

Spinning of High-Molecular-Weight Liquid Crystalline Polyarylates

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Synopsis

Attempts to spin high-molecular-weight liquid crystalline polyarylates frequently lead to decreases in strength rather than increases as a result of draw resonance in spinning and formation of thick-thin yarns. This phenomenon is attributed to the onset of highly non-Newtonian elongational flow behavior for these polymers. However, the use of small spinneret capillaries, (≤ 6 mils diameter) maintained at temperatures below the melting point of the polymer but above the freezing point, and selection of copolymers which have relatively low heats of fusion (≤ 10 J/g) can eliminate draw resonance and produce relatively high-strength fibers (up to about 14 dN/tex) without heat strengthening. With critical selection of polymer composition (i.e., copolymers containing phenylhydroquinoneterephthalate as the major component and 1,4-hydroxybenzoic acid plus, optionally, a small amount of another monomer as minor components), spinning of high-molecular-weight polymers can be effected above the melting point of the polymers without draw resonance. Tensile strengths as high as 18 dN/tex (as-spun) have been obtained in this way. A mechanism for these effects is proposed.

INTRODUCTION

The discovery that liquid crystalline solutions of aromatic polyamides can be spun to highly oriented high strength, high modulus fibers without the need for subsequent drawing was followed by the finding that similarly high as-spun fiber orientation could be achieved in the melt spinning of thermotropic polyarylates. These aromatic polyesters are frequently prepared from the diacetates of aromatic diols such as hydroquinone (HQ), phenylhydroquinone (PhHQ), chlorohydroquinone (ClHQ) and 1-4 dihydroxybiphenyl (DHB) which are reacted with aromatic dicarboxylic acids such as terephthalic acid (T) or 2,6 naphthalene dicarboxylic acid (N). In addition, aromatic hydroxy acids such as *p*-hydroxybenzoic acid (PHB) or 2,6 hydroxynaphthoic acid (PHN) have been used. Copolymers from some of these monomers with poly(ethylene terephthalate (PET) which form liquid crystalline melts have also been investigated.¹⁻³ It has generally been necessary to spin the liquid crystalline polyarylates at low to moderate molecular weight and then subject the fibers to heat treatment to increase their molecular weight and strength. Thus,^{4,5} polymers with inherent viscosity (η_{inh}) typically less than 3 were spun to fibers with tensile strength of ≤ 7 dN/tex (8 g/den). After prolonged staged heat treatment of relaxed yarn under nitrogen, much higher strengths were observed.

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In an example with ClHQ-T/N (70/30), spun yarn with $2.1\eta_{inh}$ and tensile strength/modulus (T/M) = 5.8/483 dN/tex (6.6/547 g/den) was heat-treated at gradually increasing temperatures (290°C max) for 17.5 h. Heat-treated fibers had T/M = 26.5/465 dN/tex (30/527 g/den) and were too insoluble to measure η_{inh} . In another example with a different copolymer of ClHQ-T, an increase in η_{inh} from 2.2 to 10 was found as fiber strength increased from 3.9 to 17.7 dN/tex. Heat treatment on a bobbin was carried out with alumina-coated yarn (coatings of graphite and talc are also disclosed) to minimize interfilament sticking, which is also controlled by staged temperature increase. In another example,⁶ PhHQ-T homopolymer spun yarn with $\eta_{inh} = 1.8$ had T/M = 5.1/417 dN/tex (5.8/473 g/den). On staged heat treatment for 18 h (325°C max), T/M = 25/627 dN/tex (28.4/710 g/den). The same polymer gave, in another study,⁷ as-spun T/M = 3.4/397 dN/tex (3.8/450 g/den) and heat-treated T/M = 28/803 dN/tex (32/910 g/den). This particular composition is notable for having high strength retention (up to 70%) at 150°C.

In some cases, higher η_{inh} polymers have been spun, although it is not certain that the value reported for one composition can be directly compared with others. For example,⁸ the composition PHB/PHN (80/20) was spun at 5.7 η_{inh} (measured at 0.1% concentration in pentafluorophenol) to give as-spun T/M = 10.7/477 dN/tex (12.1/541 g/den). We have reason to believe that η_{inh} measured by this procedure is higher for a given molecular weight than for measurements at 0.5%. In addition, there can be differences which are due to the polymers themselves (this will be discussed later). In any event, heat treatment at 250°C for 50 h resulted in fibers with T/M = 17.7/485 dN/tex (20/550 g/den).

As we have described above, the heat treatment process tends to be somewhat lengthy and subject to process difficulties such as filament sticking unless great care is used in establishing the proper temperature profile and/or suitable lubricants are used. Therefore, the objective of the research reported here was to determine the factors which limit spinnability of higher molecular weight liquid crystalline polyarylates and find approaches for maximizing tensile properties with such polymers.

