JOURNAL OF APPLIED POLYMER SCIENCE VOL. 17, PP. 3779–3794 (1973)

Poly(vinyl Alcohol) Hydrogels. Formation by Electron Beam Irradiation of Aqueous Solutions and Subsequent Crystallization

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Synopsis

Aqueous solutions of poly(vinyl alcohol) were submitted to varying doses of electron beam irradiation. By modification of the classical Flory-Huggins equations appropriate to the initial state of solution of the polymer, the molecular weight between crosslinks, M_c, was calculated as a function of radiation dose, initial polymer concentration, and temperature. Following crosslinking in the solution state, crystallization was induced by dehydrating the network at temperatures above 90°C. Following dehydration, the polymer network was reequilibrated with water and its tensile properties compared with identically prepared hydrogels not subjected to crystallization by dehydration. Greatly enhanced values of ultimate tensile strength and resistance to tear result from the treatment producing crystallization, compared with those of the crosslinked but not previously dehydrated gels.

INTRODUCTION

The last few years have seen a growing interest in hydrophilic polymer networks for application as biomedical polymers. There exists the problem however, of achieving sufficiently high tensile strengths in materials whose water content may be between 60 and 95 wt-%. This paper presents results of research to develop poly(vinyl alcohol) (PVA) hydrogels by initially crosslinking with electron beam irradiation, then reinforcing the materials using the crystallizability of PVA.

Crosslinking of PVA–H_2O Solutions

Considerable experimental evidence exists illustrating that anhydrous PVA film, irradiated below the glass transition temperature, undergoes molecular scission rather than crosslinking.[1–4] Irradiation above T_g has been shown to lead instead to crosslinking as the primary reaction[5,6] due to increased main-chain mobility.

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Berkowitch et al.[7] demonstrated that PVA–H_2O solutions above a concentration range of 0.32–0.67 g polymer/100 ml of solution became crosslinked under irradiation to produce a macrogel. Danno[8] confirmed these results producing brittle, gelatinous materials with a critical concentration of 0.36 g polymer/100 cc for samples of 1740 degrees of polymerization. Sakurada and Ikada[9–12] studied extensively the effect of parameters such as oxygen concentration, polymer coil conformation, molecular weight, and solution additives on the gelation dose and critical concentration of PVA–H_2O solutions.

These studies, though valuable for understanding the fundamental physical-chemical events occurring during the crosslinking process, do not provide the necessary data to understand the crosslinking of more concentrated solutions to produce materials with useful physical properties. This present work provides these data.

EXPERIMENTAL

This work dealt with crosslinking of 5–30 wt-% PVA–H_2O solutions; estimation of the molecular weight between crosslinks, M_c, by equilibrium swelling measurements; crystallization of these PVA networks by dehydration to achieve mechanical reinforcement; and evaluation of Young's modulus and ultimate tensile strength of the uncrystallized and crystallized network gels in equilibrium with distilled water.

Elvanol, 73-125G grade (du Pont), PVA, a fully hydrolyzed grade with less than 1% head-to-head units, was used in this experimental work. Intrinsic viscosity measurements at 25°C and the Mark-Houwink equation,[13]

$$[\eta] = 5.95 \times 10^{-4} \bar{M}_v^{0.63} \text{dl/g}$$

yielded a viscosity-average molecular weight of 193,000. Assuming a most probable molecular weight distribution yielded a $\bar{M}_n$ of ca. 100,000. (According to Wu,[19] $\bar{M}_w$ and $\bar{M}_n$ determined by gel permeation chromatography are respectively 184,800 and 88,800. Burke[2] reacetylated this grade of poly(vinyl alcohol) and submitted the poly(vinyl acetate) thus regenerated for gel permeation chromatography[20] in tetrahydrofuran. The resulting estimated molecular weight averages, *as the acetate*, are: $\bar{M}_w$ = 287,000 and $\bar{M}_n$ = 139,000, corresponding to nearly 140,000 and 70,000, respectively, as the alcohol.[21] Clearly, the most probable distribution $\bar{M}_w/\bar{M}_n \cong 2$ is confirmed. Inasmuch as the exact value of $\bar{M}_n$ becomes important only when the molecular weight between crosslinks, M_c, is comparable, the uncertainty in the value of the PVA used is believed to be of minor consequence.)

Degassed PVA and H_2O were placed in a 60 × 15-mm culture dish in a nitrogen-purged glove box, and the dish was wrapped tightly with Saran Wrap and placed in an 85°C oven for 25 hr to dissolve the PVA. The solutions were once again placed in the oxygen-free glove box, the Saran Wrap was removed, and the solutions were covered with 0.25 mil Mylar

film. Samples of 5, 10, 15, 20, and 30 wt-% PVA were prepared in this manner.

Irradiation was performed by passing the samples on a moving belt under the open window of a Van de Graaff accelerator at the High Voltage Research Laboratory at M.I.T. (We acknowledge with gratitude the extensive assistance of Mr. Kenneth Wright and Professor John Trump.) This machine delivered 3 MeV electrons at 0.15 megarads/sec (Mrad/sec). Irradiations were done at 0° (ice-water bath), 30°, 60°, and 85°C (heated glycerine bath). The total radiation dose ranged from 3 to 15 Mrad.

