

Differential Scanning Calorimetry of Crystallized PVA Hydrogels

NIKOLAOS A. PEPPAS and EDWARD W. MERRILL, *Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, 02139*

Synopsis

Crosslinked poly(vinyl alcohol) hydrogels produced via electron beam irradiation of aqueous PVA solutions were crystallized via a two-stage dehydration-annealing process to produce swollen hydrogels of varying degrees of crystallinity. Evaluation of the degree of crystallinity of these hydrogels was done by differential scanning calorimetry (DSC) analysis. The swollen hydrogels had degrees of crystallinities varying between 30% and 50% depending on the temperature-time history of the specimens.

INTRODUCTION

Crosslinked networks of poly(vinyl alcohol) (PVA) produced from aqueous PVA solution by irradiation or chemical crosslinking have been recently developed,^{1,2} and their physical and mechanical properties have been studied^{3,4} as a function of crosslinking conditions. These materials are too fragile to be useful for any practical applications, unless reinforced in some way. Induction of partial crystallization by a two-stage dehydration-annealing process is a reinforcement process recently proposed.⁵ Following such a procedure, the material upon reswelling in water has greatly enhanced mechanical strength. Evaluation of the crystallinity of the final hydrogel was done using differential scanning calorimetry (DSC) analysis on typical heat-treated specimens.

STRUCTURES OF CROSSLINKED CRYSTALLIZED PVA HYDROGELS

The poly(vinyl alcohol) hydrogels used in this study consist of PVA primary molecules in aqueous solution (10-15 wt-% polymer) crosslinked by irradiation. Their crosslinking density ρ (expressed as moles per cm³) is defined as the reciprocal of the product of the specific volume of the polymer \bar{v} and M_c .

Dehydration and heating of the crosslinked PVA induces crystallite formation. The crystallites are presumed to be of the fringed micelle type. Certainly no evidence of spherulitic crystallization is found. These crystalline sites act as additional crosslinks upon application of external stresses, redistributing them equally among the initial crosslinks and the introduced crys-

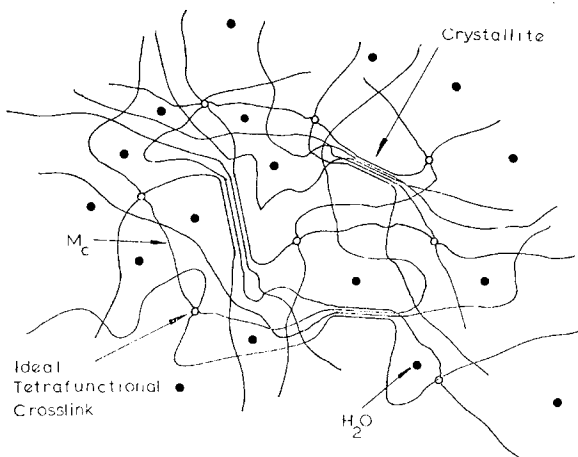


Fig. 1. Structure of crosslinked crystallized PVA hydrogels swollen in water.

tallites. A simplified figure of a typical crystallized network is shown in Figure 1.

The formation of the crystallites depends on the heat treatment conditions and on the crosslinking density of the network before crystallization. Thus, an internal relation between the average length of a polymer chain between two crosslinks and the thermodynamically minimum favorable length of a crystallite controls the formation of crystallites in the network.

Swelling characteristics of PVA networks in water after crystallization are functions of the previous history of the network. The water molecules penetrate only the amorphous (noncrystalline) regions. Thus, the crystalline regions remain essentially unaffected by the water at room temperature, as demonstrated by proving that crystallinity was not changed through swelling.^{6,7}

EVALUATION OF CRYSTALLINITY OF PVA HYDROGELS

The methods of evaluation of the crystalline content of PVA are based on the different values of some measurable properties of this polymeric material, depending on the crystalline content of this material.