EXPERIMENTAL

The polyarylates were prepared in laboratory glass equipment by well known procedures.^{4,6,9} For example, the diacetate(s) and aromatic dicarboxylic acid(s) and the acetate of the hydroxy acid (occasionally used as a copolymer component) were combined in a 1-liter, 3-neck round-bottom flask to produce about 300 g of polymer. About 4 mol % excess of the diacetate was added to compensate for loss during the polymerization and provide a polymer with about equal acetate and carboxyl end groups to maximize the rate of subsequent solid-phase polymerization. A catalyst (e.g., 0.02% sodium acetate) was also added. This catalyst also served as a buffer to minimize degradation reactions and color formation which are acid-catalyzed. The flask was equipped with a stirrer, a nitrogen inlet port, a distillation head, and a vessel to collect the acetic acid which is evolved as the polymerization proceeds. After a thorough purge of oxygen, the vessel was placed in a Woods metal bath at, for example, 310°C and held under a slight vacuum. When the mixture was

molten, except for some undissolved terephthalic acid, the stirrer was turned on at 30 rpm. Acetic acid was collected for about 30 min and then the temperature was increased gradually to the final polymerization temperature (e.g., 330°C) while the pressure reduced to 0.15 mm Hg over a period of about 1 h. The batch was held at this pressure for a few minutes. The pressure was then brought to atmospheric with nitrogen and the polymerization flask was removed from the heating bath. After cooling, the polymer was isolated, pulverized, analyzed, and then subjected to solid-phase polymerization. Values of η_{inh} were typically about 2.0 (see below) but ranged from 0.5 to 3, depending on the details of the process.

Solid-phase polymerization was carried out in a laboratory vacuum oven operated at 0.5 mm Hg. It was generally preferable to raise the oven temperature gradually to permit crystallization and some polymerization to occur before the final temperature was reached, and this reduced the tendency for particles to stick together. For example, temperature was increased from 192 to 280°C over a 9-h period and then the polymer was maintained at 280°C for an additional 21 h to increase η_{inh} from 2.0 to 7.2.

Inherent viscosity was usually determined at a concentration of 0.5 g of polymer in 100 mL of solvent. For most polymers, the solvent used was 1,1,1,3,3,3-hexafluoroisopropanol (HFIP)/CHCl₃ (50/50 by vol). Some polymers were not readily soluble in this solvent and pentafluorophenol (PFP) was used at a polymer concentration of 0.1 g/100 mL solvent. Since η_{inh} generally increases as concentration is reduced, polymers of a given molecular weight usually have a higher η_{inh} with the PFP (0.1%) measurement (e.g., 4.5 vs. 3.5). In addition, we have noted much higher than expected values of η_{inh} for polymers containing PHB as a component. This may be the result of a stiffer chain or of some association of polymer chain segments even in the very dilute solution. The effect is very pronounced for the solid-phase polymerized polymers. For polymers in which PhHQ-T was the major component and only stiff comonomers were used to depress the melting point, the relationship shown in eq. (1) was found for η_{inh} (HFIP/CHCl₃) vs. \bar{M}_n .

$$\eta_{inh} = 1.66 \times 10^{-4} \bar{M}_n^{1.04} \quad (1)$$

\bar{M}_n was determined from end group analysis (carboxyl, acetate, and hydroxyl) for polymers which were prepared with minimum hold-up time in the melt. The hydroxyl ends arise from incomplete acetylation of the diol and from degradation during melt prepolymerization but they do react to allow increase in molecular weight during subsequent solid-phase polymerization by elimination of diol. We are not certain whether these polymers were completely free of branching (see below).

Spinning was carried out in a small laboratory press spinner, usually with a single hole spinneret. In this process, the pressure applied was controlled to adjust the linear density (tex) of the fiber for any given spinning speed. In the experiments discussed below, a range of spinneret variables was examined: diameters from 0.18 to 0.64 mm, length to diameter ratios (L/D) of 1–38, and entry angles of 28–180°. We were able to melt the polymer at one temperature and spin it at another (lower or higher).

Melt viscosities were determined with an Instron rheometer with a capillary L/D of 40. The results are frequently reported normalized to a shear stress of

10^4 Pa. However, in some cases, we used the spinning experiments to estimate melt viscosity as well as the activation energy for viscous flow. While we are reasonably confident of the calculated activation energies, the absolute values of melt viscosity have to be considered as rough estimates since we have had to correct for rather substantial entrance pressure drops which are common with liquid crystalline polymer solutions or melts and are a large portion of the total for L/D of 2–5. We have also normalized the results to a fixed shear stress (e.g., 6×10^5 Pa) on the assumption of a power law exponent of 0.5. It should be pointed out that, for a non-Newtonian fluid, the activation energy of viscosity at constant shear stress is greater than that determined at constant shear rate by the factor $1/n$ or a factor of 2 for $n = 0.5$.

POLYMER QUALITY

Since the tensile strength of a fiber depends on molecular weight (\bar{M}_n), we must be concerned that changes in η_{inh} reflect corresponding changes in \bar{M}_n . The fact that high temperatures ($> 300^\circ\text{C}$) are frequently required in the polymerization and spinning of thermotropic polyarylates raises a concern that degradation will complicate the level and uniformity of tensile properties. Thus, we must be concerned not only with degradation resulting in chain cleavage but with the possibility of branching reactions which will affect both η_{inh} and melt viscosity for a given level of end groups and \bar{M}_n . Furthermore, melt viscosity may be more strongly affected by branching than is η_{inh} .

In many of our experiments, we concentrated on the polymer PhHQ-T and copolymers based on it because its homopolymer melting point (341°C) is lower than many of the other polyarylate homopolymers. With PhHQ-T/PHN (96/4) we found, in experiments run on the spinner (0.636 mm spinneret, $L/D = 2$), that at 342°C , η_{inh} (0.1% in PFP) decreased almost linearly with time (e.g., from 5.25 to 4.4 in 6.5 h). The rate of η_{inh} loss was almost the same at 360°C . However, the melt viscosity kept increasing and that rate was much higher at 360°C . The results are shown in Figure 1 with the absolute values of viscosity estimated as discussed above by taking the entrance pressure drop as

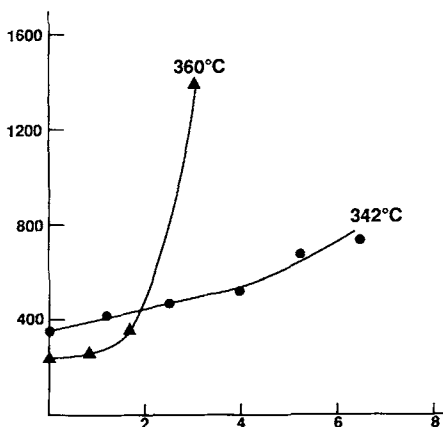


Fig. 1. Degradation and branching of PhHQ-T/PHN (96/4). Melt viscosity vs. time. ● 342°C , ▲ 360°C . Ordinate: viscosity (Pa-s); Abscissa: time (h).

