A new drawing technique for nylon-6 by reversible plasticization with iodine

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(Received 28 December 1984)

A new technique to draw nylon-6 is developed by using iodine as a reversible plasticizer. This is based on the ability of the α-crystals to transform fully to γ-crystals by treatment with an aqueous KI_3 solution. Drawing is performed on the intermediate nylon-6-I complex and iodine is subsequently removed with sodium thiosulphate to generate back a transparent, drawn nylon-6. At 55°C, a 790% elongation has been obtained, considerably higher than previously reported for nylon-6. A dynamic mechanical study of the undrawn complex showed an α-transition at 41°C–53°C. Above this temperature, it is rubbery and can be easily stretched. Wide-angle X-ray diffraction scans show the complete disappearance of nylon-6 crystalline peaks, indicating a fully amorphous structure. Drawing of the complex produced new diffraction peaks, implying a strain-induced crystallization to a new crystal structure. This new structure is shown to be monoclinic with the a-axis expanded to 17.2 Å to accommodate iodine intercalated between the nylon-6 chains.

(Keywords: drawing; nylon-6; iodine; crystals; complex; plasticization)

INTRODUCTION

Of the important commerial thermoplastics, nylon-6 is among the most difficult to draw to high ratio and tensile modulus. Generally, drawing processes result in a maximum draw of about 5, comparing this with polyethylene which can be drawn 250× leading to a remarkable reported tensile modulus of 222 GPa[1]. The highest reported modulus of drawn nylon-6 is 14 GPa[2], only a small fraction of its calculated theoretical modulus of 262 GPa[3]. Nylon-6, however, has a high melting point of 225°C; a high modulus nylon-6 would therefore potentially have a much wider temperature range application than a high modulus polyethylene would. An advancement in ultra-drawing nylon-6 thus represents a challenge.

The inability to ultra-draw nylon-6 is largely due to the presence of intermolecular hydrogen bonding between adjacent amide groups[4]. Hydrogen bonds exist in both crystalline and amorphous regions and have an activation energy of $\sim 8\ \mathrm{kcal\ mol^{-1}}$. They act as quasi-crosslinks, inhibiting the sliding of chains along the hydrogen bond plane during drawing. Drawing thus occurs mainly in the softer amorphous phase. With strain-induced crystallization, drawing is further restricted.

As a result, special processes have been developed to improve the ductility of nylon-6. One of these is a reversible plasticization concept that involves imbibing nylon-6 with liquid ammonia[5] which is subsequently removed after solid-state coextrusion. The plasticizer, therefore, does not have any deleterious effect on the final properties of the drawn polymer. However, plasticization with liquid ammonia occurs only in the amorphous phase[6], with crystals still inaccessible to drawing. In this work, we pursue the reversible plasticization concept using iodine as a plasticizer for entry in both amorphous and crystalline phases.

Nylon-6 is polymorphic and exists in several crystal forms, the most important of which are the α- and γ-crystals. Both have monoclinic unit cell structure with difference in the direction of hydrogen bonds between adjacent chains. The α-crystal has hydrogen bonds between antiparallel chains whereas the γ-crystal has bonds between parallel chains. It has been reported that a transformation of the α- to γ-crystals can be achieved by treatment with an iodine and potassium iodide solution followed by iodine removal by titration with sodium thiosulphate[7]. The crystal transformation is complete in both undrawn and drawn nylon-6, and without a loss of orientation[8]! This crystal transformation implies that the hydrogen bonds in both the amorphous and crystalline phases in the intermediate iodine complex must be disrupted to allow chain rotation and a mobility to generate the γ-crystals. With this as a basis, we developed a method for drawing the nylon-6–iodine complex. The iodine acts as a reversible plasticizer and is removed after drawing by titration with sodium thiosulphate solution to generate back nylon-6 of controlled crystal forms.

EXPERIMENTAL

Nylon-6 film ($[\eta] = 1.04$ in 85% formic acid) was used as obtained from Dr T. Kunugi of the University of Yamanashi, Japan. The film was 130 μm thick: it is isotropic with no measurable birefringence and of γ-crystal form. Annealing of this film at 200°C for 3 h converts the γ-crystal to α-crystal. It was found that both the α- and γ-nylon-6 readily absorbed iodine and the complexes of both showed similar drawing behaviour. The unannealed γ-nylon-6 was used for study.

