

Stirring-Induced Solution Crystallization of Ultra High Molecular Weight Polyamide 6

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Synopsis

Unstable solutions of ultrahigh molecular weight polyamide 6 have been prepared by adding a nonsolvent to the polymer solution. Crystallization of the polyamide from such a solution proceeds very slowly. It has been found, however, that vigorous stirring of the unstable solutions induces rapid fibrous crystallization of the polymer. The fiber mat consists of irregularly shaped fibers. A low temperature and a high stirring rate are among the conditions necessary to obtain a high yield of fibrous material. The fibers formed upon stirring have a higher molecular weight than the polyamide 6 molecules which remain in the solution. The melting point of the fibers depends on the speed of the paddle stirrer. The differential scanning calorimetry (DSC) thermogram reveals higher melting temperatures of the fibrous material if higher stirring rates have been applied.

INTRODUCTION

A nearly perfect alignment of the polymer molecules along the fiber axis is necessary for obtaining a fiber with a high tensile strength and a high modulus. Stirring-induced solution crystallization has been found to be a way to obtain fibers that may fulfil the above conditions. The method has been described by Pennings et al.¹ They made polyethylene fibers with the now well-known shish kebab structure. This implies that there are molecules present that are at least partly highly oriented.²⁻⁴ Stirring-induced crystallization with low molecular weight polyamide 6 results in fibrous crystals having a length of only 5 μm .⁵ Thanks to the availability of polyamide samples with a molecular weight higher than 250,000, we succeeded in obtaining fibers of considerably greater length.

EXPERIMENTAL

Polymer Samples

Ultrahigh molecular weight polyamide 6 (UHMW PA 6) was prepared by anionic polymerization of caprolactam. The details of the synthesis fall outside the scope of this article.^{6,7} Samples were prepared with molecular weights ranging from 10^5 to 10^6 .

Light Scattering

The molecular weight M_w of the UHMW PA 6 samples was determined with the aid of a Fica 50 light scattering apparatus at a wave length of 546.1

nm. The refractive index increment dn/dc amounts to 0.217 mL/g⁸ for the polymer in 2,2,2-trifluoroethanol (TFE)

The key problem of light-scattering measurements with the high-molecular-weight samples is to filter the solutions properly in order to meticulously remove any dust and simultaneously to avoid filtering off a high-molecular-weight polymer fraction. After many trials, the following procedure has been adopted.

The solvent TFE was thoroughly filtered over a 0.2 μm filter before use and the all-glass equipment was rinsed with clean TFE. Each concentration was prepared separately and, if necessary, with mild heating at 50°C. The solutions were then filtered over a 1 μm filter without applying pressure.

The concentrations used were as low as 0.05–0.15 g/L because at higher concentrations too much dust is introduced. Still lower concentrations lead to irregular measurements, probably as a result of polymer adsorption to filter or glass wall. The light scattering was determined for five concentrations, at angles between 30 and 135 degrees, measurements at larger angles usually being less accurate.

The equation for the light scattered by a polymer solution is

$$\frac{K_c}{R_\theta} = \frac{1}{M_w P(\theta)} + 2A_2c + \dots \quad (1)$$

in which the symbols have their usual significance. Based on the above equation, a computer calculation of the Zimm plot was made, giving the molecular weight by a double extrapolation: to zero angle and zero concentration.

Viscometry

For the viscosity measurements the UHWM PA 6 was dissolved in freshly distilled *m*-cresol. The chosen polymer concentrations, usually in the range of 0.01–0.25 g/dL depended on the molecular weight of the sample. It was found necessary to apply the Hagenbach correction for kinetic energy effects on the effluent time. The best fit for the measurements was obtained by applying Martin's equation^{9,10}

$$\ln(\eta_{sp}/c) = \ln[\eta] + kc[\eta] \quad (2)$$

in which the symbols have the well-known meaning. The relation between $[\eta]$, expressed in dL/g, and M_w , as found by light-scattering measurements, is in good agreement with that of Tuzar et al.¹¹

$$[\eta] = 5.26 \times 10^{-4} M_w^{0.745} \quad (3)$$

Solvents and Nonsolvents

Formic acid (Baker Analyzed[®]) and freshly distilled *m*-cresol were used as solvents for the polyamide. It was required to add a nonsolvent to the polymer solution in order to obtain fibrous material by stirring. As nonsolvent use was made of several liquids such as acetone (unpurified), methanol



Fig. 1. Paddle stirrer with fibrous UHMW PA 6; magnification $\times 0.7$.

