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The Effect of Ionizing Radiation on Acrylamide-Methylenebisacrylamide Gels

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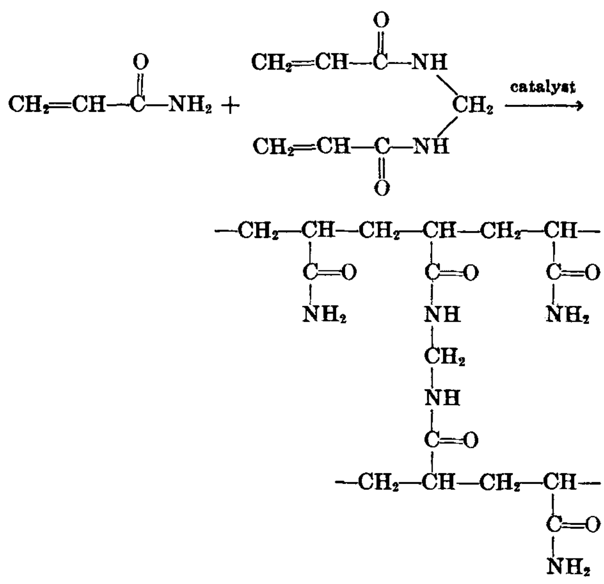
Introduction

Aqueous solutions of acrylamide-methylenebisacrylamide mixtures will form rigid gels if polymerized by free radicals.[1] Crosslinked polyacrylamide molecules are formed:



The process of polymerizing these monomers in situ has found industrial application in the field of soil stabilization.[2-4] Stabilization of soil adjacent to nuclear reactors and stabilization of radioactive waste products have been applications suggested for polymeric materials. Because of its ease of in situ polymerization, the acrylamide-methylenebisacrylamide system should lend itself to this type of application provided the polymer network is not seriously degraded by the radiation present in the stabilized area. The experiments reported in this paper demonstrate the effects of ionizing radiation on the acrylamide-methylenebisacrylamide polymer network.

Experimental

The gels were formed by adding 1 g. of ammonium persulfate (J. T. Baker Chemical Co., analytical reagent grade) and 1 g. of tetramethylethylenediamine (Ames Laboratory) to 500 ml. of an aqueous acrylamide-methylenebisacrylamide (American Cyanamid Co.) solution and casting the solution between two 12 by 12-in. Lucite acrylic resin plates separated by a $^1/_4$-in. rubber gasket. An acrylamide-methylenebisacrylamide ratio of 95/5* and total monomer concentrations of 10, 6, and 4% were studied. Gelation occurred one to two minutes after casting. This gelled membrane was cut into 2 by 4 in. specimens, and the latter were heat-sealed into polyethylene bags.

The packaged gel specimens were irradiated with 3 m.e.v. electrons from a type KS Van de Graaff accelerator. The packages were placed in thin aluminum trays, and these were reciprocated under the beam by a conveyor until the desired dose had been administered. Suitable precautions were observed to guarantee that the temperature of the samples would not rise above 40°C. The machine parameters employed were as follows: 3 m.e.v., 300 or 600 μa. beam current, 15 in. scan, 210 i.p.m. conveyor speed. The two currents cited provided doses of 0.25 or 0.5 $\times$ 10^6 rad. per pass, respectively. To insure complete penetration and to provide greater uniformity of dose, each sample was turned over after having received one-half of its prescribed dose. The doses administered constituted a geometrical series from 0.45 to 57.60 Mrad., and it is estimated that they were uniform to within $\pm 10\%$ throughout the sample. After irradiation, the samples were observed and two $^3/_4$-in. circular disks cut from each. These disks were immersed in water until they had reached constant weight. The amount of swelling was then related to the dose to which the sample had been subjected.

Results

Figure 1 shows the doses received by the gels and pictures the gels immediately after irradiation. Several noticeable changes are observed: with each series, gel cleavage (internal cavitation) occurred after 3.6 Mrad. (D_4); cleavage increased and the gel shrank as higher doses were administered; syneresis occurred, with water being lost from the gel; the polyethylene bags expanded (D_7–D_9) indicating gas evolution; and finally the gels broke apart into smaller pieces.