Since the specimens were prepared by irradiation of aqueous solutions of PVA of specified concentration, it was necessary to determine the relaxed volume (volume at which crosslinks were introduced) and the equilibrium swollen volume (volume after sample has been allowed to achieve its equilibrium uptake of water). The relaxed volume was determined by weighing the samples in air, then quickly in water. The samples were then placed in distilled water at 90°C for 24 hr to "melt" residual crystallites and to extract any sol fraction. Sol fraction was always less than 0.5% and therefore subsequently neglected. The samples were then placed in distilled water at 30°C, and the gain in water was measured after equilibrium was achieved. (Flory χ_1 factors were available at 30°C.) The samples were then dried in an air oven at 90°C for 72 hr and the weight of polymer measured. This allowed the calculation of the volume fraction of polymer in the relaxed and swollen state:

$$V_p = \frac{W_p}{\rho_p} \qquad v_{2,r} = \frac{V_p}{V_r} \qquad v_{2,s} = \frac{V_p}{V_s}$$

where W_p = weight of polymer, ρ_p = bulk density of polymer, V_p = volume of polymer, V_r = volume of relaxed gel, V_s = volume of swollen gel, $v_{2,r}$ = volume fraction polymer of relaxed gel, and $v_{2,s}$ = volume fraction polymer of swollen gel.

In addition to drying the PVA samples, the heating at 90°C served to crystallize the PVA. When the now crystallized samples were placed in distilled water at 30°C, their water contents when swollen were considerably less than before crystallization. This volume fraction was also measured:

$$v_{2,c,s} = \frac{V_p}{V_{c,s}}$$

where $V_{c,s}$ = volume of crystallized, swelled gel, and $v_{2,c,s}$ = volume fraction polymer of crystallized, swelled gel.

Samples prepared in 160 × 15-mm culture dishes were cut with an ASTM standard $\frac{1}{4}$-in. neck die and tested on a table model Instron (Model TM) to break. Stretching was done in a water bath at 30°C to prevent drying out of the samples at a strain rate of 0.2 in./min. The initial Young's modulus, ultimate tensile strength, and % elongation at break were measured.

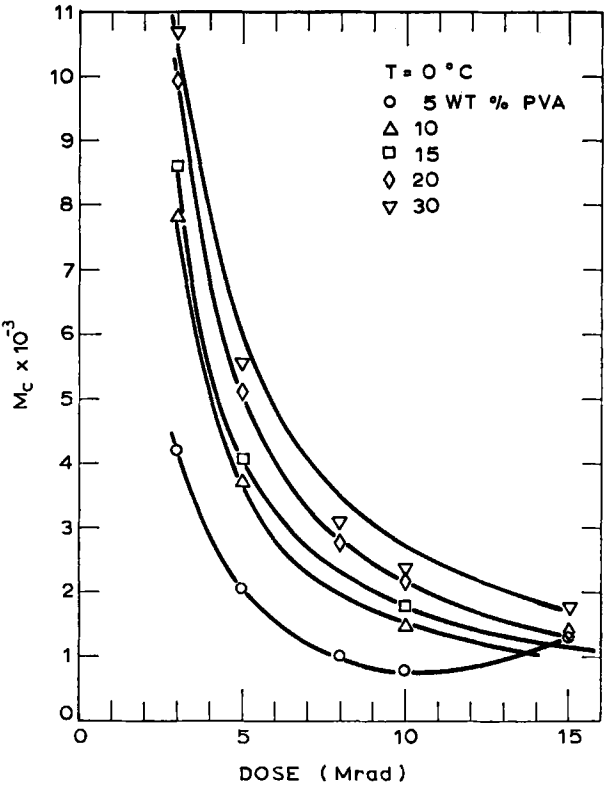

Fig. 1. M_c as function of dose and polymer solution concentration, 0°C.

RESULTS AND DISCUSSION

Evaluation of M_c

Since to the authors' knowledge no relation exists to evaluate the value of M_c for polymers crosslinked in solution, one had to be derived. Flory[14] has developed a relationship to evaluate the molecular weight between crosslinks, M_c, for polymers crosslinked in the bulk state via equilibrium swelling measurements. Following closely Flory's derivation, a modification was made taking into account that the crosslinks were introduced between polymer chains of number-average molecular weight $\bar{M}_n$, as the polymer existed in a solution of volume fraction $v_{2,r}$. The detailed derivation appears in the Appendix:

$$\frac{1}{M_c} = \frac{2}{\bar{M}_n} - \frac{\frac{\bar{v}}{V_1}\left[\ln(1 - v_{2,s}) + (v_{2,s}) + \chi_1 (v_{2,s})^2\right]}{(v_{2,r})\left[\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{2,s}}{v_{2,r}}\right)\right]}$$

where $\bar{v}$ = specific volume of polymer and V_1 = molar volume of solvent.