(unpurified), distilled water, butanol (Baker Analyzed[®]), and γ -butyrolactone (Janssen Chimica).

Dissolution and Stirring Procedures

First, 0.3 g of the UHMW PA 6 sample was put into the vessel (see Fig. 1) followed by the addition of 30 mL of either formic acid or *m*-cresol. With formic acid; the polymer dissolved completely after standing in the acid overnight. In the case of *m*-cresol, the solution was also heated at 50°C for 2 h with gentle stirring. In Table I the solvent/nonsolvent mixtures are given, including the volume percentages of nonsolvent, which gave large masses of fibrous material upon stirring.

To prevent local crystallization, the nonsolvent was slowly added at a metering rate of 0.4 mL/min, while agitating with a paddle stirrer at 100 rpm (see Fig. 1). After addition of nonsolvent the mixture was stirred at a specific

TABLE I
Solvent mixtures suitable for stirred crystallization of UHMW PA 6 solutions.
Amounts of nonsolvent expressed in volume percentages

Solvent	Nonsolvent (%)			
Formic Acid	Acetone 68.4	Butanol 62	Water 40	
<i>m</i> -Cresol	Acetone 65	Butanol 65	Methanol 60	Butyrolactone 40

TABLE II
Standard Conditions for Making Crystalline Fibrous Material
by Stirring a UHMW PA 6 Solution

M_w of UHMW PA 6 sample	8.3×10^5
Polymer concentration	0.3%
Volume ratio formic acid/acetone	31.6/68.4
Stirring rate	1500 rpm
Stirring time	45 min
Temperature	Ambient temp (20°C)

rate between 100 and 1500 rpm. From the many possible solvent/nonsolvent combinations and stirring speeds a set of parameters was chosen as standard condition; these are given in Table II.

Treatment of UHMW PA 6 Fractions

The detection of the polymer fraction was performed by viscometric measurements. To this end the fibrous material around the stirrer was thoroughly rinsed with a mixture of formic acid/acetone in a volume ratio of 35/65 to remove the original solution mixture, which still contained dissolved polymer molecules. The fibrous mat was then washed with acetone at 40°C for 24 h (according to the same procedure the yield of fibrous material, expressed in weight percentages of originally dissolved polymer, was determined).

The polymer remaining in the solution was precipitated with an excess of acetone. The precipitate was then collected by filtration, washed with acetone, and dried as stated above. Finally, the molecular weight was determined by viscometry as described above.

Turbidity Determination

The polymer dissolved in the solvent/nonsolvent mixtures is not thermodynamically stable; the solutions become turbid in the course of time. As a measure of the stability the extinction at 436 nm was determined as a function of time with the aid of a Beckman Model 24 spectrophotometer. The polymer concentration was 0.3%, the same as in the above mentioned standard condition.

Fiber Characterization

Owing to the very irregular shape of the fibers, only two characterization methods could be used successfully: Differential scanning calorimetry (DSC) was performed with the Du Pont 990 Thermal Analyzer, while the scanning electron microscopy (SEM) was done by a SEM Philips 505.

RESULTS AND DISCUSSION

Influence of Process Conditions on the Formation and Properties of Fibrous Material

As mentioned in the preceding paragraph, the UHMW PA 6 solutions, which are suitable to develop fibrous polyamide crystals by stirring, are not