Sample G_3D_8 was opened under dilute hydrochloric acid and the resulting basicity and lost water determined. It was found that the gel had shrunk to almost one-third its original weight (38%). Approximately 2.2 mole-% ammonia was determined by titration. Sample G_3D_9 was immersed in dilute hydrochloric acid for six days to assure complete penetration and neutralization of trapped ammonia. This time the mole per cent ammonia was found to be 23.2%, thus indicating that considerable hydrolysis had

* This acrylamide to methylenebisacrylamide ratio is sold by the American Cyanamid Co. as Cyanogum-41 gelling agent.

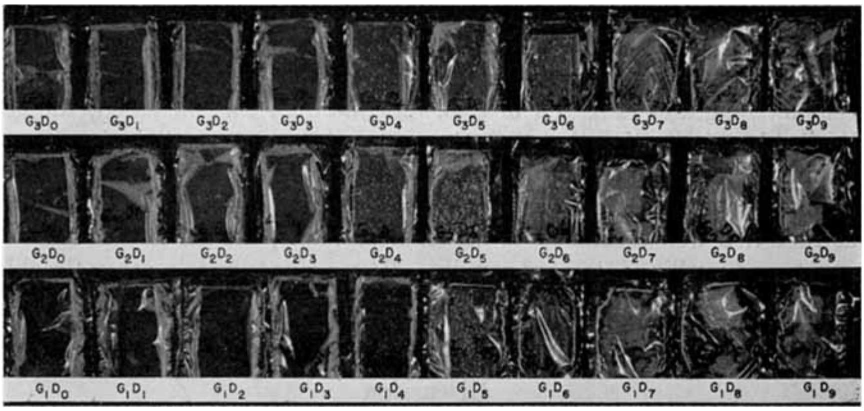


Fig. 1. Irradiated Cyanogum-41 samples.

G_3 = 10% Cyanogum-41
G_2 = 6% Cyanogum-41
G_1 = 4% Cyanogum-41

D_0 = Control
D_1 = 0.45 Mrad.
D_2 = 0.90 Mrad.
D_3 = 1.80 Mrad.
D_4 = 3.60 Mrad.
D_5 = 7.20 Mrad.
D_6 = 14.40 Mrad.
D_7 = 28.80 Mrad.
D_8 and D_9 = 57.60 Mrad.

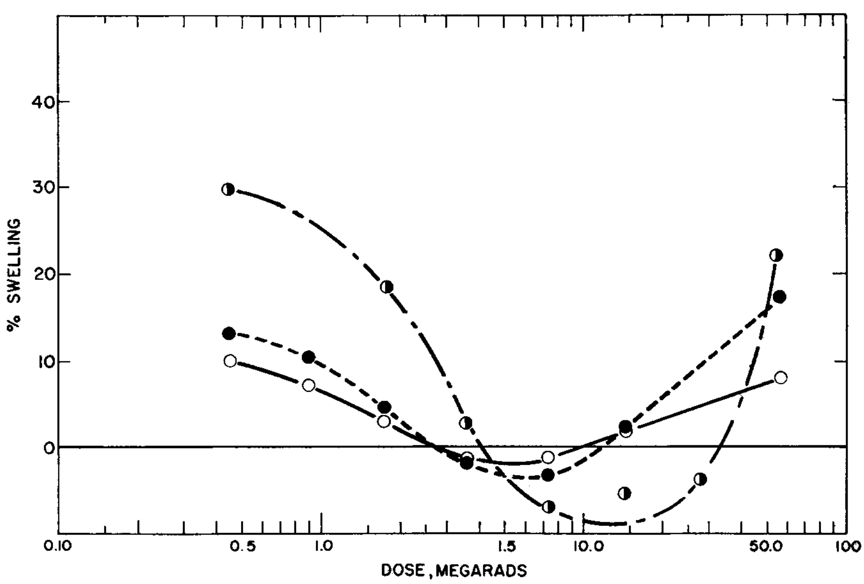


Fig. 2. Per cent swelling of gel vs. total irradiation: (○) 10% Cyanogum-41, (●) 6% Cyanogum-41, (◑) 4% Cyanogum-41.

taken place. An unirradiated control sample was not hydrolyzed in dilute hydrochloric acid.