Constants used in this work were: $\bar{v} = 0.788$ cc/g,[15] $\chi_1 = 0.494$, and $V_1 = 18$ cm³/mole. The χ_1 factor cited was determined at 30°C.[15] As is well known, the χ_1 factor is not only a function of temperature other than the inverse relationship suggested in the original formulation of Flory[14] (p. 509), it is a function of volume fraction polymer. However, the percentage variation in χ_1 over the range of, say, 2 to 15 vol-% polymer is not nearly as serious as in systems containing high volume percentages of polymer. (See, for example Fig. 111 of ref. 14.) Further, there is reason to expect that with two types of polymer–solvent interactions possible in this system (hydroxyl–water hydrogen bonding in addition to —CH_2–water interaction), the χ_1 factor might be a complex function of polymer tacticity. Other values of χ_1 are reported[22,23] for PVA–water solutions. The value used was taken because the temperature–volume fraction conditions are closest to those of this study.

M_c as Function of Irradiation Dose, Concentration, and Temperature

Values of M_c calculated via the above equation are shown in Figures 1–4 plotted as M_c versus total irradiation dose for a fixed temperature and variable concentration. As can be seen, M_c decreased, i.e., degree of cross-

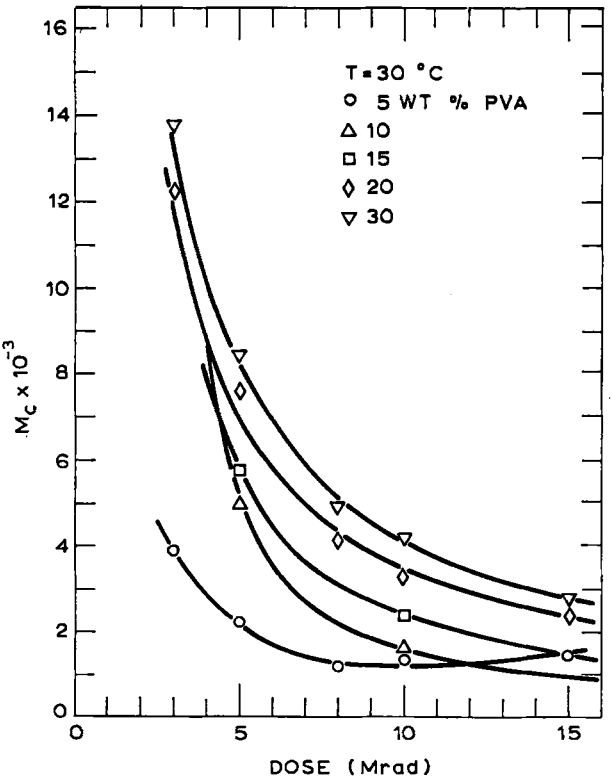

Fig. 2. M_c as function of dose and polymer solution concentration, 30°C.

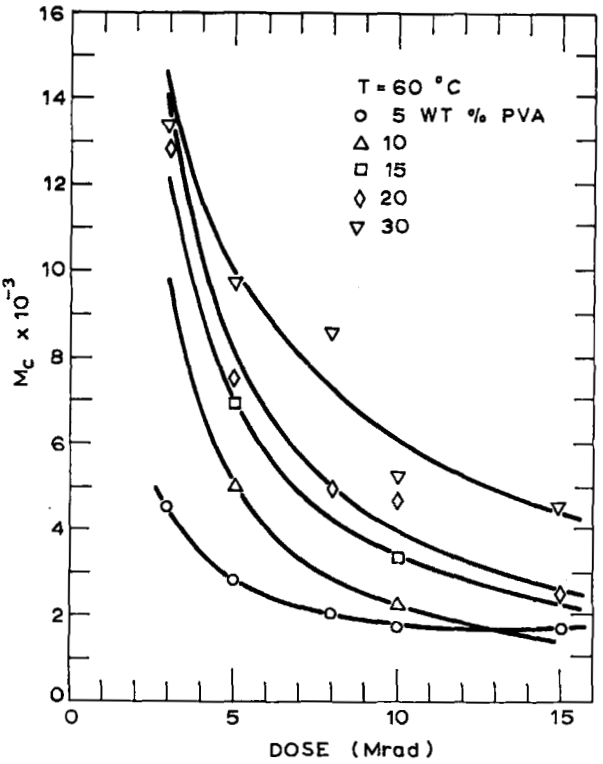

Fig. 3. M_c as function of dose and polymer solution concentration, 60°C.

linking increased, as the irradiation dose increased. Note that the 5% samples apparently had increasing M_c's at higher dose. A plot of $1/M_c$ versus dose for the 10–30 wt-% samples yielded straight lines which were used to plot the M_c versus-dose lines. In addition, as the polymer solution concentration decreased, M_c uniformly also decreased.

The swollen gels that were produced were clear (not translucent) gels which were somewhat fragile. A number of them were marred by gas bubbles immediately after irradiation, clear evidence for gas formation during irradiation.

Replotting the data as in Figure 5 shows that as irradiation temperature increased, the degree of crosslinking decreased. This was true for all five concentrations tested.

