Crystallization Kinetics of Poly(vinyl Alcohol)

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Synopsis

The kinetics of crystallization of solvent-free poly(vinyl alcohol) were investigated by isothermal crystallization at temperatures of 142–192°C, for up to 18 min. The crystallization isotherms were analyzed by Avrami's theory. The magnitude of the exponent n was almost constant (0.67–0.71) in the range of 142–182°C, increasing to 1.53 for crystallization at 192°C. Based on thermodynamic analysis of the isotherms and the crystallite growth rate, there are strong indications that crystallization of PVA is one-dimensional. In the absence of water or other swelling agents, kinetic hindrances predominate due to the interactions of the hydroxyl groups. Therefore, the maximum attainable weight fraction of crystallized PVA is considerably lower than that of hydrated PVA samples. Additional parameters affecting the growth rate are discussed, including the degree of undercooling and the average chain length, as controlled by crosslinking.

INTRODUCTION

The crystallization mechanism and kinetics of poly(vinyl alcohol), henceforth designated as PVA, have been studied by numerous investigators under various experimental conditions in the presence or absence of solvents.[1] Crystallization of hydroxyl-containing polymers, such as PVA, is of special interest due to the strong kinetic hindrance associated with formation of ordered macromolecular structures in these polymers.

It is believed that, during annealing of PVA, hydrogen bonding impedes the crystallization process. Crystallization from dilute or concentrated solutions of PVA is also complicated by the formation of supermolecular structures, which have been explained either as globular gel-like formations or as pseudocrystalline regions. Frenkel and his associates have given a rather complete account of this behavior.[2]

For semicrystalline PVA samples, the melting point has been reported between 202°C and 240°C depending on the method of preparation and conditions of hydrolysis[3,4] and on the average molecular weights and conditions of heat treatment.[5–8] Atactic PVA is usually 20–35% crystalline,[1] but, upon drawing or annealing above the glass transition temperature, its crystallinity can increase up to 55%, especially in the presence of diluents, such as water, ethylene glycol, etc.[9–13]

Growth of single crystals of PVA was first achieved by Mochizuki and his associates[14–21] by isothermal crystallization from dilute aqueous solutions and by Monobe and Fujiwara by crystallization from dilute solutions of triethylene glycol and related polyols.[22] The crystals belong to the monoclinic system with a unit cell consisting of two monomeric units.[23] The lamella thickness of a crystallite

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is around 100–125 Å, as estimated from the length of the shadow of electron micrographs. Parallel lamellae were obtained from PVA crystallized from aqueous solutions at temperatures above 180°C,[18–20,24] while spherulitic structures were formed from PVA crystallized in polyol solutions, such as ethylene glycol at 130–175°C.[25] Packter and Nerurkar[26] observed spherulitic growth when crystallizing PVA films cast from concentrated polyol solutions. The final size of the spherulites increased as the temperature of evaporation increased from 120°C to 180°C.

Numerous publications testify in favor of crystallizability of PVA even in the absence of diluents. Bessonov and Rudakov[5] showed that when PVA is cooled from the melt, it crystallizes exhibiting definite birefrigence patterns. Bunn[27] was the first to show that the side hydroxyls of PVA macromolecular chains are so small that they can be interchangeable with hydrogens in the crystalline lattice. Hence, the steroregularity has little effect on the crystallization process of PVA and its X-ray pattern. Therefore, atactic PVA can crystallize up to 65%.[28] Experiments by Kenney and Willcockson[4] showed, indeed, that increased syndiotacticity does not appear to lead to higher crystallinity, although growth of crystallites of syndiotactic-rich PVA seems to occur at a higher growth rate under flow-induced crystallization conditions.[29]

Crystallization of PVA films and fibers proceeds faster in the presence of a diluent, such as water, as shown by the studies of Sakurada and his associates,[30–35] Peppas and Merrill,[9–13] Packter and Nerurkar,[36,37] and others.[38–49]

Despite the previous work, there exist many unanswered questions on the mechanism of crystallization of PVA in the presence or absence of water. Recently, the crystallization behavior of uncrosslinked and crosslinked PVA from hydrated films was investigated to establish the mechanism of crystallization.[12,13] An Avrami-type crystallite growth dependence was observed, in agreement with similar isothermal crystallization behavior for other more crystallizable polymers.[43–46] Whereas in uncrosslinked polymers the molecular weight of the polymer did not affect significantly the crystallization behavior, the same was not true for crosslinked polymers. Formation of crystallites in crosslinked polymers depends on the degree of crosslinking; very densely crosslinked systems do not crystallize under any conditions. Thus, an internal relation between the minimum crystallite size ζ and the end-to-end distance between two crosslinks $(\bar{r}_c^2)^{1/2}$ controls the growth of crystallites in heat-treated networks in the presence of water.

