

## Gelation of Poly(ethylene Oxide) Solutions by Gamma Radiation: Effects of Molecular Weight and Irradiation Conditions\*

R. A. VAN BREDERODE† and F. RODRIGUEZ, *School of Chemical Engineering, Olin Hall, Cornell University, Ithaca, N. Y. 14850*

### Synopsis

Reticulation of a dilute aqueous solution of poly(ethylene oxide) in a  $^{60}\text{Co}$  gamma-radiation field yields a weak gel which is characterized by its damped sinusoidal oscillation in a free-swinging torsion pendulum. A storage and a loss modulus are calculated from the log decrement and frequency of oscillation, and the crosslink density is obtained from the storage modulus using the kinetic equation of rubber elasticity. The number of crosslinks added to the polymer per 100 eV of energy absorbed in the polymer above and below the gel point and the fraction of gamma energy absorbed directly by the polymer were determined from the dose-to-gel and modulus data. The effect of oxygen on the crosslinking reaction and the temperature on the gel's mechanical properties were experimentally observed.

### INTRODUCTION

In previously reported work, the gelation of dilute solutions of a high molecular weight poly(ethylene oxide), PEO, by gamma radiation was described.<sup>1</sup> The study of reticulation beyond the point of incipient gel formation was carried out by mechanical measurements of the modulus of the gel after it had been exposed to various doses of radiation. A Voigt model for the gel's viscoelastic behavior was used to define the storage and loss moduli and the crosslink density was calculated from the kinetic equation of rubber elasticity. The actual measurements were of frequency of oscillation and log decrement in a torsion pendulum using cone-and-plate geometry. The cone-and-plate assembly also served as an irradiation vessel. Both the irradiation vessel and the torsion pendulum have been described.<sup>2</sup> Some minor changes in the irradiation vessel were made in the present work.

Exposure of deoxygenated aqueous solution of PEO to  $^{60}\text{Co}$  gamma radiation yields a crosslinked gel network provided that a minimum concentration and molecular weight are exceeded. The mechanism involves radical

\* Presented before the Division of Polymer Chemistry, 158th Meeting of American Chemical Society, New York, September 1969.

† Present address: Esso Research and Engineering Co., Baytown, Texas.

formation on the polymer chain either by a direct action of the high energy radiation on the polymer, or by indirect attack on the polymer by solvent-derived radicals. The salient features of irradiation demonstrated earlier<sup>1</sup> are (a) a radiation dose to gel,  $D_g$ , (b) a linear increase in modulus with dose above  $D_g$ , and, finally, (c) a maximum "plateau" modulus  $G_p'$  achieved with a certain dose  $D_p$ . Irradiation beyond  $D_p$  does not change the modulus from  $G_p'$ .<sup>1</sup>

Extending previously reported work on the storage modulus and log decrement of PEO gels, these gel properties have been studied as functions of polymer concentration and molecular weight, oxygen concentration in the inert cover gas, and measurement temperature. In addition, the dose to gel has been determined from the theoretically expected modulus at the gel point and the efficiency of crosslinking calculated below and above the gel point. Preliminary work has begun on the effect that varying irradiation temperatures and dose rates have on the modulus.

### EXPERIMENTAL PROCEDURE

The poly(ethylene oxide) used was provided (Union Carbide Corp., N. Y.) in four molecular weight grades, as indicated in Table I. Solution storage and degassing prior to irradiation is described in a previous paper.<sup>1</sup>

TABLE I  
Poly(ethylene Oxide) Polymers Studied

Polymer	Union Carbide Designation	$M_v$	Plateau dose $D_p$ for 1% soln, Mrad
I	Polyox Coagulant	3,900,000	0.85
II	Polyox WSR-301	2,500,000	0.85
III	Polyox 3-WHG-101-A	850,000	1.95
IV	Polyox WSR-35	302,500	2.6

The viscometer assembly<sup>2</sup> has been slightly modified. The O-ring was replaced by a slightly greased step fitting to prevent seizing of the O-ring on the sleeve. The sleeve now fits directly over a step cut into the base plate. The acrylic sleeve was also replaced with a constant bore glass sleeve to eliminate the degradation and crazing which occurred after prolonged exposure in the gamma field.

A heated plate provided with a temperature controller and vacuum holes was substituted for the vacuum table<sup>2</sup> when the temperature dependence of the storage modulus was studied.

