

# Molecular weight distribution and mass changes during polyamide hydrolysis

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Samples of polyamide 6, 11 and 12 have been hydrolysed at various temperatures ranging from 80 to 120°C in water baths of pH ranging from 0 to 4. The polymer degradation was monitored by steric exclusion chromatography (SEC), viscometry and gravimetry. SEC data indicate that the polydispersity of the polyamides tested does not increase during ageing. This can be considered as proof of the homogeneity of the reaction. Average molecular weight data from SEC or viscometry appear to be consistent with a random chain scission process, however gravimetry (at least in the case of relatively soft conditions, for instance  $\text{pH} \geq 4$ ) indicates a high monomer yield. These apparently contradictory results are tentatively explained by the equilibrated character of hydrolysis. Acid–amine pairs resulting from hydrolysis events would recombine easily when both belong to macromolecular fragments. When one fragment is the monomer or a low oligomer, it can escape easily from the cage and the corresponding recombination yield is decreased. The monomer extraction by water complicates the gravimetric behaviour, especially in the most severe hydrolysis conditions. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Hydrolysis of linear polycondensates<sup>1–4</sup> such as polyesters<sup>5–9</sup>, polycarbonates<sup>10,11</sup> or polyamide<sup>12</sup> is often considered as a good example of a random chain scission process<sup>13</sup>. Detailed investigation reveals however that the reality is more complicated. If a random chain scission occurs, a weight gain of 18 g per mole of hydrolysis event must be observed. This is difficult to reconcile with the weight loss described previously at relatively low conversions<sup>14</sup>. In this recent article on the hydrolysis of polyamide 11 (PA11), we have shown that the process is highly influenced by the temperature and the acidity of the medium and is characterised by especially high monomer yields. There are many possible explanations of this surprising behaviour among which the two simplest ones are the coexistence of:

- (1) a depolymerisation process and a random chain scission;
- (2) a more or less homogeneous slow and a localised fast hydrolysis process.

As previously shown, the monomer/oligomer yield can be theoretically estimated from comparison of the mass gain rate and the chain scission rate. However experimentally, complications due to the extraction of monomers/oligomers by water are encountered<sup>14</sup>. Some new elements of discussion on these processes are presented from a detailed study of SEC, viscometry and gravimetry data. This is the first step to the proposition of a pertinent kinetic model and thus to lifetime prediction<sup>15</sup>.

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## EXPERIMENTAL

### Materials and solutions

PA11 BESNO TL grade, with  $T_m = 190^\circ\text{C}$  and  $d = 1.03 \text{ g cm}^{-3}$  was provided by Atochem. Pellets of neat PA 11 were vacuum dried at 80°C for 8 hours. Samples were then moulded at 220°C, 10 MPa for 30 min and slowly cooled at 5°C min<sup>-1</sup> to form plaques of 1 mm thick.

Immersion of PA 11 samples was performed in solutions with different acidities *ca.* pH 0, 2 and 4. Solutions at pH 0 were obtained with HCl 1 N. Two other solutions were prepared by dilution in 1 l of distilled water under the following conditions:

- pH 2 (1.68): 12.7 g of potassium tetraoxalate;
- pH 4: 10.12 g of potassium hydrogenphthalate.

### Steric exclusion chromatography

SEC measurements were performed with a Waters 150C using benzoic alcohol eluant, two columns (Plgel 10  $\mu\text{m}$  cross linked polystyrene) and a differential refractometer. The flow rate was 1 ml min<sup>-1</sup>. The concentration of polymer solutions was fixed at 0.5 wt% and dissolution was at 130°C. A universal calibration was carried out with three different standard polymers: polystyrene, polytetrahydrofuran and polyoxomethylene.