The effect of polymer concentration is readily explainable in terms of the effect of free radicals generated from the solvent (H_2O), SH, on the polymer chains, PH, as reported, for example, by Henglein.[16] These events are postulated as follows:

Radical Initiation

$$PH \rightsquigarrow P\cdot + H\cdot \quad (1)$$

$$SH \rightsquigarrow S\cdot + H\cdot \quad (2)$$

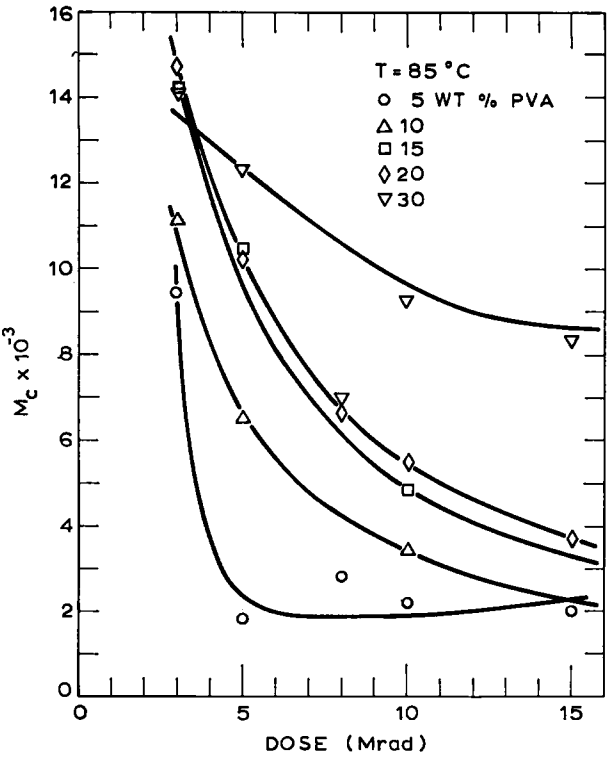

Fig. 4. M_c as function of dose and polymer solution concentration, 85°C.

Radical Transfer

$$S\cdot + PH \rightarrow SH + P\cdot \tag{3}$$

Crosslinking

$$P\cdot + P\cdot \rightarrow P - P \tag{4}$$

Degradation

$$P\cdot_{x+y} \rightarrow P_x + P_y \tag{5}$$

Network formation results from a competition between reactions (4) and (5). Polymer free radicals P· result from both reaction (1) by primary initiation of the polymer radical and by (3), transfer of a radical from the solvent radical S· to polymer molecule. Easily, then, a high concentration of solvent radicals will cause a large increase in the number of polymer radicals formed. To further amplify this, Table I shows the change in the ratio of moles of water to moles of vinyl alcohol segments present. The ninefold change in the ratio adds credence to the radical transfer mechanism.

TABLE I
Ratio of Moles of H_2O to Moles of $-(-CH_2CHOH-)-$ Segments

Concentration of solution, wt-% PVA	5	10	15	20	30
Moles H_2O/moles $-(-CH_2CHOH-)-$	46.4	22.0	13.9	9.8	5.7

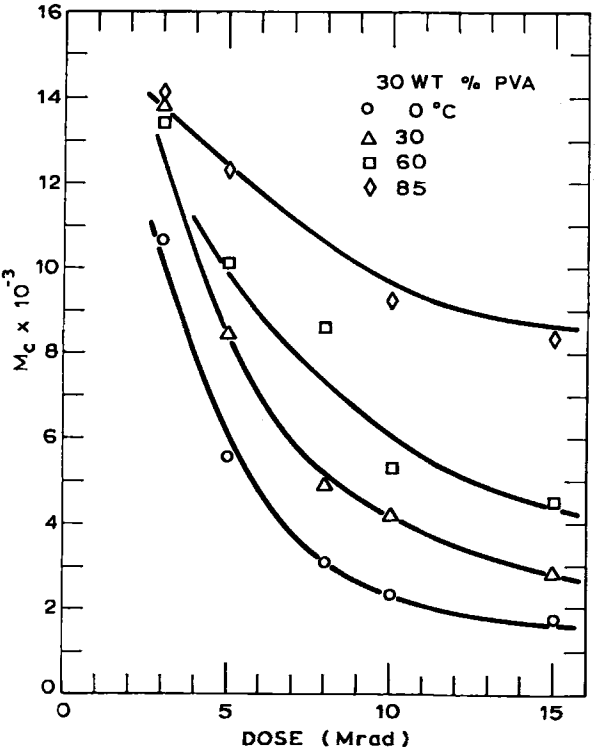

Fig. 5. M_c as function of dose and irradiation temperature, 30 wt-% PVA.

The effect of temperature on crosslinking of PVA–H_2O solutions required some additional data before interpretation was possible. PVA was cast from a 10 wt-% water solution to form 5-mil-thick films, substantially anhydrous, which were irradiated at 0°, 50°, and 100°C with doses over a range of 5 to 20 Mrad. The films were then dissolved in water and the intrinsic viscosity was measured at 25°C with a Ubbelohde viscometer. The data, intrinsic viscosity $[\eta]$ versus dose D, are plotted in Figure 6. The intrinsic viscosity shows a uniform decrease with dose and with increased irradiation temperature. If network formation is viewed as a competitive process between reactions (4) and (5), then increased scission (4) will cause higher values of M_c. The tendency of the PVA main chain to undergo —C—C— scission at higher temperatures of irradiation is in accord with the increase of M_c noted as the irradiation temperature of the PVA–H_2O solutions was increased.

