maximum in the gel permeation curve is at 3800. There are appreciable amounts of polymers at molecular weights of 1000 or lower that were not present in the original samples. This suggests that the limiting degree of polymerization depends on the initial molecular weight distribution and is either much lower than previously reported or perhaps non-existent.

ACKNOWLEDGEMENT

R. S. Porter expresses appreciation to the Army Research Office for support of US contribution to this study.

## REFERENCES

1 Casale, A., Porter, R. S. and Johnson, J. F. *Rubber Chem. Technol.* 1971, **44**, 534
2 Rodriguez, F. and Winding, C. C. *Ind. Eng. Chem.* 1969, **51**, 1281
3 Smith, W. H. and Temple, H. W. *J. Phys. Chem.* 1968, **72**, 4613

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# Variation of the glass transition temperature of nylon-6 with changing water content

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## INTRODUCTION

During the course of an examination of the effect of water content on the properties of nylon-6, it was found that the values quoted in the literature for the glass transition temperature of nylon-6 ($T_g$) varied considerably. The range of values quoted are summarized in *Table 1*. It was suspected that the disagreement between the values quoted was probably due to variations in the water contents of the samples tested. It was therefore decided to determine the $T_g$ of dry nylon and to examine the effect of water content on this parameter.

## EXPERIMENTAL

The material used was a commercial grade of nylon-6 in the form of moulding granules*. Samples having various water contents were prepared by exposing the granules to environments of known relative humidity (r.h.), for a period of six months. Granules in the 'as received' condition and 'dried' over silica gel were also examined. The environments were produced in closed vessels by the use of selected saturated (aqueous) solutions of common salts maintained at a fixed temperature, and, in the case of 'dry' conditions, silica gel. The weight percentage of water in each sample was determined by vacuum distillation[1].

*Table 1* Comparative table of literature values for the glass transition temperature of nylon-6

| Method | $T_g$ (°C) | Reference |
|---|---|---|
| Dielectric loss | −120 to −50 | 6 |
| Penetrometry | −66 | 7 |
| Sonic modulus | −50 and 70 | 8 |
| Mechanical loss | 37 | 9 |
| Infra-red absorption | 37 to 46 | 10 |
| Differential thermal analysis | 45 | 11 |
| Dilatometry | 41 to 54 | 2 |
| Mechanical loss | 65 | 12 |
| Dilatometry | 75 | 13 |
| Dielectric loss | 0 (wet), 75 (dry) | 14 |
| Dilatometry | 0 (wet), 75 (dry) | 14 |
| Viscoelastic properties | 91 | 15 |

The measurements of the $T_g$s of the samples were made using a dilatometric technique. The containing fluid used in the method was mercury. Volume expansion of the cell was measured both by heating and cooling at a rate of approximately 0.25°C/min. Several values for the point of inflection of the volume–temperature plots were obtained by repeatedly heating and cooling each sample. These values agreed to within ±1°C.

## RESULTS AND DISCUSSION

The results obtained are summarized in *Table 2*, in which the environment r.h., water content and $T_g$ for each sample are listed. From these data, a graph of $T_g$ against sample water content was constructed (*Figure 1*). This graph does not show the expected steady decrease in $T_g$ with increasing water content, but levels off between 2.5 and 5.0 (% w/w) water content. This plot is in agreement with the findings of Kaimin *et al.*[2] who ascribed this fall in the $T_g$ of the nylon-6 to the plasticizing effect of the water. However, Fox[3] has defined a plasticizer in terms of the following equation:

*Table 2* Effect of environment upon the equilibrium water contents and glass transition temperature of samples of nylon-6

| R.h. (%) | Water content (% w/w) | $T_g$ (±1°C) |
|---|---|---|
| (a) | 0.35 | 94 |
| (b) | 0.70 | 84 |
| 12 | 1.17 | 71 |
| 33 | 1.99 | 56 |
| 44 | 2.70 | 45 |
| 55 | 3.47 | 43 |
| 66 | 4.45 | 40 |
| 86 | 6.61 | 23 |
| 97 | 10.33 | −6 |

a, 'dried' over silica gel; b, tested as received

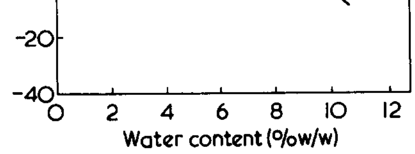

*Figure 1* Effect of water content on the $T_g$ of nylon-6

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* Akulon M2W, natural grade, manufactured by Akzo Chemie Ltd.

$$\frac{1}{T_g^s} = \frac{W}{T_g} + \frac{W^p}{T_g^p}$$

where $W$ and $W^p$ are the weight fractions of the pure polymer and pure plasticizer respectively, $T_g$, $T_g^p$ and $T_g^s$ are the glass transition temperatures of the pure polymer, pure plasticizer and plasticized sample respectively.