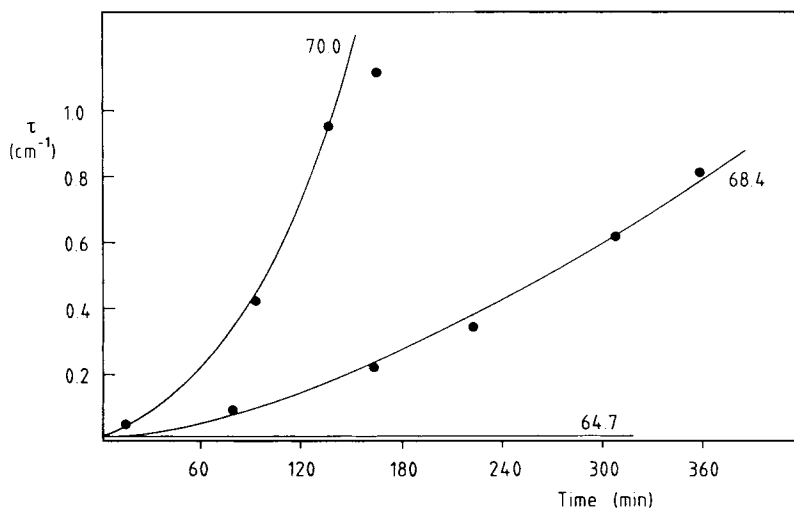


Fig. 2. Turbidity at 436 nm as a function of time for UHMW PA 6 solutions in formic acid/acetone mixtures. Molecular weight 8.3×10^5 ; UHMW PA 6 concentration 0.3%; acetone concentrations if vol % as indicated in the figures.

thermodynamically stable. The instability of the solutions is demonstrated in Figure 2, in which the turbidity as a function of time is given for three UHMW PA 6 solutions with different formic acid/acetone compositions. The turbidity is caused by the relatively slow generation and growth of the polyamide crystals. As could be expected, the turbidity increases faster with greater amounts of nonsolvent in the mixture. It is of importance to distinguish clearly the slow crystallization of a stagnant solution from the fast crystallization induced by stirring. Therefore, some care must be taken in the

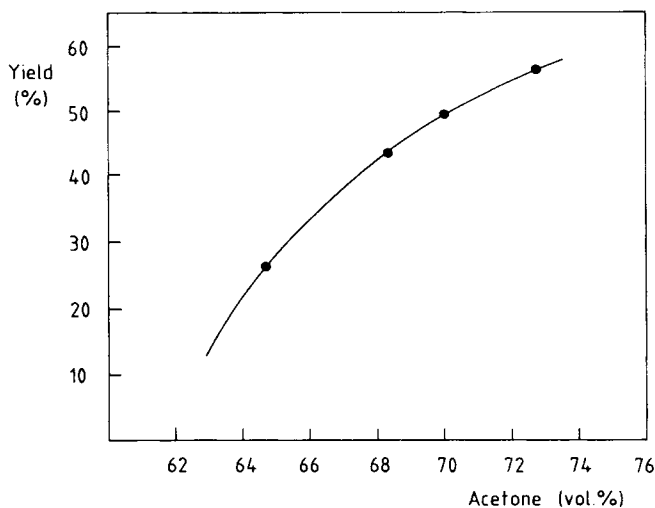


Fig. 3. Yield of fibrous material in weight percentages of the total amount of originally dissolved UHMW PA 6 in formic acid at various amounts of added acetone as nonsolvent. For other stirring conditions see Table II.

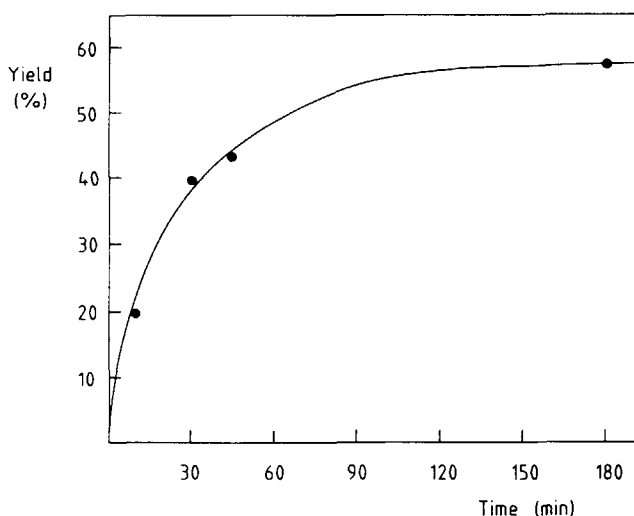


Fig. 4. The yield of fibers during stirring in the course of time. For other conditions see Table II.

