

# Solid-State Polymerization Vis-à-Vis Fiber Formation of Step-Growth Polymers. I. Results from a Study of Nylon 66

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## SYNOPSIS

This study is directed toward synergistic integration of processing of nylon 66 fibers with solid-state polymerization. The following two goals are sought through the incorporation of solid-state polymerization after the initial shaping operation: eliminating some of the processing problems in the production of high molecular weight, high performance industrial fibers and attainment of improved mechanical properties via high molecular weight. Successful solid-state polymerization has been achieved with as-spun fibers of nylon 66 and molecular weights up to 280,000 g/mol have been obtained from a starting molecular weight of 40,000 g/mol. It is shown that much of the ductility of the starting fiber can be retained, or even enhanced, with solid-state polymerization. Simulated drawing experiments using a thermal deformation analysis technique show an increase in the drawing potential of the solid-state polymerized fiber as compared to the starting material. This has important implications regarding the ultimate properties that can be achieved in fibers of condensation polymers. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

It has been well-known in the polymer industry for the last three decades that it is possible to increase the degree of polymerization of certain condensation polymers, especially polyamides and polyesters, by heating them to a temperature between glass transition and melting in an inert atmosphere or in vacuum. This type of reaction is termed solid-state polymerization (SSP) because the end groups react to increase the molecular weight while the material retains its solid state.<sup>1-5</sup> SSP is widely used to produce relatively high molecular weight in polymers such as nylon 6, nylon 66, and polyethylene terephthalate (PET).<sup>6,7</sup> However, achieving very high molecular weights and successful processing of step-growth, condensation polymers have remained relatively unsuccessful. Beyond moderate molecular weights, fabrication processes for solid-state polymerized high molecular weight polymers are limited to solution-based routes to avoid excessive degradation

of molecular weight that might occur in melt-based routes.<sup>8</sup>

Although the *process* of achieving high molecular weight through thermally induced SSP of polymer chips is relatively simple, it is often extremely difficult to achieve very high molecular weights; the chip's relatively large dimensions increase the probability of reaction of the condensation product in the polymer. Also, subsequent processing of such high molecular weight material is made difficult by the consequent generation of high pressures during extrusion, chances for melt fracture, and thermo-mechanical degradation of molecular weight. Additionally, in processes such as fiber spinning, it can lead to an increase in frequency of filament breakage due to excessive stresses in extensional flow of the polymer.<sup>9</sup>

To overcome the above-mentioned inherent limitations of the process of producing high molecular weight fabricated products from solid-state polymerized chips, an alternative route has been explored by some researchers. This consists of extruding (shaping) a low or medium molecular weight polymer and then polymerizing it further in the "shaped" solid-state, that is, in the fabricated form. The

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problems of processing high molecular weight material are thus eliminated. However, this alternative route would be appropriate only if the solid-state polymerized material possesses the characteristics necessary for either direct use or subsequent processing. Otherwise, achieving an increase in molecular weight would be counterproductive. For example, in fiber formation, the ductility required for drawing to achieve superior mechanical properties is often lost upon polymerization of the extruded filament in the solid state.

Much of the reported work on SSP pertains to nylon 6, nylon 66, and PET. Although little data have appeared in the literature, it is believed that the final stage in the generation of high mechanical properties in fibers of liquid crystalline aromatic polyamides and polyesters is governed to a large extent by SSP.

Several earlier studies have explored SSP of nylon 6 chips.<sup>10-12</sup> Monroe<sup>13</sup> patented a process for producing a polycarbonamide fiber by SSP. Griskey and Lee<sup>14</sup> studied the kinetics of SSP in nylon 66 at temperatures ranging from 90 to 135°C and found that the rate of the reaction was of the form

$$\frac{dM_n}{dt} = kt^n,$$

with  $n = -0.5$  and activation energy of  $\sim 13$  kcal/mol.

Chen et al.<sup>15</sup> studied the mechanism of SSP of nylon 66 chips by formulating equations for combined diffusion and chemical reactions, and concluded that the chemical reaction was the rate controlling step in nylon 66 SSP at temperatures ranging from 120 to 200°C.

The earliest reference to postextrusion SSP is to a patented process by Tyron for SSP of PET filament.<sup>16</sup> He heated undrawn PET fibers in a slow stream of nitrogen at temperatures ranging from 200 to 260°C and obtained intrinsic viscosity of at least 0.6 dL/g from a starting intrinsic viscosity of 0.3–0.4 dL/g. He observed a doubling of the rate of condensation for every 10°C rise in annealing temperature. Luise patented a process for producing high tenacity and high modulus fibers of the liquid crystalline polymers, poly(chloro-1,4-phenylene-terephthalate/4,4'-oxydibenzoate), poly(chloro-1,4-phenylene 4,4'-oxydibenzoate), and copoly(chloro-1,4-phenylene/dichloro-1,4-phenylene *trans*-1,4-cyclohexane dicarboxylate) by SSP of as-spun fibers.<sup>17</sup> He annealed the fibers to temperatures 20°C below the melting point from 5 s to several hours and observed an increase of the fiber tenacity from

2 to 3 to at least 10 g/denier. The increase in strength was attributed to increase in molecular weight that was seen through an increase in inherent viscosity and loss of solubility. In contrast to this, he observed that heat treatment of drawn and undrawn PET fibers produced fibers of lower tenacity. Lee<sup>18</sup> studied SSP in fibers of a liquid crystalline polyester prepared from hydroxy benzoic acid and hydroxy naphthoic acid. In experiments conducted at temperatures around 260°C from 1 to 12 h, he observed an increase in tenacity of the fibers from 10 to 27 g/denier. He attributed the increase in tensile strength to the increase in molecular weight through SSP and to the simultaneous annealing induced increase in crystal perfection.

Fakirov et al.<sup>19</sup> investigated the effect of vacuum annealing on drawn and undrawn nylon 6 bristles at temperatures around 200°C. They observed an increase in the molecular weight and a decrease in the polydispersity of the samples with increasing time of SSP. They reported a moderate increase in the tensile strength of the undrawn and drawn bristles after annealing. It was attributed not only to the increase in molecular weight but also to the narrowing of molecular weight distribution and increase in crystallinity. Kiyotsukuri and Tada<sup>20</sup> investigated the structure and properties of drawn commercial nylon 66 fibers after polymerizing them in a nitrogen atmosphere or in vacuum at temperatures ranging from 195 to 253°C. They reported a significant increase in molecular weight with heating in vacuum whereas the increase was minimal in nitrogen. A reduction in tensile strength, modulus, and breaking elongation with heat treatment, except for heating in vacuum at 253°C that led to little change in elongation, was also reported.