The complex was prepared by immersing the nylon-6 film in 1N KI_3 solution for 48 h at room temperature. It was then air dried. Stress–strain measurements were made

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with an Instron tensile tester, equipped with environmental chamber, at strain rate 0.01 $\min^{-1}$. Dynamic mechanical measurements were made using a Toyo Dynamic Viscoelastometer Model DDV-II.

Wide-angle X-ray scan of the complex was obtained with a Siemen D-500 diffractometer equipped with scintillation counter, operating at 30 mA, 40 kV and using a CuKα radiation with Ni filter. Scanning was made on undrawn complex and at increasing elongation with a stretcher attachment in the diffractometer at room temperature.

Photographic techniques using a Statton flat film with 5 cm sample-to-film distance and a Weissenberg camera of 57.3 mm diameter were used to supplement the diffractometer data.

RESULTS AND DISCUSSION

Although the transformation of α-crystal of nylon-6 to the γ-form by treatment with aqueous KI_3 solution has been reported as early as 1958[9], previous studies emphasized the determination of the γ-crystal structure[10–12] and on the mechanism in which it is generated. We review here the mechanism that has been proposed since this new drawing technique is based on the chain mobility of the complex outlined in the mechanisms.

Frayer, Koenig and Lando[13], noting the structural arrangement of the α- and γ-nylon-6 chains, suggested that if the tight amide folds at the lamellar surface act as pivots and with alternating chains in the α-form rotated 180°, the methylene groups will then match properly and with the amide groups twisted in proper direction to form hydrogen bonding between parallel chains, a γ-structure will be obtained. Such a proposal involved large scale movement of the chains and the breaking and remaking of hydrogen bondings; however, it did not consider the role of iodine in the transformation.

Arimoto[12] proposed a mechanism involving iodine entering the crystalline region and coordinating with the oxygen of the amide group to form a complex. Such coordination destroys hydrogen bonds and the amide group is preferentially twisted out-of-plane with respect to the fibre axis. On removing iodine, hydrogen bonds form between the nearest amide groups in parallel chains giving a pleated sheet γ-structure.

An alternate mechanism involving I_3^- ion was proposed by Matsubara and Magill[14] from infra-red study of the complex. Their study also used *N*-methylacetamide–iodine complex as a model and led to the same conclusion as Doslocilova and Schneider[15] that the triiodide ion is coordinated to the nitrogen of the amide group with protonation of K^+ or H^+ ions at the oxygen atom.

The above mechanisms were further reviewed by Abu-Isa[16] who found that when a thin nylon-6 film is exposed to iodine vapour alone, the infra-red spectrum obtained is similar to that of the complex obtained from KI_3 solution treatment, except in the degree of severity. Complex formation with iodine vapour alone, though, is possible but proceeds very slowly. This finding suggests that molecular iodine is capable of complex formation. We are not aware of further studies to substantiate whether molecular iodine or I_3^- ion is involved in the complex formation with nylon-6.

Arimoto[17] also found that when non-polar solvent KI_3 solution is used, the amount of absorbed iodine was very much smaller than those in polar solvents at the same iodine concentration. Matsubara and Magill[14], however, found that the i.r. spectra was unaffected. It is well known that when iodine dissolves in a polar solvent, it complexes with the solvent to give a brown solution of I_3^- ions in equilibrium with I_2, whereas it dissolves in non-polar solvent to give purple solution of molecular iodine[18]. From these studies of solvent effect, the ability of nylon-6 to absorb strongly and to produce significant change in the i.r. spectra only in a polar solvent indicates, though not conclusively, that I_3^- ion is largely responsible for the complex formation.