It was the objective of this work to investigate the kinetics and mechanisms of crystallization of poly(vinyl alcohol) in the solvent-free state under isothermal conditions, for crosslinked and uncrosslinked PVA samples, using differential scanning calorimetry and examining the possible Avrami-type growth.

EXPERIMENTAL

Uncrosslinked Samples

The poly(vinyl alcohol) used in this study was supplied by DuPont de Nemours and it was Elvanol, grade 73-125G of number average molecular weight $\bar{M}_n$ = 88,880, weight average molecular weight $\bar{M}_w$ = 184,800, and polydispersity index of 2.08. This PVA grade had less than 0.4% acetyl groups, less than 0.1% carbonyl

groups, less than 0.1% 1,2-glycol groups, and a maximum of 5% volatiles. The samples used were atactic.[9]

Accurately measured quantities of PVA of approximately 10 mg were weighed in aluminum pans and placed in the sample holder of a differential scanning calorimeter (model DSC-1B, Perkin Elmer, Norwalk, Conn.), and the sample cover was tightly secured. The temperature scale was calibrated with pure indium and lead samples.

After purging with nitrogen for 45 min, each PVA sample was melted at 230°C at a scanning speed of 10°C/min to eliminate any crystalline phase initially present in the sample. The sample was cooled rapidly at a scanning speed of 80°C/min to the predetermined crystallization temperature, ranging from 142°C to 192°C, where it was isothermally crystallized for periods of 1–25 min, under nitrogen.

At the end of this crystallization (annealing) process the temperature was raised at a rate of 10°C/min, and the melting isotherm was recorded. Rates of 1.25°C, 2.5°C, 5°C, and 20°C/min were also used in selected experiments. The melting temperature T_m and the heat of melting ΔH^* were determined by standard techniques and recorded for all samples.

To investigate the alleged dehydration and eventual decomposition of the PVA samples upon the first melting at 230°C,[47] thin films of PVA (15 μm thick in dry state) were prepared by casting of a 10 wt % aqueous solution of PVA as described before.[48] These samples were dried to constant weight at 40°C for 20 days, and they were subsequently treated in heating chambers under conditions similar to the DSC-treated samples. Infrared spectra were obtained in an IR spectrophotometer (model 237, Perkin-Elmer) for the detection of bands characteristic of partial degradation.

Crosslinked Samples

To investigate the effect of the molecular weight between crosslinks on the crystallization kinetics of PVA, crosslinked PVA samples were prepared by a chemical crosslinking technique using glutaraldehyde, as described by Peppas and Benner elsewhere.[49] Chemical crosslinking of 10 wt % aqueous PVA solutions was followed by swelling analysis of the prepared swollen networks. Samples with number average molecular weight between crosslinks, $\overline{M}_c$, of 1,085 ± 30, 4,160 ± 50, and 6,160 ± 60, were prepared.

These samples were dehydrated up to constant weight at 40°C for 10 days. Subsequently, isothermal crystallization was performed as before.

Analysis of Crystallization Isotherms

The degree of crystallinity vs. time dependence was analyzed using the Avrami theory of crystallization. The normalized degree of crystallinity, $X(t)$, of the PVA samples was determined from the plots of the DSC using eq. (1),

$$X(t) = X_t/X_\infty = \int_0^t \left(\frac{dH}{dt}\right) dt \bigg/ \int_0^\infty \left(\frac{dH}{dt}\right) dt \qquad (1)$$

