of the nitriles in the PAN pyrolysis, resulting in short zip lengths on preoxidation. Both 2% and 6% styrene loadings will be assessed.

b. Poly(acrylonitrile-co-itaconic acid)

Itaconic acid, one of the Courtaulds precursor comonomers, is expected to act as a nitrile polymerization initiator via nucleophilic (anionic) attack of the unshared pair of electrons of the -OH oxygen on the nitrile carbon under pyrolysis conditions:



The azomethine can then propagate down the chain. The acid functionality is also expected to take part in, rather than block, the propagation reaction via an aldol-type condensation:



Both -OH groups would then be available for continuing the nitrile polymerization sequence. A unique factor in itaconic acid is that the two acid functionalities offer ample opportunity for interchain nitrile polymerization initiation as well as intrachain zipping. The bulk of the itaconic acid comonomer should also have interesting effects on the solid state structure of the copolymer at the two planned loading levels (2% and 6%).

c. Poly(acrylonitrile-co-acrylic acid) and poly(acrylonitrile-co-methacrylic acid)

Acrylic acid should have similar nitrile zip initiation capabilities as itaconic acid, but without the bulk and complexity of structure. The comonomer imparts some hydrophilicity to the copolymer with heavier loadings resulting in a water-soluble material. Methacrylic acid has a "greasier" nature than acrylic acid, due to the hydrophobic methyl group, and should therefore not slow down coagulation and disrupt the structure as much as the non-methylated analog in spinning the copolymer into an aqueous bath. The inductive (hyperconjugative) effect of the methyl group should also adversely effect the nucleophilic capability of the -OH electron pair, and the hyperconjugation capability (electron donation) should destabilize the developing negative charge on the oxygen, raising the energy to alkoxide formation and thereby slowing the reaction rate. The bulky nature of the methyl group should also affect the packing in the solid state structure versus the acrylic acid copolymer. The latter has to be balanced against the coagulation behavior of the two copolymers. Loadings of 2% and 6% of the two comonomers with AN will be investigated.

Although a final decision has not yet been reached, the preferred route of polymerization for the copolymers appears to be modified suspension. The polymerized PAN should have higher $\overline{M}v$ and lower end group initiator concentration. The hydrophilicity of two of the proposed comonomers, itaconic acid and acrylic acid, may, however, dictate modification of the basic polymerization procedure worked out with pure AN. Feed ratios are also being investigated in the bench-scale apparatus, based on the reported reactivity ratios of the respective monomers.

B. Spinning Trails

Several spinning trials were made with a 15 hole spinneret in order to recognize and eliminate the spinning problems. Absence of gel particles in the spinning solution, control of the coagulation bath composition (solvent to non-solvent ratio) and temperature, and proper circulation of the coagulation solution (essentially laminar cocurrent flow) are the most critical factors in ensuing uninterrupted production of good quality filaments. For our purpose, good quality is defined by the absence of pores inside the filaments in the range of resolution of our scanning electron icroscope (100 Å or higher) and by uniformity of mechanical properties of filaments produced at different times in a given trial. These trials have also shown that any effort to change the morphology of the as-spun fiber by changing the coagulation bath composition and temperature affects the quality of the fiber produced. For this reason the coagulation conditions will be determined in the future to give optimum quality of filaments produced and morphological differences will be introduced only through changes in the conditions and the extent of drawing in the gel state and in the plasticized drawing stage.

Typical spinning conditions for the 15 hole spinnerets are as follows:

Polymer Used:	PAN (supplied by Monsanto, containing VA as comonomer).
Dope concentration:	22 wt.% in DMF
N_2 pressure:	20 psi
Polymer Solution Output:	0.06 cc/min./hole
Spinneret hole diameter:	.006"
Jet stretch:	1.
Coagulation bath composition:	60:40 DMF:H_2O
Coagulation bath temperature:	27°C
Speed of godet I:	11 ft./min.
Wash water temperature:	45°C
Draw bath temperature:	98-99°C
Tenacity of single filament:	4 gpd

Experiments are currently being conducted with the 360 hole (3 mil diameter) spinneret. Some work is also underway with a 100 hole, 3 mil spinneret.