Even though none of the above mechanisms are satisfactorily confirmed, it is certain that hydrogen bonds in both crystalline and amorphous regions are interrupted and there is considerable chain mobility in the nylon-6-I complex during the transformation. Using this idea, a new reversible plasticization method of drawing nylon-6, with the possible unravelling of chains from previously unaccessible crystalline regions may be developed to give high draw ratio. Iodine can then be subsequently removed by reacting with sodium thiosulphate solution. The temperature and solvent used in the reaction determine the type of crystal, α or γ formed finally[16]. Using water/ethylene glycol mixture at below 35°C, γ-crystal is formed. Above 50°C, α-crystals are formed, whereas between 35°C–50°C, a mixture of both crystals is reported. The reaction condition can thus be used to control the type of crystals desired in the drawn nylon-6.

Drawing and mechanical properties

The wet complex film immediately after treatment in an aqueous KI_3 solution is swollen and soft. It can be easily stretched by hand and shows necking. A stress–strain curve of such film tested with an Instron tensile tester at room temperature is shown in *Figure 1*. It has a very low yield stress of 5 MPa and necks at 20% elongation. It strain hardens on further stretching and breaks at 550% elongation with a strength of 16 MPa. It is remarkable to note that complexing with iodine changes drastically the drawing behaviour of nylon-6. A stretched, wet film, on releasing the load, will retract slightly from elastic recovery and contraction from deswelling on solvent evaporation.

A dried complex film is however very much stiffer. To help determine the temperature range for effective drawing, dynamic mechanical properties were measured

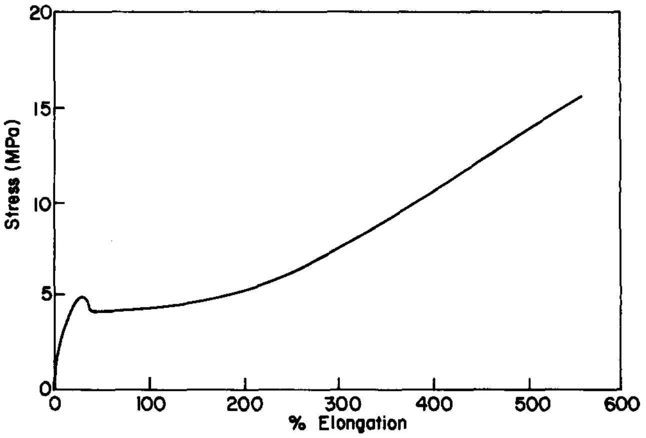


Figure 1 Stress–strain curve of a wet nylon-6-I complex film, tested immediately after immersing in 1N aqueous KI_3 solution for 48 h

with a Rheovibron at three different frequencies of 11, 35 and 110 Hz. Plots of dynamic mechanical loss tan δ results are shown in *Figure 2*. The curves at 35 and 110 Hz are displaced vertically for visualization. Two loss peaks are found for the complex. A small peak occurs at about $-40°C$; its maximum does not shift appreciably with change of frequency. The second loss peak is of much higher magnitude, with maximum tan δ of 0.2. The maximum occurs at 41°C at 11 Hz, increasing to 53°C at 110 Hz. Up to 60°C, the results are reversible. However, above 80°C, the complex shows irreversible viscous flow.

In an untreated γ-nylon-6, dynamic mechanical study gives three relaxation peaks[19]. The highest α-relaxation is the glass transition, T_g, which is 80–90°C. T_g of nylon-6 is strongly influenced by water content, which can reduce it drastically. β-Relaxation occurs at $\sim -40°C$ and is associated with the presence of water. Its magnitude decreases when water content in nylon-6 is reduced. The γ-relaxation of crankshaft motion of the methylene chains in the amorphous phase at $\sim -120°C$ is, however, not observed for the complex. Thus, comparing the dynamic mechanical properties of the complex with those of γ-nylon-6, we identify the relaxation temperature at 41°C of the complex as the α-relaxation which has been depressed by the plasticizing effect of iodine and the presence of some water as is evidenced from the appearance of a small β-relaxation peak. The α-relaxation of the complex is also detected in a differential scanning calorimeter (d.s.c.), which shows prominent second order transition at a lower temperature of 32.5°C.