Calorimetric methods are indirect methods for calculating the degree of crystallinity ($x\%$) of a PVA sample by evaluating the heat of fusion of a particular sample (ΔH^*) and comparing it to the heat of fusion of an 100% crystalline PVA (ΔH_c).

In the case of several polymers, the calorimetric methods cannot apply because they decompose before melting. For this reason, it is necessary to use a system of the polymer with one of its solvents (in the case of PVA, water) and apply Flory's theory on the depression of the melting point in order to calculate the heat of fusion.⁸

In DSC, the temperatures of the tested sample and the reference are maintained at an equal or fixed differential level during the analysis, and the variation in power input required to maintain the level during a transition is measured.

Melting of PVA usually takes place over a range of temperatures, since the crystallites surrounded by amorphous regions have a range of sizes. The size distributions are dependent on the thermal history of the samples.

Other factors that broaden the melting range of PVA are the presence of diluent and the stereoisomeric types of the chain of the polymer.

EXPERIMENTAL

This work mainly includes the application of the DSC analysis on the particular sample of PVA hydrogels. The initial crosslinked PVA hydrogels are produced by irradiation via electron beams as has already been reported.^{4,5,9} The samples used in this work are reported in Table I.

The PVA used in this study was Elvanol R73-125G grade (du Pont) having the highest commercially available molecular weight of $\bar{M}_n = 88,800$ as calculated by gel permeation chromatography. It contains less than 0.7% acetyl groups, less than 4% head-to-head units, and less than 0.1% carbonyl groups. It contains more than 70% atactic form, but its stereoregular analysis is not available.

The samples after irradiation were dehydrated by a slow drying rate process at $23^\circ \pm 1^\circ\text{C}$ and R.H. 40% for 24 hr in a dust-free environment. This initial dehydration process was followed by an annealing process of heating above the glass transition temperature ($T_g = 85^\circ\text{C}$) of PVA¹⁰ with subsequent slow cooling. The annealing process was performed under various conditions of temperature (90–135°C) and time (15–120 min). After the heat treatment, the samples were swollen in water at 30°C.

For the calorimetric analysis, a Perkin-Elmer DSC-1 instrument was used.¹¹ It was calibrated with indium for the high temperatures (melting temperature 155°C at 5°C/min) and with palmitic acid (64°C at 5°C/min). Since the T_m of the gels was expected to be around room temperature, we used the lower temperatures cover of the DSC-1 instrument which covered the range of -100°C to $+400^\circ\text{C}$.

The hydrogel to be analyzed was cut with a round die of internal diameter 6 mm, and this disk (which weighed 8–15 mg) was placed in the pan, covered with an aluminum sample pancover, and pressed in the sample pan crimper so that it made a pellet including the sample. The pellet was placed on the right-hand sample holder, while an empty pan with cover was placed on the left-hand sample holder as a reference sample. The low-temperature cover was placed on the top of the sample holders. After dry nitrogen was allowed to pass through the instruments for about 15 min, the coolant (liquid nitrogen) was introduced; upon temperature equilibration, the run was started.

A typical thermogram of a run of one of the hydrogel samples is shown in Figure 2. All the thermograms were taken between -100°C and $+250^\circ\text{C}$. The thermogram is characterized by peak A which refers to the melting of the crystallites of the crosslinked network in the presence of the diluent and by peak B which refers to the melting of PVA upon recrystallization due to the increase of the temperature during the test. For the calculation of the area under the peak and for estimation of the melting point of the gel (T_m), a graphic method, as shown in Figure 2, was used.¹²

Experiments were done on the effects at the scanning speed on the shift of

TABLE I
Samples Used in this Work, Condition of Irradiation, and Crosslinking Parameters

Condition of irradiation			M_c	$\rho \times 10^4 = \frac{1}{vM_c} \times 10^4$
$C_c, \%$	$T_c, ^\circ\text{C}$	D_c, Mrads		
10	30	3	9370	1.35
10	30	5	4770	2.66
10	0	5	3765	3.37
10	0	10	1495	8.49
15	0	3	8420	1.51
15	30	5	5715	2.22
15	30	10	2190	5.80

