

The Preparation and Properties of Poorly Ordered (Amorphous) Polyamide Films

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Synopsis

A poorly ordered film, easily stretched by hand and thin enough for infrared spectroscopic investigations, has been produced using a simple melt quenching technique. Drawing of samples has been shown to induce increases in molecular orientation with small increases in molecular order, and annealing has been found to decrease the extent of molecular orientation while increasing molecular order. The absorption of water has been found to induce similar changes to those brought about by annealing.

INTRODUCTION

Various workers have used solvent casting techniques¹⁻³ for the preparation of polyamide films. Modifications of this technique by Koshimo⁴⁻⁶ involved the initial casting of a film from solvent, followed by melt quenching in cold carbon tetrachloride. Other methods⁷ have used a mixture of Dry Ice and acetone as the quenching medium, while a blown film system and a melt pressing technique have also been used.⁸ This latter process involved the pressing of molten polyamide between stainless steel plates which had previously been coated with a thin layer of silicone oil to prevent polymer adhesion. When this process was followed by quenching, a much less well-ordered specimen resulted.⁹ Many variations on such methods have been reported, one of which describes the use of PTFE-coated plates for pressing the polyamide samples.¹⁰

EXPERIMENTAL

Films cast by the above methods in this laboratory exhibited characteristics which showed that the experimental techniques used were not ideal. The method of production was found to influence the physical and structural characteristics of the polyamide film, and in practice the force required to draw such a film of a given thickness showed a considerable variation and was found to be governed by the production technique used. Some samples were easily drawn by hand, while others required such high forces as could only be obtained from industrial testing equipment. Films cast from solvents could not be drawn, and in every case film rupture immediately occurred on drawing.

X-Ray diffraction data and infrared spectra show the presence of highly ordered molecular regions within solvent-cast films, but such regions are randomly arranged. The x-ray diffraction photograph of an undrawn solvent-cast film of nylon 6 is shown in Figure 1. Diffraction patterns indistinguishable from this were also obtained from films produced by published methods.¹⁻¹⁰

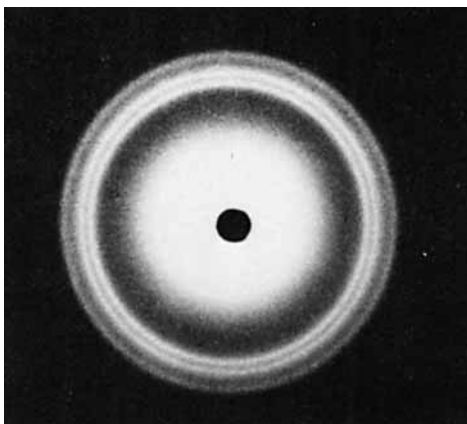


Fig. 1. X-Ray diffraction photographs of an undrawn solvent-cast film of nylon 6.

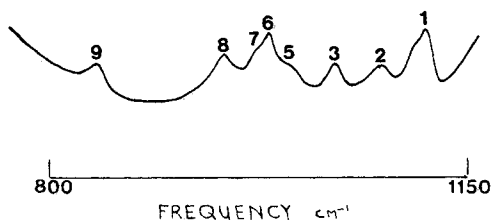


Fig. 2. Infrared absorption spectrum of an undrawn solvent-cast film of nylon 6.

The 0.38-, 0.36-, and 0.32-nm spacings are clearly visible as sharply defined rings, indicating a high degree of order and random molecular orientation within the film. This lack of molecular orientation was found in all undrawn films whichever method of preparation was used. In Figure 2, the corresponding infrared absorption spectrum recorded between 800 and 1150 cm^{-1} is shown. The main absorption peaks and their corresponding frequencies are listed below:

Peak number:	1	2	3	4	5	6	7	8	9
Frequency, cm^{-1}	1118	1075	1029	1002	974	959	952	928	836

Peaks 3, 6, 7, 8, and 9 have been assigned by the authors from work carried out in this laboratory,¹¹ and as yet unpublished, to crystalline or highly ordered regions of the film. These peaks are clearly shown in Figure 2.

On this basis, therefore, investigations were initiated to develop a more satisfactory method for the preparation of poorly ordered film samples.

