The Photochemical Degradation of 6 Nylon. I*

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The photochemical degradation of nylon has been the subject of several recent publications[1-3]. This topic has been under investigation in this laboratory for some time, and the author has found that the photochemical degradation of 6 nylon is accompanied with considerable decrease in molecular weight and increase in water soluble material. The water soluble material of nylon consists of monomers and oligomers. In this paper it is attempted to elucidate the mechanism of the photochemical degradation of 6 nylon from the relationship between molecular weight and the amount of monomer produced.

Various Possible Modes of Linear Polymer Degradation

Grassie and Melville[4] made a consideration of various possible modes of molecular weight change the starting point in their study of the reaction. Before appreciable amounts of monomer appear in a random scission process in large molecules, the number-average molecular weight of the residue is reduced to a small fraction of its initial value. This behavior is represented by AD in Fig. 1. Another suggestion was that the bonds joining the end units to the rest of the chain might be particularly vulnerable and thus exclusively broken. Such a process has been called stepwise depolymerization and would result in decrease in molecular weight, directly proportional to the amount of monomer produced. This behavior is represented by AC in Fig. 1.

A third possible depolymerization mechanism is the exact reverse of polymerization. Initiation would consist of chain scission resulting in the production of radicals. These would then rapidly lose monomer until they had completely disintegrated. If these degrading radicals had a lifetime of the order of those of the growing radicals in polymerizing systems (approximately 10^{-3} —10 sec.), virtually all the monomer units would exist at any instant as free monomer or unchanged polymer. No great change in the molecular weight of the residue would therefore be expected throughout the whole course of the reaction. This mechanism is represented by AB in Fig. 1.

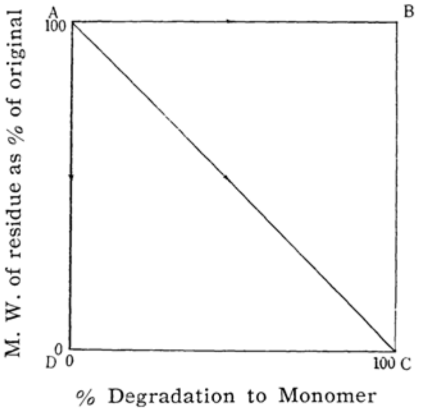

Fig. 1. Theoretical reaction curves for possible depolymerization mechanisms (Grassie and Melville).

Experimental

Scoured and heat-set nylon taffeta of 70^{D} $34^{fil.}$ 6 nylon yarn (Amilan) was used in these experiments. Samples of the fabric were irradiated in a Fade-Ometer for various periods of time and then the amount of water-soluble material and the degree of polymerization of the sample were measured.

1) *The measurement of the amount of water soluble material.*—Half a gram, of irradiated nylon taffeta was dried in vacuo over phosphorous pentoxide for 24 hr. and weighed. After 4 hr. extraction with water in a Soxhlet extractor, decrease in the weight of the sample was referred to as the amount of water soluble material.

2) *The measurement of the degree of polymerization.*—Number-average degree of polymerization $\overline{P}_n$ is calculated from intrinsic viscosity

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[1] B. G. Achhammer et al., *J. Appl. Chem.*, **1**, 301 (1951).

[2] R. A. Ford, *Nature*, **176**, 1023 (1955).

[3] M. Schwemmer, *Textil-Rundschau*, **11**, 1, 70, 131 (1956).

[4] N. Grassie and H. W. Melville, *Proc. Roy. Soc.* **A 199**, 1, 14, 24 (1949).

TABLE I

WATER-SOLUBLE MATERIAL AND NUMBER AVERAGE DEGREE OF POLYMERIZATION OF IRRADIATED NYLON

Exposure time (hr.)	0	10	20	40	60	80	120
Sample weight (mg.)	490	458	487	487	487	484	488
Water-soluble (%) Material	0.7	0.8	1.1	1.9	2.9	3.6	5.6
$[\eta]$ Before extraction	1.02	0.70	0.50	0.33	0.17	0.30	0.19
$[\eta]$ After extraction		0.73	0.65	0.42	0.31	0.34	0.23
$\overline{P}_n$ Before extraction	131	76	47	26	10	22	12
$\overline{P}_n$ After extraction		81	68	36	23	27	15

$[\eta]$ which is measured in *m*-cresol at 25.00°C. Thus $\overline{P}_n=127.4\,[\eta]^{1.435}$ 5).

Results

All the results are summarized in Table I.

Fig. 2 shows the increase in amount of water-soluble material and the decrease in intrinsic viscosity during irradiation. The increase in amount of water-soluble material is approximately proportional to the exposure time, while the decrease in intrinsic viscosity is rapid at the beginning of exposure. It might be due to the presence of water-soluble material that the intrinsic viscosity after extraction always shows a little higher value than that before extraction.