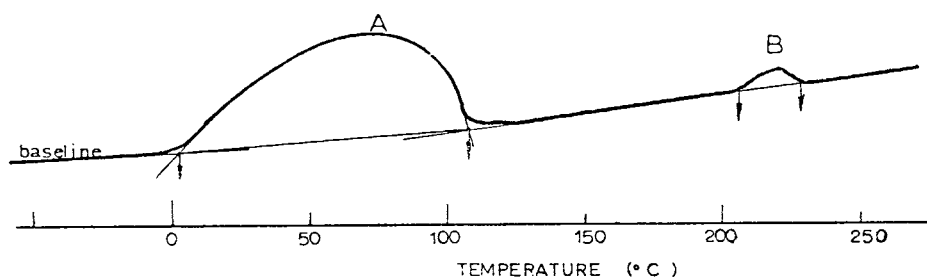


Fig. 2. Typical DSC thermogram of a PVA hydrogel.

the melting points of the examined hydrogels as well as on the reproducibility of the results. The melting point of PVA was calculated from the peak B of the typical thermogram as shown in Figure 2.

RESULTS AND DISCUSSION

Evaluation of the Heat of Fusion ΔH_c

Flory's expression¹³ for the crystalline melting point depression by the addition of a diluent to a linear, flexible, noncrosslinked polymer is

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_c} \right) \left(\frac{V_u}{V_1} \right) (v_1 - \chi_1 v_1^2) \quad (1)$$

where T_m = melting point of the polymer-diluent gel, T_m^0 = melting point of pure polymer, V_u = molar volume of the polymer repeating unit, V_1 = molar volume of diluent, v_1 = volume fraction of the diluent, χ_1 = the chi factor as defined by Flory,¹³ and ΔH_c = the heat of fusion of the 100% crystalline PVA. In eq. (1) it is assumed that χ_1 is independent of the polymer volume fraction $v_2 = 1 - v_1$. The χ_1 factor is expressed at temperature T_m as¹³

$$\chi_1 = \frac{BV_1}{RT_m} \quad (2)$$

where B is the interaction energy density characteristic of the solvent-solute pair. Thus, the equation becomes

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0} \right) / v_1 = \left(\frac{R}{\Delta H_c} \right) \left(\frac{V_u}{V_1} \right) \left(1 - \frac{BV_1 v_1}{RT_m} \right). \quad (3)$$

In the case of crosslinked samples, T_m^0 refers to the particular samples with crosslinked density, so that the appropriate value of T_m^0 has to be used.

If the introduction of crosslinks does not chemically alter the polymer nor perturb the equilibrium between polymer crystal units and polymer units surrounded by solvent, i.e., the amorphous phase, then plots of $(1/T_m - 1/T_m^0)/v_1$ versus v_1/T_m should give straight lines. Using the intercept and the slope of these lines, the terms ΔH_c and B could be calculated.

Sakurada et al.¹⁴ reported a χ factor of 0.494 at 30°C for the system PVA-water (calculated from vapor pressure data), being constant in the concentration range at $v_2 = 0-0.15$. This arithmetic value was used in the present study, where hydrogels with polymer volume fractions between 0.05 and 0.14

TABLE II
Effect of Scanning Speed on T_m^0 (Peak B)^a

Scanning speed, °C/min	T_m^0 , °C
5	213
10	211
20	198
40	192
80	192

^a Sample no. 62, $M_c = 8420$, $x = 47.63\%$, PVA = 48.52%.

TABLE III
Effect of Repeated Heating-Cooling Cycles on T_m^0 ^a

Cycle no.	T_m^0 (heating), °C	T_m^0 (cooling), °C
1	197.2	186
2	197.3	186.2
3	196.2	186.5
4	195	188.3

^a Sample no. 62, $M_c = 8420$, $x = 47.63\%$, PVA = 48.52%, scanning speed, 20°C/min.