In Figure 2, data are presented to show the relationship between per cent swelling and radiation dosage. As the dose was increased, the gel swelled less, indicating that the polymer became more crosslinked. Crosslinking increased to a point where, even though immersed in excess water, original water in the gel was forced out (negative swelling). Eventually, as radiation was continued to higher dose levels, the gel network broke apart, and swelling increased rapidly. These effects were most noticeable with the less concentrated gels (G_1 series, 4% acrylamide-methylenebisacrylamide gels).

Discussion

These results indicate that acrylamide-methylenebisacrylamide gels are noticeably affected by ionizing radiation at dose levels above about 2.0 Mrad. Crosslinking appears to commence immediately upon subjection to radiation. A tighter polymer network is formed until eventually the polymer chains are ruptured. Water is forced out of the gel as tightening continues. Hydrolysis of the amide linkage occurs, and ammonia escapes from the gel. Simultaneously, hydrolysis of the methylenebisacrylamide linkage probably takes place, breaking the molecule into smaller pieces.

The dose rates employed in these experiments were quite high and in the vicinity of 0.5 to 1 Mrad./sec. It is quite likely that the radiation damage observed is representative of that which would occur at the dose levels studied irrespective of the type of ionizing radiation employed providing the dose rates also remain the same. However, it is possible that less extensive damage might be observed at these same total dose levels if the irradiations were carried out at much lower dose rates (order of magnitude lower, for example) so as to permit the gel structure to accommodate some of the changes effected by the radiation.

It is a pleasure to acknowledge the contributions of Messrs. G. Butler, E. L. McCarthy, and C. F. Spiers who assisted with the radiation experiments.

References

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Synopsis

Acrylamide–methylenebisacrylamide gels (95/5 monomer ratio) of 10, 6, and 4% total monomer concentration were subjected to from 0 to 57.6 Mrad. of ionizing radiation. With increasing radiation dosage, the gels first shrink because of further crosslinking, then rupture and break into gel particles. At a dose rate of 0.5 to 1 Mrad/sec., the gels will absorb about 5 Mrad. before degradation begins. Weaker gels (4%) will absorb more irradiation before they degrade than will stronger gels (10%).

Résumé

Des gels d'acrylamide–méthylènebisacrylamide (le rapport des monomères est 95/5) de concentration totale en monomère de 10, 6 et 4%, ont été soumis à des radiations ionisantes allant de zéro à 57.6 mégarads. En augmentant la dose des radiations les gels retrécissent tout d'abord à cause de pontages ultérieurs; ensuite il y a rupture et séparation en particules de gel. Pour une vitesse de dose de 0.5 à 1 mégarad par seconde, les gels absorberont environ 5 mégarads avant que ne commence la dégradation. Des gels plus faibles (4%) absorberont, avant de se dégrader, plus de radiations que les gels plus consistants (10%).

Zusammenfassung

Acrylamid–Methylenbisacrylamid-Gele (Monomerverhältnis 95/5) mit einer Gesamtmonomerkonzentration von 10, 6 und 4 Prozent wurden einer ionisierenden Bestrahlung von 0 bis 57,6 Megarad unterworfen. Bei steigender Bestrahlungsdosis schrumpften die Gele vorerst wegen weiterer Vernetzung, bekommen dann Risse und zerfallen in Gelteilchen. Bei einer Dosigeschwindigkeit von 0,5 bis 1 Megarad pro Sekunde absorbieren die Gele ungefähr 5 Megarad, bevor der Abbau einsetzt. Weichere Gele (4%) absorbieren eine grössere Strahlungsdosis bis zu Beginn des Zerfalls als festere Gele (10%).

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