Method

Nylon 6 was chosen as the first specimen. Pellets of nylon 6 were sandwiched between two pieces of aluminum foil, previously coated with a thin layer of Nujol to act as a lubricant, and this foil sandwich was inserted by hand between the jaws of the hydraulic press which had been preheated to 240°C using electrically heated jaw plates. A small part of the foil was left extruding from the jaws to facilitate removal from the press.

A pressure of approximately $2.5 \times 10^7 \text{ N m}^{-2}$ was applied to the sample, the total pressure being increased from atmospheric over a period of about 3 sec,

and this pressure was maintained for a period of 10 sec. When the pressure was applied for a longer period than this, sample discoloration indicative of degradation occurred; and if a shorter period was used, air pockets were found to be trapped within the sample film.

The foil protruding from the press jaws was gripped with forceps near to the end of the pressing period; and when the hydraulic pressure was released, the foil was rapidly transferred into a bath of liquid nitrogen placed adjacent and slightly below the aperture of the jaws. The time taken between removal of the pressure and removal of the sandwich from the jaws was estimated as 1 sec, while that involving removal and immersion in liquid nitrogen was approximately 0.5 sec.

Due to variations in the surfaces of the jaw plates of the press, film thicknesses were found, from optical techniques, to vary over the sample within the range 10 to 25 μm .

The procedure was repeated with other polyamides when, in each case, poorly ordered films were successfully produced.

RESULTS AND DISCUSSION

The x-ray diffraction photograph and infrared absorption spectrum of a nylon 6 film prepared by the above method are shown in Figures 3 and 4, respectively, which show considerable differences from Figures 1 and 2. In place of the three sharply defined rings seen in Figure 1, one diffuse ring with an approximate spacing of 0.36 nm is present in Figure 3. From the infrared

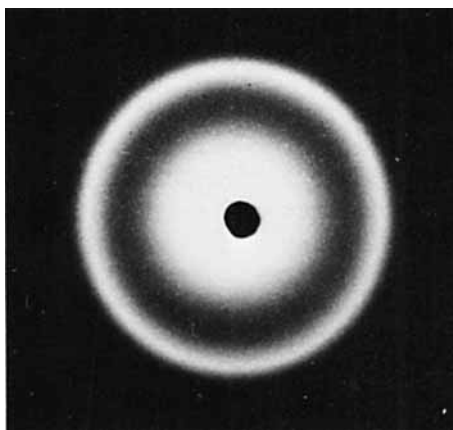


Fig. 3. X-Ray diffraction photograph of an undrawn "amorphous" film of nylon 6.

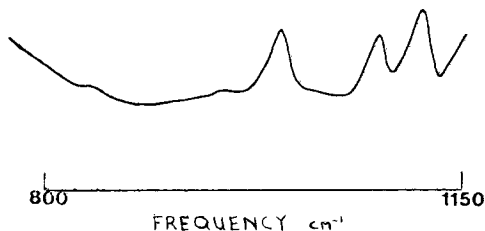


Fig. 4. Infrared absorption spectrum of an undrawn "amorphous" film of nylon 6.

absorption spectrum shown in Figure 4, we can see on comparison with Figure 2 that peaks 3, 6, and 7 have disappeared, while peaks 8 and 9 are much less intense. Since all of these absorption peaks have been shown to correspond to crystalline regions of the film,¹¹ the infrared spectrum indicates that a poorly ordered film has been prepared. It may be concluded from x-ray and infrared measurements, therefore, that the film exists in a state of disorder with poor molecular orientation.

In this preparative technique, air and moisture were removed from the foil "sandwich" during the heating and pressing, so that any tendency for oxidative degradation to occur was minimized. Nujol was chosen as the lubricant. The use of PTFE and silicone oil as previously reported⁸⁻¹⁰ were considered, but both were found to be unsatisfactory in tests carried out in this study. At the high temperature required, PTFE was found to degrade and turn brown, so that on quenching, the polyamide samples were found to be contaminated with degraded PTFE. Silicone oil, however, proved to be an efficient lubricant, but it was found from infrared data to be included in the polymer film produced. Figure 5 shows the infrared spectrum of a nylon 6 film prepared by the new technique, with the exception that silicone oil was used as a lubricant. On comparison with Figure 4, the strong absorption band of silicone oil centered near 1080 cm^{-1} is clearly in evidence.