Problems have been encountered in obtaining good spinning solutions on a consistent basis. Small gel particles resulting from incomplete dissolution of the polymer can cause blocking of the in-line dope filter or plugging of spinneret holes. Purchase of a thermostatted high shear mixer for improved dope preparation would help in eliminating this problem.

C. Morphological Characterization of Precursors

Work has centered primarily around IR dichroism and wide and small angle X-ray diffraction for characterization of order in the PAN filaments. Though several experimental difficulties have been encountered with respect to IR dichroism measurements on fibers, the technique does look promising in characterising orientational order in PAN fibers. The main difficulty has been due to excessive surface scattering which significantly reduces the intensity of the $-C\equiv N$ stretching band. An immersion cell is being built to mount the filaments in a non-interacting medium of refractive index comparable to that of PAN. Correlations between orientation functions obtained from IR dichroism and wide angle X-ray diffraction will be sought. Sonic modulus as another method for characterizing molecular orientation is being examined.

Detailed analysis of techniques for identifying defect distributions will begin after PAN samples begin to be produced on a regular basis.

Samples of good quality filaments differing in molecular orientation are being produced by incorporating different levels of stretch in the gel state and in the plasticised drawing stage. These samples will be characterized by the techniques mentioned above and the properties in tension will be measured. Stabilization with varying degrees of contstraint (at different axial stress levels) and temperature profiles will be carried out prior to carbonization. The morphological techniques, especially IR dichroism and X-ray diffraction, will be used for determining changes in orientational order at every stage.

D. Stabilization Studies

Several commercially available PAN based precursors have been processed through stabilization lines to check performance and provide samples for comparison with laboratory prepared polymers. Samples of Courtaulds, Draylon T, and a carbon fiber precursor manufactured by duPont were used for these studies. To establish the stabilization profile for these precursors, the maximum temperature in Section 1 of the stabilization line was determined by increasing the temperature until fiber destruction occurred. The temperature was then reduced by 10%. Temperature of the second section was determined in a similar fashion. Finally the third section temperature was set at the lowest level that would give complete stabilization of the fiber as determined by exposing the fiber to a match flame (fiber which does not burn in this test can be considered stabilized).

The optimized profiles for each of the three precursors are shown in Figure 5. In general the Courtaulds fiber requires the mildest stabilization conditions with Draylon T while the duPont fiber was capable of higher temperature stabilization. The Draylon T required the highest temperature in the final section to achieve complete stabilization.

The procedure for optimizing temperature profiles appears to work satisfactorily and will be used with the laboratory precursors.

V. PROPOSED WORK DURING SECOND YEAR

The following PAN polymers and copolymers will be prepared and carefully characterized:

	PAN	PAN/Itaconic Acid	PAN/Styrene
Solution	100%	98%/2%	98%/2%
Emulsion	100%	98%/2%	98%/2%
Solution	-	94%/6%	94%/6%
Emulsion	-	94%/6%	94%/6%

These polymers will be converted into fiber under conditions that give dense, uniform fibers with minimym void content. These fibers will be stabilized under temperature conditions determined as described earlier. Maximum possible tension will be applied to the fibers during the stabilization process. These stabilized fibers will be converted to carbon fiber under maximum possible tension with residence time of 4 minutes at two different carbonization temperatures (approximately 1500 and 2600°C).

The 98% AN, 2% Itaconic acid emulsion polymerized copolymer will be used for studies of the effect of stretch during various phases of the fiber spinning-stabilization process. The precursor can be stretched in four steps in the carbon fiber process (i.e., in the stabilization bath, prior to collapse of the gel structure, after collapse of the gel structure and during stabilization). Previous studies have suggested that maximum stretch is associated with the best carbon fiber properties but the effect of distribution of the stretch among these four possible points in the process has not been extensively examined.

All prepared carbon fiber samples will be characterized by X-ray diffraction, measurement of tensile properties, electron microscopy, and in some cases surface area and pore size and volume distribution. The observed properties will be correlated with the polymer chemical compositions, fiber spinning, and stabilization conditions.

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