### POLYMER CONCENTRATION AND MOLECULAR WEIGHT

The plateau modulus,  $G_p'$  rises, as shown in Figure 1, with the 2.25 power of the concentration. At the lowest concentration (0.25 wt-%), the rise in

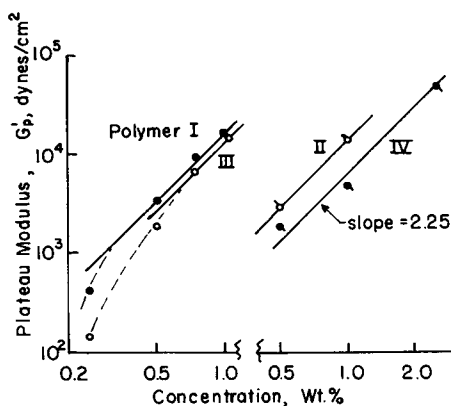


Fig. 1. Variation of plateau modulus,  $G_p'$ , with concentration for polymers of Table I.

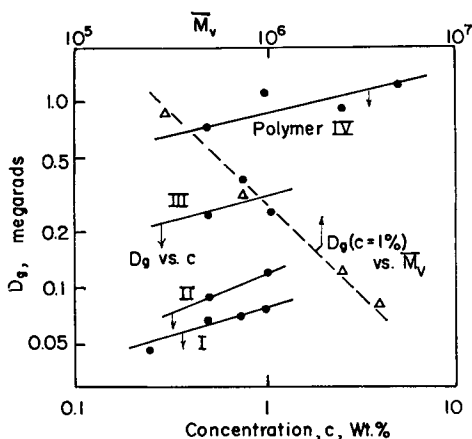


Fig. 2. Dose to gel,  $D_g$ , as a function of concentration  $c$  and of original molecular weight  $\bar{M}_v$ .

modulus with concentration is more rapid, but this may be due to a concentration limitation in the gel structure which does not appear above 0.5 wt-%. A dependence of the modulus on the second or third power of polymer concentration has been noted for aluminum soap and gelatin gels.<sup>3,4</sup> The dependence of modulus on molecular weight at a given concentration (above 0.5 wt-%) corresponds to a 0.3 power. The dependence on molecular weight is greater than can be accounted for by the increase of chain ends in the network at lower molecular weights. Perhaps the broad distributions noticed in these polymers include a substantial amount of low ends which do not participate in network formation.

The modulus expected when there is one crosslink per two initial viscosity-average molecular weight molecules can be calculated<sup>5</sup> and may be used to define the dose to gel a PEO solution,  $D_g$ , when the modulus versus the total dose received in the solution is known. Despite the difficulty of the

measurement involved, the dose to gel appears to rise slowly with concentration as shown in Figure 2, over the concentration range 0.25 to 1.0 wt-% PEO. Both Charlesby<sup>6</sup> and more recently King and Ward<sup>7</sup> notice an upswing in  $D_g$  at concentrations less than 2%. This could be due to the well-known concentration limitation on gel formation where the dose to gel rises rapidly as the polymer molecules become discontinuous across the solution. However, in this study no increase in the dose to gel with decreasing concentration is observed even as low as 0.25 wt-% PEO as Figure 2 indicates. The experimenters feel that this discrepancy may be due to the inherent difficulty in establishing a gel point by the flow-no flow approach as opposed to the definition of gel point from a concentration and molecular weight-dependent modulus. An irradiation-induced PEO gel is initially pituitous but evolves upon irradiation to the brittle condition at or near the dose to achieve the plateau modulus. However, a low concentration gel will generally appear "tighter" during all stages of crosslinking than will a low molecular weight polymer gel. This makes the definition of dose to gel very subjective when visually using its flow characteristics to define the gel point.

One theory of gel formation (see eq. (1) below) indicates that, at constant concentration, the dose to gel is expected to be inversely proportional to molecular weight. Replotting the data for the dose to gel (also shown in Fig. 2 for a 1 wt-% solution) indicates that the dose to gel as determined by the modulus expected at the gel point does indeed follow the inverse dependence of  $D_g$  on  $M$ . This inverse dependence has also been shown to apply to poly(vinyl alcohol) above the region of concentration limitation to gel formation.<sup>8</sup>