### Viscometry

Table 1 indicates the quantity of PA 11 dissolved in *m*-cresol as a function of the calculated concentration. A viscometer with automatic measurement has been used. Measurements have been made at 20°C. The coefficient of flow is determined with a capillary tube (Ubbelohde type) and is proportional to the viscosity of the solution *i.e.*  $\eta = \alpha t$ . By measuring the viscosity of both the solvent

**Table 1** Relation between weight and concentration of PA11 in *m*-cresol

Concentration (g dl <sup>-1</sup> )	0.5	0.4	0.3	0.2	0.1
<i>m</i> <sub>polyamide</sub> (mg)	96.71	77.37	58.03	38.68	19.34

and the solution in the same tube, the relative viscosity is

$$\eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0}$$

**Gravimetry**

Disc samples of 14 mm diameter and 2 mm thick were vacuum dried at 80°C for 2 days. They were weighed (*m*<sub>0</sub>) and placed in an acid solution. After *t* days of immersion, they were vacuum dried at 80°C for 1 week and weighed again (*m*<sub>t</sub>). The weight variations (%) during hydrolysis are given by

$$\frac{m_0 - m_t}{18m_0} \times 100$$

**RESULTS AND DISCUSSION**

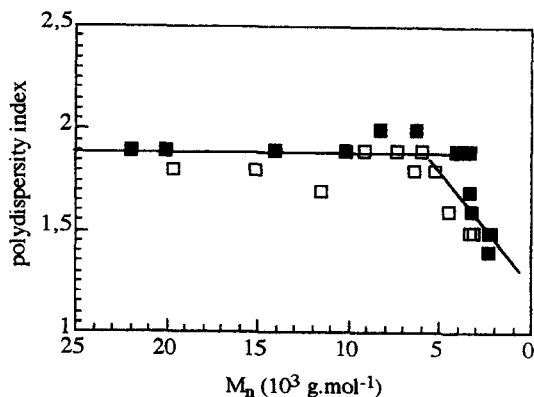
**SEC results**

As shown previously, hydrolysed samples of polyamides can contain variable amounts of monomer and oligomers, depending on exposure conditions<sup>14</sup>. These low molecular mass species have not been detected by SEC in our chosen conditions. Thus, the SEC data only relate to the macro-molecular part of the samples.

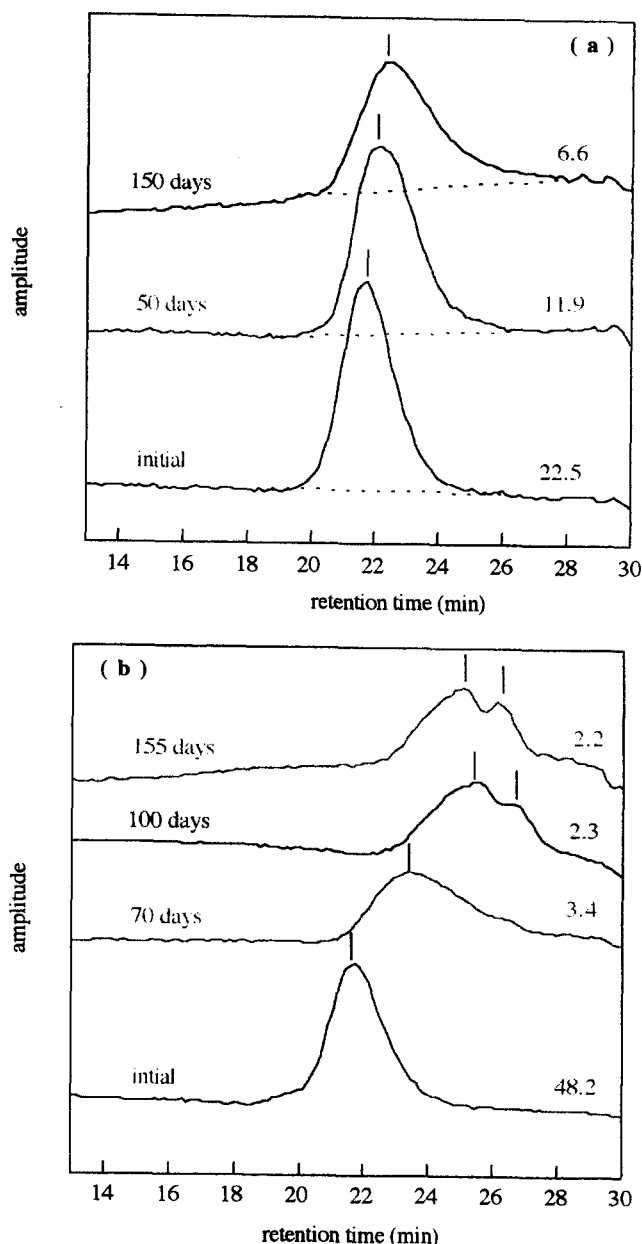
The analysis of the polydispersity index (Figure 1) implies a separation of the hydrolytic process according to the level of conversion.