where X_t and X_∞ are the weight fractions of crystalline PVA at times t and ∞, respectively. These weight fractions were determined by dividing the heat of
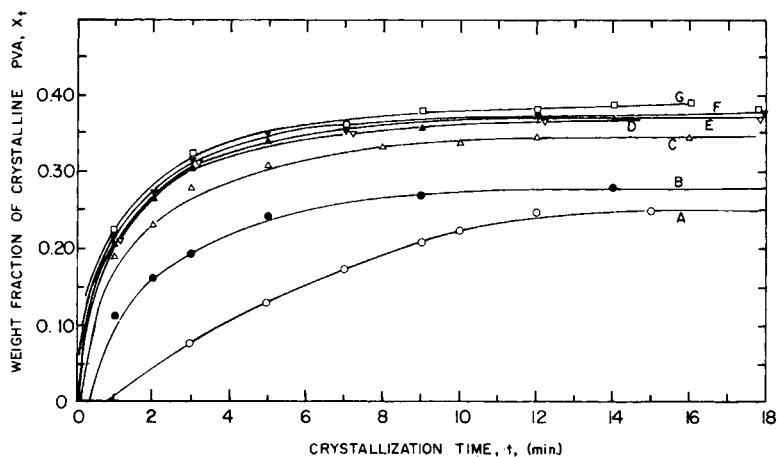
Fig. 1. Weight fraction of crystallized uncrosslinked solvent-free PVA vs. time of crystallization. Curves: (A) 192°C; (B) 182°C; (C) 172°C; (D) 167°C; (E) 162°C; (F) 152°C; (G) 142°C.

fusion of a partially crystallized sample, ΔH^*, by the heat of fusion of the hypothetical 100% crystalline PVA sample, ΔH_u. For example, X_t can be expressed according to eq. (1) as

$$X_t = \Delta H^*/\Delta H_u \qquad (2)$$

The value of ΔH_u has been previously determined[10] as 138.6 J/g of repeating unit.

The Avrami equation can be written as

$$X(t) = 1 - \exp(-kt^n) \qquad (3)$$

where k is the kinetic growth rate constant (min^{-n}) and n in an exponent characteristic of the mechanism which controls the crystallization process. Equation (3) can be written also in a form useful for determination of the parameters k and n:

$$\ln\{-\ln[1 - X(t)]\} = \ln k + n \ln t \qquad (4)$$

The growth rate constant k can also be determined from the half-time [time when $X(t) = 0.5$] τ and from the average value of n, as

$$k = \ln 2/\tau^n \qquad (5)$$

RESULTS AND DISCUSSION

Crystallization Kinetics

Isothermal crystallization of uncrosslinked PVA samples was performed at 142°C, 152°C, 162°C, 167°C, 172°C, 182°C, and 192°C. Typical curves of the dependence of the weight fraction of crystallized PVA, X_t, on crystallization time t are shown in Figure 1. The maximum attainable weight fraction of crystallized material X_∞ was determined from the asymptotic value of X_t at long times, and it is plotted in Figure 2 as a function of crystallization temperature T_c. Within the range of temperatures studied, a maximum X_t of 0.396 was attained in the
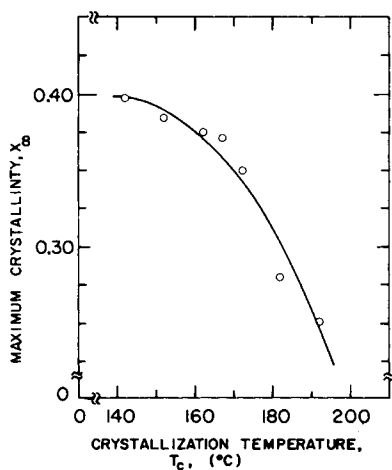
Fig. 2. Maximum weight fraction of crystallized PVA as a function of crystallization temperature.

absence of water. This value of crystallinity was considerably lower than that attained by crystallization of hydrated PVA films,[33] even if the hydrated films were crosslinked[9]; therefore, crystallization of solvent-free PVA exhibits considerable kinetic hindrances.[2]

The crystallization curves of Figure 1 exhibit an induction period for nucleation and growth, which increases as the crystallization temperature increases.
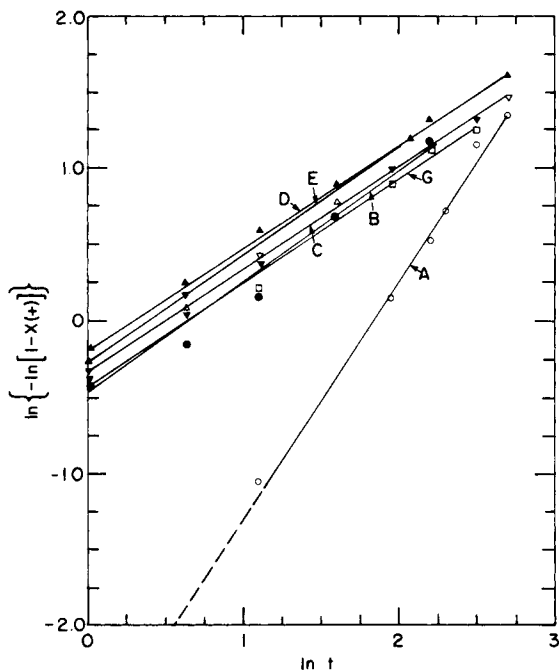