### G VALUE

Sakurada and Tkada<sup>8</sup> derived an equation relating dose to gel,  $D_g$ , to  $k$ , the fraction of water-absorbed energy that is used for crosslinking. The number of crosslinks produced in the gel per 100 eV absorbed, the  $G$  value, for crosslinking below the gel point may be calculated from this equation by plotting  $1/D_g M$  versus  $1/c$ :

$$\frac{1}{D_g M} = \frac{2AGk}{N} \left(\frac{1}{c}\right) + \frac{AG}{50N} (1 - k) \quad (1)$$

where  $A$  is the conversion factor from rads to eV,  $N$  is Avogadro's number,  $M$  is the polymer molecular weight,  $G$  is the number of crosslinks formed per 100 eV,  $D_g$  is the dose to gel, and  $c$  is the polymer concentration in wt-%. From this plot (Fig. 3), the  $G$  value is calculated to be 1.4 crosslinks per 100 eV absorbed in the polymer and compares to a value of 4.46 found by Charlesby and Kopp.<sup>6</sup> The difference is attributable to the use in the present calculations of a crosslink density of one per two initial polymer molecules at the gel point<sup>9</sup> compared to one per one by Charlesby; to the use of an average dose to gel and slightly different molecular weight by

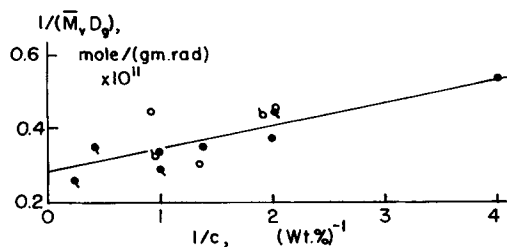


Fig. 3. Determination of  $G$  and  $k$  from eq. (1): (●) I; (○) II; (○) III; (●) IV.

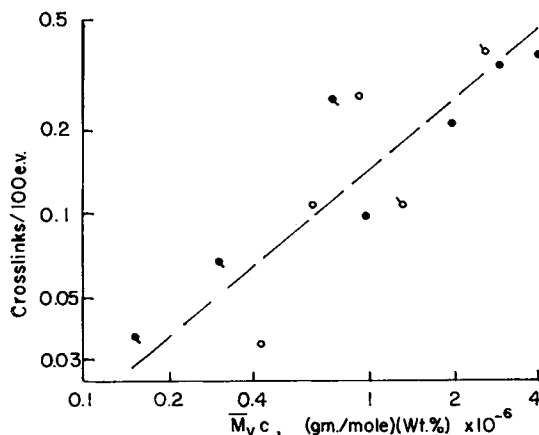


Fig. 4. Chemical yield of radiation,  $G$ , correlated with product of concentration and original molecular weight: (●) I; (○) II; (○) III; (●) IV.

Charlesby; and the inclusion in this study of indirect energy absorption by the polymer.

The fraction of energy absorbed indirectly,  $f$ , is found from

$$f = \frac{k(100-c)}{c + k(100-c)} \quad (2)$$

Using a value of  $k = 0.002$  from Figure 3,  $f$  is 30% at a 0.5 wt-% PEO concentration and 18% at 1 wt-% PEO. This is considerably less than the 90% Sakurada and Ikada<sup>8</sup> find for poly(vinyl alcohol) but is greater than Charlesby's finding that gelation of PEO takes place entirely by the direct mechanism. Above 5 wt-% PEO, however, the crosslinking appears to be almost entirely direct.

Crosslinking above the gel point is found to depend on the polymer concentration and molecular weight. From the rising portion of the modulus-versus-total-dose-received curve, the  $G$  value based on the *total energy absorbed in the system* increases with concentration. If the energy absorbed were entirely direct, this  $G$  value would rise as the first power of concentration, but the added indirect effect makes the rise more rapid than directly

proportional to concentration. Figure 4 shows that, based on the *total energy absorbed in the solution*,  $G$  ranges from 0.04 to 0.4. Assuming that the indirect energy absorption is similar to that below the gel point, the  $G$  value is corrected for indirectly absorbed energy and found to be 4 to 20 based on energy absorbed in the polymer. This is of the same order of magnitude as that found below the gel point. At the dose necessary to achieve the plateau,  $G$  abruptly drops to zero and the crosslinking apparently ceases. The plateau value of the storage persists to several times the dose to reach the plateau and suggests that no major degradation occurs in the gel. However, syneresis is observed in the plateau region. This syneresis, coupled with the extreme brittleness of the gels at the plateau, serves as a handling limitation of the study of the gels far into the plateau region.

A supramolecular open-cell structure has been proposed for these gels in which the polymer molecules form the network of the open cell.<sup>10</sup> This structure could be visualized as the chicken wire foundation of a papier-mâché model. Electron micrographs of these cells typically indicate a diameter of 1000 angströms. The walls appear to become thicker with radiation received beyond the gel point but no noticeable change occurs beyond the plateau dose.