- At low to moderate conversions (Figure 2a), the chromatograms have a single band but additional fine structure appears at high conversions (Figure 2b). It is especially apparent in the case of PA6 (Figure 3). The polydispersity index is close to 2 and remains constant.
- At high conversions, this index decreases and only the last peak from the above fine structure survives. The molar mass corresponding to this peak is above 1000 g mol<sup>-1</sup> for PA6 and PA11.

The behaviour observed at low to moderate conversions is usually interpreted as a homogeneous distribution of chain scission within the whole sample volume. There is no depth gradient linked to diffusion control of the kinetics, nor any degradation localised in microdomains because in both



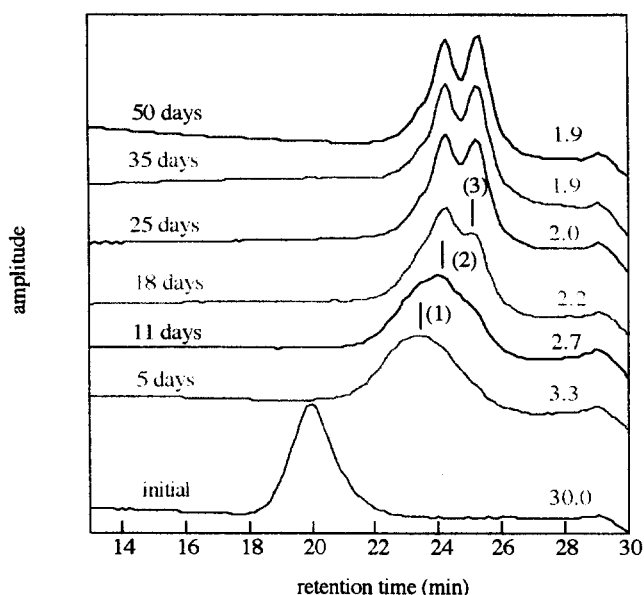
**Figure 1** Polydispersity index versus *M<sub>n</sub>* during ageing at pH 2, 120°C and pH 4, 120°C



**Figure 2** (a) SEC curves for PA11 as a function of ageing time at pH 2, 90°C; on the right side are the *M<sub>n</sub>* values in 10<sup>3</sup> g mol<sup>-1</sup>. (b) SEC curves for high viscosity grade PA11 as a function of ageing time at pH 4, 120°C; on the right side are the *M<sub>n</sub>* values in 10<sup>3</sup> g mol<sup>-1</sup>

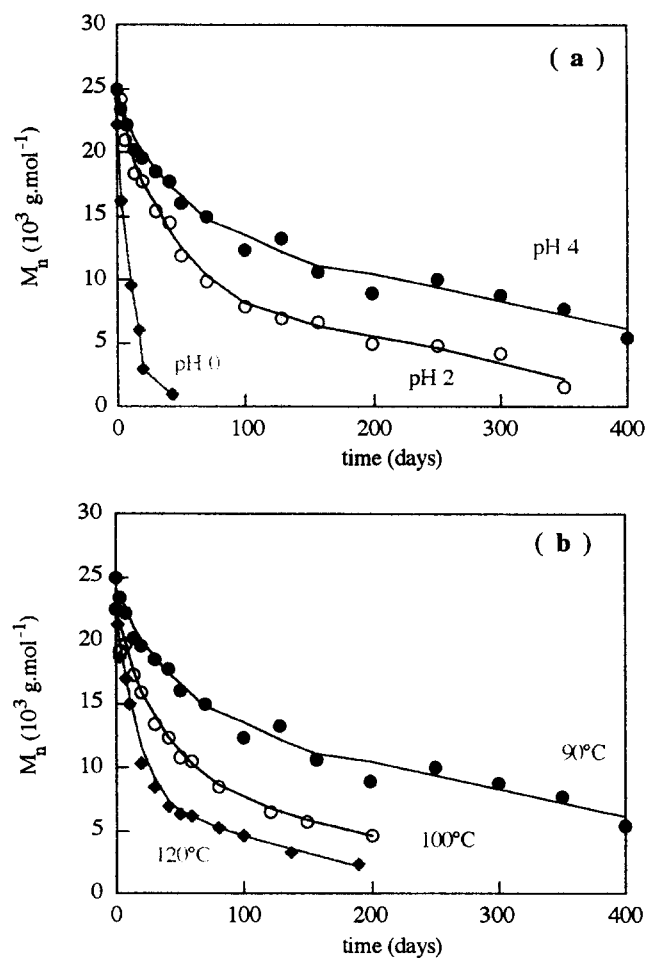
cases the polydispersity would have increased<sup>14</sup>. The constancy of the polydispersity index of 2 indicates apparently that the chain scission process is random at least at low or moderate conversions<sup>5</sup>. The decrease of this index indicates that another process is superimposed on the random chain scission.