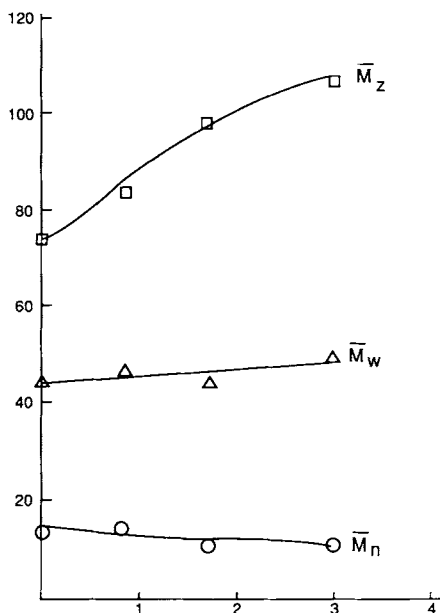


Fig. 2. Degradation and branching of PhHQ-T/PHN (96/4) at 360°C. Molecular weight averages from GPC. \circ \bar{M}_n , \triangle \bar{M}_w , \square \bar{M}_z . Ordinate: $\bar{M} \times 10^3$; Abscissa: Time (h).

75% of the total for this L/D. For this discussion, it is the change in viscosity which is of importance. It can be seen that the viscosity about doubled in 6.5 h at 342°C and increased by almost a factor of 6 at 360°C with a very fast rate of increase beyond about 2 h. Gel permeation chromatography (GPC) for these samples showed a decrease in \bar{M}_n , a modest increase in \bar{M}_w and a sharp increase in \bar{M}_z . The data for 360°C are shown in Figure 2. Here again, the absolute values may not be exactly right because of calibration uncertainties but the changes appear to be significant. It should be noted that degradation and branching are both taking place and that a branched polymer has a lower radius of gyration and η_{inh} than a linear polymer of equal \bar{M}_w . This effect is probably affecting the GPC values as well.

Another indication of degradation is the loss in tensile strength of spun fibers with increasing hold-up time in the melt. In Figure 3 we have shown an Arrhenius plot of the degradation rate expressed as average loss in tensile strength per 5 min for a variety of PhHQ/PHN copolymers and the temperature dependence seems even greater than that observed for the melt viscosity data. We have crudely estimated the activation energy of the overall process which increases melt viscosity from the results at the two temperatures and from the \bar{M}_z data and get values of about 209 kJ/mol (50 kcal/mol) for both criteria. On the other hand, the strength loss data (four temperatures) indicate an apparent activation energy of about 310 kJ/mol (74 kcal/mol). This high value may reflect the adverse effects on strength of branching per se in addition to the expected effects of chain cleavage, but is not well understood. Overall, we see that, for this polymer system, the degradation becomes relatively slow at temperatures $\leq 340^\circ\text{C}$; we therefore tried to select our polymer compositions so that we could carry out our spinning experiments at

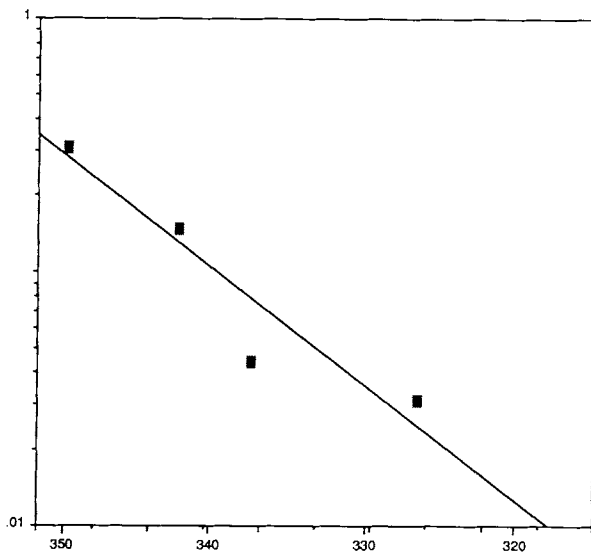


Fig. 3. Rate of strength loss in spinning vs. temperature—PhHQ-T/PHN copolymers. Ordinate: Δ strength (dN/tex)/5 min; Abscissa: polymer temperature ($^{\circ}$ C).

these temperatures and preferably at $\leq 330^{\circ}$ C to minimize or eliminate effects of degradation for hold-up times of 40 min. Finally, we note the effects of 5.5 h of exposure at 360° C on DSC curves for a PhHQ/PHN (94/6) copolymer. The initial extrudate showed a melting point of 317° C and a heat of fusion of 5.5 J/g while the degraded sample showed a slight endotherm at about 293° C and a heat of fusion of only 0.5 J/g. These changes point clearly to formation of a more highly modified "copolymer" as a result of branching. We estimate that it would take about 5 mol% of additional copolymer component to produce the change in melting point but the effect on heat of fusion is even a little greater than in normal copolymerization.

