

## Crosslinking Poly(ethylene Oxide) in Dilute Solutions by Gamma Rays

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### Synopsis

A high molecular weight poly(ethylene oxide) is gelled by radiation from a  $^{60}\text{Co}$  source. At concentrations of 0.25 to 1 wt-%, doses of 4.5 to  $7.5 \times 10^4$  rad cause gelation. The storage modulus of the gel formed increases linearly with additional dose to a plateau value and then remains constant during further irradiation. The dose needed to reach the plateau,  $D_p$  in rads, and the plateau modulus  $G_p$  in dynes per square centimeter, are related to the concentration  $c$ , in weight per cent:  $D_p = 1.05 \times 10^6 c$  and  $G_p = 1.75 \times 10^4 c^{2.5}$ . The energy absorbed by the polymer per crosslink formed is about  $80 \pm 10$  kcal/mol. The crosslink density produced by radiation is calculated from the measured modulus by using the theory of rubber elasticity. Both modulus and loss are measured in a special air-bearing, recording torsion pendulum with a cone-plate geometry.

### INTRODUCTION

The ultimate effect of radical formation in polymers by gamma radiation may be chain scission or crosslinking. The chemical nature of the polymer and the presence or absence of oxygen usually are major factors in the favoring of one result over the other. Aqueous solutions of a variety of polymers have been irradiated and reported in the literature. Most studies have involved measuring viscosity changes before gelation and the dose necessary to gel. Controlled variables have been molecular weight, concentration, presence of oxygen, pH, and addition of monomers or of proposed antirads. Polymers studied include the homopolymers of acrylic acid,<sup>1,2</sup> methacrylic acid,<sup>2</sup> styrene sulfonate,<sup>2</sup> vinyl pyrrolidone,<sup>2,3</sup> and vinyl acetate.<sup>1</sup> Also reported are poly(ethylene oxide),<sup>4-6</sup> gelatin,<sup>7</sup> and poly(vinyl alcohol).<sup>1,2,8,9</sup>

Formation of gels is favored when dissolved oxygen is excluded, although gelation can occur in the presence of oxygen despite extensive chain scission. Radiation may generate a radical on the polymer chain directly or it may generate a species in the solvent, which in turn attacks the polymer chain, giving a radical on the polymer indirectly. In the *direct* mechanism the high-energy radiation results in abstraction of a hydrogen atom from the chain, leaving a radical (unpaired electron) site on the chain.

This radical can rearrange to a more stable state by chain scission in the neighborhood of the original attack, or it may move by virtue of molecular or segmental diffusion close enough to another chain radical to form a stable covalent crosslink. In aqueous solutions radiation generates hydroxyl radicals from the water, which can, by *indirect* action, abstract hydrogen atoms from the polymer. It has been proposed by Charlesby that in solutions of poly(ethylene oxide) only the direct action is operative.<sup>4,5</sup> This conclusion is based on the variation in radiation dose required to cause gelation as polymer concentration is increased beyond the critical concentration for macroscopic gel formation. Above the critical point the dose needed to gel poly(ethylene oxide) does not increase as the concentration is increased, indicating the method of direct action. The dose for gelling some other polymers, such as poly(vinyl pyrrolidone), does increase with concentration, which is taken as evidence supporting indirect action.<sup>4</sup>

A handicap suffered by most workers is that the measurement of yield of crosslinks has been dependent on the assumption that the molecular weight of the polymer does not decrease as irradiation proceeds and that incipient gelation occurs when one crosslink has been introduced for each pair of original polymer molecules.<sup>10a</sup> Without taking into account distributions of molecular weight, chain scission, and intramolecular crosslinks, the accumulation of assumptions becomes quite vexing. Moreover, the yield of crosslinks after gelation seems not to have been investigated extensively.

In the present work the poly(ethylene oxide) used is of very high molecular weight originally, so that the complication of chain ends that do not contribute to rigidity in a network is minimized. The measurement of modulus gives a theoretically defensible estimate of the crosslink density in the postgelation regime. Similarly, the extrapolation of modulus to zero gives a rather more elegant measure of the dose to gel than does visual inspection alone.

## EXPERIMENTAL PROCEDURE

### Preparation of Samples

Poly(ethylene oxide), coagulant grade (Union Carbide Corp., N.Y.), with a viscosity-average molecular weight of about  $4 \times 10^6$ ,<sup>11</sup> was dispersed by the boiling-water technique<sup>12</sup> and dissolved by rocking at 25°C for 1 wk. Minute, insoluble impurities were removed by pressure filtration with an 0.8  $\mu$  Metrice filter (Gelman Inst. Co., Ann Arbor, Mich.). A very small amount of undissolved but swollen polymer also was retained on the filter.