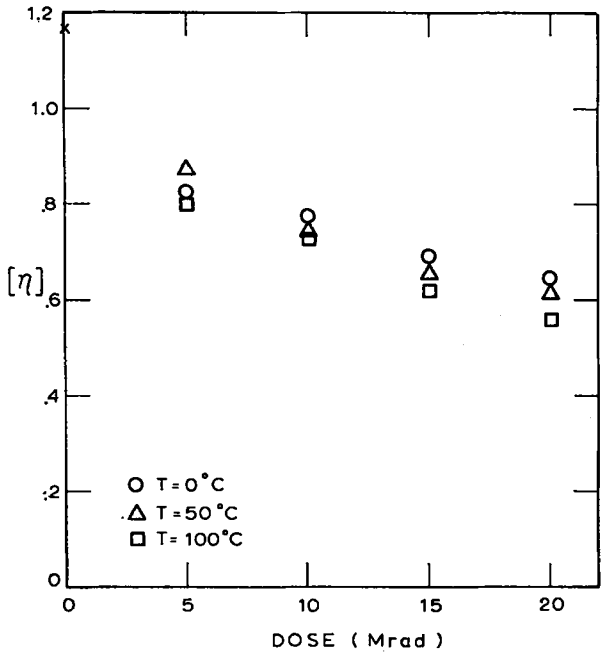

Fig. 6. Intrinsic viscosity decrease of irradiated anhydrous PVA film.

Crystallized and Uncrystallized Gels of PVA

The volume fraction of PVA in the gels swollen to equilibrium in water are shown in Figure 7 plotted as ($v_{2,c}$) versus M_c. The volume fraction ranges from 0.04 to 0.17 and is a function of both M_c and irradiated polymer solution concentration, increasing as M_c decreases and as polymer concentration increases. A number of possibilities exist to explain samples of equal M_c having different volume fractions of polymer in the swollen gel:

(1) The χ_1 value may vary with polymer concentration, which was not taken into account in this work (see above).

(2) Association of PVA chains in solution led to spontaneous gelation of 20 or 30 wt-% solutions at 30°C prior to irradiation. This association, probably crystallization of a fringed-micelle type, was evidenced by an increase in turbidity and the mechanical strength of the gels formed. Different amounts of interchain association would lead to different final volume fraction of polymer. (Subsequent DSC studies have confirmed "melt out" phenomena in these gels; crystallization-melting is probably the most significant of the three factors here enumerated.)

(3) Polymer side groups may have been changed during the irradiation procedure, i.e., exchange of —H for —OH or vice versa or formation of carboxyl groups leading to swelling in distilled water via Donnan equilibrium. The most logical explanation becomes evident from recalling that the samples were crosslinked at different volume fractions of polymer. Since the final volume fraction is controlled by elastic refractive force of

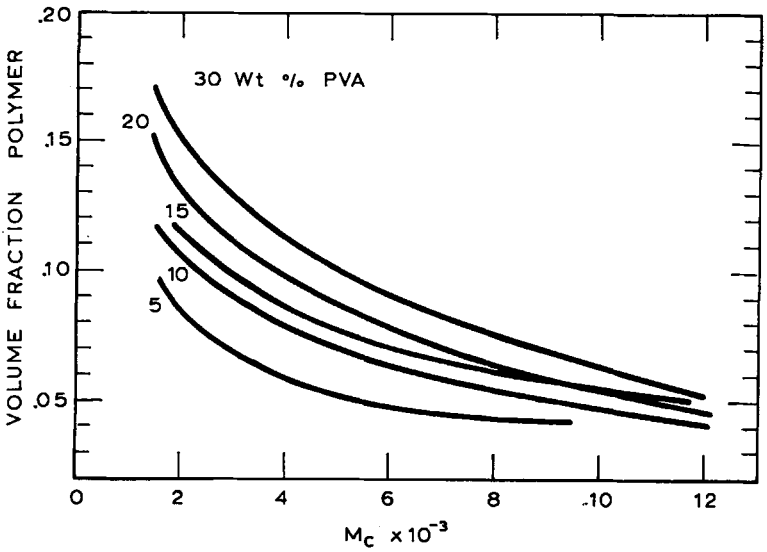

Fig. 7. Volume fraction polymer of PVA gels prior to crystallization.

the network it is logical that a different relaxed state would yield a different swollen state.

Annealing the samples at 90°C for 72 hr in an air oven changed considerably the equilibrium uptake of water, as can be seen in Figure 8 with the volume fraction of polymer ($v_{2,c,s}$) in the crystallized network–diluent mixture plotted against M_c. The volume fraction ranges between 0.1 and 0.5, achieving a maximum around $M_c = 7500$ and decreasing for higher and lower M_c values.