Examples of kinetic curves of *M<sub>n</sub>* change are shown in Figure 4. As expected, the degradation rate increases with pH (Figure 4a) and the temperature (Figure 4b). At least in the less severe conditions, the curves reveal the existence of two stages. In a first stage, *M<sub>n</sub>* decreases quasi hyperbolically with time. When it reaches values of 10 000–5000 g mol<sup>-1</sup>, the curves display a linear part or even a quasi horizontal plateau, indicating the presence of a non reactive or less reactive fraction in the sample. This last characteristic and the appearance of fine structure at high conversions (Figure 2b and Figure 3) seem to be common features of the degradation of semi-crystalline polymers since they have been observed for instance in the hydrolysis of PET<sup>1,7</sup>.



**Figure 3** SEC curves for PA6 as a function of ageing time at pH 2, 120°C; on the right side are the  $M_n$  values in  $10^3 \text{ g mol}^{-1}$ : (1)  $M_i = 4.2 \times 10^3 \text{ g mol}^{-1}$ ; (2)  $M_i = 2.6 \times 10^3 \text{ g mol}^{-1}$ ; (3)  $M_i = 1.0 \times 10^3 \text{ g mol}^{-1}$

The shape of the SEC chromatograms at high conversions can be explained by the well known folded chain structure of crystalline lamellae<sup>16</sup>. In fact, hydrolysis occurs only in the amorphous phase. If chain scission occurs at chain folds,



**Figure 4** (a) Influence of acidity (pH) on  $M_n$  at 90°C as a function of time. (b) Influence of the temperature on  $M_n$  at pH 4 as a function of time

i.e. at the crystallite surface, the length of the chains is a multiple of the lamella thickness. In the case of PA6, the three peaks which appear in SEC chromatograms during prolonged ageing (Figure 3), correspond to molar mass of 4200, 2600 and  $1000 \text{ g mol}^{-1}$ , respectively. This agrees reasonably with the hypothesis of multiple values. The peaks at 4200 and  $2600 \text{ g mol}^{-1}$  disappear progressively and only the peak at  $1000 \text{ g mol}^{-1}$  remains. This last one is presumably attributed to the lamella thickness, i.e. around eight monomeric units for PA6 and four units for PA11<sup>17</sup> and PA12. In severe conditions, or at long times in softer conditions, the molar mass continues to decrease slowly, which could be linked to crystallite erosion by progressive release of the monomer units close to the surface or by hydrolytic attack of the chain located at the crystal–water interface. These phenomena are interesting for morphological studies but they lack interest from the practical point of view since the mechanical properties are lost long before the appearance of the fine structure in SEC chromatograms.