From the maxima of tan δ curves, log$f$ (frequency) is plotted against the reciprocal relaxation temperature, $1/T$, (*Figure 3*) to give the Arrhenius activation energy ΔH_a of 17 kcal mol^{-1}. Kunugi[20] reported from the stress relaxation of oriented nylon-6 that the Arrhenius plots of shift factor were represented by two straight lines having a break point at 80°C–110°C, corresponding to the temperature of the breakdown of hydrogen bonds in the amorphous region. ΔH_a above this temperature range was 17 and 33 kcal mol^{-1} for nylon-6 drawn 3- and 4-fold respectively. A value of 34 kcal mol^{-1} was also reported by Hoashi and Andrews[19]. The measured ΔH_a for the complex is low compared with the reported values. This low ΔH_a implies greater molecular chain mobility. By analogy, this must be resulting from the plasticizing effect of iodine with the interruption of intermolecular hydrogen bondings.

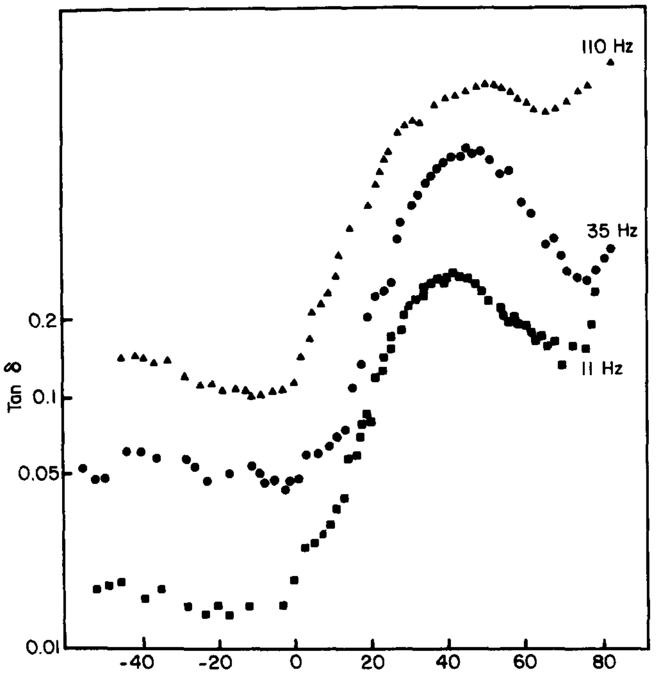


Figure 2 Loss factor tan δ for undrawn nylon-6-I complex at frequencies 11, 35 and 110 Hz

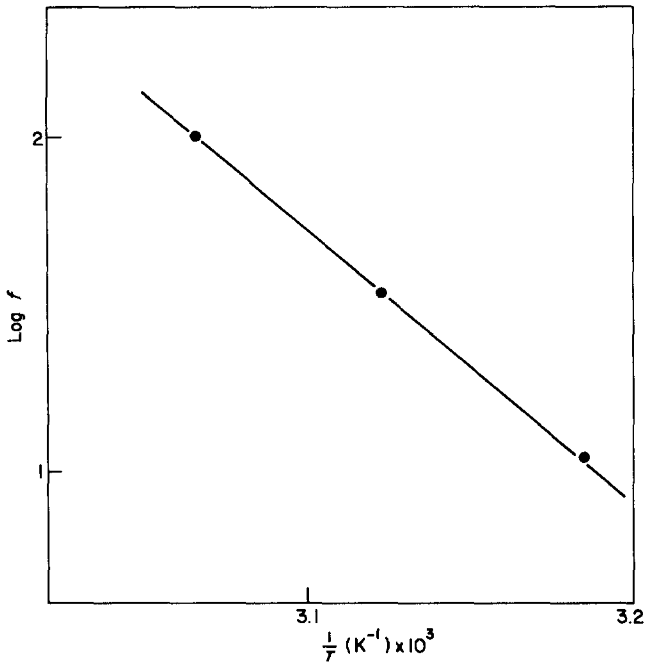


Figure 3 Arrhenius plot of log$f$(frequency) vs. $1/T$ for undrawn nylon-6-I complex