The possibility of inducing SSP in as-spun fibers, with subsequent drawing to improve their mechanical properties, had not been explored until Knorr<sup>21</sup> patented a process for producing high tenacity nylon yarns via this route. The process was the melt-spinning of an as-spun fiber, followed by a thermal annealing step for increasing the molecular weight and changing the crystalline characteristics of the as-spun yarn, and finally a drawing step for increasing the tenacity of the yarn. However, Knorr's patent does not reveal much fundamental information regarding the polymerization processes and drawing. Such knowledge can be of value in designing a process to derive maximum mechanical performance from the solid-state polymerized fiber of high molecular weight.

We report here results from the initial phase of a study of SSP and drawing of a broad class of melt-

spun polyamides and polyesters. The kinetics of SSP in the fiber form and the morphology and properties of the fibers after SSP were studied. The drawing potential of the solid-state polymerized fibers has also been determined through a simple but versatile "controlled force" thermal deformation analysis (TDA) experiment.

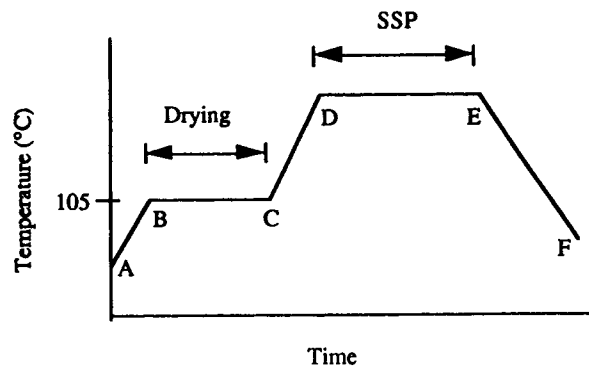
## EXPERIMENTAL

### Materials

A series of melt-spun fibers of nylon 66, nylon 6, nylon 46, and PET were studied with respect to the morphology and properties that can be generated via postextrusion SSP. The results reported here are from experiments with a melt-spun nylon 66 fiber. The material specifications are given in Table I.

### SSP (Annealing) Experiments

Skeins of nylon 66 fibers were placed in an oven (30 × 3 × 7.5 cm) and heated to 105°C in an atmosphere of nitrogen for 1 h to dry the samples. The temperature of the oven was then raised to the SSP temperature at a rate of 20°C/min and maintained for the required period of time. The temperature variation was maintained below ±2°C. The temperature controller was then switched off and the samples were allowed to cool in the stream of nitrogen to room temperature. The nitrogen flow rate was maintained constant at 0.85 m<sup>3</sup>/h throughout the experiment. An additional experiment was also conducted with the filaments wound around a frame to determine whether such a dimensional constraint



**Figure 1** Time-temperature profile for annealing (SSP) experiments. Details are given in text.

would affect mobility of the chain segments and, therefore, SSP.

Figure 1 shows the time-temperature profile used in the SSP experiments. In order to obtain an estimate of the extent of SSP during the heating and cooling intervals in these experiments, samples were also heated to the respective SSP temperatures and cooled immediately to room temperature at the same rate as used in earlier experiments. The assumption used in establishing the "zero time" base from this experiment is that the influence of the duration of part DE (in Fig. 1) on SSP during part EF is negligible. As will be seen later from the experimental data, any deviation of experimental response from this assumption is likely to be small.

### Molecular Weight, Morphological Parameters, and Mechanical Properties

The flow time of a solution of concentration 0.25 g/dL in 90% formic acid at 25°C was measured and the intrinsic viscosity was calculated using the following equations

$$[\eta] = \frac{2}{c} (\eta_{\text{rel}}^{1/2} - 1)$$

$$\eta_{\text{rel}} = \frac{t_{\text{solution}}}{t_{\text{solvent}}}$$

where  $c$  is the concentration of the solution and  $t$  is the time of flow.<sup>22</sup> The viscosity average molecular weight was then calculated using the Mark-Houwink equation. The constants  $K$  and  $\alpha$  values used for the nylon 66/formic acid system were  $35.3 \times 10^{-5}$  dL/g and 0.786, respectively.<sup>23</sup>

Changes in the fiber length, usually shrinkage, due to heat treatment were measured by changes in

**Table I** Material Specifications of Nylon 66 As-Spun Fiber for SSP

Molecular weight ( $M_v$ )	40,000 g/mol
Spinning speed	300 m/min
Linear density	7000 dtex (6300 denier)
No. of filaments	210
Tenacity	1.01 cN/dtex (0.93 g/denier)
Elongation at break	412%
Birefringence	0.015
Melting point (DSC peak)	258°C

dtex and denier are the weight in grams of 10,000 and 9000 m of fiber, respectively. 1 g/denier = 1.0889 cN/dtex.

the linear density. Linear density is expressed as dtex or denier, the weight in grams of 10,000 or 9000 m, respectively.

The refractive indices with polarization parallel and perpendicular to the fiber axis were measured using a transmitted light interference microscope with light of wave length 550 nm. Birefringence,  $\Delta n$ , and isotropic refractive index,  $n_{\text{iso}}$ , were computed from these measurements as follows.

$$\Delta n = n_{\parallel} - n_{\perp}$$

$$n_{\text{iso}} = (n_{\parallel} + 2n_{\perp})/3$$

where  $n_{\parallel}$  and  $n_{\perp}$  are the refractive indices parallel and perpendicular to the fiber axis.

Flat plate wide angle X-ray diffraction photographs of the samples were obtained with a Rigaku-Geigerflex sealed tube X-ray generator. The radiation used was Ni filtered  $\text{CuK}_{\alpha}$ . Power of 1.12 kW and exposure time of 3 h were used.

The melting point, crystallization temperature, and the enthalpies of melting and recrystallization were determined using a Perkin-Elmer DSC-4 differential scanning calorimeter. The heating and cooling runs were carried out at a rate of  $20^{\circ}\text{C}/\text{min}$ .