preparation of the solution mixtures. The nonsolvent must be added with stirring to prevent crystallization by locally high concentrations of nonsolvent. On the other hand, agitation must be gentle to avoid crystallization induced by stirring. After addition of the proper amount of nonsolvent, the solution should be visually clear. Then stirring can be started at higher rates to induce the formation of the fibrous crystals. Following this method of preparation, a number of solvent/nonsolvent combinations was made, as given earlier in Table I, to obtain metastable UHMW PA 6 solutions. For the various combinations, however, the differences in stirring conditions and resulting fiber masses are only gradual. As mentioned above, we selected a set of standard conditions, which are compiled in Table II. In a series of experi-

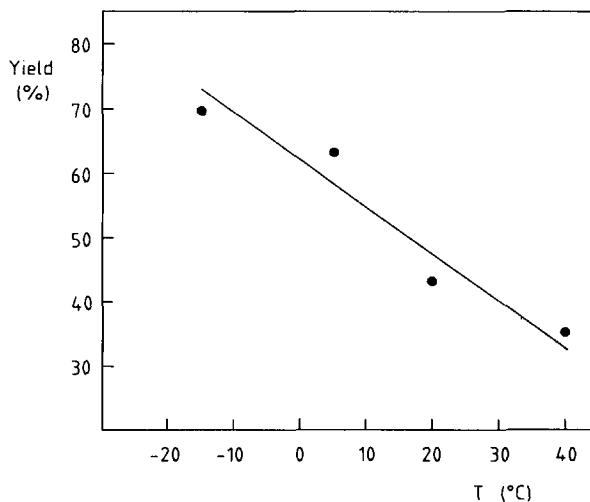


Fig. 5. The influence of temperature on the yield of fibers (see Table II).

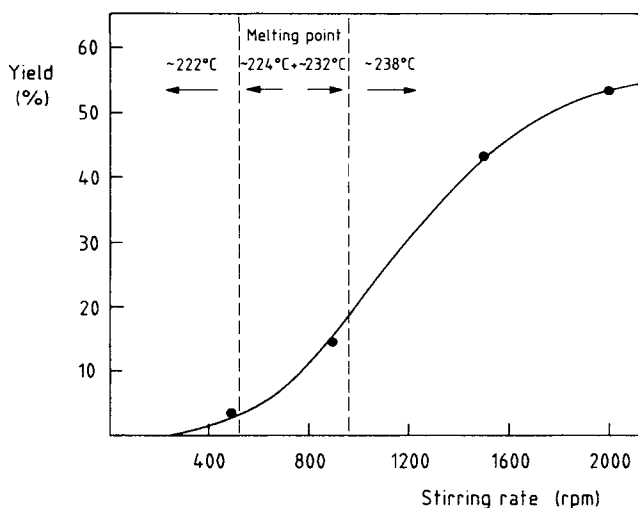


Fig. 6. The yield of fibrous material as a function of the stirring rate (see Table II). Melting point boundaries of fibers obtained at different stirring rates are indicated in the figure.

ments the yield of fibrous material, expressed in weight percentages of originally dissolved polymer, was determined under various process conditions. This was done by varying one of the standard conditions and keeping the other parameters constant. In Figure 3, the yield is shown at various amounts of acetone as nonsolvent. Even at a concentration of 64.7% acetone, an appreciable amount of fibrous crystals can be collected after 45 min of stirring, while in a stagnant solution (see Fig. 2) no increase in turbidity could be detected after such a short time. The yield obviously increases with increasing amounts of nonsolvent.

Figure 4 demonstrates the rapid increase in the yield during stirring at 1500 rpm. No clear induction time was detectable before the generation of the first tiny fibers. After 10 minutes of stirring, quite a large mass of fibers has developed. The influence of the temperature on the yield of fibers is shown in Figure 5. The increasing yield at decreasing temperature can be attributed to the worsening of the solvent quality of the formic acid/acetone mixture by lowering the temperature. The increase in yield of fibrous material with the rate of stirring is illustrated in Figure 6. As indicated in this figure, the melting points of the fibers depend on the stirring speed. Figure 7 gives the DSC thermograms of three fiber samples prepared at three different stirring rates: The sample made at 300 rpm has the "normal" melting point of 222°C for polyamide 6. For the sample prepared at 960 rpm, the melting point has not only slightly shifted to 224°C but, moreover, a peak at 232°C has developed. The last sample, collected after stirring at 1500 rpm, shows only one melting peak at 238°C. A speculative explanation of this phenomenon will be given in the following paragraph. In Figure 8, the yield of fiber mass is plotted against the molecular weight of a series of polyamide 6 samples. The absence of any fiber formation for $M_w < 2.5 \times 10^5$ cannot merely be ascribed to the fact that the solvent composition is relatively "better" for the lower molecular weight samples. In a separate experiment with a sample with