#### Viscometric results

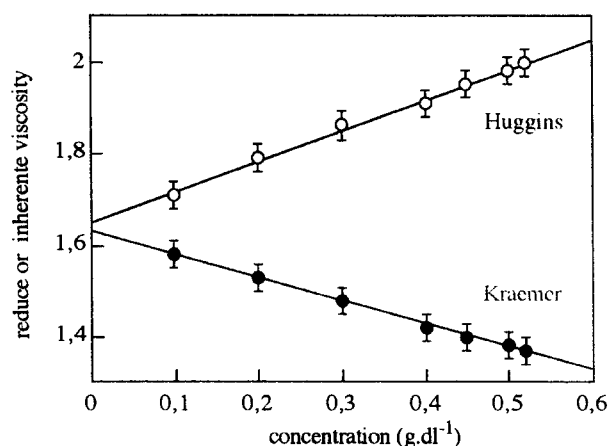
Viscometry has been performed in the case of PA11. Single point measurements have been used to determine the intrinsic viscosity  $[\eta]$  using the well-known Huggins or Kraemer relationships:

$$\text{Huggins : } \frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \quad (1)$$

$$\text{Kraemer : } \ln \frac{\eta_{rel}}{c} = [\eta] + k_K [\eta]^2 c \quad (2)$$

where  $c$  is the concentration,  $\eta_{sp}$  and  $\eta_{rel}$  are respectively the specific and relative viscosity. These relationships have been checked in the case of non degraded samples (Figure 5). The values of Huggins ( $k_H$ ) and Kraemer ( $k_K$ ) constants are given in Table 2. For degraded samples, the Huggins constant  $k_H$  is almost independent of ageing since it varies from 0.21 to 0.55 with a mean value at 0.38. This feature is in a good agreement with the literature<sup>18,19</sup>.

Correlation between SEC results ( $M_n$  or  $M_w$ ) and viscometry ( $[\eta]$ ) has been made using the well-known Mark–Houwink relationship  $[\eta] = KM^a$ . In the literature, values of  $K$  are in the range  $1.35\text{--}18 \cdot 10^{-4}$  and  $a$  in the range 0.654–0.96 for polyamide–*m*-cresol systems<sup>12</sup>. There is a relatively good logarithmic correlation between  $[\eta]$  and  $M_w$  determined by SEC (Figure 6) despite the fact that the viscosity is probably influenced by the presence of monomers and oligomers not taken into account by SEC



**Figure 5** Determination of intrinsic viscosity of the initial PA11

**Table 2** Intrinsic viscosity calculated from Huggins and Kraemer relationships

Equation	$[\eta]$ (dl g <sup>-1</sup> )	$k$
Huggins	1.62	0.27
Kraemer	1.61	-0.19
Average	1.618	$\Delta k = 0.45$

measurements. In fact, as the low molecular weight species were observed by viscometry, a modification of the slope is apparent for the low viscosities.

*Gravimetric results*

Some examples of kinetic curves of mass change are shown in *Figure 7a, b* and *c*. The polymer behaviour is influenced by the conditions of immersion. In soft conditions used in this work (pH 4 all temperatures, pH 2 low temperatures), its mass decreases in hard conditions (pH 2 high temperatures, pH 0 all temperatures). Two processes are obviously involved in a such behaviour:

- (1) mass gain due to hydrolysis (18 g per mole of event);
- (2) mass loss due to the extraction of low molar mass chain fragments.

When the mass increases, the number  $n_t$  of chain scission per mass unit is given by:

$$n_t = \frac{m_0 - m_t}{18m_0} \quad (3)$$

where  $m_0$  and  $m$  are respectively the initial and final sample mass. Indeed, this value is an underestimate if there is a mass loss due to monomer release.

From SEC data, one can determine another  $n_t$  value:

$$n_t = \frac{1}{M_{n,t}} - \frac{1}{M_{n,0}} \quad (4)$$

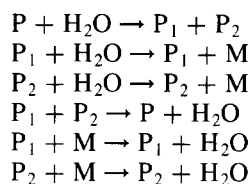
The kinetic curves corresponding to both modes of determination of  $n_t$  have been plotted in *Figure 8* for the experiment at pH 2 and 90°C. The whole hydrolysis rate (gravimetry) appears to be more than 10 orders of magnitude higher than the random chain scission rate (SEC).

These results could be interpreted as an especially fast

degradation located in microdomains. However, the polydispersity data do not support such a model and so it can be discounted. In the case of vinylic or acrylic polymers, such behaviour would be explained by the coexistence of random chain scission and depolymerisation, this latter being more than 10 orders of magnitude faster than the former one<sup>13</sup>.