The strength, elongation to break, modulus, yield stress, and strain were calculated from the load-elongation curves obtained with an Instron tensile tester, Model No. 1125. A strain rate of  $5.7 \text{ min}^{-1}$  ( $0.095 \text{ s}^{-1}$ ) and a gage length of 3.5 in. (8.9 cm) were used.

## Drawing of Solid-State Polymerized Fibers

The role of stress in the process of drawing can be simulated by a TDA as a preliminary experiment prior to continuous drawing.<sup>24,25</sup> This analysis involves the measurement of changes in length of filaments when they are subjected to a constant axial force and heated rapidly to a temperature between glass-transition and melting temperatures,  $T_g$  and  $T_m$ . The experimental apparatus (shown in Fig. 2) consists of a temperature controlled tubular heater mounted on a mobile platform with wheels that can be moved rapidly over rails to enclose the loop of filaments being tested. The fiber loop is connected at each end to Kevlar yarns, one of which is connected to a fixed support while the other is passed over a smooth pulley and connected to a weight. A pointer is attached to the moving end so that the deformation can be read against a scale. The deformation of the Kevlar yarn is negligible when compared to that of the filament loop in all experiments. Two kinds of experiments were performed with this apparatus.

## Nonisothermal Deformation Analysis

A specific force is applied to the fiber by hanging a weight to the free end of the Kevlar yarn. The fiber is then enclosed by the heater at room temperature. The temperature of the heater is then ramped at the desired rate. Deformation of the fiber with time is obtained from a record of the position of the pointer against the scale using a video camera. This

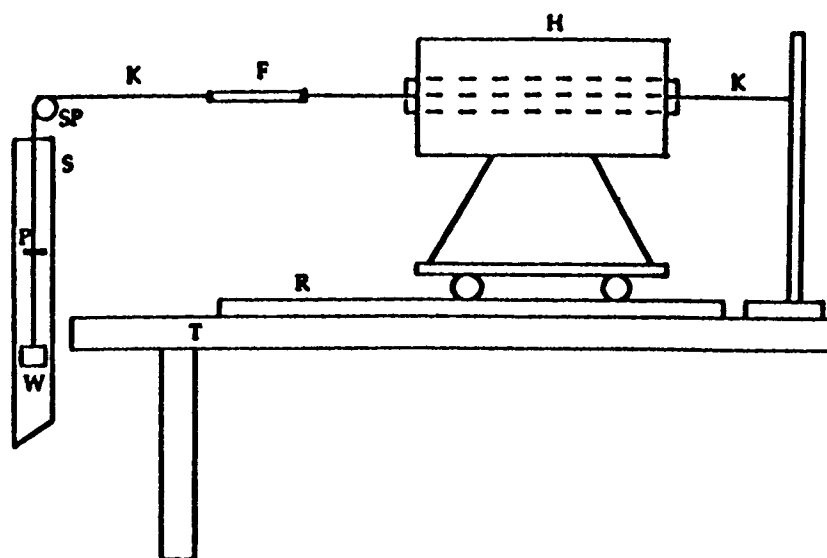


Figure 2 Schematic of the apparatus for thermal deformation analysis.

**Table II** Intrinsic Viscosity and Molecular Weight of Nylon 66 Fibers after SSP at Different Temperatures and Times

Temp (°C)	Time (min)	IV (dL/g)	$M_v$ (g/mol)
As-spun Nylon 66		1.43	40,000
220	15	1.83	53,000
220	30	1.81	52,000
220	45	1.89	55,000
220	60	2.05	61,000
220	120	2.20	66,000
230	15	1.98	58,000
230	30	2.18	66,000
230	45	2.32	71,000
230	60	2.47	77,000
230	180	3.36	115,000
240	15	2.16	63,000
240	30	2.61	83,000
240	45	2.94	97,000
240	60	3.36	115,000
240 <sup>a</sup>	60	3.32	113,000
240	240	4.98	190,000
250 <sup>b</sup>	0	1.61	45,000
250	15	2.70	87,000
250	30	3.23	109,000
250	45	4.28	156,000
250	60	4.66	174,000
250	120	6.72	278,000

IV, intrinsic viscosity.

<sup>a</sup> Sample heat treated with constraint against shrinkage.

<sup>b</sup> Sample heated to 250°C and cooled without being held at peak temperature.

analysis is carried out to determine the temperature range for conducting isothermal deformation studies.

### *Isothermal Deformation Analysis*

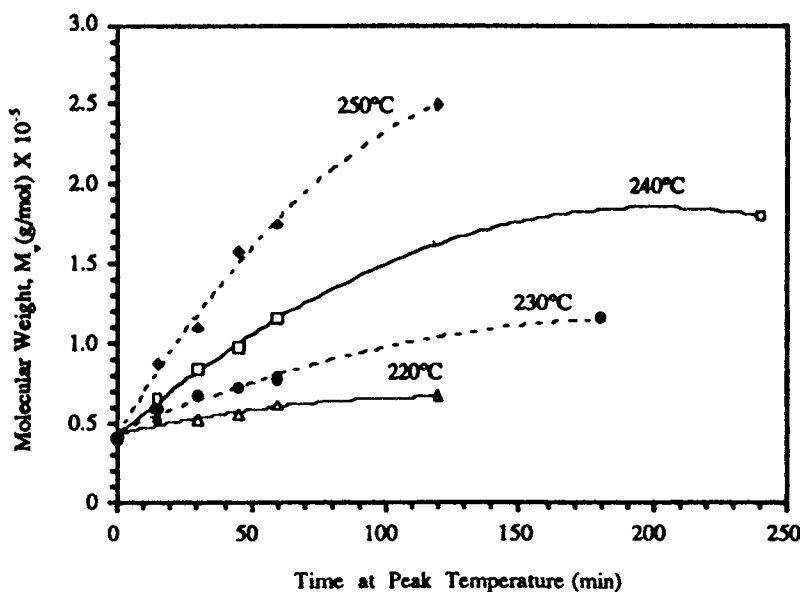
The temperature of the heater is set and a constant weight is hung from the fiber loop. The heater is then moved rapidly over the fiber loop so that it is completely enclosed, maintained in this position for a period of 5 s, and withdrawn rapidly. The accompanying deformation is obtained from the initial and final positions of the pointer against the scale.