SPINNING

In initial examination of the spinning behavior of copolymers based on PhHQ-T, we found that tensile strength increased linearly with η_{inh} up to about 2.5 to 2.8. On the average, maximum strengths of about 9.7 dN/tex (11 g/den) were reached, and occasionally a little higher. When η_{inh} increased to 3 or higher (sometimes as low as 2.5), a sharp decrease in strength occurred and one could readily observe pulsations of the threadline. On closer examination, a region of sharp neckdown a few centimeters from the spinneret was apparent. At $3.4\eta_{inh}$, the oscillations became pronounced at a spin stretch factor (SSF) of 11. At higher η_{inh} , the oscillations were observed at SSF as low as 4. Since the extruded free fall sample was uniform in thickness, this was clearly not a case of melt fracture but an example of draw resonance. While the spinning filament was cooled by the ambient air, the amount of cooling in the vicinity of the neck was not very large. This will be discussed further below.

Theoretical analysis of isothermal spinning¹⁰⁻¹² has indicated that, for Newtonian elongational flow, the critical attenuation factor (AF) for onset of draw resonance is about 20. AF equals SSF times the bulge area expansion ratio. It should be noted that there is little or no bulge in the spinning of high-molecular-weight polyarylates. Other analyses¹³⁻¹⁵ have predicted that, for power law fluids, the critical AF decreases as the power law exponent (n) decreases. For example, critical AF is calculated to be 4.8 for $n = 0.5$ and 2.8 for $n = 0.3$. Solutions of the rheological equations for isothermal spinning of power law fluids are available.¹⁶ The relation between threadline stress (f) and rate of elongation (dv/dx) is shown in eq. (2)

$$f = k(dv/dx)^n \quad (2)$$

where v is the threadline velocity, x is the distance, and k is a constant related to but not equal to apparent elongational viscosity unless $n = 1$. The threadline force $F = fA$ where A is the cross-sectional area of the filament and is constant in the absence of inertial or drag forces. With the conservation equation $v = w/A$, where w is the throughput in cm^3/s , we get, for the area reduction profile, the result shown in eq. (3), for n not equal to 1.

$$\frac{[A_0^p - A^p]}{[A_0^p - A_c^p]} = x/x_c \quad (3)$$

where x_c is the point where neckdown stops for some reason (e.g., stress- or orientation-induced crystallization), A_c is the cross-sectional area and $A_0/A_c = \text{AF}$ at this point. The exponent $p = n^{-1} - 1$. For the Newtonian case ($n = 1$), $\ln(A_0/A)$ is linear with distance. The calculated neckdown profiles are shown in Figure 4 for several values of n and $\text{AF} = 20$. Inspection of eq. (3) shows that, for example, if $n = 0.2$ ($p = 4$) and $\text{AF} = 10$, the attenuation between $x = 0.99x_c$ and x_c is a draw ratio of 3.2 (6.3 for

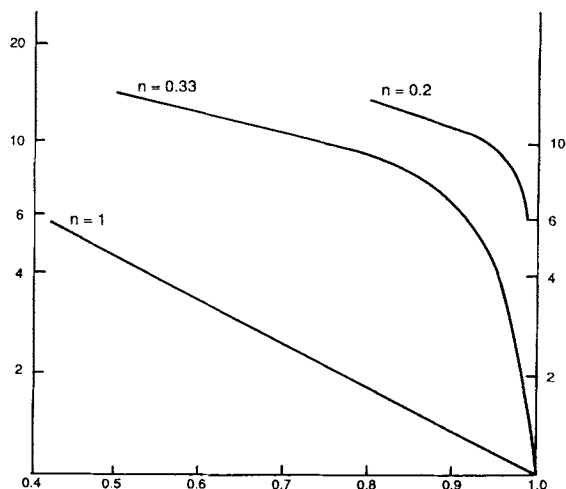


Fig. 4. Neckdown patterns for isothermal spinning of power law fluids. Numbers on curves are power law exponents. Ordinate: x/x_c ; Abscissa: A/A_0 .

AF = 20). Thus, we believe that the neck and the propensity for draw resonance both derive from a low power law exponent for the higher molecular weight thermotropic polyarylates. We should mention at this point that with these high viscosity polymers, because of the fairly low spinning speeds used and the short distance from the spinneret at which the neck and pulsations occur, the contributions of inertial and drag forces are minimal so that the rheological solution should be valid.

Upon further investigation of the draw resonance problem, we discovered that, with selected copolymers, and using spinneret temperatures below the melting point of the polymer but above the DSC crystallization temperature draw resonance could be eliminated.⁹ To achieve smooth spinning under these conditions, it was necessary to select polymers whose DSC heat of crystallization (on cooling from the melt) was less than 10 J/g to avoid solidification in the spinneret. In addition, these conditions were not effective in eliminating draw resonance if the spinneret capillary diameter exceeded 0.635 mm (25 mil). Moreover, the degree of supercooling required could be reduced when capillary diameters were reduced to 0.15 mm (6 mil) or less. DSC curves were obtained with a Du Pont 1090 Differential Scanning Calorimeter. When the polymer showed multiple melting peaks, the highest major peak was cited as the melting point (T_m).

