

## Photodegradation in Solution

In a recent paper on the photodegradation of polyacrylonitrile in solution,<sup>1</sup> 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  $I_{\text{abs}}$  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,<sup>1</sup> 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.<sup>1</sup> 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.<sup>2</sup>

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  $\phi$  is the quantum yield.

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

Eq. (10) in the quoted paper<sup>1</sup> 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

- Jellinek, H. H. G., and W. A. Schlueter, *J. Appl. Polymer Sci.*, **3**, 206 (1960).
- Jellinek, H. H. G., *Degradation of Vinyl Polymers*, Academic Press, New York, 1955, p. 20.

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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<sup>1,2</sup> 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,<sup>3,4</sup> 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. Newman<sup>5</sup> 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-