The polymer solution was stored at 3°C to inhibit bacterial growth. When needed for irradiation the solution was deoxygenated by shaking for 45 min while drawing a vacuum. Then the evacuated flask was flooded with nitrogen. The solution, blanketed with nitrogen, could be

transferred to a cone-plate viscometer especially prepared for this work. Briefly, an acrylic plastic sleeve is used to contain the polymer solution between the base plate and truncated cone, while any excess is removed via two vents. A visual check is made through the transparent sleeve, to ensure that no bubbles are trapped between the cone and plate. Finally, a spacer is set on top of the sleeve to ensure accurate horizontal and vertical alignment of the cone.

The viscometer with sleeve and spacer is then set inside an irradiation vessel for easy handling in the Cornell University Gamma Facility, a 5700-Ci  $^{60}\text{Co}$  gamma source. The steel-encapsulated  $^{60}\text{Co}$  source in the form of cylinders 0.380 in. in diameter by 8 in. was calibrated by the Fricke chemical dosimeter (ASTM D 1671-63) to give an absorbed dose in water of about 9600 rad/min at the center of a circular metal rack with a 4 in. radius. The strength of field varies in a known manner with the vertical position at the center of the circle and was calculated to vary insignificantly within a 1-in. horizontal radius from the centerline. Because the Cornell source must be raised from an underground well and positioned each time in the circular rack, the unirradiated polymer samples are protected from stray radiation behind a 6-in. lead wall before and after exposure in the known field. The vessel is purged with wet nitrogen through the irradiation as added insurance against any oxygen's diffusing into the polymer solution in the viscometer.

### Measurement of Dynamic Properties

A torsion pendulum has been designed<sup>13</sup> with an air-lubricated bearing to support a moment arm and the cone of a cone-and-plate viscometer. The frequency of oscillation,  $\omega$  (radians per second) and logarithmic decrement  $\lambda$  of the irradiation-formed gel can be recorded after the cone is given a small initial displacement.

The complex modulus  $G^*$  of the gel, the storage modulus  $G'$ , and the loss modulus  $G''$  are related as follows:<sup>14</sup>

$$G^* = G' + iG'' \quad (1)$$

$$G' = 3I\phi f^2 [1 + \lambda^2/(4\pi^2)] / (2\pi R^3) \quad (2)$$

$$G'' = 3I\phi f^2 \lambda / (2\pi^2 R^3) \quad (3)$$

where  $I$  = moment of inertia of the oscillating system,  $\phi$  = angle between the cone and plate, and  $R$  = the radius of the cone.

### Calculation of Crosslink Density and Radiation Yield

In the swollen gel the effective number of polymer chains per unit volume,  $N$ , in moles per cubic centimeter of gel, theoretically is given by<sup>15</sup>

$$N = G'/RT \quad (4)$$

where  $G'$  is in dynes per square centimeter and  $RT$  is  $2.46 \times 10^{10}$  dyne-cm/mol at 23°C. There is one crosslink for every two polymer chains,

assuming no loose ends. Evidence has been found that  $N$  calculated from mechanical measurement of  $G'$  overestimates the number of polymer chains by as much as 50%.<sup>16</sup> A polymer chain is defined here as a segment fixed at each end by a crosslink.

In order to calculate the yield of crosslinks produced by the radiation dose that causes incipient gelation in poly(ethylene oxide) Charlesby has assumed that<sup>5</sup> (a) there is negligible chain scission up to the point of gelation, so that the initial viscosity-average molecular weight can be used, (b) one crosslink has been introduced for each primary molecule, and (c) only the energy absorbed by the polymer is effective in generating crosslinks. His calculations lead to a yield ( $G$  value) of 4.46 crosslinks per 100 eV of energy absorbed by a poly(ethylene oxide) of  $M_v = 240,000$ , corresponding to an absorbed energy of 515 kcal/mol of crosslinks.