The form of the curves in Figure 8 is explainable by the effect of crosslinks on the ability of the chains to crystallize. Below $M_c = 7500$, increased crosslinks yield decreased crystallization and thus decreased polymer volume fraction in the final gel. The interference of crystallization by crosslinks is documented by Meares[17] and Mandelkern.[18] The initial increase in $v_{2,c,s}$ as M_c decreased from 12,000+ to 8000 can be explained by tetrafunctional crosslinks acting as stress-bearing points protecting crystallites from being "melted out" as the network swells.

The effect of initial polymer solution concentration is somewhat more difficult to explain. In going from 30% to 10%, the water content in the final swollen gel from which crystallization was done increases. Crystallization from a more dilute solution allows the formation of larger crystallites due to increased chain mobility during crystallization. The large number of free radicals formed in the 5% solutions may have led to degradation introducing free chain ends which prevent cyrstallization or may so alter the repetitive symmetry by substitution as to make the sequence noncrystallizable.

Much of the evidence for crystallization is inferential because of difficulty of obtaining x-ray evidence in the water-swollen PVA networks. The

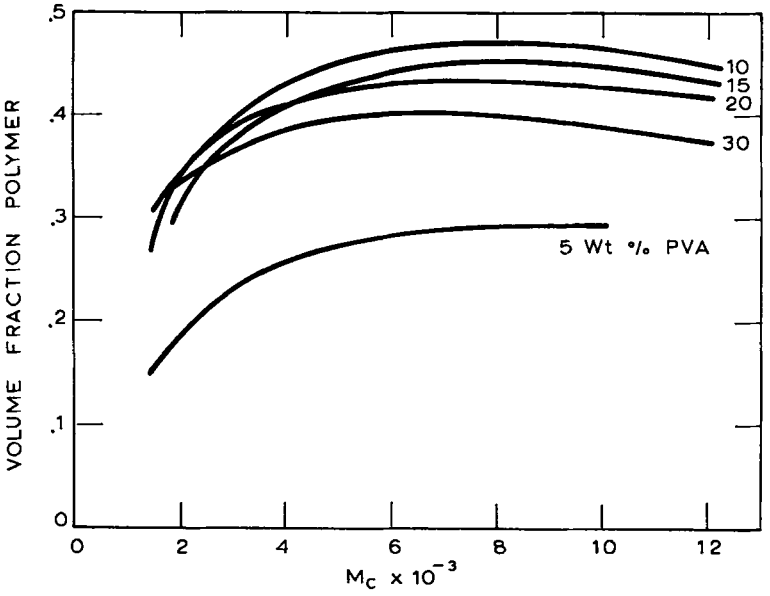

Fig. 8. Volume fraction polymer of PVA gels after crystallization.

"crystallized" gels are turbid whereas the fully swelled gels are clear, lending evidence for crystallization. When the crystallized gels are placed in 90°C for 24 hr, then in 30°C water, they swell back up to their original water contents favoring crystallization as opposed to intermolecular dehydration. As previously mentioned, 20% and 30% solutions, uncrosslinked, gel spontaneously, more than likely due to crystallization.

The two sets of samples differ drastically in their physical properties, with the swollen samples being fragile (low tear resistance) while the crystallized samples are extremely tough, capable of being bent 180° without breaking. This suggests the presence of crystallites of the "fringed micelle" type rather than the more brittle spherulitic crystal type. The marked improvement of strength by crystallization is in accord with the generally accepted theory that reinforcement of network polymers occurs only through multifunctional fix points, viz., microcrystallites of the "fringed micelle" type, reinforcing filler (carbon in polybutadiene) or discrete phase separated domains (styrene in styrene–butadiene–styrene triblock copolymers).

Tensile Properties

The values of Young's modulus at small deformations (E_0 = initial tensile modulus) are listed in Tables II and III and plotted in Figures 9–11 as E_0 versus dose, irradiation temperature, and polymer solution concentration. The uncrystallized samples have initial tensile moduli of 10^5–10^6 dynes/cm^2 with crystallization increasing this to 10^6–10^7 dynes/cm^2. E_0 for the uncrystallized gels increased with dose and decreased as solution

concentration and irradiation temperature increased, i.e., E_0 increased as M_c decreased. The values of E_0 for the crystallized samples followed the opposite trend, i.e., increased as M_c increased owing to longer segments of chain being able to participate in crystallization.