Fig. 3. Logarithmic plots of normalized degree of crystallinity, $X(t)$, vs. time of crystallization, according to eq. (4). Lines: (A) 192°C; (B) 182°C; (C) 172°C; (D) 167°C; (E) 162°C; (F) 152°C; (G) 142°C.

TABLE I
Isothermal Crystallization Kinetics Analysis According to Avrami Theory

Crystallization temp T_c (°C)	Maximum crystallinity X_∞	Kinetic const k (min^{-n})	Exponent n	Half-time of crystallization τ (min)	Melting temp T_m (°C)
142	0.396	0.645	0.67	1.13	199.5
152	0.385	0.675	0.68	1.05	202.1
162	0.376	0.710	0.69	0.98	205.0
167	0.372	0.820	0.71	0.81	206.5
172	0.351	0.780	0.71	0.89	206.7
182	0.280	0.640	0.67	1.21	207.4
192	0.256	0.060	1.53	5.00	212.8

The kinetics of PVA crystallization were further analyzed by plotting the normalized degree of crystallinity, $X(t)$, as calculated from eq. (1), vs. crystallization time, using eq. (4). Figure 3 shows these linear plots for all crystallization conditions studied.

From the intercepts and slopes of these lines, values of the growth rate constant k and the exponent n were calculated and reported in Table I. The same table shows the maximum crystallinity attained, X_∞, for each crystallization process, and the melting temperature is determined from the DSC data.

To investigate possible degradation or dehydration of the PVA samples in the range of experimental conditions studied here, IR spectra were obtained for selected samples, especially those crystallized at high temperatures. Figure 4 shows the IR spectrum of a sample crystallized at 192°C for 15 min, as compared to a noncrystalline PVA sample. There is no evidence of degradation, dehydration, or related reactions, apart from the considerable change of the height of the peak at 1141 cm^{-1}. This peak is crystalline-sensitive, and its importance in quantitative analysis of PVA crystallinity has been discussed before.[48]

Increase in the crystallization temperature increases the melting point of PVA according to a linear dependence; similar behavior has been observed for other polymers with low crystallizability, such as poly(vinylidene fluoride) and poly(vinyl chloride)[50,51] (see also Fig. 5). The kinetic growth constant k exhibits a maximum in the range of 165°C as shown in Table II, and it drops considerably
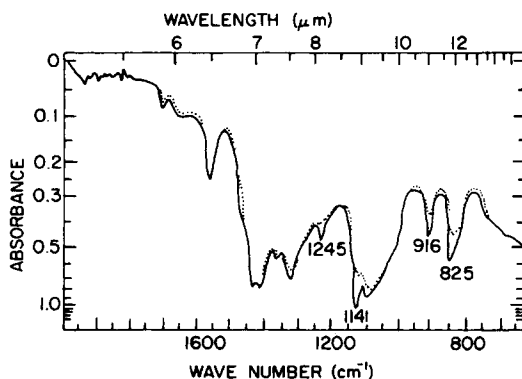

Fig. 4. Infrared spectra of uncrosslinked solvent-free PVA samples before ($\cdots\cdots$) and after (——) crystallization at 192°C for 15 min. The 1141 cm^{-1} band is crystalline phase-sensitive.
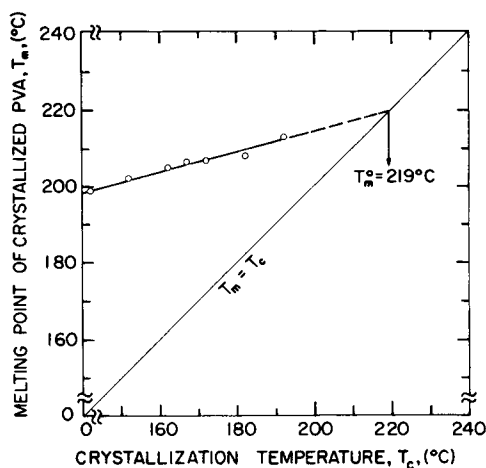
Fig. 5. Effect of crystallization temperature, T_c, on the melting point of annealed samples. The equilibrium melting point T_m^0 is determined by intersection with the $T_m = T_c$ line.

at high temperatures of crystallization (i.e., at low degrees of undercooling, ΔT).