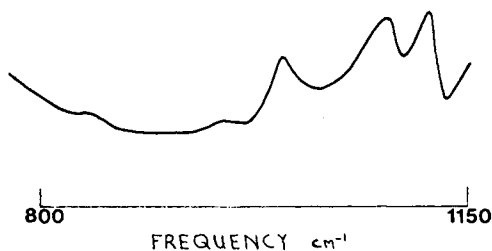


Fig. 5. Infrared absorption spectrum of an undrawn "amorphous" film of nylon 6 prepared using silicone oil as a lubricant.

The presence of Nujol could not be detected from infrared spectra, when this material was used in the preparation of polyamide films, and such spectra, as shown in Figure 4 for nylon 6, are identical to those of films prepared without lubricant. When no lubricant was used, only a 2% success rate in "amorphous" film preparation was achieved, since in most cases drawing of the polymer occurred during separation from the aluminum foil.

Efficient quenching is an essential part of the technique, since without it, regions of high molecular order are produced and the polymer film is difficult to stretch. X-Ray diffraction data of such poorly quenched specimens are similar to those shown in Figure 1 in which regions of high molecular order exist with random molecular orientation. Similarly, the infrared absorption spectrum of poorly quenched films shows a likeness to that shown in Figure 2. When liquid nitrogen is used for quenching, however, samples are produced which are more "amorphous" than those produced by any other quenching media. Solvent quenching was found from infrared examination to contaminate the films obtained.

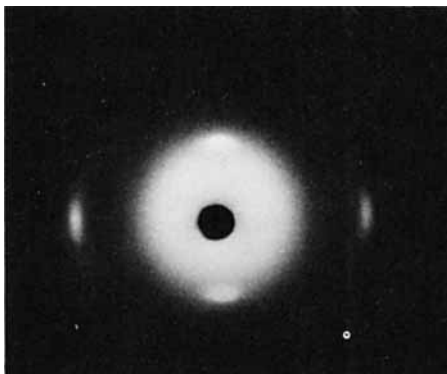


Fig. 6. X-Ray diffraction photograph of an "amorphous" film of nylon 6 drawn to 300% extension.

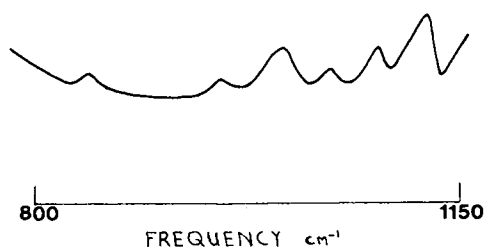


Fig. 7. Infrared absorption spectrum of an "amorphous" film of nylon 6 drawn to 300% extension.

Film Properties and Treatments

Drawing

The films produced by this technique are easily drawn by hand, and this induces "necking." When "necking" ceases, the films are found to have stretched approximately 300%, and any further extension can only be effected by the use of industrial testing equipment. During the drawing process, an increase in molecular orientation is brought about, together with a small increase in order within the films. Figure 6 shows the x-ray photograph of a film of nylon 6 drawn to 300% extension, when diffuse spots, which are clearly seen at 0.36 nm on the equator and 0.65 nm on the meridian, indicate an increase in molecular orientation. In addition, the corresponding infrared spectrum (Fig. 7) shows a small increase in the intensity of the crystalline peaks when the films are drawn by hand.

A drawn sample of nylon 6 film was examined using polarized infrared radiation, and the spectrum of the film was recorded for perpendicular and parallel polarization with respect to the draw direction in the film. The results of such measurements are shown in Figures 8 and 9, respectively. The crystalline peaks become better resolved, and it is notable from Figures 8 and 9 that crystalline peaks 3 and 6 are predominantly perpendicular, while crystalline peak 8 is almost wholly parallel in character. The weak band 2a at 1040 cm^{-1} , shown in Figure 9, which is only detectable in untreated samples when polarization studies are undertaken, also appears as a shoulder on peak 3 in Figures 10 and

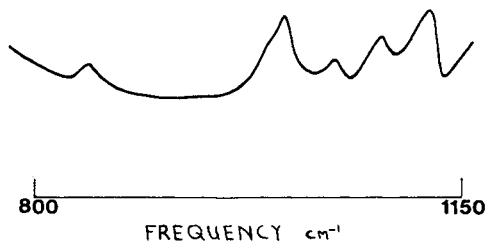


Fig. 8. Infrared absorption spectrum of an "amorphous" film of nylon drawn to 300% extension, recorded for perpendicular polarization with respect to the draw direction in the film.