## RESULTS AND DISCUSSION

### Kinetics of SSP

Viscosity-averaged molecular weights of the solid-state polymerized nylon 66 fibers are given in Table II. It can be seen clearly from Figure 3 that there is a substantial increase in molecular weight at higher temperatures of SSP. Molecular weights up to 280,000 g/mol have been achieved by SSP from a starting molecular weight of 40,000 g/mol. The molecular weight obtained here is much higher than those reported in the literature.

It is also evident that temperature has a significant effect on the rate of SSP. It can be seen that even after a period of 3 h at 230°C the molecular weight increased up to only 115,000 g/mol, a level



**Figure 3** Effect of time and temperature of SSP on molecular weight.

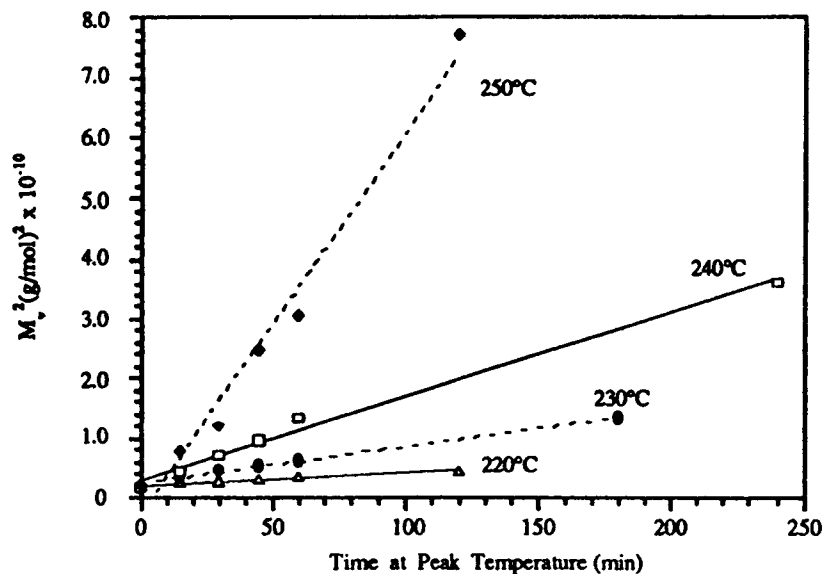


Figure 4 Kinetics of nylon 66 fiber SSP.

reached after just an hour at 240°C. The effect of temperature in increasing the reaction rate is apparently due to the increased mobility of the functional groups at higher temperatures.

There is only small increase in the molecular weight, from 40,000 to 45,000 g/mol during the heating and cooling intervals at 250°C (Table II). At other temperatures there was no significant polymerization during the heating and cooling intervals.

It is evident from the data presented in Figure 4 that the kinetics of SSP at and above 220°C follows

simple self catalyzed step-growth polymerization kinetics as the rate of the reaction can be described by

$$-\frac{d[M]}{dt} = k[M]^3$$

where  $[M]$  is the concentration of the functional group and  $t$  is the time of reaction. The relation between the final and the initial degree of polymerization is then given by

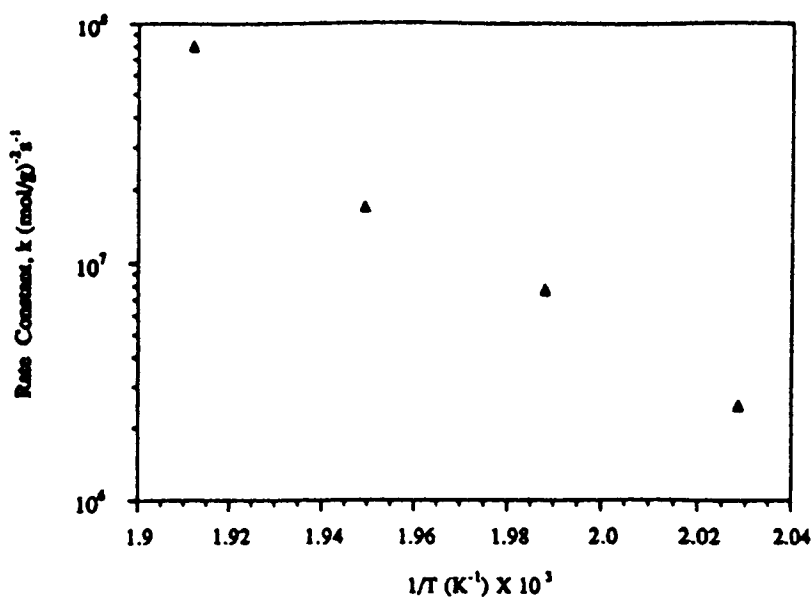


Figure 5 Arrhenius plot for nylon 66 fiber SSP.

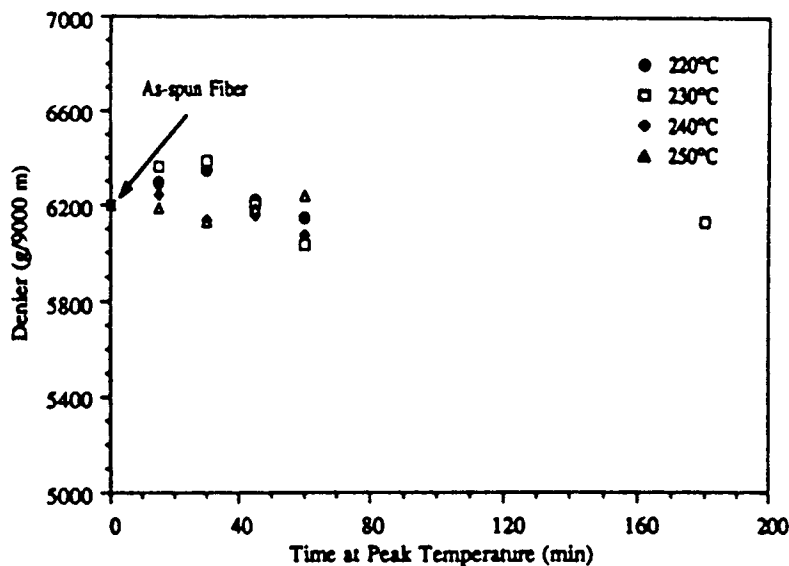


Figure 6 Linear density of fibers after SSP.