## RESULTS AND DISCUSSION

The storage modulus  $G'$  increases linearly to an upper limit with radiation dose after a certain minimum dose is exceeded (Fig. 1). The linearity of such plots encourages the choice of the intercept with the abscissa as being the "dose to gel," which is more commonly measured by visual inspection of the sample. As irradiation is continued, the gels become progressively stronger and also stiffer, until the plateau is reached beyond which further irradiation does not increase the modulus. The character of the gel is observed to change from weak and pituitous near the gelation point to brittle just before the plateau. The brittle gels in the plateau region are easily broken into small shards when handled, unlike the gels at lower

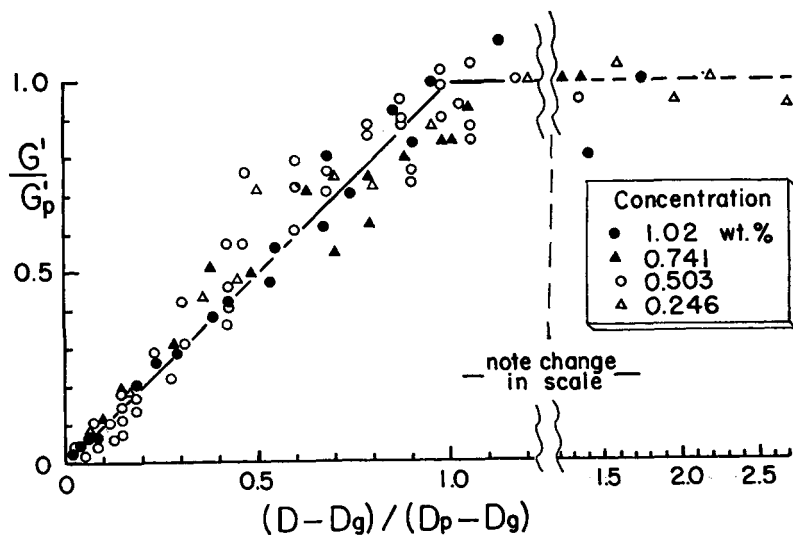


Fig. 1. Reduced modulus as a function of reduced dose for four concentrations of poly(ethylene oxide) in water. The constants  $G'_p$ ,  $D_g$ , and  $D_p$  are listed in Table I.

doses, which sustain large deformations and remain cohesive. Qualitatively, the same linear behavior is observed at various concentrations (Fig. 1). The values of the characteristic parameters gelation dose  $D_g$ , plateau-dose  $D_p$ , and plateau modulus  $G'_p$  are given in Table I for the concentrations studied.

TABLE I  
Characteristic Radiation Parameters

Concn. $c$ , wt-%	Gel. dose $D_g$ , rad ( $\times 10^{-5}$ )	Plat. dose $D_p$ , rad ( $\times 10^{-4}$ )	Plat. mod. $G'_p$ , dyn/cm <sup>2</sup> ( $\times 10^{-3}$ )	Absorbed energy per crosslink, $E_c$ , kcal/mol
0.246	0.45	2.00	0.44	92
0.503	0.75	5.85	3.5	87
0.741	0.75	8.0	9.2	69
1.02	0.75	10.0	15.7	71

The gelation dose is constant above the lowest concentration. The plateau parameters may be represented (Fig. 2) as

$$D_p = 1.05 \times 10^6 c \quad (5)$$

$$G'_p = 1.75 \times 10^4 c^{2.5} \quad (6)$$

where  $c$  is in weight per cent polymer,  $D_p$  is in rads, and  $G'_p$  is in dynes per square centimeter. The dependence of modulus on concentration is not of an unusual order. The rigidity of gelatin gels is roughly proportional to the square of the concentration,<sup>17</sup> and the dynamic modulus of aluminum

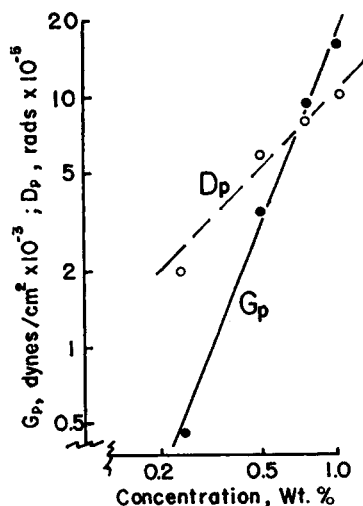


Fig. 2. The plateau modulus  $G'_p$  and plateau dose  $D_p$  vary with the concentration to the  $5/2$  and the 1 order, respectively [eqs. (5) and (6)].

soaps gels in organic solvents is proportional to the concentration raised to the 2.5 power.<sup>18</sup> At gelation any polymer system consists of a gel phase and a sol phase, the former increasing at the expense of the latter as crosslinking continues. One can estimate the size of the sol fraction from relationships summarized by Flory.<sup>10b</sup> For example, the plateau modulus for the lowest concentration listed in Table I corresponds to a molecular weight between crosslinks [eq. (4)] of about  $10^4$ . Since the original molecular weight is more than  $10^6$ , this means that, even when the modulus is only 10% of the plateau modulus, there are more than 10 crosslinked units per molecule. The sol fraction corresponding to such a high crosslink index is less than  $10^{-4}$ . It seems reasonable to assume, then, that the increase in modulus that we see is the result of continued crosslinking of a gel and that conversion of sol to gel is virtually complete even at the lowest measured moduli.