As an example, for a PhHQ-T/PHN (85/15) copolymer ($T_m = 301^\circ\text{C}$, $T_c = 222^\circ\text{C}$, $\Delta H_c = 1.6$ J/g) with $\eta_{inh} = 4$ and spun through a 0.38 mm (15 mil) or 0.18 mm (7 mil) capillary, 2.5 cm filament tensile strength increased from 5.9 dN/tex (6.7 g/den) to 9.7 dN/tex (11 g/den) as spinneret temperature was reduced from 290°C to 280°C . For a 90/10 copolymer of the same components with $\eta_{inh} = 5.4$, spun through a 0.10 mm (4 mil) spinneret, tensile strength increased from 9.9 dN/tex (11.2 g/den) to 12.8 dN/tex (14.5 g/den) as spinneret temperature decreased from 320°C to 280°C . Severe draw resonance was encountered with a 350°C spinneret. This composition had $T_m = 323^\circ\text{C}$, $T_c = 238^\circ\text{C}$, and $\Delta H_c = 2.4$ J/g. In other spins with this composition, one occasionally saw maximum properties at 295°C with a gradual decrease as spinneret temperature was reduced to 280°C . With smaller spinneret capillaries, the general trend was for the optimum temperature to increase as the extent of copolymer modification with PHN decreased (e.g., 295°C for 10 mol% to 324°C for 4 mol% and a little higher for 3 mol%). Under optimum conditions, tensile strength increased with increasing η_{inh} up to about 6–7. Among the best results was a spin with PhHQ-T/PHN (96/4) with $\eta_{inh} = 6.9$ which was melted with a short holdup time at 350°C and spun through a 0.125-mm (5 mil) capillary maintained at 324°C at 37 m/min. The 0.88 tex (7.9 den) filaments had an average tensile strength of 13.8 dN/tex (15.6 g/den). T_m for this polymer was about 348°C and T_c was about 251°C while ΔH_c was 2.1 J/g. However, thermal stability would probably not be suitable for this composition if longer holdup times were required. As we will show in more detail later, these strengths do not represent the full potential for the molecular weights involved.

Draw resonance was eliminated by supercooled spinning for other copolymers of PhHQ-T as well as for other polyarylates.⁹ For example, ClHQ-T/PHN (75/25) with 6.3 fiber η_{inh} (PFP-0.1%) with $T_m = 307^\circ\text{C}$, $T_c = 235^\circ\text{C}$, and $\Delta H_c = 2.9$ J/g showed strong draw resonance when spun with a 330°C

spinneret but yielded uniform fibers with 9.4 dN/tex (10.7 g/den) tensile strength when spun with a 280°C spinneret (0.38 mm or 15 mil diameter) at 93 m/min. PhHQ-T homopolymer, which melts at 341°C, freezes at 286°C, and has a ΔH_c of 21 J/g cannot be spun below the melting point without breakdown because of incipient freezing in the capillary. However, draw resonance is only mild at 350°C. Nevertheless, we believe that homopolymer may be unsuitable from the standpoint of thermal stability. The value of ΔH_c decreases rapidly as mol% PhHQ-T in the copolymer decreases reaching 10 J/g for 3 mol% modification (with PHN) and 1.5–3 J/g for 10–20 mol%. Data on the effect of copolymer modification on the DSC melting point of PhHQ-T-based polymers, expressed in the form of the Flory equation are shown in eq. (4) (least-squares line) with the assumption that the extent of polymerization (p) is 0.99:

$$1/T = 1/T_0 + 2R/\Delta H_f \bar{P}_n \quad (4)$$

$$= 1.606 \times 10^{-3} + 1.00 \times 10^{-3}/\bar{P}_n \quad (4a)$$

where T is in K and ΔH_f is the heat of fusion per repeat unit (2 ester groups) of the homopolymer at $p = 1$. From this we deduce that the heat of fusion of the homopolymer is about 16700 J (4000 cal) per repeat. Since the sample of homopolymer we tested had a DSC heat of fusion of about 10,500 J (2500 cal) per repeat, we can estimate that its crystallinity before melting was about 63%.

The maximum spinneret temperature for avoiding draw resonance decreases with increasing capillary diameter for a variety of polymer compositions. For example, for PhHQ-T/PHN (90/10) it decreases from 330°C for a 0.076 (3 mil) diameter capillary to 289°C for a 0.20 (8 mil) capillary and about 280°C for a 0.635 (25 mil) capillary. We believe this to be a result of the small, but significant amount of cooling which occurs in the first 5–10 cm from the spinneret for the smaller capillaries. Our calculations indicate that, for 0.076 to 0.89 mm capillaries, convection is the rate-limiting step in cooling. For an assumed 100°C temperature difference between the initial filament temperature and the air in the region just below the spinneret and an assumed constant shear stress (constant capillary L/D) and a jet velocity (cm/s) = $500r$ (r is the radius of the capillary), we estimate that the temperature decrease per cm of path decreases from about 24°C for 0.076 mm (3 mil) to 2°C for a 0.38 mm (15 mil) capillary. Thus the greater cooling rate for the smaller capillaries seems to be stabilizing.