While Figure 4 indicates that the  $G$  value is best correlated against the product  $M_w c$ , the authors can advance no hypothesis for including  $M_w$  in this way.

### LOG DECREMENT

As indicated in a previous paper,<sup>1</sup> the log decrement,  $\lambda$ , decreases rapidly to an asymptotic value for gels irradiated beyond the gel point. The magnitude of the asymptote is found to depend on both the polymer concentration and initial molecular weight. It is shown in Figure 5 that at constant concentration, a higher initial molecular weight PEO corresponds to a lower asymptotic value of  $\lambda$ . Similarly, but not shown, at constant

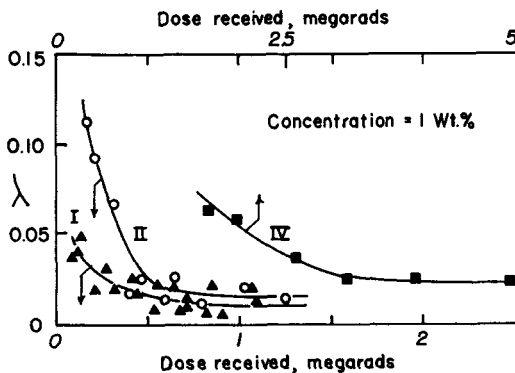


Fig. 5. Log decrement (measure of damping) as a function of radiation dose. Plateau dose for each polymer is listed in Table I.

molecular weight  $\lambda$  eventually reaches a lower value at higher concentrations. Thus the viscous loss is reduced by decreased numbers at chain ends inherent in the gels of high molecular weight and also by the increased numbers of polymer molecules throughout the solution. Calculation of the number of crosslinks per initial polymer molecule from the kinetic equation of rubber elasticity<sup>1</sup> also confirms that there are more crosslinks formed under conditions of higher molecular weight in higher concentration. These crosslinks tend to reduce the viscous loss from loose polymer ends.

### MEASUREMENT TEMPERATURE

The gel properties were measured at  $25 \pm 1^\circ\text{C}$ , but if gels conform to the kinetic equation of rubber elasticity as postulated,<sup>1</sup> the modulus should be directly proportional to the absolute temperature of measurement,  $T$ .

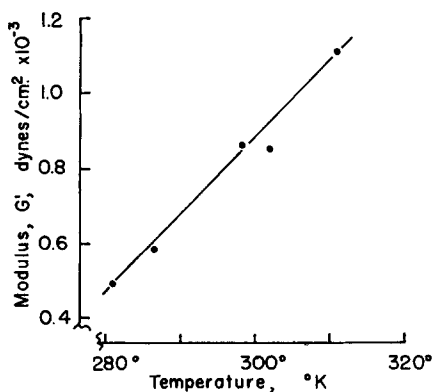


Fig. 6. Linear relationship between modulus and temperature (but intercept is not zero). Polymer III;  $c = 0.5$  wt-%; dose, 0.7 Mrad.

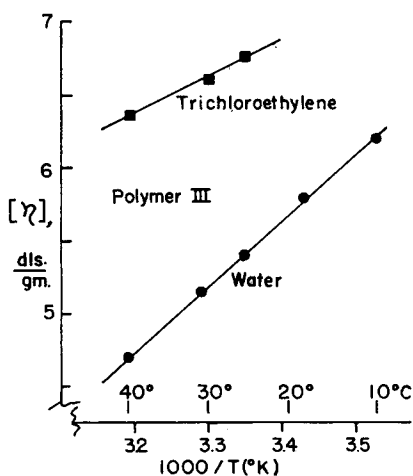


Fig. 7. Intrinsic viscosity dependence on temperature of polymer III.

Over a range from 6°C to 38°C, the modulus is found to increase faster than directly proportional to  $T$ , indicating additional crosslinking which increases with temperature, as shown in Figure 6. Intrinsic viscosity determinations for PEO in water, Figure 7, indicate that at higher temperature the polymer molecule is contracting in volume. An upper theta temperature at about 90°C is known for PEO in water.<sup>11</sup> The additional crosslinks in a gel at elevated temperature may then be attributed to "hydrophobic bonding" which stiffens the gel.

Because all other measurements of modulus were carried out at 25°C, the contribution of the hydrophobic bonds to the measured modulus is considered a constant value when the number of crosslinks added per 100 eV of gamma energy, the  $G$  value, is calculated.