The plateau values of radiation dose and modulus can be combined to give the energy absorbed directly by the polymer per crosslink produced,  $E_c$ . Since there is one crosslink for every two polymer chains of eq. (4), and the crosslink density increases linearly with dose above the dose needed for incipient gelation (Fig. 1),

$$E_c = 2(D_p - D_g)cRT/G'_p \quad (7)$$

The concentration  $c$  is needed in the calculation to convert the total dose absorbed per gram of gel to dose absorbed per gram of polymer, since we have assumed only a direct effect of the radiation striking the polymer to produce crosslinks. The values of  $E_c$  in Table I thus represent the energy directly absorbed beyond the gelation point that produces a crosslink. They show only a modest change with concentration and, even if we are overestimating the number of crosslinks by as much as 50%, the energy per crosslink via direct radiation is still uncomfortably below the dissociation energy for the carbon-hydrogen bond. Two such bonds with energies of 100 kcal/mol each would be needed for one crosslink in the absence of indirect radical formation.

The dose to gel of 515 kcal/mole calculated from the article by Charlesby and Kopp diverges quite widely from the values of  $E_c$  calculated here for crosslinking above the gelation point. From the present work a calculation similar to Charlesby's, with the use of an average value of  $0.75 \times 10^5$  rad for  $D_g$  and a molecular weight of  $4 \times 10^6$  gives an energy to gel,  $E$  (gelation), of 710 kcal/mol.

There are several rationalizations for the tenfold difference in  $E_c$  calculated from the plateau and from incipient gelation doses. If the molecular weight of the primary molecules has been greatly diminished by chain scission, then many more crosslinks are needed to cause gelation. For a given dose to gel this means that  $E_c$  based on original molecular weight is overestimated. Furthermore, the molecular weight used by us is 16 times higher than that of Charlesby, is more sensitive to radiation, and would be expected to degrade more readily.<sup>19</sup> The difference between Charlesby's

$E_c$  (gelation) of 515 and the present one of 710 is consistent with this mechanism. A second possibility is that crosslinking is very inefficient before gelation and very efficient after gelation. This seems unlikely, because the diffusion of one chain radical to another is not enhanced in a gel. In fact, the decreased termination between chain radicals is the seat of the well-known Tromsdorff effect in vinyl polymerizations.

At any rate, an exclusively direct effect (formation of radicals utilizing only the energy absorbed by the polymer) as proposed by Charlesby seems to be an untenable viewpoint. Indirect radical formation on the polymer is due to hydrogen and hydroxyl radicals produced by the radiolysis of water, probably as an adjunct to the direct effect. If  $G$  is defined as the

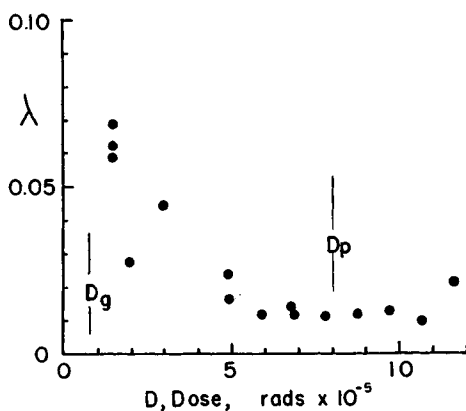


Fig. 3. Energy dissipation represented by the log decrement  $\lambda$  decreases after gelation dose  $D_g$  but shows no discontinuity where the modulus stops changing,  $D_p$ . Concentration is 0.741 wt-% of polymer.

number of crosslinks produced per 100 eV of energy absorbed by the polymer, a  $G$  value for exclusively direct action of the radiation is calculated to be 33 when  $E_c$  equals 70 kcal/mol, compared to 4.46 reported by Charlesby. Combining the energy of the direct and indirect actions,  $G = 0.33$  for the 1% solution, based on the total energy absorbed in the solution.

One would expect that immobilization of polymer in a network should decrease the energy-dissipating capability of the system. At the gelation point the measure of energy dissipation,  $\lambda = \pi G''/G'$ , decreases very rapidly as the dose exceeds the minimum (Fig. 3). That the system continues to become more resilient as radiation proceeds is not unexpected, since loose chain ends and long polymer segments are being eliminated. On the other hand, there is no apparent discontinuity in the loss curve at the plateau dosage.

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