$$X_n^2 = X_{n_0}^2 + 2[M_0]^2kt$$

where  $X_n$  and  $X_{n_0}$  are the final and initial average degree of polymerization,  $[M_0]$  is the initial concentration of the functional groups, and  $k$  is the reaction rate constant. If we assume equimolar ratio of the functional groups at the beginning of SSP and the molecular weight distribution of the system remains equal to that of a typical step-polymerization reaction, then the reaction rate constants at the four different temperatures can be calculated from the slopes of the straight lines in Figure 4. The calculated reaction rate constants are

$$k = 5.0 \times 10^6 \text{ (mol/g)}^{-2} \text{ s}^{-1} \text{ at } 220^\circ\text{C}$$

$$k = 6.2 \times 10^7 \text{ (mol/g)}^{-2} \text{ s}^{-1} \text{ at } 230^\circ\text{C}$$

$$k = 1.9 \times 10^8 \text{ (mol/g)}^{-2} \text{ s}^{-1} \text{ at } 240^\circ\text{C}$$

$$k = 4.9 \times 10^8 \text{ (mol/g)}^{-2} \text{ s}^{-1} \text{ at } 250^\circ\text{C}.$$

From Figure 5 the activation energy for SSP is calculated to be 57 kcal/mol. It should be realized however, that this activation energy has been determined from data ranging over just 30°C.

Comparison of the results of annealing of the as-spun fibers under constraint and in free condition

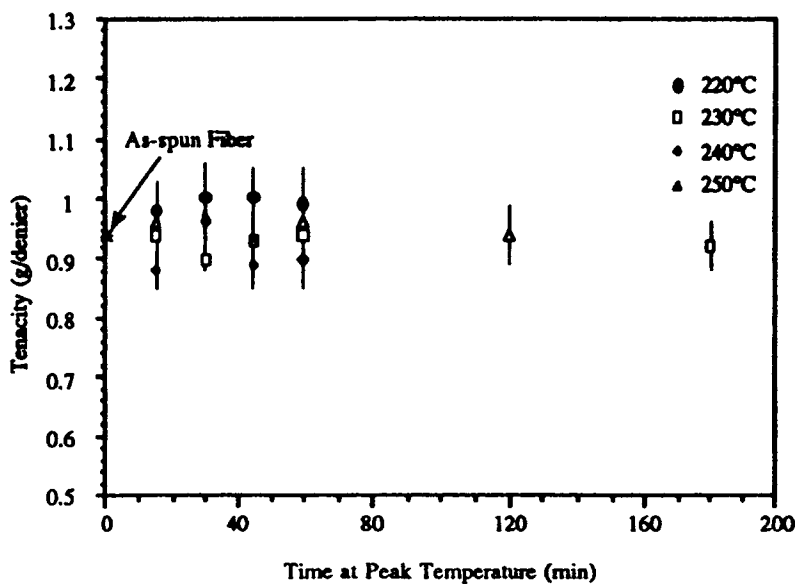


Figure 7 Tensile strength of nylon 66 fibers after SSP.

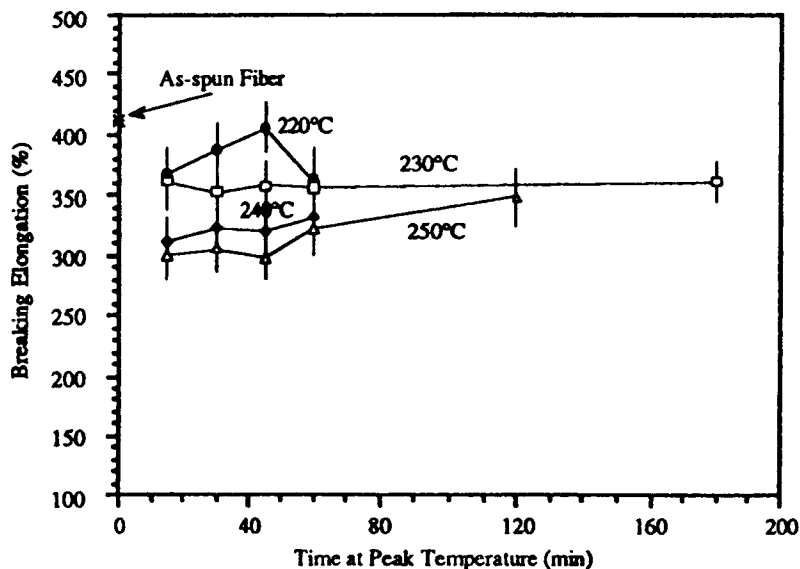


Figure 8 Elongation to break of nylon 66 fibers after SSP.

at 240°C for 1 h from Table II shows that similar extents of increase in molecular weight are obtained by performing the SSP of as-spun fibers under both conditions. This is probably due to the combination of the fact that diffusion of only end groups is required to facilitate SSP of nylon 66 and the as-spun fiber exhibits relatively little shrinkage during annealing without any constraint, thus indicating that the orientational environment around the end groups is not influenced by the presence or absence of a dimensional constraint. This observation has a practical significance because it suggests the feasi-

bility for conducting continuous, albeit slow, SSP of these as-spun fibers.

#### Mechanical Properties and Morphology of Solid-State Polymerized Fibers

From the linear densities of the fibers after SSP (Fig. 6) it is seen that there was no significant shrinkage during SSP of these fibers. It should be noted here that significant crystallization exists in the as-spun fibers of nylon 66. It is now well understood that such crystallization occurs preferentially