TABLE IV
Melting Point Depression in PVA Networks Due to Crosslinking

PVA solution concentration, wt-%	M_c	$\rho \times 10^4$, moles/cm ³	T_m^0 , °C
10%	1495	8.49	208.6
	3765	3.37	208.2
	4770	2.66	210
	9370	1.35	212.2
	∞	—	218.3
15%	2190	5.80	200
	5715	2.22	204
	8420	1.51	211
	∞	—	216.5

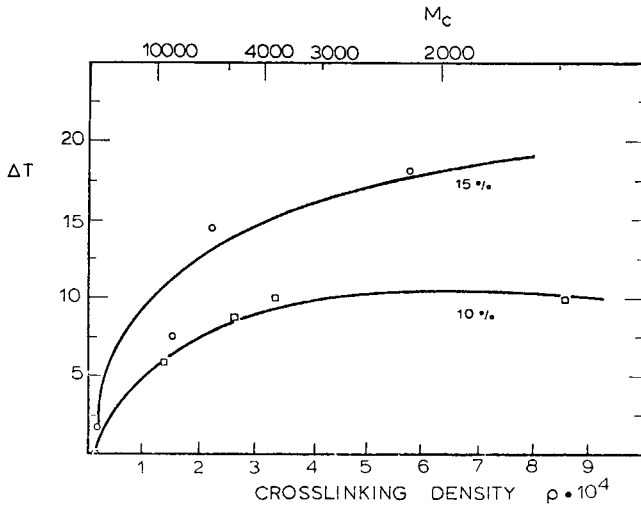


Fig. 3. Melting point depression because of crosslinking in crosslinked PVA networks.

were studied. It is in considerably good accordance to the one of $\chi = 0.49$ calculated by Hamada and Nakajima¹⁵ (from melting point depression experiments).

Different samples of M_c between 1495 and 9370 from two different initial solution concentrations of 10% and 15% in PVA, heat treated at different conditions, were studied. They were compared to the uncrosslinked crystalline PVA films prepared in the same way. For the purpose of elimination of er-

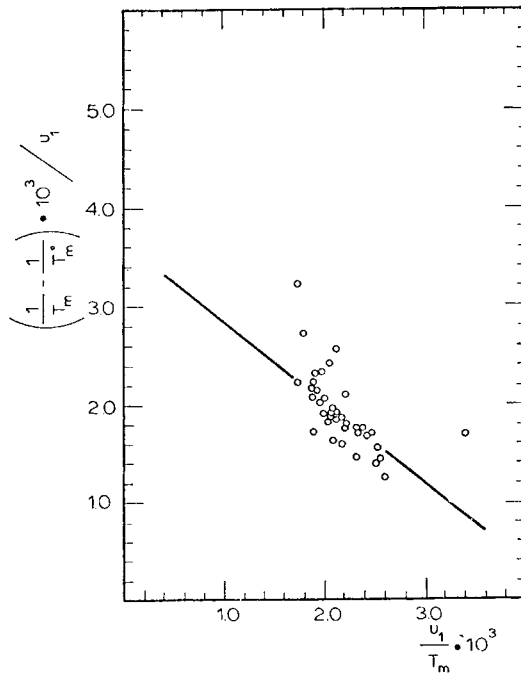


Fig. 4. Application of Flory's theory for the calculation of ΔH_c from DSC data.

rors because of different testing conditions, all the samples were tested with a scanning speed of 5°C/min. It was found that the scanning speed affects greatly the apparent melting point, shifting the melting curves (Table II). Repeated cycles of melting of the PVA did not show significant change of the melting point of PVA, as shown in Table III.