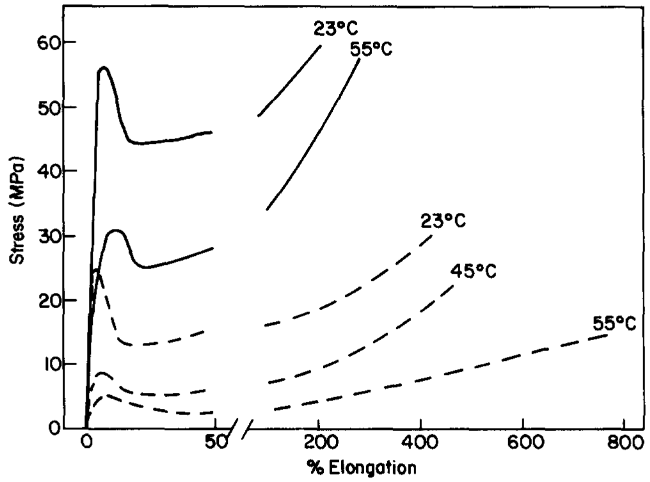


Figure 4 Stress–strain curves for γ-nylon (solid lines) and nylon-6-I complex (broken lines) at temperatures below and above the α-relaxation of the complex

Figure 4 shows the stress–strain curves of nylon-6 and its iodine complex at temperatures below and above the α-relaxation. The solid lines are nylon-6, which shows high yield stress of 55 MPa and breaks at 180% elongation at room temperature. Increasing the draw temperature to 55°C lowered the yield stress but did not increase the elongation at break appreciably. At room temperature, the yield stress of the complex is comparatively low, 24 MPa, and decreases with increasing temperature. At 55°C, the complex shows rubbery behaviour and elongates to 790% before breaking. This is a much higher draw than is possible for an untreated nylon-6. Drawing behaviour at 55°C is very similar to drawing of the wet complex at room temperature (*Figure 1*) except in the higher elongation at break. Thus the presence of water provides an additional plasticizing effect. Above 80°C, the complex exhibits viscous flow; drawing does not produce signification orientation.

Table 1 lists the modulus, % crystallinity from d.s.c. and crystal orientation function, f_c obtained from complex drawn and washed under fixed length with sodium thiosulphate solution at room temperature. Removal of iodine under this condition gives γ-crystal form. The orientation function was obtained from the azimuthal scan of the (020) reflection in a wide-angle X-ray diffractometer. Orientation produced is high with $f_c > 0.978$. For a perfect orientation, $f_c = 1$. For drawing at room temperature, draw ratio and modulus obtained are comparable to reported values from drawing at elevated temperature. Drawing at 55°C gives higher draw of 7.5 × with relatively high modulus of 6.0 GPa. % crystallinity in all cases increases by 15–27% from the 27% crystallinity of initial untreated nylon-6.

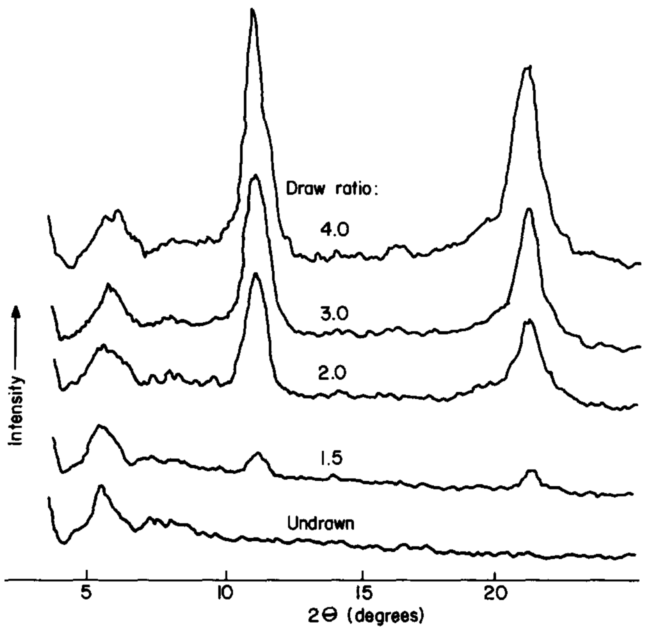


Figure 5 Wide-angle X-ray diffractometer scan of an undrawn nylon-6-I complex and at increasing draw ratio at room temperature