The half-time of the crystallization processes was determined from the lines of Figure 3 at $X(t) = 0.50$ and plotted for all temperatures in Table I.

Crystallization Mechanisms

Despite the limitations of the Avrami theory which have been previously analyzed by many investigators (see, for example, Ref. 52), it is possible to obtain valuable information about the crystallization mechanism of certain polymers by examining the dependence of the exponent n and the growth rate constant k on temperature of annealing. Joint information on these two terms may provide details of the nucleation and growth processes during crystallization, in addition to micrographic and X-ray analysis.

Values of the exponent n for these PVA crystallization experiments were almost constant (between 0.67 and 0.71) in the range of crystallization temperatures between 142°C and 182°C, and increased to $n = 1.53$ for isothermal crystallization at 192°C, i.e., close to the melting point of PVA. The values of this exponent may suggest that the rate-controlling mechanism of the growth of crystallites

TABLE II
Effect of Degree of Undercooling on Crystallization Kinetics

Crystallization temp T_c (°C)	Degree of undercooling $\Delta T = T_m^0 - T_c$ (°C)	Melting point T_m (°C)	Logarithm of kinetic const, $\ln k$
142	77	199.5	−0.44
152	67	202.1	−0.39
162	57	205.0	−0.345
167	52	206.5	−0.195
172	47	206.7	−0.25
182	37	207.4	−0.45
192	27	212.8	−2.80

is the diffusion of macromolecules to or from the growth surface of the crystallites, as long as instantaneous, homogeneous, one-dimensional, fibrillar crystallization is observed.[52-54]   Indeed nucleation of PVA has been shown to be homogeneous[30-32], and one-dimensional, fibrillar crystallization has been reported by several investigators,[24,39,40] based on X-ray and electron-microscopic studies. Diffusional limitations are to be expected in crystallization of PVA in view of the fact that hydroxyl group interactions are so strong in the case of hydroxyl-containing polymers that the mobility of macromolecular chains before they approach the growing crystal is strongly impeded.

Experimental analysis using the Avrami theory with constant exponent n frequently exhibits large deviations from predicted values at long times.[52]   This deviational behavior is observed at X_t higher than 0.35 for polymers that do not crystallize easily.   It is described as secondary crystallization, characterized by different values of exponent n, and it results in crystallites which are substantially deformed due to strong stresses developed in the polymer.[45,54]   However, in the case of solvent-free PVA, our data showed only primary crystallization and no significant secondary crystallization (see also Fig. 3).

Growth Rate of PVA

The magnitude of the growth rate constants k (see Tables I and II) can provide information about the growth of PVA crystallites.   To analyze the growth behavior, an extension of the Turnbull–Fisher nucleation theory can be used,[55] in a fashion similar to the one employed by Ohta et al.[51] for poly(vinyl chloride), whereby the growth rate is expressed according to eq. (6):

$$k = k_0 \exp(-\Delta F_1/RT_c) \exp(-\Delta F_2/RT_c) \tag{6}$$

Here k_0 is a constant, independent of temperature, ΔF_1 is the energy of activation for diffusion of molecules, and ΔF_2 is the energy of activation for formation of crystallites.

The activation energy ΔF_1 can be expressed, by application of the WLF equation,[55] as

$$\Delta F_1 = \frac{17,300 \, T_c}{51.6 + T_c - T_g} \tag{7}$$

where T_g is the glass transition temperature of PVA, which was determined to be $85 \pm 1°C$ for the samples used in this work.

