Notes to the Editor

Mechanical degradation of polymers: the limiting degree of polymerization

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INTRODUCTION

It is well established that polymer molecules can be degraded mechanically both in the bulk phase and in solution. Degradation is a chemical process for which the energy of activation is supplied mechanically. Commonly during mechanical degradation the molecular weight decreases rapidly in the initial portion of the reaction and then the rate decreases until an apparent limiting molecular weight is reached. The limiting value usually is a function of experimental conditions. The concept of a limiting degree of polymerization, or critical molecular weight, for any polymer species below which degradation will not take place regardless of the experimental conditions has been widely employed. Limiting degrees of polymerization have been reported for polyisobutylene, polystyrene, poly(methyl methacrylate), polypropylene, poly(vinyl chloride), DNA and other polymers by a number of authors. A review covers previous work in this area in detail[1]. However, the view that there is a specific limiting degree of polymerization, *LDP*, that depends only on the polymer has been disputed. The other proposed mechanisms may be summarized as (a) an *LDP* exists but its value varies with the initial molecular weight distribution of the polymers and (b) that no *LDP* exists but instead there is a decreasing probability of bond rupture with decreasing molecular weight[2].

Table 1 Elution volume vs. molecular weight

Counts	Molecular weight	Counts	Molecular weight
25	1.8×10^6	33	9.5×10^4
26	1.2×10^6	34	5.8×10^4
27	8.5×10^5	35	4×10^4
28	5.7×10^5	36	2.8×10^4
29	4×10^5	37	1.9×10^4
30	2.7×10^5	38	7.5×10^3
31	1.8×10^5	39	1.9×10^3
32	1.25×10^5		

Many of the previously reported studies determined average molecular weights or used kinetic data to determine limiting degree of polymerization. Gel permeation chromatography is a convenient technique to determine molecular weight distribution of both the starting and degraded polymer.

EXPERIMENTAL

The narrow molecular weight distribution polystyrenes were obtained from Pressure Chemical Company, Pittsburgh, Pennsylvania. Concentration of the solutions was 20 g/l. Tetrahydrofuran was the solvent and was freshly distilled from KOH.

Table 2 Degradation of polystyrene, molecular weight 1 800 000

Irradiation time (min)	No. of counts to peak maximum	Molecular weight	Molecular weight (%)
0	25	18×10^5	0
5	25.8	13×10^5	27.78
10	26.8	9×10^5	50.0
15	27.35	7.5×10^5	58.33
20	27.85	6.3×10^5	65.0

Table 3 Degradation of polystyrene, molecular weight 19 800

Irradiation time (min)	No. of counts to peak maximum	Molecular weight	Loss of molecular weight (%)
0	37	19×10^3	0
30	38.25	5×10^3	73.68
60	38.4	4×10^3	78.95
90	38.4	4×10^3	78.95
120	38.45	3.8×10^3	80.0

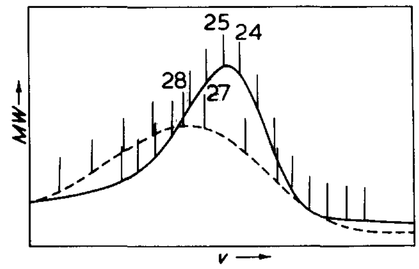

Figure 1 Degradation of polystyrene, *MW*: 1 800 000. – – – –, Degraded polystyrene; ———, undegraded polystyrene

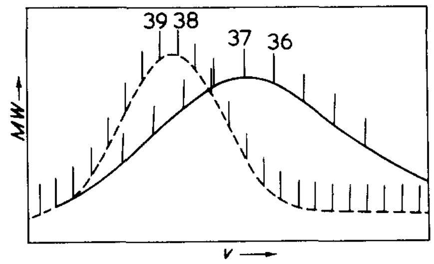

Figure 2 Degradation of polystyrene, *MW*: 19 800. – – – –, Degraded polystyrene; ———, undegraded polystyrene

Ultrasonic energy was supplied by a Brownwill Biosonik probe operating at 20 kHz. Nominal power rating was about 28 W. The samples were maintained at 10° ± 3°C.

Molecular weight distributions were determined by gel permeation chromatography in the conventional manner.

RESULTS AND DISCUSSION

Tables 2 and *3* and *Figures 1* and *2* present representative data. The high molecular weight polystyrene degrades rapidly at first then has a decreasing rate. Doubtless further degradation could be observed with increasing time. Under very similar conditions, Smith and Temple[3] found a polystyrene with initial molecular weight of 841 000 decreased to 27 800 after 88 h. However, it seems improbable that the *LDP* will be much below 100.

When the low molecular weight polystyrene 19 800 is irradiated the qualitative pattern is the same. After 120 min the molecular weight at the 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

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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].

The measurements of the T_gs 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.

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

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

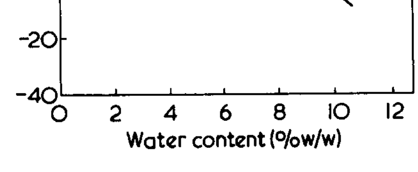

Figure 1 Effect of water content on the T_g of nylon-6

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