TABLE II
Tensile Data for Uncrystallized Gels

C, wt-% PVA	T, °C	D, Mrad	E_0, 10^6 dynes/cm²	UTS, 10^5 dynes/cm²	$(l/l_0)_{break}$
10	0	3	.316	1.813	1.841
		5	.813	2.737	1.408
		8	1.437	1.583	1.117
		10	2.187	2.644	1.136
		15	3.405	2.724	1.093
10	30	10	1.329	1.612	1.138
	60		1.150	1.852	1.215
15	0	10	2.118	2.960	1.155
20			1.737	3.000	1.194
30			1.798	9.896	1.791

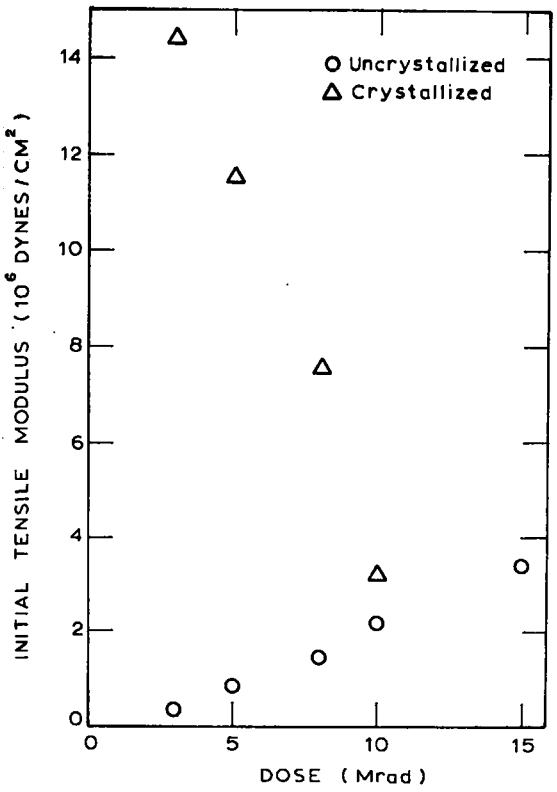

Fig. 9. Effect of dose on initial tensile modulus of uncrystallized and crystallized gels.

TABLE III
Tensile Data for Crystallized Samples

C, wt-% PVA	T, °C	D, Mrad	E_0, 10^6 dynes/cm²	UTS, 10^5 dynes/cm²	$(l/l_0)_{break}$
10	0	3	14.45	>280	4.149[a]
		5	11.52	41.65	1.492
		8	7.564	12.58	1.180
		10	3.25	7.25	1.248
10	30	10	3.678	8.87	1.248
	60		1.904	6.95	1.360
	85		3.742	17.77	1.497
15	0	10	20.98	100.3	1.906
20			31.67	51.52	1.234
30			46.87	>119.6	>1.147[b]

[a] Exceeded maximum gauge length.
[b] Exceeded load cell capacity.

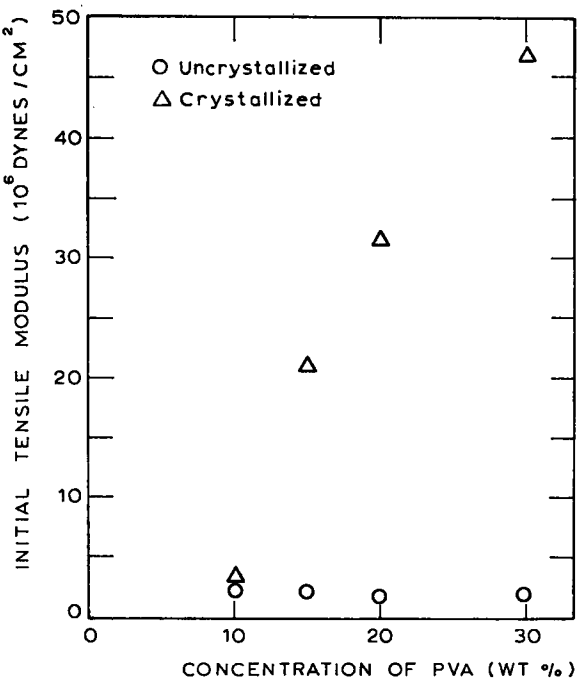

Fig. 10. Effect of polymer solution concentration on initial tensile modulus of uncrystallized and crystallized gels.

Crystallization improved the ultimate tensile strength from 10^5–10^6 dynes/cm² to 10^6–10^7 dynes/cm², approximately tenfold, and the per cent elongation at break increased from 9–80% to 20–400%. The values of ultimate tensile strength and per cent elongation at break do not correlate well with dose, temperature, or concentration owing to minor imperfections causing premature break.

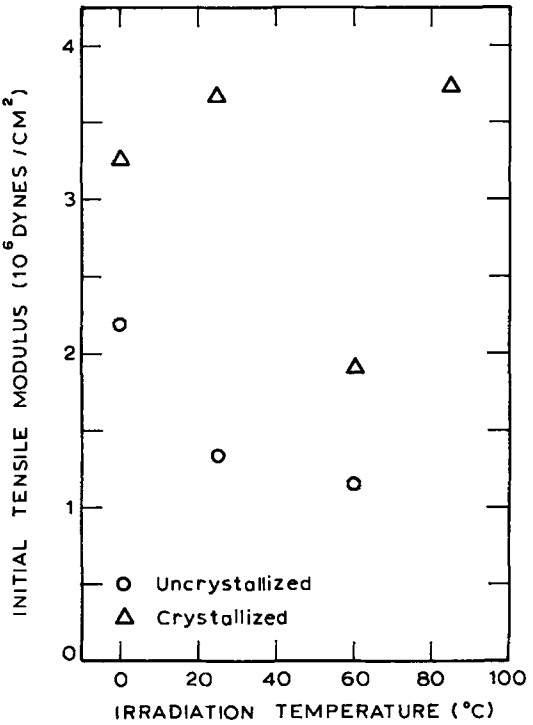

Fig. 11. Effect of irradiation temperature on initial tensile modulus of uncrystallized and crystallized gels.