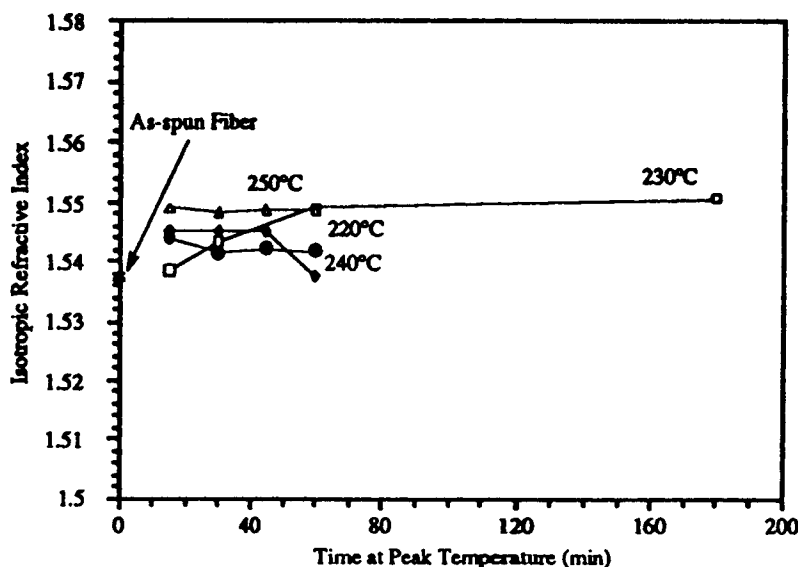
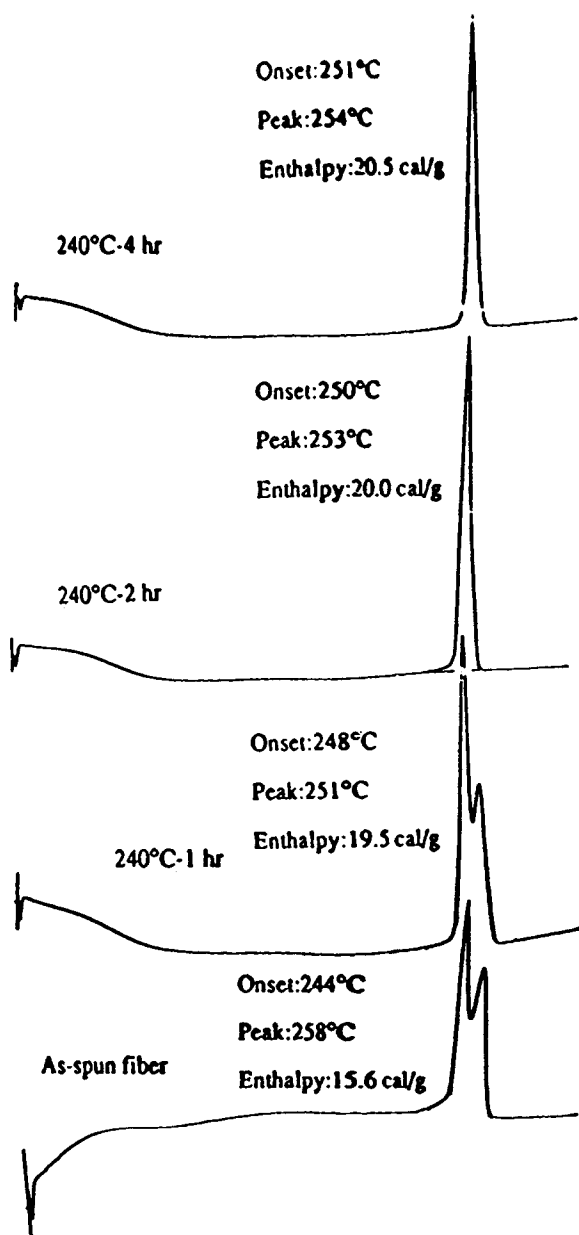


Figure 9 Isotropic refractive index of nylon 66 fibers after SSP.

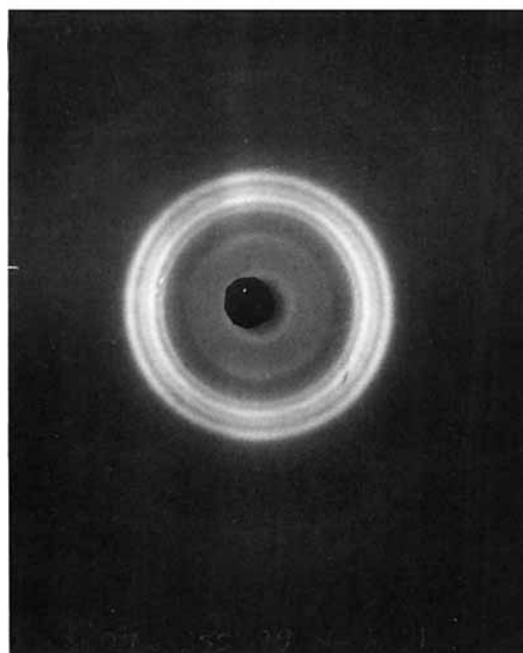
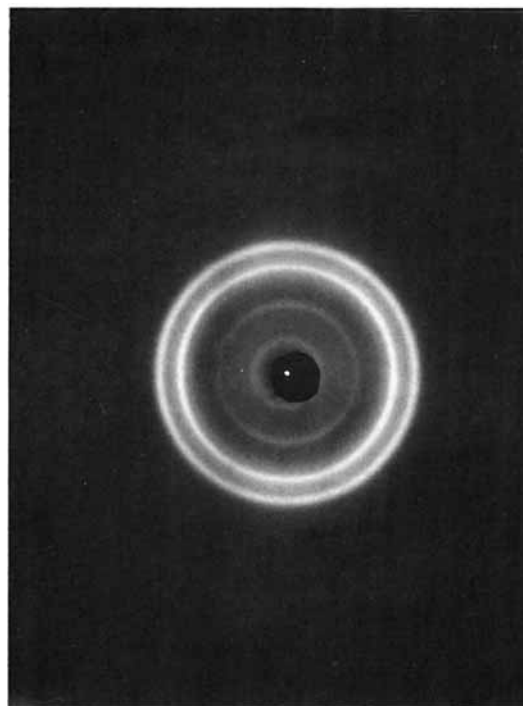


among the oriented segments, thus reducing the shrinkage potential of the as-spun fibers.<sup>26-28</sup>

The tensile strength and elongation to break of the SSP fibers are shown in Figures 7 and 8, respectively. With the increase in temperature of heat treatment, there is a slight decrease in the elongation to break *measured at room temperature* due to increased crystallization at higher SSP temperatures. This increase in crystallinity is revealed by isotropic refractive index measurements (Fig. 9). Much of the initial ductility of the fiber is retained after SSP.



**Figure 10** DSC heating thermograms of as-spun nylon 66 and fiber solid-state polymerized at 240°C.



**Figure 11** Wide-angle x-ray diffraction photographs of (a) as-spun nylon 66 fiber and (b) fiber solid-state polymerized at 240°C for 1 h.

The tensile strength (shown in Fig. 7) remains essentially unchanged after SSP. Simultaneous relaxation and crystallization of the segments in the amorphous regions takes place during the process

of SSP and these are reflected in the morphology and mechanical properties of the fibers.

