

Spectrophotometric determination of gelation dose in the γ -irradiation of polyacrylonitrile (PAN)

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INTRODUCTION

Irradiation of vinyl polymers with high energy radiations leads to the formation of chain scissions and/or crosslinks. When the number of crosslinks per chain exceeds the number of chain scissions by a factor of at least 2, polymer chains start to form insoluble networks¹. The first appearance of insoluble polymers during irradiation is designated as the gelation dose, D_g , the dose required for the onset of gelation. D_g is generally found either by viscometric or solubility methods. If a polymer develops a colour upon irradiation, this behaviour can be used to determine the D_g by spectrophotometric methods. In the thermal degradation of PVC, Ivan *et al.*² showed that reproducible gel point values can be determined by a photometric method. In this study it is shown that the gelation dose of PAN irradiated with γ -rays, can be determined spectrophotometrically.

EXPERIMENTAL

The PAN sample used in this study was prepared by free radical bulk polymerization of purified acrylonitrile monomer at 60°C using AIBN as the initiator. The viscosity average molecular weight of the sample is 6.6×10^4 as determined in DMF at 25°C using the relation³: $[\eta] = 39.2 \times 10^{-5} M^{0.75}$.

Polymer samples in the form of solid chips were irradiated in evacuated glass ampoules in the Gammacell 220, a ^{60}Co - γ irradiator. The dose rate of $0.307 \text{ Mrad h}^{-1}$ was determined by conventional Fricke dosimetry⁴. After the irradiation, the samples were immediately dissolved in DMF to avoid post irradiation effects which were observed to be of great importance⁵. Exactly equal concentrations of DMF solutions of irradiated PAN samples were filtered through G₃ type Gooch crucibles. The visible spectra of the filtrates were taken with a Beckman DB-GT double beam u.v. visible spectrophotometer.

To find D_g from gel fractions, the gels obtained from the above filtration procedures were dried in a vacuum oven at 40°C to constant weight. The gel fractions were calculated as the ratio of the weight of insoluble fraction to total weight.

RESULTS AND DISCUSSION

When PAN is irradiated with ionizing radiations in the presence of air, mainly chain scission takes place. However, when irradiation is carried out in vacuum or in the absence of air, crosslinking predominates⁶. During the

degradation of PAN (either thermal or radiative), formation of conjugated sequences of double bonds imparts to this polymer a yellow to red colour⁷. As long as the coloured species remain soluble, the solution of degraded PAN also develops a similar colour. During the course of the degradation however, through the formation of crosslinks, some of the degraded (coloured) polymer molecules start to become insoluble. If crosslinking is absent, colour formation associated with degradation should increase as the degree of degradation increases. This is found to be the case.

Together with the onset of gelation however, degraded (coloured) molecules find themselves attached to the insoluble part, causing the intensity of the filtrates to decrease. The initial increase of the colour of polymer solution in the pregel region and its decrease after the formation of gels can be used to determine the gelation dose photometrically. In Figure 1 the absorbance values of DMF solutions of irradiated PAN samples at 360 nm are plotted against dose. A point of discontinuity in the curve is apparently seen and this corresponds to the dose of gelation, D_g . The D_g value of the PAN sample used in this study was also determined using gel fraction values plotted in Figure 2. The dose required for the first

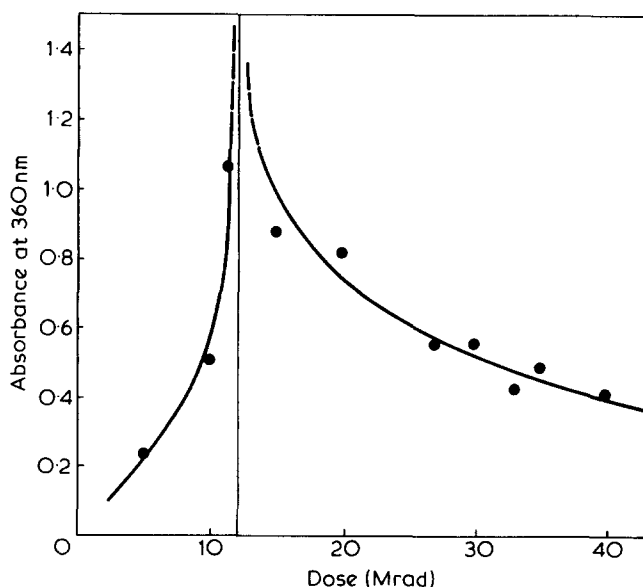


Figure 1 The absorbance values at 360 nm of γ -irradiated PAN solutions as a function of dose

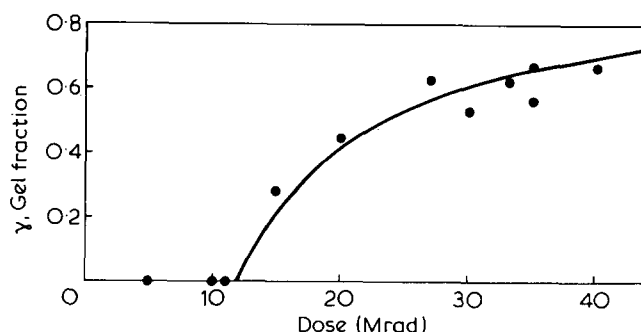


Figure 2 Determination of gelation dose D_g of γ -irradiated PAN using the gel fraction method

appearance of gels determined by this method gives nearly the same value as obtained by photometric method—12 Mrad.

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COMMENTS

Flory-Schulz distribution does hold for reversible polycondensation

Comments on the articles on reversible nylon-6 polymerization by S. K. Gupta *et al.*

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Reading two articles^{1,2} invites some comment (*Polymer* 1981, **22**, 387; *Polymer* 1981, **22**, 481).

FLORY-SCHULZ DISTRIBUTION

The general idea put forward in these articles is that the Flory-Schulz distribution in polycondensation holds only when the forward reaction is taken into consideration, whereas deviations should occur when the backward reaction is also included. To prove this hypothesis the authors borrow rate and equilibrium constants from the literature and by using rate equations for the monomer (S_1) and for a chain of length n (S_n) they calculate the number distribution during reaction. They find a maximum for $n=2$ if the backward reaction is also taken into consideration and thus conclude the distribution differs from a F.S. distribution. An F.S. distribution is found by the authors only in those cases where the backward reaction is neglected.

Flory in his book does not make any assumption about forward and backward reactions but only defines the probability for any functional end group to be free as p or

to be connected as $(1-p)$, independent of chain length. As a consequence the result of the authors is in contradiction with their own and the identical assumption of equal reactivity. Therefore, there may be some errors in the authors' equations.

They define the rate constants k_1 and k_2 for condensation and hydrolysis, successively, based on concentrations of functional groups.

The equation for the monomer then becomes:

$$\frac{d[S_1]}{dt} = -2k_1[S_1] \sum_{n=1}^{\infty} [S_n] + 2k_2[W] \sum_{n=2}^{\infty} [S_n]$$

The factor 2 in the first term originates from the two possibilities of reacting an S_1 with an S_n (both having two end groups). The authors state, however, that for $S_n=S_1$, this factor should be unity and from their calculations it can be assumed that they indeed took that factor as equal to unity. However, also in that case the factor should have the value of 2.

The explanation is as follows: a factor 2 should be added because of the two end groups in one S_1 molecule