*Proposed scheme of hydrolysis*

In the case under study, the following simplified scheme is proposed to explain the observed behaviour:



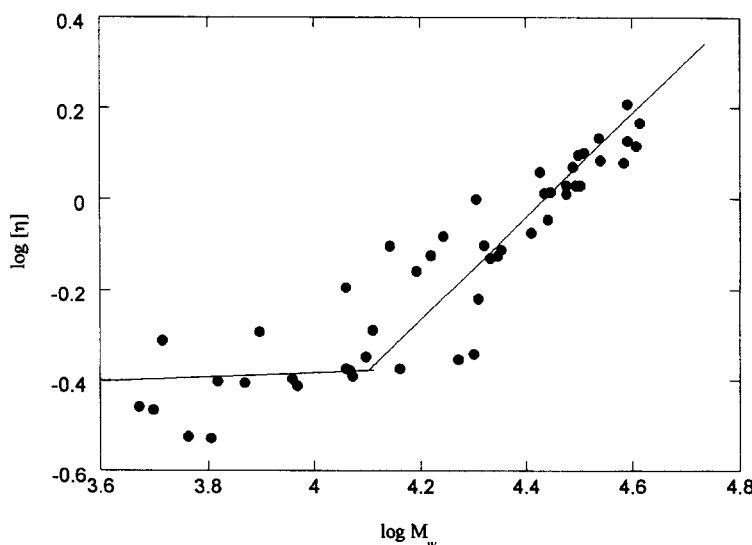
where P is the polymer undergoing a random attack, P<sub>1</sub> and P<sub>2</sub> are respectively an amine or a carboxylic acid chain end in a macromolecule and M is the monomer. The whole hydrolysis rate as determined from mass gain in 'soft' conditions is then:

$$\begin{aligned} \frac{dH}{dt} = &k_R[P] + k_1[P_1] + k_2[P_2] - k_T[P_1][P_2] \\ &- k_1'[P_1][M] - k_2'[M][P_2] \end{aligned} \quad (5)$$

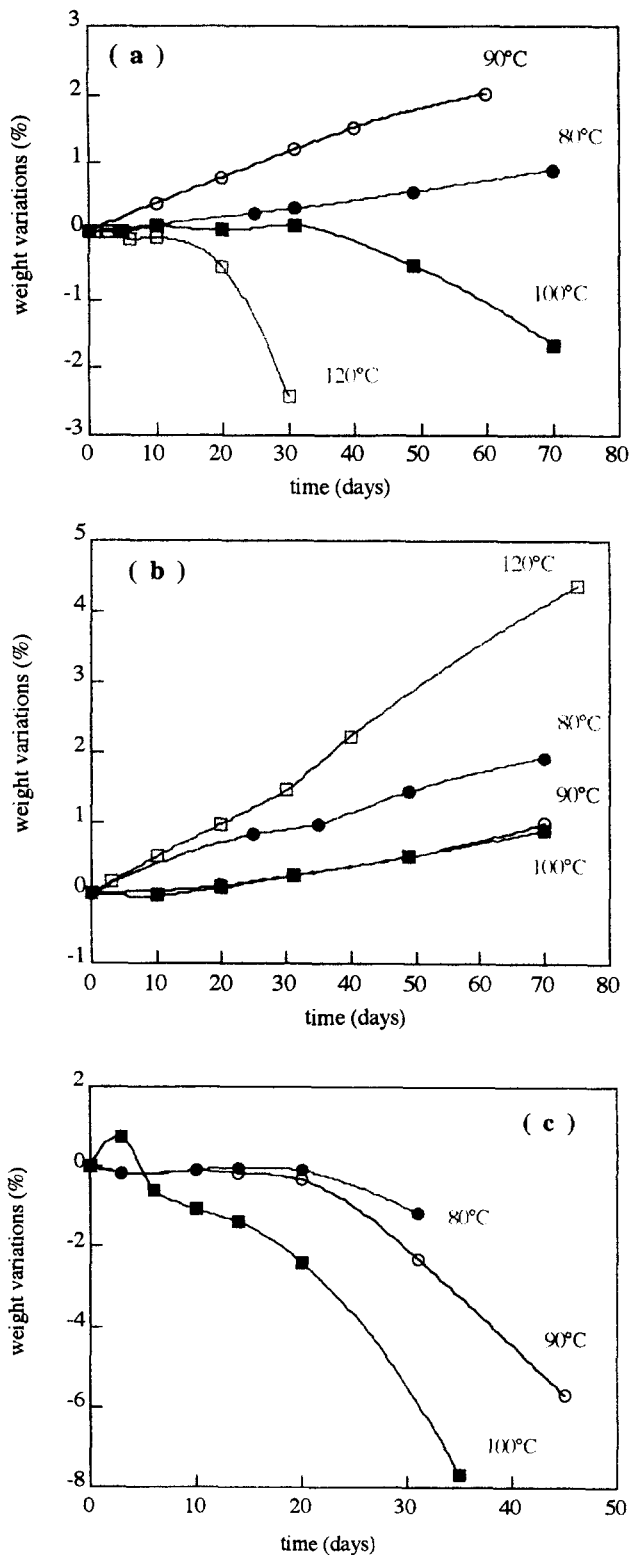
where  $k_R$ ,  $k_1$  and  $k_2$  are pseudo first order rate constants. The water concentration is supposed constant otherwise the degradation would be heterogeneous as a result of diffusion control.