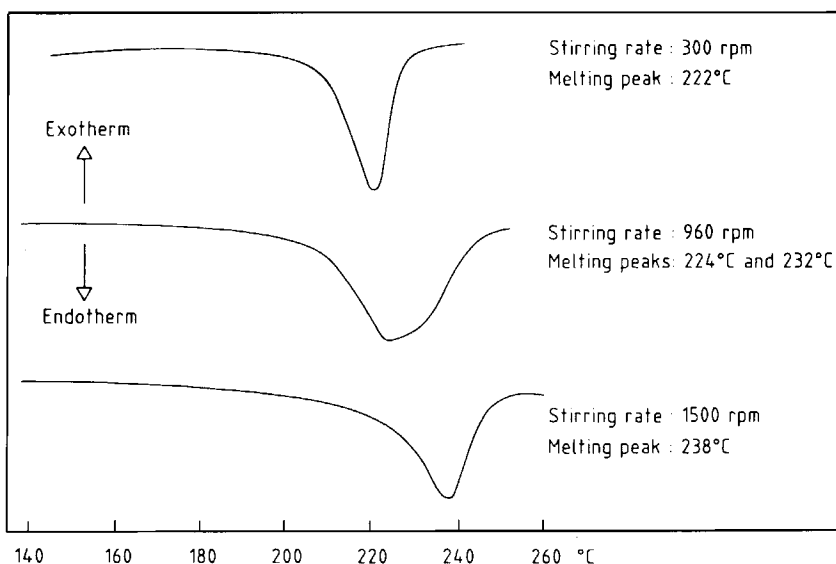


Fig. 7. DSC thermograms of UHMW PA 6 fibers prepared under standard conditions, but at different stirring rates (DSC heating rate 20°C/min).

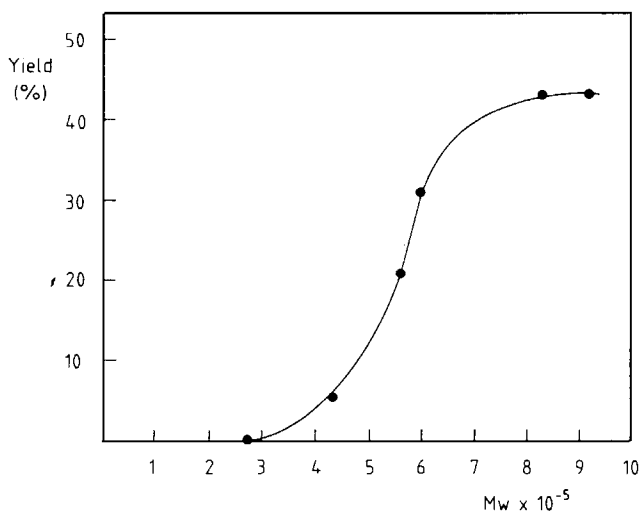


Fig. 8. Dependence of the fiber mass yield on M_w (see Table II).

$M_w = 250,000$, a large excess of acetone was added gradually during stirring at 1500 rpm. Although the solutions became very turbid, no fibers were formed at all.

Regarding the molecular weight dependence of the yield, it is not surprising that, similar to polyethylene¹², fractionation occurs in the process of stirring-induced crystallization. The PA 6 fiber mat has a higher molecular weight than the polymer that remains in the solution. The results of the fractionation on two samples are collected in Table III. Therefore, it is not only from polyethylene, but from UHMW PA 6 as well, that fibrous crystals can be

TABLE III
 Fractionation by Stirring Two Samples A and B of a UHMW PA 6^a

	Sample A $M_w 10^{-5}$	Sample B $M_w 10^{-5}$
Original UHMW PA 6 samples	8.0	5.0
Fibers obtained by stirring	9.1	7.6
UHMW PA 6 remaining in the solution	5.4	3.9

^a For stirring conditions see Table II.