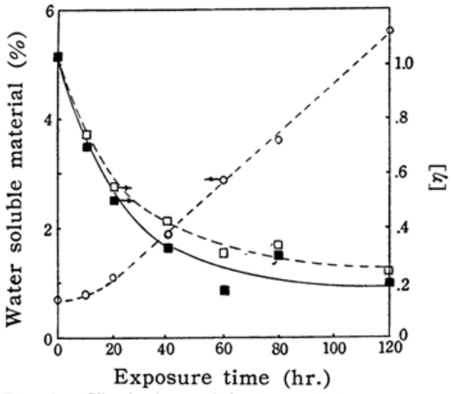

Fig. 2. Variation with time of the amount of water-soluble material and intrinsic viscosity (○ water soluble material, ■ intrinsic viscosity before extraction, □ intrinsic viscosity after extraction).

The relationship between the amount of water soluble material and the number-average degree of polymerization after extraction is shown in Fig. 3. Monomer is not the only water-soluble material produced. From the analogy of Fig. 1, however, it is deduced that the molecular chain of nylon is randomly split off by light.

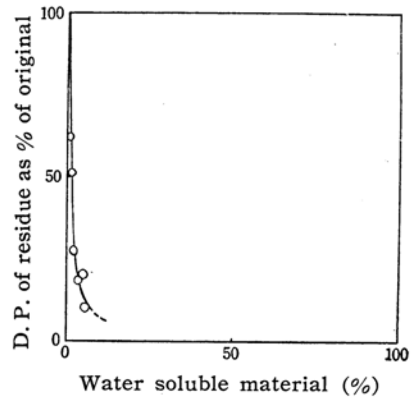

Fig. 3. Relationships between the amount of water-soluble material and the number-average degree of polymerization of residue.

Discussion

A theory regarding the random breaking of polymer chain has been elaborated by a number of workers. The theory makes it possible to obtain mathematical expressions for the various size distributions at definite stages of the degradation process. Here is cited Hoshino and Watanabe's 6) theory from which the relationship between the amount of monomer or oligomer produced and the number-average degree of polymerization is derived in the following way.

Supposing the molecular size distribution at initial stage follows Flory's distribution. That is

$$N=N_p{}^{x-1}(1-p) \qquad (1)$$

where N_x is the number of molecules

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5) O. Fukumoto, *J. Polymer Sci.*, **22**, 263 (1956).

6) K. Hoshino and M. Watanabe *J. Chem. Soc. Japan, Pure Chem. Sec.*, **70**, 170 (1949); *J. Am. Chem. Soc.*, **73**, 4816 (1951).

TABLE II

WEIGHT FRACTION OF OLIGOMERS DURING RANDOM DEGRADATION

Number-average degree of polymerization	Degree of degradation	Weight fraction of (%)			
		Monomer	Dimer	Trimer	Total
130					
65	0.0078	0.023	0.046	0.068	0.137
130/3	0.0155	0.054	0.105	0.154	0.313
26	0.0310	0.148	0.285	0.410	0.843
130/9	0.0620	0.479	0.892	1.245	2.616

$p=0.9923$ Initial degree of polymerization 130

composed of x monomer units, N is the total number of molecules and p is the extent of reaction. In a case where the bonds of all chains in the mixture at any given time are equally accessible to reaction independent of both their position in a chain and the length of their parent chains, the molecular weight distribution after degradation is given by

$$N_y(\alpha)=N[1-p(1-\alpha)]^2[p(1-\alpha)]^{y-1}(1-p)^{-1} \tag{2}$$

where $N_y(\alpha)$ is the number of molecules composed of y monomer units at the degree of degradation α. Substituting 1, 2, 3 etc. for y in equation (2), one can calculate the fraction of monomer, dimer, trimer etc. respectively at any degree of degradation. The results are summarized in Table II.

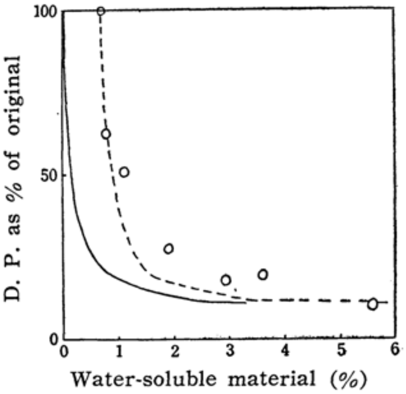

Fig. 4. Theoretical curve and observed relationship between the amount of water-soluble material and the number average degree of polymerization.
—— theoretical
- - - corrected
○ experimental

When the total weight fraction of monomer, dimer and trimer is plotted against number-average degree of polymerization, one can obtain the full line in Fig. 4. Observed values are represented by points. Taking it into account that a sample before degradation already has water-soluble material of 0.7%, one can reasonably say that the corrected value (dotted line) shows good agreement with the observed value.

Summary

1) The photochemical degradation of 6 nylon was investigated through the measurement of intrinsic viscosity and the amount of water-soluble material of 6 nylon taffeta irradiated for various periods of time in Fade-Ometer.

2) The intrinsic viscosity or the number-average degree of polymerization decreases rapidly at the initial stage, while the amount of water-soluble material increases approximately in proportion to the exposure time.

3) It is deduced from the relationship between the number-average degree of polymerization and the amount of water-soluble material that the molecular chain of 6 nylon is randomly split off by light. The relationship is well explained by the theory of random breaking of the polymer chain.

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