At low pH values (*Figure 7c*), the initial period of mass gain disappears almost totally. This result is linked to the difference between the mass gain during a hydrolysis event (18 g per mole) and the mass lost by monomer extraction (183.3 g per mole). If a monomer is extracted, 10 scissions must have occurred to compensate and to keep a constant weight. It can be concluded that a constant weight (= 0) is indicative of a hydrolysis rate 10 orders of magnitude faster than the extraction rate. This relation is only verified for monomeric species.

In extreme conditions, hydrolysis is so fast that it becomes diffusion controlled. In this case, monomer diffusion out of the sample would become faster since it is

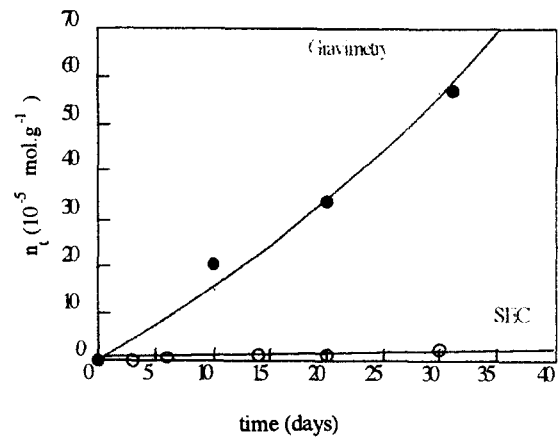


**Figure 6** Relationship between  $[\eta]$  and  $M_w$  according to the Mark-Houwink law



**Figure 7** (a) Weight variations of PA11 samples hydrolysed at pH 2 between 80 and 120°C. (b) Weight variations of PA11 samples hydrolysed at pH 4 between 80 and 120°C. (c) Weight variations of PA11 samples hydrolysed at pH 0 between 80 and 100°C

essentially formed in a superficial layer. In this case, however, the heterogeneity of degradation would lead to a polydispersity increase, which is not clearly seen in SEC chromatograms. However, the molar mass ( $M_w$ ) of the surface and the core of a sample immersed at pH 0 are respectively equal to  $21\,400\text{ g mol}^{-1}$  and  $2300\text{ g mol}^{-1}$ . These results indicate clearly that the hydrolytic process in



**Figure 8** Number of chain scissions per mass unit during PA11 hydrolysis at pH 2, 90°C as determined by gravimetry and SEC

hard conditions is heterogeneous. In the following, only the homogeneous case will be considered.

The rate of chain scission as determined by SEC is:

$$\frac{dn_t}{dt} = k_R[P] - k_T[P_1][P_2] \quad (6)$$

Experimentally, it has been found that

$$\frac{dH}{dt} \gg \frac{dn_t}{dt}$$

which leads to the following alternative.