TABLE IV
 Comparison Between Stirring Conditions for Polyamide 6 and Polyethylene

	Polyamide 6	Polyethylene
Molecular weight	$> 2.5 \times 10^5$	0.9×10^5
Solvent	Mixtures (see Table I)	<i>p</i> -xylene
Temperature	20°C	104.5°C

obtained by hydrodynamically induced crystallization. There are, however, some striking differences in the stirring conditions as shown in Table IV.

The fibrous crystals of polyethylene can be obtained by dissolving the polymer in a single solvent, in this case *p*-xylene, and stirring at 100°C, that is below the solubility temperature of the crystals. Similarly, one might dissolve polyamide 6 in, for instance, 1,4-butanediol at 160–170°C and stir the solution at a somewhat lower temperature. However, at these high temperatures, the polyamide 6 will—like in any other solvent—be seriously degraded. We have chosen therefore the “good” solvents formic acid and *m*-cresol. These single solvents cannot be deep-cooled to worsen the solvent quality as they solidify at, respectively, 8° and 11°C. The use of solvent/nonsolvent mixtures appears to be the only way to obtain fibrous material from polyamide 6 by stirring-induced crystallization.

Mechanism of Fiber Formation

As mentioned previously, the UHMW PA 6 solutions to be stirred must be unstable. In such solutions, separation into a polymer-rich and a polymer-poor phase occurs in the course of time. The polymer-rich phase contains more or less perfect UHMW PA 6 crystals.

The generation and growth of these crystals are rather slow (see Fig. 2). It turns out that stirring the solution accelerates these processes, and fibrous material develops in the form of a fiber mat. The following molecular process steps for the formation of the fiber mat may take place repeatedly: collision, extension, crystallization, recoiling, and entangling. Enhancement of the collision frequency in a shear field can be visualized in the following way. If one goes from one flow layer to the next one in the direction perpendicular to the velocity, the molecules in such adjacent layers will pass one another more frequently as the velocity gradient is higher, thus leading to a greater collision probability. The effectiveness of the collisions will be enhanced by two

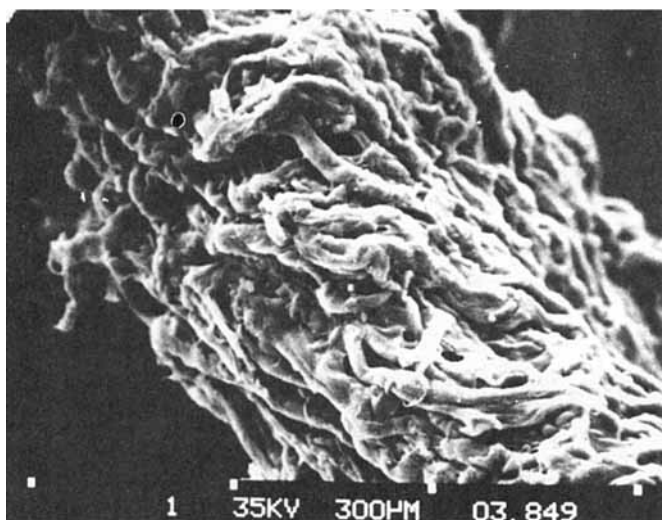


Fig. 9. Scanning electron micrograph (SEM) of UHMW PA 6 fiber. Stirring rate 135 rpm.

phenomena: (1) flow-induced crystallization and (2) formation of entanglements.

In a turbulent flow, which is certainly the case when the solution is agitated with a paddle stirrer, macromolecules are highly extended.^{13,14} The free energy of the originally coiled molecules increases when they adopt an extended conformation.¹⁵ The higher free energy induces crystallization of polymer chain segments when they come into contact with one another, causing the molecules to fuse together.