X-ray diffraction studies

Wide-angle X-ray diffractometer scan of the undrawn complex is shown in *Figure 5*. A single weak, broad new peak at $2\theta = 5.3°$ (d-spacing = 16.7 Å) is obtained. This new peak is observed for complex regardless of the starting nylon-6 being α- or γ-form. In α-nylon-6, strong (200) and (002 + 202) diffraction occurs at $2\theta = 20.2°$ and 24.0° respectively, and γ-nylon-6 has (200) and (002) diffractions at $2\theta = 21.8°$ and 22.7° respectively. All these crystalline peaks are absent in the complex, which is proof of the disruption of crystallinity and implies that iodine or I_3^- ion goes into both amorphous and crystalline phases, likely due to the ability to complex with the amide groups as a driving force.

On drawing the complex, weak diffraction peaks appear at $2\theta = 11.43°$ and 22.93°. Neither of these two new peaks are related to the crystalline peaks of the parent nylon-6. Their intensities increase with drawing, becoming very strong at draw ratio 4. The low angle peak at $2\theta = 5.3°$ also shifts slightly to higher angle of 5.6°. The appearance of these new diffraction peaks is unique for the nylon-6-I complex, whether initially an α- or γ-nylon-6 is used. Thus the complex has a unique structure of its own. From the d-spacings, the 22.93° peak is a second order diffraction of the 11.43° peak. This diffraction has also been observed for both iodine-doped *cis*- or *trans*-polyacetylene and is characteristic of iodination[21]. The spacing is reasonably close to the sum of the spacings of the most intense diffractions in the precursor polyacetylene and the van der Waals diameter of iodine, and was suggested to be the interplanar spacing between iodine layers separated by a close-packed plane of polyacetylene. However, we observe more diffractions for the drawn nylon-6-I complex to index differently.

Table 1 Properties of drawn γ-nylon-6 after removal of iodine with sodium thiosulphate solution at room temperature

Draw temperature (°C)	Draw ratio	Modulus (GPa)	Crystallinity (%)	Orientation function f_c
23	3.5	3.4	42.2	–
23	4.0	3.9	44.9	0.978
23	4.5	4.1	43.3	0.984
23	5.3	4.5	44.3	0.987
55	7.5	6.0	53.9	0.985

The appearance of the low-angle peak in the undrawn complex at $2\theta = 5.3°$ is significant. It has a d-spacing of 16.7 Å and provides intermolecular chain information without going into more detailed radial distribution function. Taking the van der Waals radii of the methylene groups in the nylon-6 chain as 2.0 Å and that of iodine or ionic radius of I_3^- as 2.15 Å,[22] the packing of iodine between nylon-6 chains give a dimension of 8.4 Å. If this is repeated at the adjacent chain, the total dimension would be 16.6 Å, close to the observed d-spacing. An alternating arrangement of iodine and nylon-6 chains can be surmised. Intercalation of iodine between chains would most likely have occurred between the hydrogen bond planes. For an α-nylon-6, this is the (001) plane with 8.01 Å spacing, for γ-nylon-6, this plane is (100) and the spacing is 9.33 Å. When iodine or I_3^- ions are intercalated between the hydrogen bond planes, c-axis of α-nylon-6 will expand to 16.61 Å and a-axis of γ-nylon-6 will expand to 17.93 Å. The first dimension is close to the observed d-spacing while the latter is greater by 1.23 Å. The γ-nylon-6 has a less close-packed structure with packing density of 0.707 compared with 0.75 for the α-crystal[23]. Since we observe the same d-spacings for both their complexes and therefore possibly the same complex structure, the complexing of iodine or I_3^- ion with the γ-nylon-6 amide groups could cause closer packing and slight reduction in the van der Waals radii, and therefore a smaller dimension for the expanded a-axis than would be expected from simple addition. Therefore intercalation between the hydrogen bond planes is very likely in the complex formation. Since there is only one weak reflection indicating lateral packing of iodine alternation between nylon-6 chains, the undrawn complex has a mesomorphic structure.