- (1) 'Recombination' reactions ( $k_T, k'_1, k'_2$ ) play a negligible role and  $k_1$  and/or  $k_2$  is (are) considerably higher than  $k_R$ . The amide groups located at the chain ends are considerably more reactive than the other amide groups so that depolymerisation occurs. This hypothesis seems to be difficult to justify in mechanistic terms. As a matter of fact, there are only two ways for the chain end group (amine or carboxylic acid) to exert such an influence on the nearest amide group:

- inductive effect, but it cannot be transmitted through a polymethylene sequence;
- backbiting process, but it is difficult to imagine in the case of PA11.

- (2) 'Recombination' reactions between macrofragments are highly favoured whereas recombination between a chain end and a monomer is less favoured. In this case, it can be written that:

$$k_1[P_1] + k_2[P_2] \gg k_R[P] - k_T[P_1][P_2] \quad (7)$$

and

$$k'_1[P_1][M] + k'_2[P_2][M] < k_T[P_1][P_2] \quad (8)$$

so that

$$\frac{dH}{dt} \gg \frac{dn_t}{dt}$$

Most of the amine–acid pairs resulting from random hydrolysis events 'recombine' in a cage as a result of the relatively low mobility of the macrofragments and the sterically favourable conditions. In contrast, for hydrolysis events occurring near the chain ends, the 'cage effect' is less efficient. The small chain fragments created have a high mobility and can escape from the cage without recondensation.

## Quantification of the monomer in PA11

The rate of monomer loss must depend on its actual concentration, its affinity in the matrix and the sample thickness  $L$ . The mass balance can be described:

$$\frac{1}{m} \frac{dm}{dt} = 18 \frac{dH}{dt} - M_m \frac{d[M]}{dt} \quad (9)$$

where  $m$  is the sample mass,  $dH/dt$  is the whole hydrolysis rate,  $M_m$  the monomer mass and  $d[M]/dt$  the rate of monomer release.

The monomer accumulation in the matrix is given by:

$$\frac{d[M]}{dt} = r([M]) - D \frac{d^2[M]}{dx^2} \quad (10)$$

where  $r([M])$  is the rate of monomer formation determined from the mechanistic scheme,  $D$  is the monomer diffusivity and  $x$  the depth of the layer under consideration. The rate of monomer formation is obviously an increasing function of the chain end concentration, e.g. the hydrolysis conversion. An example of this relation has been given in *Figure 6a*. The sample mass first increases and then decreases. At the maximum of the curve, it can be written:

$$\frac{d[M]}{dt} = \frac{18}{M_m} \frac{dH}{dt} \quad (11)$$

This means that more than 10% of the hydrolysis events must create monomer molecules ( $M_m = 183.3 \text{ g mol}^{-1}$  for PA11).

Only the case of monomer is considered here but the reasoning could be applied to dimers and other low oligomers. It is, however, noteworthy that  $D$  must decrease exponentially with the molar volume<sup>20</sup>, e.g. with the degree of polymerisation so that monomer release must be noticeably favoured in comparison with higher oligomers.

## CONCLUSION

The polyamide hydrolysis has been followed simultaneously by SEC, viscometric and gravimetric measurements. From the SEC results, the polydispersity does not increase in the initial period of ageing, indicating a homogeneous (uniform) degradation in the whole sample volume. At high conversions, quasi monodisperse species appear. They correspond to the chain segments present in the crystalline lamellae after complete destruction of the amorphous phase, including chain folds.

Gravimetric data obtained in relatively soft tested conditions (temperature  $< 100^\circ\text{C}$ , pH  $> 4$ ) indicate that

the whole hydrolysis rate is considerably higher than the one determined from SEC or viscosimetric measurements. This can be explained by the existence of a depolymerisation like process. This 'depolymerisation' is a 'recombination', e.g. amide reformation from amine-acid pairs in the cage. If one fragment is monomeric (or eventually oligomeric), the 'recombination' is not favoured and it can easily escape from the cage. Only such a mechanism seems to take into account at the same time characteristics of random chain scissions and of depolymerisation, e.g. decrease of the average molar mass with a constant polydispersity and high monomer yield.

The gravimetric study is complicated by the occurrence of monomer extraction by the water bath. Mass loss becomes predominant sooner and sooner as the severity of hydrolysis conditions increases.

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