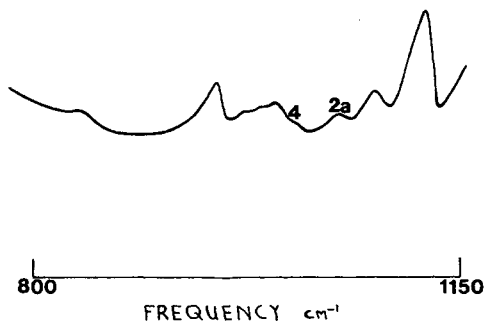


Fig. 9. Infrared absorption spectrum of an "amorphous" film of nylon 6 drawn to 300% extension, recorded for parallel polarization with respect to the draw direction in the film.

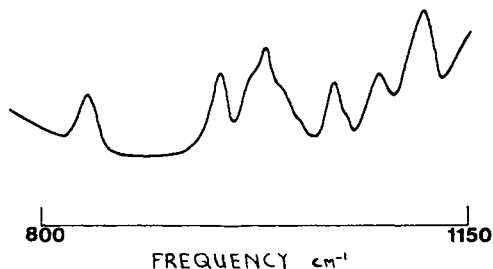


Fig. 10. Infrared absorption spectrum of an undrawn "amorphous" film of nylon 6, annealed at 200°C for 30 min.

11, which show the infrared spectra of annealed films of nylon 6. This band has been assigned along with peak 8 as a crystalline peak, which exhibits "parallel" dichroism.

The infrared absorptions of the "amorphous" films prepared by the method described above are initially nondichroic and exhibit spectra which are identical to that shown in Figure 4. However, small and apparently random differences in dichroism were measured in the spectral peaks initially, but these were related to the position from which the sample was cut from the disc of polymer produced during the melt quenching technique. Such differences were found to be more marked when the film preparation was carried out near the melting point of the polymer, and were due to the viscous streaming of the polymer from the position of the original chip on the application of pressure. Samples prepared at temperatures 20°C and above the melting point, however, did not exhibit this dichroism owing to the lower viscosity of the polyamide during the preparative technique.

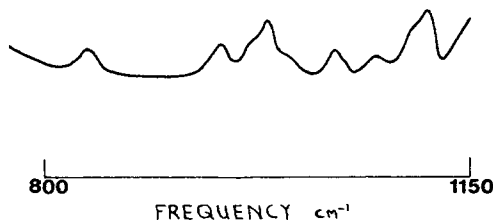


Fig. 11. Infrared absorption spectrum of an "amorphous" film of nylon 6 drawn to 300% extension and annealed at 200°C for 30 min.

Annealing

The annealing of drawn and undrawn film samples of "amorphous" nylon 6 produces an increase in order, but measurements of dichroism show no evidence of increase in molecular orientation. Figures 10 and 11 show the infrared spectra of undrawn and drawn films of nylon 6 annealed at 200°C for 30 min. It can be seen when Figures 4 and 10 are compared that the crystalline peaks 3, 6, 7, 8, and 9 exhibit an increase in intensity on annealing and that the crystalline peak 2a appears as a shoulder on peak 3, while the x-ray diffraction pattern of the undrawn annealed sample is similar to that shown in Figure 1. In addition, after annealing, the undrawn sample was found to exhibit little infrared dichroism. It is thus confirmed that the annealing process has induced the formation of regions of high molecular orientation. However, the infrared spectrum of an undrawn sample shown in Figure 10 is similar to that of Figure 2, and the x-ray diffraction pattern obtained from the same sample is identical to that obtained from samples produced by previously published methods.¹⁻¹⁰ Hence, it is clear that the annealing of samples prepared by the technique described in this paper induces a structure similar to that obtained from solvent-cast and melt quenching techniques described in earlier publications.

A comparison of Figures 2 and 11 indicates that there is little difference between the structure of solvent-cast films and stretched and annealed samples prepared by the method described here. Comparison of a spectrum of a drawn and annealed sample (Fig. 11) with that of a drawn sample (Fig. 7) indicates that all crystalline peaks increase in intensity on annealing. Measurements of dichroic ratios of drawn samples indicated that the dichroism of the oriented groups was not further enhanced by the annealing process, and in some instances the recorded changes indicated that a decrease in orientation had taken place. The increase in order after annealing is borne out by x-ray evidence, as shown in Figure 12, where a sharpening of the diffraction pattern in a drawn film is evident. Hence, the drawing process induces increased molecular orientation with a small increase in molecular order, as seen from increases in the intensities of crystalline peaks in Figure 7, while annealing increases the extent of molecular order in both drawn and undrawn samples while decreasing molecular orientation in the drawn samples.