The melting point of Elvanol 73-125 G used in these experiments has been reported as 218–219°C.⁴ The melting point is a function of crosslinking density, and Mandelkern has shown¹⁶ that the depression of the melting point is higher the higher the degree of crosslinking. The melting points T_m^0 for different crosslinking densities were calculated from the thermogram as shown in Table IV. Thus, the depression of the melting points are plotted as a function of the crosslinking densities as shown in Figure 3.

From the data of T_m from the thermograms, a straight line is drawn as in Figure 4, and $\Delta H_c = 1.05$ kcal/mole and $B = 24.90$ cal/cm³ are calculated. This value is within the range of ΔH_c between 0.56 and 2.47 kcal/mole that have been reported by Finch¹⁷ depending on the method of evaluation.

Scattering of the experimental points can be mainly attributed to variation of the tacticity of the samples. Although it is known that the PVA used is mostly amorphous, the exact analysis of stereoregularity is not available. Thus imperfections arising from amorphous parts of the chains as well as the actual state of the "ends of the crystallites," i.e., the regions where the chains are in an intermediate state may affect the calculation of ΔH_c .

Actually, ΔH_c is expected to vary somewhat with crosslinking density (especially for very densely crosslinked networks), and, as predicted by Mandelkern,¹⁶ the higher the crosslinking density, the lower ΔH_c will be because of the imperfections of the networks and because the probability that a crystallite will form will be less. However, the variation of ΔH_c due to crosslinking is not expected to be more than 10%.¹⁶

EVALUATION OF THE DEGREE OF CRYSTALLINITY

The calculation of the heat of fusion of the particular tested samples ΔH^* was done by measuring the areas of the corresponding thermograms and converting them to kcal/mole. In this way, the degree of crystallinity could be evaluated as

$$x = \frac{\Delta H^*}{\Delta H_c} \quad (4)$$

Table V includes some of the results. They show the effect of the annealing conditions as well as the crosslinking densities on the degree of crystallinity. The degrees of crystallinity vary between 20% and 70%, depending on the annealing conditions. It is mostly the increase of the annealing temperature (within the ranges of annealing times tested) that is responsible for the crystallization.

It is to be noted that the samples annealed at 135°C and 120°C for 90 min showed a very high degree of crystallinity of 62.74 and 71.10, respectively. These values are difficult to explain, especially in view of the fact that the initial PVA was amorphous.¹⁸

A possible explanation is that, due to vigorous annealing conditions, there

TABLE V
Crystallinity of Certain PVA Hydrogels as Judged from DSC

M_c	Annealing conditions		Crystallinity from DSC
	$T, ^\circ\text{C}$	t, min	
1495	90	30	23.40
	105	30	33.45
3765	90	60	30.02
	90	90	31.59
	105	90	53.10
	120	30	49.65
	135	90	62.74
4770	90	30	35.61
	105	60	46.80
	120	30	50.12
	120	90	71.10
9370	90	30	39.93
	90	60	43.10

is a partial formation of conjugated double bonds, as shown by the IR spectra of these samples, where CO formation is evident.

It is also evident that lower crosslinking density (higher M_c) favors the crystallization, mainly because a minimum critical length of a polymer chain is necessary for the formation of a crystallite and, the higher this length (higher M_c), the more probable that more crystallites will form.

It is evident that change of scanning speed of the experiment affects the area of the peak (i.e., ΔH^*) and the onset from the baseline (i.e., T_m); but in the present study, these variations were not significant because of the choice of an appropriately low scanning speed (see also Table II).

CONCLUSIONS

From this study, it is concluded that:

1. Crosslinked PVA networks submitted to a dehydration annealing process can be reinforced by partial crystallization to form crystallized PVA hydrogels.
2. Evaluation of the degrees of crystallinity of the materials by DSC showed that they are functions of the annealing conditions and the crosslinking density. The value of $\Delta H_c = 1.05$ kcal/mole calculated for the 100% crystalline PVA is in good agreement with other reported values, and it does not seem to depend on the crosslinking density.

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