The activation energy ΔF_2 can be expressed in terms of parameters characteristic of the crystallite dimensions and the thermodynamics of crystallization[56] as

$$\Delta F_2 = \frac{4b \, \sigma_s \, \sigma_e}{\Delta H_u} \times \frac{T_m^0}{\Delta T} \tag{8}$$

where b is the thickness of a monomolecular layer, σ_s and σ_e are the surface free energies of the side and end planes of the crystal, and ΔT is the degree of undercooling, expressed as

$$\Delta T = T_m^0 - T_c \tag{9}$$

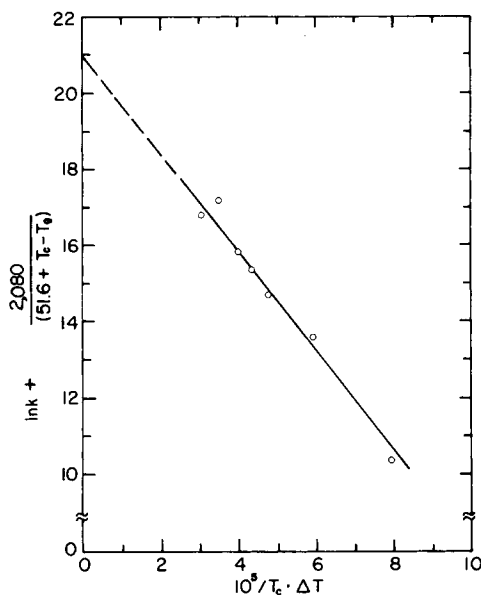The equilibrium melting temperature T_m^0 is related to the crystallization tem-

Fig. 6. Effect of undercooling on the kinetic growth rate constant k.

perature T_c and to the melting temperatures of the individual samples, T_m, by eq. (1):

$$T_m = T_m^0 - \tfrac{1}{2}\,\beta\,(T_m^0 - T_c) \tag{10}$$

It was determined as $T_m^0 = 219°C$ by extrapolation, as shown in Figure 5.

Therefore, from eqs. (6), (7), and (8) one can obtain

$$\ln k = \ln k_0 - \frac{17{,}300}{R(51.6 + T_c - T_g)} - \frac{C_1}{\Delta T \cdot T_c} \tag{11}$$

where C_1 is a constant characteristic of the PVA structure and incorporating the parameters of eq. (8), $R = 8.314$ J/mol $\cdot$ K, and all the temperatures are expressed in K.

Since k_0 is independent of temperature, a plot of $\ln k + 17{,}300/R(51.6 + T_c - T_g)$ vs. $1/\Delta T \cdot T_c$, in the range of temperatures between T_m^0 and T_g, should give a straight line. Table II summarizes data on the degree of undercooling of the crystallization experiments, and Figure 6 presents the linear relationship

TABLE III
Isothermal Crystallization of Solvent-Free Crosslinked PVA

Crosslinking $\overline{M}_c$ (g/mol)	No. repeat units between crosslinks	Crystallization conditions		Crystallinity X_t
		Temp (°C)	Time (min)	
1085	25	192	15	0.030
		182	15	0.030
4160	95	192	15	0.035
		182	15	0.038
6160	140	192	15	0.042
		182	15	0.046

of eq. (11). By extrapolation we found $k_0 = 1.32 \times 10^9\ \mathrm{min}^{-1}$. The linear relationship of eq. (11) and the qualitative agreement of the data of Table III with the theory described by eq. (6) are additional indications of one-dimensional growth geometry, which was expected from the values of exponent n.

Crosslinked Samples

An additional physical hindrance to the crystallization is the molecular weight of the macromolecular chains. In addition to kinetic hindrance due to hydroxyl interactions and low crystallizability of solvent-free uncrosslinked PVA, short chains of PVA will have to overcome the energetic barriers of the critical chain length required for the formation of crystallites. Table III summarizes characteristics of the solvent-free PVA networks employed, and selected values of the weight fraction of crystallized PVA, X_t, obtained at specified crystallization conditions.

Since differential scanning calorimetry has a lower limit of detection of $X_t = 0.03 - 0.04$, these data cannot be further analyzed. Highly and moderately crosslinked PVA systems did not exhibit crystallization, although their swollen counterparts are known to crystallize readily.[9]

CONCLUSIONS

Uncrosslinked poly(vinyl alcohol) samples can crystallize in the absence of diluents to yield degrees of crystallinity which are well below the values of hydrated, uncrosslinked samples. The kinetic data can be analyzed by the Avrami theory. Crystallization of PVA at temperatures between 142°C and 192°C is one-dimensional, and the chain mobility is affected by the time and temperature of crystallization.

The degree of undercooling and the chain length are important factors in the crystallization process. Indeed, moderately or highly crosslinked dry PVA samples exhibit very little crystallinity.

In conclusion, this work quantifies the physical predictions of Frenkel and his collaborators[2] about the importance of hydrogen-bonding and other hydroxyl interactions in the crystallization of polar polymers.

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