Figure 6 shows the rotation photograph of a complex drawn 4 ×. Three layer lines are found with a fibre identity

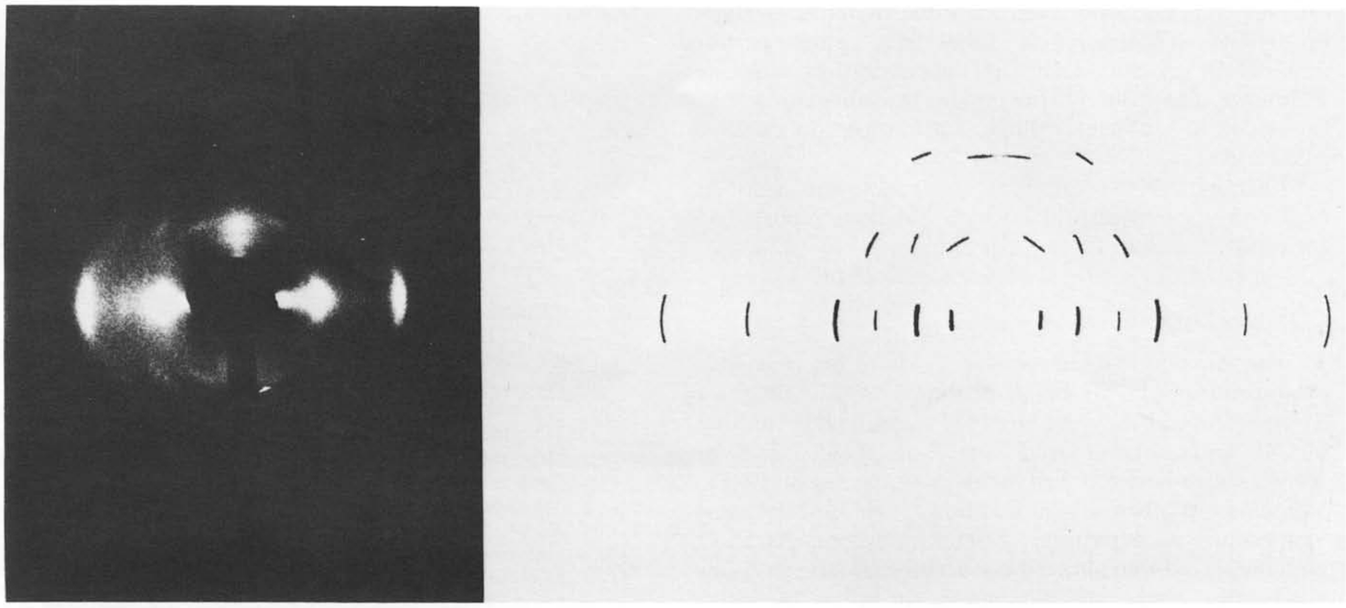
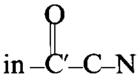


Figure 6 Rotation photograph of a nylon-6-I complex drawn 4×

period of 16.66 Å. This is the repeat distance of the chain axis and is equivalent to two monomer units. Using standard bond angles and distances, a fully extended planar zig-zag nylon-6 monomer unit is 8.7 Å. Rotation of the amide group about C′–C bond in  $-\overset{\overset{\displaystyle O}{\|}}{C'}-C-NH-$ out-of-plane by 69° for two monomer units gives this observed identity period. This rotation is 2° more than that reported for a γ-nylon-6[10]. Because of the rotation of the amide groups, the layer line corresponding to 8.33 Å spacing was not observed. The observed reflection can be indexed with a monoclinic unit cell with $a = 17.2$ Å, $b = 16.66$ Å, $c = 8.52$ Å and $\beta = 115°$ (*Table 2*). The a-axis of the original γ-nylon-6 expands to accommodate the intercalation of iodine or I_3^- ion. Because of complexing between amide groups with iodine or I_3^-, the amide group is twisted out-of-plane, shortening the chain axis and changing the interaxial angle. *Figure 7* shows a space filling model of one quarter of the unit cell viewed in the a–c plane. When the setting angle of the nylon-6 chain is 5°, iodine with van der Waals radius of 2.15 Å can be accommodated easily between the chains.