It is evident that any effect of cooling will depend on the temperature dependence of elongational viscosity so that this property should have a bearing on the propensity for draw resonance, especially with smaller capillaries. While we have not determined this, we have determined the activation energy of shear viscosity from spinning experiments as discussed above. The results, obtained in the shear stress range of $2\text{--}6 \times 10^5$ Pa, have all been normalized to a constant shear stress of 6×10^5 Pa, with assumption of a power law exponent of 0.5. The results for a variety of PhHQ-T/PHN copolymers (see Fig. 5) indicate an activation energy of about 105 kJ/mol (25 kcal/mol) for the temperature range 281–326°C. The value would be half that

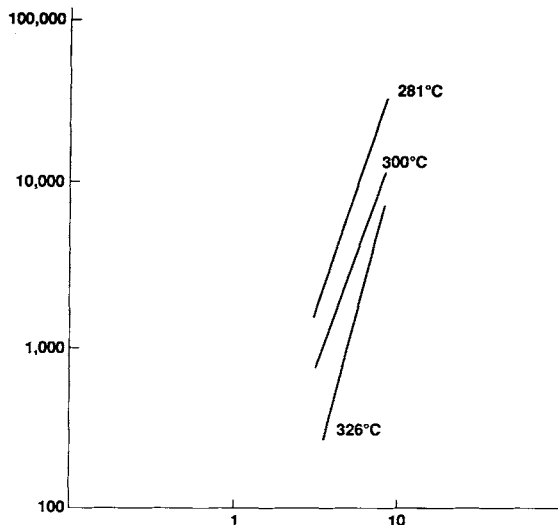


Fig. 5. Melt viscosity estimates from spinning. Entrance corrected. Normalized to shear stress of 6×10^6 dynes/cm². PhHQ-T/PHN copolymers. Ordinate: melt viscosity (poise); Abscissa: η_{inh} .

for data normalized to a constant shear rate. The log-log plot of melt viscosity versus η_{inh} had slopes ranging from 2.9 to 3.9 and averaged 3.3. Thus the average Mark-Houwink exponent was about 3.4, based on the 1.04 value cited above for the exponent in the relation between η_{inh} versus \bar{M}_n . This is somewhat lower than the value of about 4.7 deduced from other Instron rheometer measurements with lower η_{inh} polymers which were normalized to shear stress of 10^4 Pa. From the spinning experiments, we deduced an entrance-corrected viscosity of 300 Pa-s for 6.8 η_{inh} polymer at 326°C and a shear stress of 6.6×10^5 Pa. For a power law exponent of 0.5, the viscosity would be 10 times greater at a shear stress of 6×10^3 Pa.

For our highest strength fibers, in the η_{inh} range of 4–7, we found that we could achieve spin stretch factors of about 36 for 0.635 mm (25 mil) capillaries and an average of 18 for 0.10 mm (4 mil) capillaries. Thus the lowest filament linear densities we could achieve were 11 tex (100 denier) for the former and 0.44–0.67 tex (4–6 denier) for the latter. Higher SSF resulted in threadline breakdowns. On the average, the minimum attainable linear density increased with the 1.6 power of capillary diameter. We found no significant effects of capillary L/D in the range of 1–10 on tensile properties with a 0.127 mm (5 mil) capillary. Similarly, we found no strong effect of entrance angle on properties. However, with L/D of 5, the pressure drop across the capillary increased by a factor of about 1.8 as entrance angle decreased from 60° to 45°. At 30°, the pressure increased sharply by an additional factor of about 6. This indicates that the “natural entry angle” may be in the range of 50–60°.

When we introduced a bent chain component such as isophthalic (I) acid into the PhHQ-T copolymer system, we found that the degree of supercooling required to suppress draw resonance increased markedly. For example, with 12 mol% PHN and 5 mol% PhHQ-I, the borderline spinneret temperature for draw resonance was 254°C, below the DSC freezing point (266°C) and temper-

atures as low as 241–246°C gave optimum properties. It is likely that spinning was possible at these temperatures because ΔH_c was very low (1.5 J/g). A tensile strength of 8.0 dN/tex (9.1 g/den) was achieved with $2.7\eta_{inh}$ fiber. This η_{inh} represents a somewhat higher molecular weight than for the previously mentioned polymers since the polymer is more flexible. This effect supports the idea that a two-phase (anisotropic/isotropic) structure in the melt may be contributing to the low power law exponent. The fact that the critical temperature also decreases with increasing PHN concentration in the absence of bent chain components (see above) indicates that this ostensibly stiff component is interfering with liquid crystal formation in the PhHQ-T system, possibly because of steric effects.

Since we observed the unexpected reduction in critical spinneret temperature with increasing concentration of PHN in copolymers of PhHQ-T, we decided to examine copolymers with PHB which might interfere less with liquid crystallinity because of its relative compactness. In a series of initial spinning experiments with PHB concentrations of 10–20 mol%, we were able to spin without draw resonance at a spinneret temperature well above the melting point (e.g., 353–355°C), provided that relatively small spinneret capillaries were used¹⁷ (≤ 0.152 mm or 6 mil diameter). In fact, with spinneret temperatures much below 350°C, spinning performance was poor as were tensile properties, not because of freezing but because of an extraordinary increase in melt viscosity.

In these initial experiments with the PhHQ-T/PHB copolymer system, tensile strength increased linearly with increasing η_{inh} reaching a high of 16.6 dN/tex (18.8 g/den) at $6.2\eta_{inh}$. The DSC melting behavior of these copolymers which had been solid-phase polymerized was marked, in many cases, by multiple melting endotherms and a rather broad melting range, with a rather shallow descent of the temperature for complete melting versus PHB concentration. This temperature decreased linearly with PHB content from about 353°C for homopolymer to about 330°C for 20 mol% PHB. The onset of melting, however, decreased from about 340°C to 275°C over the same concentration range and there were as many as 3–8 separate endotherm peaks at the higher modifications. The heat of fusion decreased with increasing comonomer content as with the PHN copolymers, but not as steeply (e.g., about 14 J/g for 10 mol% PHB and values ranging from 8 to 18 J/g for 15%). It should be noted that we use the convention that n mol% is n moles of PHB per $100-n$ moles of PhHQ-T (or $100-n$ moles each of its two components). From the heats of fusion we estimate that the crystallinity of the 15 mol% modification ranges from 15 to 30%. This, along with the viscosity behavior (to be discussed in more detail below) has led us to postulate that the polymers may be variably blocky. The driving force for this blockiness may be the high melting point of poly-PHB, and the continuing occurrence of interchange reactions during solid-phase polymerization.

