

Photodegradation in Solution

In a recent paper on the photodegradation of polyacrylonitrile in solution,¹ the degradation could be represented as a random scission process with a rate of breaking links expressed as follows:

$$-dn/dt = kI_0n \quad (1)$$

where n is the number of C—C links in the main polymer chains at time t , I_0 the incident light intensity, and k a rate constant. This rate law represents the experimental results quite satisfactorily; however, it is desirable to generalize the treatment. For this purpose, the rate of breaking links can be expressed by,

$$-dn/dt = k_1I_{\text{abs}} \quad (2)$$

where I_{abs} is the absorbed light intensity and n the concentration of C—C links (number per unit volume). For a given polymer sample, the initial concentration of links n_0 is proportional to the weight concentration (in grams/liter) of the polymer. If only a very small number of links is ruptured during degradation, which is actually the case for the experiments on polyacrylonitrile,¹ and provided Beer-Lambert's law holds, then

$$-dn/dt = k_1I_0(1 - e^{-k_2nl}) \quad (3)$$

where k_2 is a constant and l the width of the reaction cell. Further $k_2nl = 2.303E$, where $E = \log(I_0/I)$ is the optical extinction of the solution and I the transmitted light intensity. As $1 - e^{-k_2nl}$ is a constant, the eq. (3) reduces to:

$$-dn/dt = k_3I_0 \quad (4)$$

where k_3 is a constant. Integration of eq. (4) yields

$$n_0 - n = k_3I_0t \quad (5)$$

Introducing, $s = (P_0/P_t) - 1$, the average number of breaks for each original chain, P_0 and P_t being the initial number-average chain length and number-average chain length at time t , respectively, one obtains:

$$n_0 - n = Ns = k_3I_0t$$

or

$$Ns = N[(P_0/P_t) - 1] = k_3I_0t$$

which can be transformed to:

$$s/P_0 = (1/P_t) - (1/P_0) = k_4I_0t \quad (6)$$

where N is the concentration of polymer chains in the system and k_4 is a constant. Eq. (6) is identical with eq. (7) in the quoted paper.¹ It represents a degradation reaction where the rate of breaking links is independent of chain length and position of the links. That such a reaction is a random scission process has to be shown for instance by intrinsic viscosity measurements and proof that monomer is not formed.²

If a polymer sample is considered over a range of concentrations and constant I_0 (only a small number of scissions are considered), then the rate constants k_3 are a function of n_0 and are given by

$$k_3 = k_1(1 - e^{-k_2nl})$$

or

$$k_3 = k_1(1 - e^{-2.303E}) \quad (7)$$

Hence k_3 or $n_0k_4 = k_3$ plotted against $1 - e^{-2.303E}$ should give a straight line, if the process remains the same over the whole concentration range (e.g., random scission only).

If e^{-k_2nl} is nearly equal to one (this means that light absorption is small), then

$$e^{-k_2nl} \cong 1 - k_2nl$$

and

$$-dn/dt = k_1I_0k_2n_0l = kI_0n_0 \quad (8)$$

or

$$s/P_0 = (1/P_t) - (1/P_0) = kI_0t = \phi I_0k_2t \quad (9)$$

where ϕ is the quantum yield.

Eq. (8) corresponds to eq. (1), which was also given in the quoted paper,¹ and eq. (9) to eq. (7) in the same paper.¹

Eq. (10) in the quoted paper¹ should read,

$$-dn/dt = (k_3/4k_2)[-k_3 \pm (k_3^2 + 8k_2k_1n)^{1/2}]$$

The expression for n^* , the number of radical chain ends, should be corrected correspondingly.

References

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Note on the Cold Drawing of Nylon 66

Much of the development of the theory of cold drawing in amorphous and semicrystalline polymers^{1,2} has centered about the role of heat conduction, the work of drawing being concentrated in a very short length of specimen (the neck) and causing the temperature of the neck to rise considerably above the ambient temperature. Efforts to explain the basic cause of cold drawing by purely thermal considerations have led to difficulties, however. As has been emphasized by several investigators,^{3,4} cold drawing is not eliminated in certain polymers, even at extremely low rates of extension or under conditions of good thermal contact with the surrounding medium. Newman⁵ recently observed that high density polyethylene will continue to draw at a neck even when the extension is applied in small increments, with time allowed between increments for thermal equilibrium to be established.

In the course of drawing experiments conducted in various organic liquids, it was found that a number of polymers will draw at a neck in some media but not in others. The experiments were carried out at room tempera-

ture with a simple tensile tester operating at a constant rate of extension, in which the filament is completely immersed in the liquid just prior to extension. In Table I are given some results obtained with approximately 13-den. filaments of undrawn, pigmented nylon 66, at a (nominal) rate of extension of 100%/min. Both stresses refer to the original denier; the drawing stress refers to the minimum stress recorded immediately after necking. As suggested by Vincent,⁴ the ratio of yield stress to drawing stress is a useful measure of the cold-drawing tendency, increasing values of the ratio above unity indicating a greater tendency toward cold drawing.

TABLE I
Yield Stress and Ratio of Yield Stress to Drawing Stress for Undrawn Nylon 66 in Organic Liquids (Gauge Length 1 in., Jaw Speed 1 in./min.)

Liquid	Yield stress, g./den.	Yield stress drawing stress
(Air)	0.45	1.03
<i>n</i> -Heptane	0.43	1.04
Carbon tetrachloride	0.45	1.06
Diethyl ether	0.38	1.19
Chloroform	0.35	1.28
Acetone	0.32	1.03
Ethanol ^a	0.36	1.33
Methanol	0.12-0.28	1.00-1.87
Ethylene glycol	0.39	1.52
Water	0.26	1.24

^a Multiple necks formed.

The results indicate that the character of the drawing process does not change on passing from air to inert, non-polar liquids (heptane, carbon tetrachloride), despite the much improved thermal contact of the fiber with its surroundings. There is also, in general, an increasing tendency toward cold drawing as the polarity of the liquid increases, in addition to a reduction in the yield stress. It is noteworthy that the effect of the various liquids on the stress ratio for undrawn nylon 66 almost exactly parallels the known swelling action of these same liquids.⁶ Chloro-

form, for example, which is less polar than acetone, causes longitudinal swelling of nylon, whereas acetone does not.

Soaking the filaments for 5 min. in the organic liquids mentioned, prior to testing in air, had no permanent influence on the fiber structure, as judged by x-rays or subsequent tensile properties. With methanol, both necking and nonnecking behavior occurred with different specimens, leading to the wide range of values indicated in Table I. Here the smaller denier specimens tended to exhibit lower yield stresses and lower stress ratios.

It would appear in these experiments that the adiabatic nature or otherwise of the drawing process does not play an important role in deciding whether extension takes place homogeneously or inhomogeneously. It seems more reasonable to ascribe the influence of the liquids to their specific effect in lowering the tangent modulus of the "true" stress vs. extension curve in the vicinity of the yield point.⁴ Liquids which allow or enhance necking probably do so by conferring additional mobility on the amorphous regions of the fiber, whose role in the flow process begins at the yield point.

These few observations provide no test of Newman's suggestion⁵ that flow occurs more readily at the neck because of the different state of orientation in this region, but are consistent with the more general viewpoint expressed by Hookway⁷ that the cold-drawing phenomenon is intimately connected with the mobility of the amorphous regions.

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