Future Work

Work is presently being conducted on the crystallization of PVA networks. Variables of interest include annealing temperature, heating time, and drying rate.

CONCLUSIONS

1. Water solutions of PVA from 5–30 wt-% polymer can be crosslinked with 3 MeV electrons, with the degree of crosslinking increasing for increasing dose, decreasing solution concentration, and temperature of irradiation.

2. The strength of water-swollen PVA networks can be greatly increased by annealing above the glass transition temperature to allow crystallization of the PVA subchains.

Appendix

Derivation of Equilibrium Swelling Equation

Starting with a swollen network, the sample is swelled further to equilibrium in a solvent. The equilibrium criterion is

$$\mu_1 - \mu_1^0 = \frac{\delta \Delta F}{\delta n_1} = 0 \tag{1}$$

where μ_1 = chemical potential solvent in gel, μ_1^0 = chemical potential of solvent in bulk, and $\Delta F = \Delta F_{mix} + \Delta F_{el}$, where F = free energy, F_{mix} = solution mixing contribution, and F_{el} = elastic retractive force of network contribution.

Calculation of ΔF_{mix}:

From Flory,[14] the free energy of mixing of a solvent and a polymer network is

$$\Delta F_{mix} = kT[n_1 \ln(v_{1,s}) + \chi_1 n_1 (v_{2,s})] \tag{2}$$

where k = Boltzman's constant, T = absolute temperature, n_1 = molecules of solvent, χ_1 = Flory polymer–solvent interaction parameter, and $v_{1,s}$, $v_{2,s}$ = volume fractions of solvent and polymer in swollen state.

Taking the derivative with respect to n_1, recalling that $v_{1,s}$ and $v_{2,s}$ are functions of n_1 and assuming simple additivity of volumes, yields

$$\frac{\delta \Delta F_{mix}}{\delta n_1} = kT[\ln(1 - v_{2,s}) + \chi_1 (v_{2,s})^2]. \tag{3}$$

Calculation of ΔF_{el}:

$$\Delta F_{el} = -T\Delta S_{el} \qquad \text{(assuming } \Delta H_{el} = 0\text{)}$$

$$S_{el} = \text{constant} - \frac{kv_e}{2}[\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3 - \ln(\alpha_x \alpha_y \alpha_z)] \tag{4}$$

where S_{el} = elastic entropy contribution, v_e = effective number of subchains in the network, and $\alpha_x, \alpha_y, \alpha_z$ = x,y,z contributions to deformation from a relaxed state; $\alpha^3 = V/V_0$ where V_0 = volume at which crosslinks were introduced.

Assuming isotropic swelling ($\alpha_x = \alpha_y = \alpha_z = \alpha$) and recalling that $V_0 = V_r$ since the crosslinks were introduced in a swollen state (V_r = relaxed volume) simplified the relationship

$$\Delta S_{el} = S_{swelled} - S_{relaxed}$$

$$\Delta S_{el} = -\frac{3kv_e}{2}[\alpha_s^2 - 1 - \ln(\alpha_s)] \qquad \text{where } \alpha_s^3 = \frac{V_s}{V_r} \tag{5}$$

$$\Delta F_{el} = \frac{3ktv_e}{2}[\alpha_s^2 - 1 - \ln(\alpha_s)].$$

This derivative may be evaluated using

$$\frac{\delta \Delta F_{el}}{\delta n_1} = \frac{\delta \Delta F_{el}}{\delta \alpha} \cdot \frac{\delta \alpha}{\delta n_1} \tag{6}$$

and

$$\alpha^3 = \frac{V_s}{V_r} = \frac{V_p + n_1 V_1}{V_r}$$

where V_p = polymer volume, and V_1 = solvent molar volume.

$$\frac{\delta \Delta F_{el}}{\delta n_1} = kTv_e \frac{V_1}{V_r}\left[\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\frac{v_{2,s}}{v_{2,r}}\right]. \tag{7}$$

The effective number of subchains is given by Flory[14] as follows:

$$v_e = \nu\left(1 - 2\frac{M_c}{M_n}\right) \tag{8}$$

where ν = total number of subchains, and

$$\nu = \frac{V_p}{\bar{v}M_c}$$

where $\bar{v}$ = specific volume of polymer.

Substituting and rearranging yields the desired result:

$$\frac{1}{M_c} = \frac{2}{\bar{M}_n} - \frac{\frac{\bar{v}}{v_1}\left[\ln(1 - v_{2,s}) + (v_{2,s}) + \chi_1(v_{2,s})^2\right]}{v_{2,r}\left[\left(\frac{v_{2,s}}{v_{2,r}}\right)^{1/3} - \frac{1}{2}\left(\frac{v_{2,s}}{v_{2,r}}\right)\right]}.$$

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Received December 21, 1972
Revised June 1, 1973