Effects of Water

When a polyamide film is exposed to a moist atmosphere or soaked in distilled water, changes in the molecular order result.^{12,13} Experiments carried out in this laboratory indicate that the effect is more marked in "amorphous" undrawn

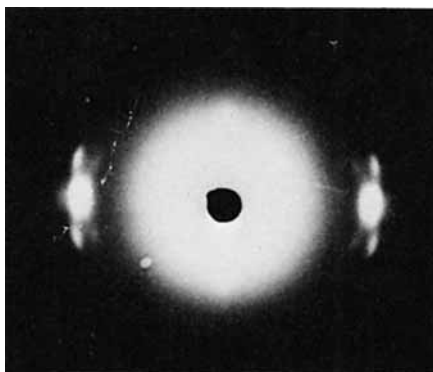


Fig. 12. X-Ray diffraction photograph of an "amorphous" film of nylon 6 drawn to 300% extension and annealed at 200°C for 30 min.

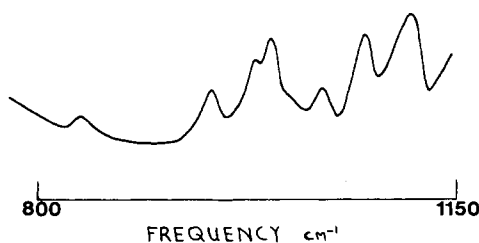


Fig. 13. Infrared absorption spectrum of an undrawn "amorphous" film of nylon 6 soaked in distilled water overnight followed by extended drying.

films than in annealed or drawn samples. Such induced changes are found to be irreversible and extended drying has little effect on the x-ray and infrared data. The original form can thus only be obtained on remelting and quenching of the film. The phenomenon of water absorption is considered to be associated with the rupture and reformation of hydrogen bonds, together with a reorientation of molecular chains, and it is evident that the water participates in this process.

Alcohols have been shown to induce the same effect, when again the changes brought about are irreversible. Figure 13 shows the infrared spectrum of an untreated "amorphous" film of nylon 6 which has been soaked in distilled water overnight, followed by extended vacuum drying over P_2O_5 at room temperature for two days.

On comparison of the spectrum of this sample with Figure 4, it can be seen that crystalline peaks 3, 6, 7, 8, and 9 have increased in intensity, which indicates that an increase in molecular order within the sample film has occurred. The x-ray diffraction pattern is similar to that of Figure 1 and hence confirms this analysis. Thus, the absorption of water by an "amorphous" sample induces the formation of a structure which is similar to that obtained from previously reported methods of film preparation. Such samples, after treatment in H_2O , exhibited little infrared dichroism, indicating that the water has little effect on the molecular orientation. On treatment of drawn samples with H_2O , a similar increase in crystalline peaks 3, 6, 7, 8, and 9 occurs. The corresponding x-ray diffraction pattern also shows increased resolution and indicates that an increase in order within the sample has occurred. As was the case when drawn samples were annealed, the absorption of H_2O by drawn samples decreased the extent of

dichroism and hence indicated that water absorption decreased the molecular orientation.

CONCLUSIONS

The above results indicate that the rate of sample quenching governs the structure of the polyamide film produced. While the preparation method described is based on an extremely rapid rate of quenching assisted by the low thermal capacity of the foil, it is also clear that sample preparation techniques described elsewhere⁴⁻¹⁰ allow the sample to anneal for a short period so that the resulting structures are similar to those of samples prepared by the method described in this paper and subsequently annealed. In addition, the absorption of water by the sample prior to examination is also shown to influence the extent of molecular order and molecular orientation. Clearly, therefore, the changes in the infrared spectra and x-ray diffraction patterns on annealing are dependent on the initial structure of the polymer, and previously reported results have been based on partially annealed samples in which water absorption may have occurred. Such variations in structure lead to anomalous deductions concerning absorption band origins, and this will be discussed in detail in a subsequent paper.

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