When the macromolecules leave an eddy and enter a domain with a lower velocity gradient they will recoil and become entangled. In the unstable solution the chains will attempt to crystallize around the entanglements.¹⁶

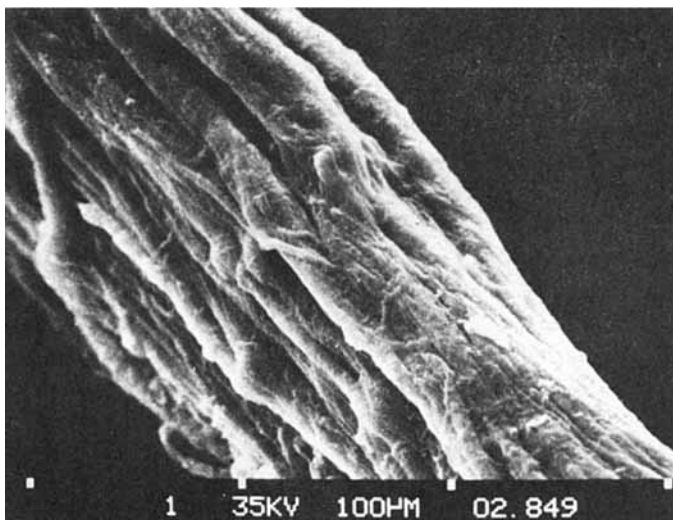
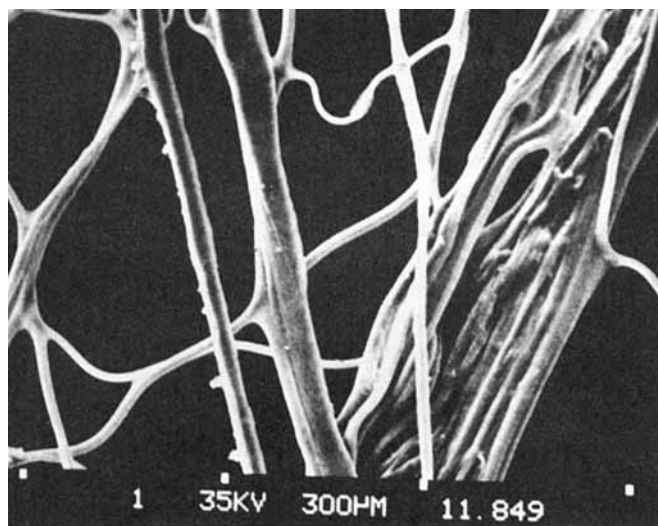


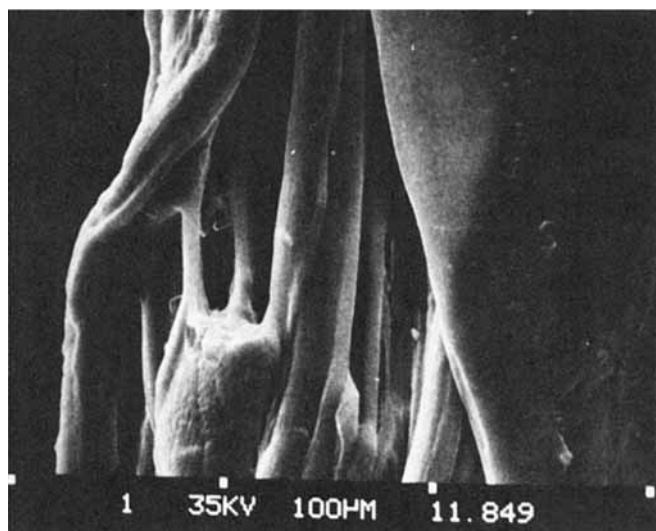
Fig. 10. SEM of UHMW PA 6 fiber. Stirring rate 850 rpm.

According to the mechanisms described above, clusters of molecules are formed, which grow to larger gel particles. Molecules below a certain size do not produce sufficient crystallites and entanglements to withstand high shear stresses. Therefore, the relatively small molecules are excluded from effective collisions and fractionation takes place. Polymers with a $M_w < 250,000$ were found to be incapable of forming fibrous material, as the formed gel breaks down in smaller fragments at high shear stress.