In assessing melt viscosity of the PhHQ-T/PHB (90/10) copolymers from spinning experiments with 0.127 mm (5 mil) capillaries with $L/D = 5$, we found, at 354°C, that viscosity increased with about the 7.5 power of η_{inh} at constant shear stress. Because of the higher viscosities at high η_{inh} , attainable SSF reduced rapidly with increased η_{inh} , particularly above about $5\eta_{inh}$, so that as η_{inh} increased from 5.0 to 6.3, minimum attainable linear density

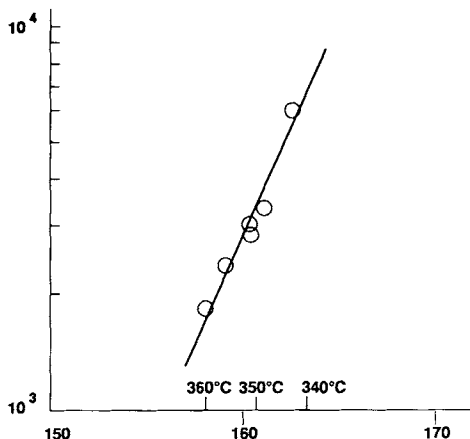


Fig. 6. Melt viscosity of PhHQ-T/PHB (90/10) vs. temperature. Normalized to η_{inh} of 5.9. Ordinate: melt viscosity (poise); Abscissa: $10^5/T$ (K).

increased from about 1 tex (9 den) to about 4 tex (35 den), but there was a great deal of scatter in attainable SSF at $6.0\eta_{inh}$. Melt viscosity measurements normalized to $5.9\eta_{inh}$, in the range of 340–360°C, indicated (Fig. 6) that the activation energy was 214 kJ/mol (51 kcal/mol), or about twice as high as that for the PHN copolymers. As indicated above, we believe that small quantities of blocks of PHB, longer than expected from random copolymerization are aggregating and acting as crosslinks and that this effect becomes more pronounced as temperature is reduced. In this connection, we have estimated the melting point of poly (PHB) as a function of block length using the Flory melting point depression equation as shown in eq. (4), except that we use R instead of $2R$ for the AB polymer which has only one ester group per repeat. We have estimated a heat of fusion (per one ester group) of 10,900 J/mol (2600 cal/mol) for this polymer based on its higher melting point versus PhHQ-T (about 550°C vs. 341°C). The calculated melting temperatures for $\bar{P}_n = 2, 3,$ and 4 are 352, 406, and 438°C, respectively.

With the PhHQ-T/PHB polymer system, introduction of small quantities of a bent chain monomer (isophthalic acid), had a drastic effect on the propensity for draw resonance, as it did for the PhHQ-T/PHN copolymers (Fig. 7). Thus, 2 mol% PhHQ-I in a copolymer containing 13 mol% PHB dropped the critical temperature of a polymer with $6.9\eta_{inh}$ (PFP) to about 338°C (draw resonance at higher temperatures) while 4 mol% reduced it to about 320°C for $4.2\eta_{inh}$ polymer. In spite of this, by spinning just below the critical temperature, we were able to prepare 2 tex (18 den) fiber at about 30 m/min with 2.5 cm filament tensile strength of 15 dN/tex (17 g/den) for the 2% modification and 13.9 dN/tex (15.8 g/den) at 75 m/min with the 4% modification.

The importance of cooling discussed above can be shown dramatically by attempts to spin a PhHQ-T/PHB (85/15) copolymer with a 0.23 mm (9 mil) capillary. For this situation, it was necessary to reduce spinneret temperature to 333°C to obtain only a mild degree of resonance. At 332–329°C the threadline was very stiff and difficult to wind even though we could produce

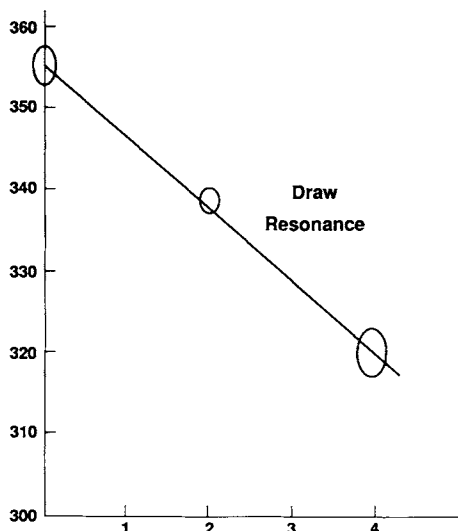


Fig. 7. Effect of isophthalic acid content on spinning of PhHQ-T/PHB/PhHQ-I terpolymers. Ordinate: optimum spinning temperature ($^{\circ}\text{C}$); Abscissa: mol% PhHQ-I.

fiber at about 15 m/min with 8.5 dN/tex (9.6 g/den) tensile strength. Thus we see that it is the cooling along with the high activation energy of viscosity which together prevent draw resonance at the higher spinneret temperatures while the high activation energy prevents the use of supercooled spinning with the larger capillaries.