Also from Figure 7, trichloroethylene is observed to be a better solvent for PEO than water, although there is also a change in intrinsic viscosity (or in molecular volume) with temperature. Water was chosen as the solvent for the studies of the radiation-induced crosslinking of PEO because it is an excellent radical producer and does not act as a radical scavenger to deactivate any radical species formed on the polymer chain by the direct mechanism of radical production.

### OXYGEN CONCENTRATION

The PEO solution was degassed for 45 min prior to irradiation. A nitrogen atmosphere was maintained over the degassed solution. Neither dry (approximately 0.1% oxygen contamination) nor prepurified (approximately 0.002% oxygen contamination) nitrogen affected the gel properties, but a 1.02% solution of oxygen in nitrogen did. The changes, as shown in Figure 8, are toward a lower plateau modulus, a less rapid rise in modulus with dose, and a higher dose to gel, all indicative of a decreased molecular weight. It then appears that above about 0.1% oxygen in nitrogen there is

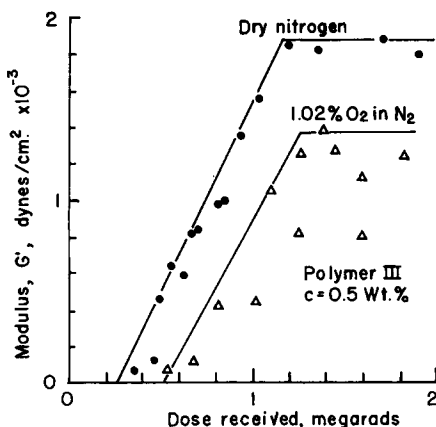


Fig. 8. Effect of oxygen in the cover gas during radiation, polymer III,  $c = 0.5$  wt-%.



a measurable amount of chain scission prior to gel formation. This gives the gel properties that make it appear as if it were formed from a lower molecular weight initial polymer.

### EXPLORATORY WORK

Irradiation of PEO solutions at various temperatures might be expected to have an effect similar to that of varying the molecular expansion by changing the pH or concentration of salt in polyelectrolytes<sup>12</sup> because of the temperature effect on the PEO molecular volume.

All of the above gels were formed at  $31 \pm 1^\circ\text{C}$ , but in changing the irradiation temperature to  $35 \pm 0.5^\circ\text{C}$ , the plateau modulus decreases by a factor of two for a 0.5 wt-% solution of polymer III. Neither the value of the dose to gel nor the rise in modulus with dose received appear to be altered at the higher irradiation temperature. Several runs at temperatures lower than  $31^\circ\text{C}$  indicate that an increased modulus is possible. It would be interesting to see if the effect on the plateau modulus by increasing the molecular expansion could be correlated with that observed for the rise in modulus for varying initial PEO molecular weights.

An increase in radiation dose rate from 7,500 to 148,000 rads/min was not found to alter the dose to gel in accordance with Charlesby's findings,<sup>6</sup> or the rise in modulus with dose received in the solution. Because the irradiation at high dose rate was carried out at a temperature less than  $31^\circ\text{C}$ , the effect of dose rate on the plateau modulus at  $31^\circ\text{C}$  was not obtained.

This work was conducted with the aid of Grant G.K.-1093 from the National Science Foundation.

### References

1. R. A. van Brederode, F. Rodriguez, and G. G. Cocks, *J. Appl. Polym. Sci.*, **12**, 2097 (1968).
2. F. Rodriguez, R. A. van Brederode, and G. G. Cocks, *J. Appl. Polym. Sci.*, **12**, 2415 (1968).
3. R. E. Levy and F. Rodriguez, *Offic. Dig. (FSPT)*, **35**, 289 (1968).
4. J. D. Ferry, *Viscoelastic Properties of Polymers*, Wiley, New York, 1961, p. 392.
5. *Ibid.*, p. 395.
6. A. Charlesby and P. M. Kopp, *Proc. Roy. Soc. (London), Ser. A.*, **291**, 129 (1966).
7. P. A. King and J. A. Ward, *J. Polymer Sci.*, to appear.
8. I. Sakurada and Y. Ikada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **42**, 22 (1964).
9. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N. Y., 1953, p. 358.
10. L. D. Johnson, M. S. Thesis, Cornell University, 1968.
11. F. E. Bailey, G. M. Powell, and K. Smith, *Ind. Eng. Chem.*, **50**, 7 (1958).
12. I. Sakurada and Y. Ikada, *Bull. Inst. Chem. Res., Kyoto Univ.*, **41**, 103 (1963).

Received August 20, 1969

Revised December 3, 1969