Isotropic refractive indices of the starting and SSP fibers are shown in Figure 9. The isotropic refractive indices of the annealed fiber samples are higher than the starting material, confirming crystallization during annealing. The isotropic refractive index increases with an increase in temperature, which again implies higher extents of crystallization at higher temperatures.

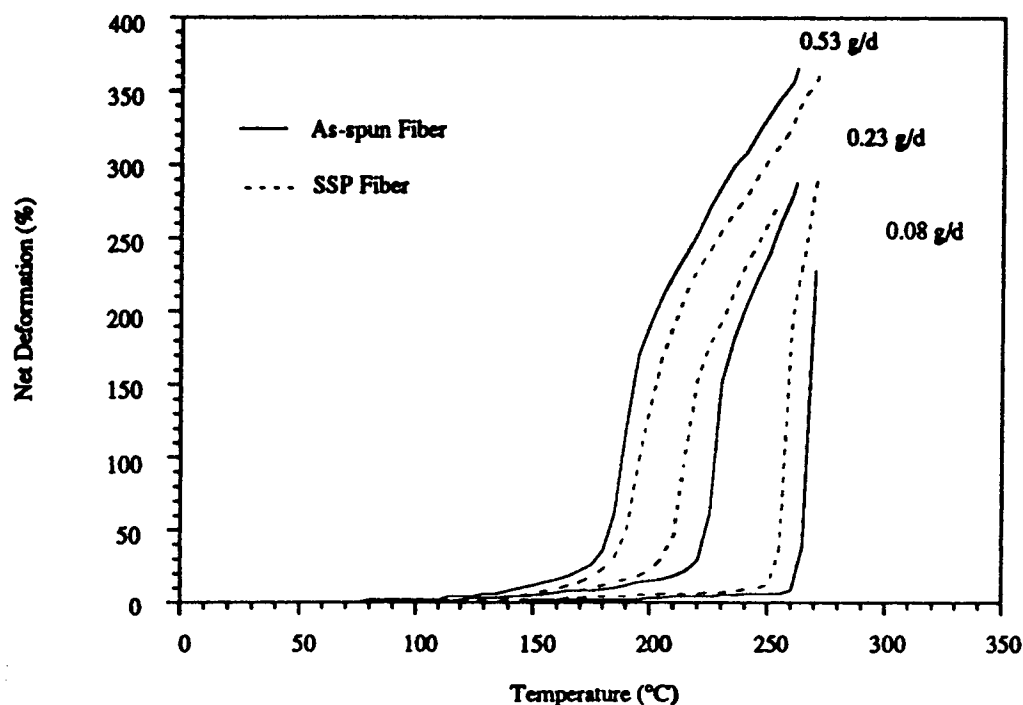
The results from calorimetric studies of the nylon 66 fibers solid-state polymerized at 240°C are shown in Figure 10. There is no significant change in the melting temperature with the change in molecular weight. This is because the influence of molecular weight on the melting or crystallization temperatures is significant only for low molecular weight materials. Because the starting material already has a relatively high molecular weight ( $\sim 40,000$  g/mol), there is no significant change in the melting point with a further increase in molecular weight. However, it can be seen clearly from the sharpness of the melting peaks that the crystal perfection and/or size should have increased with annealing. The enthalpy of melting values shown in Figure 10 confirm an increase in crystallization with annealing, as previously observed from isotropic refractive index measurements.

There is a decrease in the birefringence value of the fibers, from a starting material birefringence of 0.015 to about 0.010 after SSP. It should be noted, however, that the low birefringence of the starting material shows that it possesses only a low overall orientation to begin with, as a consequence of its low spinning speed. Well drawn and crystallized nylon 66 fibers typically show birefringence values from 0.05 to 0.06.

The wide-angle x-ray diffraction photographs of the as-spun fiber and that after SSP at 240°C for 1 h (Fig. 11) confirm that both samples are significantly crystalline and the crystalline orientation is poor in both cases, consistent with the isotropic refractive index and birefringence measurements.

### TDA

Initially nonisothermal deformation analyses (NTDA) were performed with the precursor material and the material solid-state polymerized (annealed) at 240°C for 1 h to help determine the appropriate conditions (temperature and force level) for conducting isothermal deformation studies. The NTDA experiments were conducted at a heating rate of 10°C/min. The results are shown in Figure 12. It can be seen from the plots that there is a gradual increase in the net deformation with an increase in



**Figure 12** Nonisothermal deformation analysis of as-spun and fiber solid-state polymerized at 240°C for 1 h.

temperature in the low temperature region, followed by a sudden increase. The temperature at which there is a sudden increase in elongation decreases with an increase in applied stress for both samples.

### Isothermal Deformation Analysis

Results of the isothermal TDA (ITDA) are shown in Figure 13. Higher extents of deformation could be achieved with the solid-state polymerized fiber than with the starting material. This shows clearly that the solid-state polymerized as-spun fiber has a higher drawing potential, a probable consequence of increase in molecular weight.

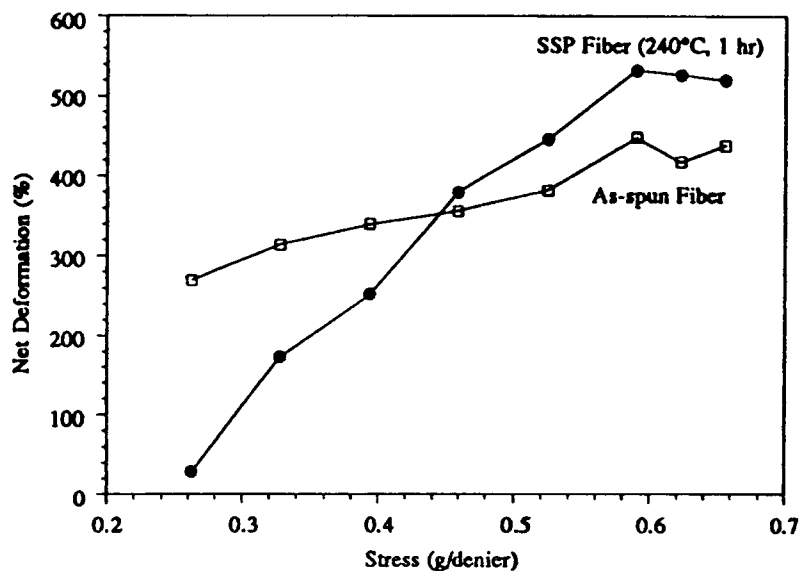
Results of the ITDA of solid-state polymerized fiber at different temperatures are shown in Figure 14. The net deformation increases with an increase in stress level at each test temperature. The net deformation increases initially with an increase in temperature but failure occurs at a lower stress level with an increase in the temperature of ITDA. It should be noted here that, in the TDA experiment (shown in Fig. 2), the momentum due to the movement of the weight increases substantially due to rapid deformation of the fiber at higher temperatures. The fiber has to absorb the kinetic energy of the weight also to prevent failure. So the force level at which the fiber breaks is not the true failure stress of the material. This might be a probable cause for the lower breaking stress level at higher temperatures.