As noted in the discussion of thermal stability, melting temperatures of 330°C give good retention of molecular weight for at least 40 min of hold-up time. Thus, it is important to separate the spinneret heating from the rest of the process so that the required high temperatures can be used with the copolymers containing PHB. In order to keep the melting point low enough to avoid thermal degradation, we also investigated several terpolymers within the PhHQ-T/PHB system. Among the third monomers investigated were 1,4-dihydroxy biphenyl (DHP) and PHN. These terpolymers could be spun without draw resonance at lower temperatures than those quoted above for the copolymers, but still well above their melting points. In one case we achieved our highest level of as-spun tensile strength with a terpolymer. Thus, with PhHQ-T/DHP-T/PAB (80/10/10) having fiber $\eta_{\text{inh}} = 9.3$ (PFP), a spinneret temperature of 324°C (0.127 mm or 5 mil diameter) and a winding speed of 28 m/min, filament tensile strength was 17.7 dN/tex (20.1 g/den) for a 1.21 tex (10.9 denier) fiber. The DSC melting point of this composition was 288°C . With a 80/5/15 composition of the same intermediates having a fiber $\eta_{\text{inh}} = 9.7$ (PFP), a spinneret temperature of about 350°C was used and a tensile strength of 16.5 dN/tex (18.7 g/den) was obtained in a 1.3 tex (11.7 denier) filament. Finally, a PhHQ-T/PHB/PHN (82/15/3) terpolymer with fiber $\eta_{\text{inh}} = 6.3$ was spun with a 330°C spinneret at 18 m/min to give 2 tex (18.2 denier) filaments with 14 dN/tex (15.9 g/den) tensile strength. The DSC melting point of this composition was about 283°C . The best tensile strengths attained for phenyl HQ-T/PHB copolymers or terpolymers versus η_{inh} are shown in Figure 8.

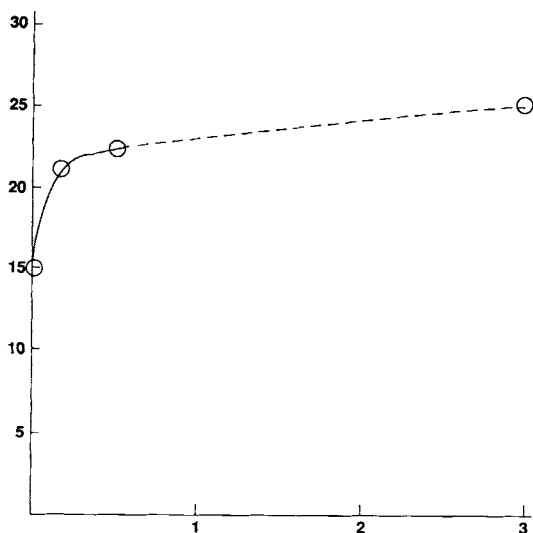


Fig. 8. Heat strengthening of $6\eta_{inh}$ PhHQ-T/PHB (90/10). Fiber strength vs. time at 300°C (plus 15–30 min warmup at ca. 290°C). Ordinate: tensile strength (g/den); Abscissa: time (h) at 300°C .

HEAT STRENGTHENING OF HIGH-MOLECULAR-WEIGHT FIBERS

The fact that the tensile strengths of as-spun high-molecular-weight fibers prepared by supercooled spinning are significantly lower than expected from extrapolation of the tensile strength versus η_{inh} line prompted us to attempt to find the cause of this deviation. Examination via scanning electron microscopy (SEM) at $2000\times$ magnification of a $6.3\eta_{inh}$ fiber from PhHQ-T/PHN (85/15) showed that the surface was relatively rough with a striated, fibrillar structure oriented along the fiber axis. On the other hand, the fiber with 17.7 dN/tex (20.1 g/den) tensile strength which had been spun with higher spinneret temperatures (i.e., well above the melting point) showed a fairly smooth surface even at $2000\times$ magnification. In spite of this, we felt that the tensile strength of these fibers should have been even higher and that they might still have strength-limiting defects.

Initially we selected a PhHQ-T/PHB (90/10) fiber whose η_{inh} was 6.0 with 13.9 dN/tex (15.5 g/den) tensile strength. This fiber was preheated at 290°C for about 30 min and then held at 300°C for various periods of time. Tensile strength increased to 18.5 dN/tex (21 g/den) in 10 min at 300°C , 19.9 dN/tex (22.5 g/den) after 30 min and 22 dN/tex (25 g/den) after 3 h. Strengthening was less reliable at 310°C . Similarly, 290°C was better than 300°C for the composition containing 15 mol% PHB. With other polymer compositions such as $7.7\eta_{inh}$ (PFP) PhHQ-T/DHP-T/PHB (80/8/12) with 15 dN/tex (17.1 g/den) tensile strength, 70 min at $265\text{--}271^{\circ}\text{C}$ increased strength by 3 dN/tex and there was no sign of filament sticking for the small size samples tested. In further study, we determined the rate of solid-phase polymerization for a variety of compositions and found that the rate of increase in η_{inh} was too slow by at least a factor of 3 to account for the observed strength increases

(e.g., in 10 min at 300°C). Therefore, we believe that some kind of flaw healing is involved. Comparison of the optimum strengthening temperatures for the few fibers tested with the DSC curves for these fibers indicates that strengthening is best carried out at the onset of the melting endotherm. Going to higher temperatures leads to filament sticking while going much lower results in much lower rates of strengthening. It is obvious that these conclusions do not apply to low-molecular-weight as-spun fibers where solid-phase polymerization is essential.

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Received July 10, 1989

Accepted September 26, 1989