It has been observed that freshly formed filaments are transparent gels. The molecules in the gel may be interconnected by crystallites and entanglements. In the course of time the fibers become opaque, pointing to further crystalliza-



(a)



(b)

Fig. 11. (a and b) SEM's of UHMW PA 6 fibers, stirring rate 1500 rpm

tion of the material. The way in which a cluster of molecules grows to a gel and subsequently to a fiber may be derived from scanning electron micrographs (SEM) [Figures 9, 10, and 11(a) and (b)]. They show fibers made at different stirring rates. To obtain fibrous material at a stirring rate as low as 135 rpm (Fig. 9), continuous stirring (for about 20 h) was necessary. The fiber is composed of small "subfibers" with a diameter of 10–30 μm . In the fiber made at 850 rpm (Fig. 10), the subfibers approximately have the same range of diameters. These subfibers, however, are more aligned in the direction of the fiber axis. The better alignment is certainly due to the higher shearing stresses applied on the fiber during stirring. Fibers made at a stirring rate of 1500 rpm are shown in Figures 11(a) and (b). Figure 11(a) shows a fiber mat which has deliberately been torn apart after its formation. Figure 11(b) illustrates the branches in an irregular fiber. The surface is rather smooth compared with the fiber made at 850 rpm (Fig. 10). The better alignment of the fibers at higher shear stresses is accompanied by the formation of more perfect and maybe larger crystals. This leads to melting points of the fibrous material which increase with increasing stirring velocity, as mentioned above (see Figs. 6 and 7). From the SEM pictures one can assume a mechanism for the development of fiber mats. A cluster of molecules or a gel may contain chain segments that are dangling in the solution. If the dangling part of a molecule is long enough, it can form entanglements and crystallites with individual molecules or clusters. This may lead to a branched growth of the gel as shown in Figure 11(b). Further growth finally gives a mat of irregular fibrous material. Finally, Figure 12 is a SEM of the surface of a fiber developed at 1500 rpm. The porous surface appears to be composed of knobs interconnected by short sticks. The knobs have a diameter of 50 nm, that is, the order of the

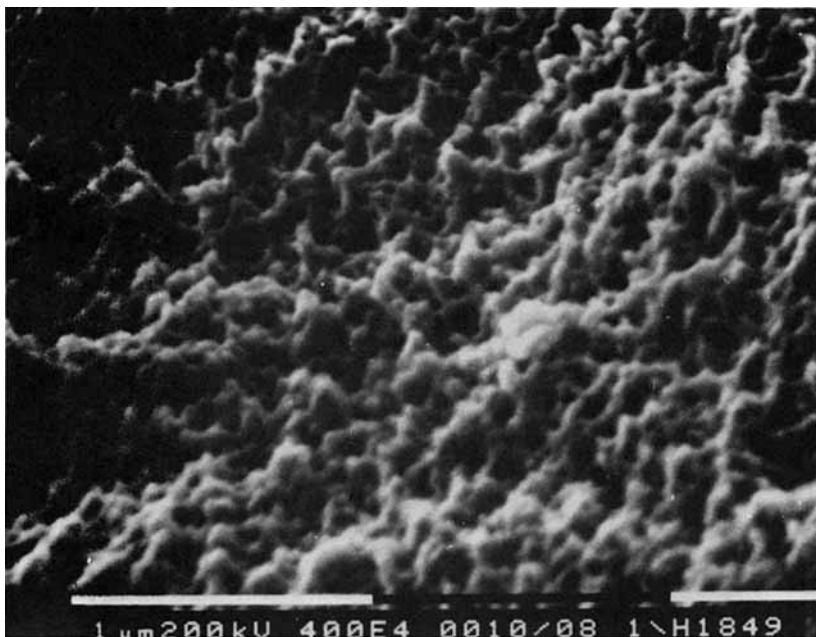


Fig. 12. SEM of a fiber surface, developed at 1500 rpm.

dimensions of the folded-chain crystals in the shish kebab structure of polyethylene.¹ In spite of the more perfect or larger crystals in the fibers made at 1500 rpm, the knobs do not look like well-ordered crystals. This may be due to the strong hydrogen bridges in PA 6; once they are formed, they cannot be easily disrupted and thus prevent the arrangement to highly ordered crystal structures.

The authors gratefully acknowledge the valuable suggestions made by Prof. Dr. A. J. Pennings. The many discussions with our colleagues have been of great assistance for both of us. We are much indebted to Mr. J. L. Markhorst, who synthesized the UHMW PA 6 samples and also performed the molecular weight determinations. Thanks are also due Mr. H. J. W. Elzerman for supplying the scanning electron micrographs.

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Received July 21, 1987

Accepted November 4, 1987