The undrawn complex shows lateral order with mesomorphic structure. Only on drawing, the complexed chains are forced to align giving a more well defined structure with definite fibre identity period. Iodine, being a heavy atom, is a very strong scatterer and dominates the observed intensities. Higher order reflections are observed indicating a high degree of regularity in the intercalated iodine. Here we do not observe the 3 Å periodicity of polyiodide as reported for poly(vinyl alcohol)–iodine complex[24] and iodine-doped polyacetylene[25]. The intercalated structure proposed here can be found in many complexes. An example is the detailed structural study of benzamide–iodine complex[26], which has I_3^- ion inserted between the benzamide dimers. The present proposed structure, though without in-depth study such as exploiting the possibility of the heavy iodine atom to do Patterson mapping, does depict the structure developed during strain-induced crystallization of the complex.

Table 2 Comparison of observed and calculated d-spacings for a nylon-6-I complex drawn 4×

	d-Spacing (Å)		
(hkl)	Observed	Calculated	Intensity[a]
100	15.56	15.57	m
300	5.20	5.20	w
001	7.73	7.73	vs
002	3.88	3.87	s
003	2.58	2.58	w
004	1.94	1.93	vw
120	7.43	7.35	m
220	5.69	5.69	w
021		5.67	
320	4.41	4.40	w
140	4.09	4.02	w
041	3.66	3.66	vw

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak

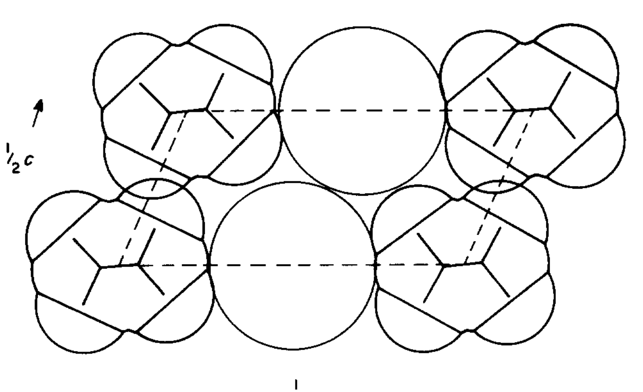


Figure 7 Space filling model of one quarter of the proposed structure in a–c plane, showing iodine intercalated between nylon-6 chains

Application to other nylons

The reversible plasticization technique proposed here can also be potentially applied to other nylons. Arimoto[17] and Matsubara and Magill[14] had extensively studied complex formation by several nylon compositions. They found that crystal transformations occur only for even–odd, odd–even and some ω-amino acid type of nylons. These nylons thus have potential for application of the reversible plasticization drawing technique. Even though the crystal transformation may not occur, this iodine technique may yet be applicable to other nylons.

Other possible reversible plasticizers can also be explored, such as phenol[19] which has been reported to transform the γ- to the α-form of nylon-6.

CONCLUSIONS

A new drawing technique for nylon-6 by reversible plasticization with iodine is proposed. A 130 μm thick nylon-6 film was immersed in a 1N aqueous KI_3 solution for 48 h. The complexed film was then drawn at temperatures between 23°C and 55°C, corresponding to temperatures below and above the α-relaxation temperature as determined from Rheovibron. At 55°C, the complexed film showed rubbery behaviour with low yield stress and high elongation at break of 790%, therefore, a much higher draw possible for nylon-6. The drawn film was washed with sodium thiosulphate solution at room temperature to remove the absorbed iodine, giving a highly oriented γ-nylon-6 with $f_c > 0.978$. Wide-angle X-ray measurements showed that the crystallinity of original nylon-6 was destroyed with the development of new diffraction peaks, giving evidence of plasticization of both the amorphous and crystalline phases. The complex showed strain-induced crystallization giving new diffraction peaks corresponding to a monoclinic structure. The a-axis expanded to 17.2 Å, a dimension sufficiently big for iodine to intercalate between the nylon-6 chains.

ACKNOWLEDGEMENTS

We wish to express appreciation to the Office of Naval Research for the support of this research and Dr T. Kunugi for supplying the nylon-6 film.

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