If the Fox equation applies, a plot of $1/T_g^s$ against $W^p$ would be a straight line. However, when a plot of $1/T_g^s$ against percentage water content was constructed (*Figure 2*), it was found to be non-linear. It is therefore apparent that the water is not behaving just as a simple plasticizer in nylon-6. This more complex picture tends to support the mechanisms proposed by Puffr and Sebenda,[4] Kawasaki and Sekita[5], for the interaction of water with nylon-6.

The plot illustrated in *Figure 2* shows three distinct regions. The central portion of this graph shows little change in the $T_g$ of the nylon-6 between 2.5 and 5% water content. Below 2.5% there is a rapid and almost linear increase in $T_g$ with decreasing water content. Similarly about 5% there is an apparently linear, but less rapid decrease in $T_g$ with increasing water content. By extrapolation of the initial linear portion of this graph to zero water content, a value of 100° ± 2°C was obtained for the $T_g$ of the dry nylon-6 granules.

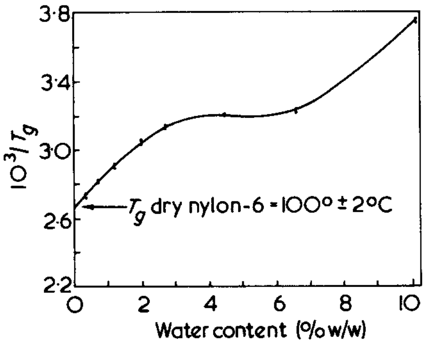

*Figure 2* Fox plot for nylon-6

The results show that the $T_g$ of nylon-6 is markedly affected by water content and this is probably the explanation for the wide range of values quoted in the literature.

ACKNOWLEDGEMENTS

Thanks are expressed to Mr J. Hawke for helpful discussions.

## REFERENCES

1 Def Stan 93-811, Annex B
2 Kaimin', I. F., Apinis, A. P. and Galvanowskii, A. Ya. *Polym. Sci. USSR* 1975, **17**, 46
3 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1**, 123
4 Puffr, R. and Sebenda, J. *J. Polym. Sci. (C)* 1976, **16**, 79
5 Kawasaki, K. and Sekita, Y. *J. Polym. Sci. (A-2)* 1964, **2**, 2437
6 Wilusz, E. B. and Karasz, F. E. *Polym. Prepr.* 584, **16**
7 Rybnikar, F. *J. Polym. Sci.* 1958, **28**, 633
8 Forster, M. J. *Text. Res. J.* 1968, **38**, 474
9 Frosini, V. and Butta, E. *J. Polym. Sci. (Polym. Lett. Edn)* 1971, **9**, 253
10 Anton, A. *J. Appl. Polym. Sci.* 1968, **12**, 2117
11 Price, F. R., Pearce, E. M. and Fredericks, R. J. *J. Polym. Sci. (A-1)* 1970, **8**, 3533
12 Thomas, A. M. *Nature* 1957, **179**, 862
13 Doak, K. W. 1967, **45**, 14
14 Shibusawa, T. *J. Appl. Polym. Sci.* 1970, **14**, 1553
15 Takayanagi, M. *Rep. Prog. Polym. Phys. Japan* 1963, **6**, 121

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# Mosaic blocks in polymer crystals – the concept of paracrystallinity

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*(Received 30 December 1976; revised 14 March 1977)*

Misunderstandings and misrepresentations in the literature[1,2] force us to clearly outline again the mosaic block concept in polymer crystals as it follows from numerous wide-angle (WAXS) and small-angle (SAXS) X-ray scattering studies.

The mosaic block concept is generally accepted for bulk polymers. However, on account of recent diffraction results from polymer single crystals it has been questioned 'as an intrinsic feature of polymer crystallization[2]. Therefore the present paper will be mainly concerned with diffraction measurements on single crystals. Two points will be stressed in the hope of clarifying the differences in explaining the diffraction results:

(1) X-ray line profile analysis proves that paracrystalline distortions define the limited sizes of the mosaic blocks called microparacrystals (*mPc*'s). Therefore the mosaic block concept does not invoke 'an intrinsic structural unit of a specific size and shape as a necessary attribute of polymer crystallization'.[2] For the same reason we do not believe the mosaic blocks in single crystal mats to be artefacts induced by sedimentation and drying.

(2) Our WAXS results on single crystal mats cannot be explained by chain obliquity, but positively prove the reality of *mPc*'s.

## BLOCK SIZE AND DEFECT CONCENTRATION

Lamellae-shaped single crystals grown from dilute solution are seen in the electron microscope to extend laterally over many microns, whereas WAXS measurements on single crystal mats usually yield much smaller values for the coherently scattering domains. Consequently, it was assumed that a lamella consists of mosaic blocks. These are separated from each other laterally by twist-boundaries resulting in a slight rippling of moiré fringes[3].

The existence of paracrystalline distortions in polyethylene (PE) single crystal mats has been verified by analysing the linewidths of a number of wide angle reflections[4] and more recently by applying a Fourier method[5]. In the latter generally applicable analysis the Fourier coefficients $A_n$ of the experimental line profiles of different orders of reflection are calculated. The logarithm of their ratio –