Clearly, the inference from the above-mentioned results has to be that a higher potential for drawing is obtained with SSP of these as-spun nylon 66 fibers. Such deformation, combined with the intrinsic contribution from the higher molecular weight, is likely to yield fibers of superior mechanical properties. However, this hypothesis needs to be validated through continuous drawing of SSP fibers. Experiments are currently in progress to determine the appropriate conditions and the range of properties that can be obtained by drawing after SSP in the fiber form.

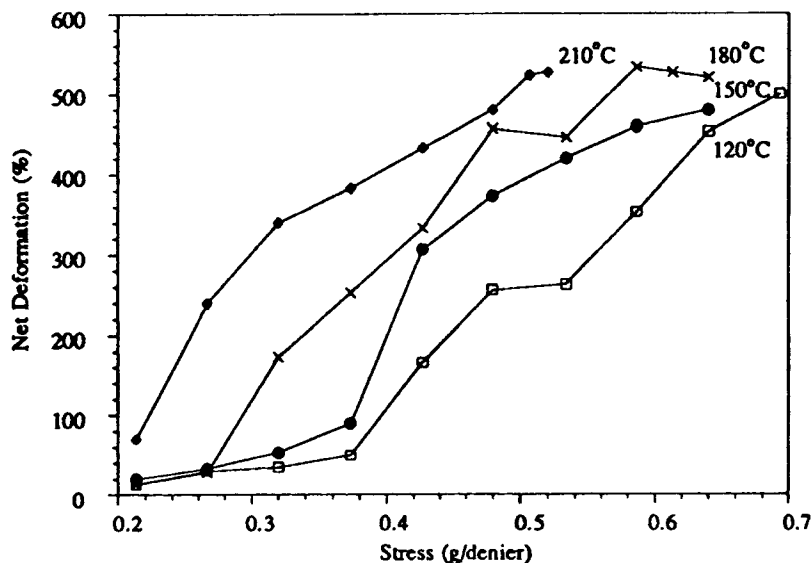
### CONCLUSIONS

Several important results have been obtained in the study conducted so far on the nature of SSP that can be carried out at the post fiber-extrusion stage. These are:

1. The rate of SSP increases significantly when the temperature is raised close to the  $T_m$  of the polymer, allowing high molecular weights to be obtained at reasonable polymerization times.
2. The SSP of nylon 66 as-spun fibers at and above 220°C follows simple self catalyzed step-growth bulk polymerization kinetics.
3. The tensile strength and the melting point of the fibers remain unchanged after SSP.



**Figure 13** Isothermal deformation analysis at 180°C of as-spun nylon 66 and fiber solid-state polymerized at 240°C for 1 h.



**Figure 14** Isothermal deformation analysis of nylon 66 ( $M_v = 115,000$ ) solid-state polymerized at 240°C for 1 h.

4. Although there is a slight drop in the elongation to break after SSP of the fibers, much of the initial ductility is retained even at room temperature. The drawing potential at higher temperatures appears to be higher for the SSP fibers, a probable consequence of the substantial increase in molecular weight.
5. There is an increase in crystallinity and crystal perfection of the fibers with SSP. It is therefore likely that at least the final stage of subsequent drawing of these SSP fibers has to be carried out at "near melting" temperatures to unravel the folded chains from the crystals and produce a drawn fiber morphology with a high density of tie chains to achieve superior mechanical properties.

It can be concluded that SSP of nylon 66 as-spun fibers prior to drawing is likely to be a viable process for the production of high molecular weight industrial fibers. Elimination of the problems associated with extrusion of high molecular weight polymer, without adversely affecting subsequent processes, is an important advance in this regard. However, postextrusion SSP would be relevant only if the substantial increase in molecular weight could be taken advantage of during the subsequent drawing process in achieving a high degree of order and consequent generation of improved mechanical properties.

It has to be clearly understood that it is the combination of the high molecular weight and the ap-

propriate morphology of the drawn fiber that would make achievement of superior mechanical properties in fibers of flexible polymers possible. It is evident from this investigation that SSP of as-spun fibers results in an increase in the crystallinity/crystal perfection in the fiber prior to drawing. On the contrary, it is common practice in the fiber industry to start with an as-spun fiber with low orientation and crystallinity and then produce an extended chain morphology with oriented crystallization by drawing in multiple stages. It is imperative to use an appropriate alternative drawing mechanism to draw the solid-state polymerized fibers and attain a morphology with increased density of bridging segments between crystals.

Postextrusion SSP will be of even greater significance in the class of step-growth polymers where high molecular weight cannot be obtained by melt polymerization due to excessive degradation reactions. In such cases, postextrusion SSP would facilitate the achievement of higher molecular weights due to the relatively shorter polymerization times involved as compared to SSP of the polymer. A typical example of this class of polymer would be the polyamide, nylon 46, produced by condensation of tetramethylene diamine and adipic acid.

Preliminary investigations conducted in our laboratories on SSP of nylon 46 as-spun fibers at a temperature of 260°C for 1 h show that intrinsic viscosity, in formic acid at 25°C, up to 3.0 dL/g could be obtained from a starting material intrinsic viscosity of 1.4 dL/g. As observed earlier with nylon

66, the ductility of the fiber (room temperature breaking elongation) was retained after SSP that would facilitate subsequent drawing to produce fibers with increased mechanical properties.<sup>29</sup>

The study reported here has served to identify the critical issues associated with postextrusion SSP. Different mechanisms for drawing these high molecular weight solid-state polymerized fibers are currently being studied in our laboratories. These include a combination of drawing at near melting temperatures, different rates of drawing, and drawing with or without a plasticizer to facilitate the unraveling of the chains from the crystals to produce an extended chain morphology.

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