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## The Effect of Molecular Weight on the Retrogradation of Amylose

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THE EFFECT OF MOLECULAR WEIGHT ON THE  
RETROGRADATION OF AMYLOSE

by

Darryl O'Daye

Thesis submitted to the  
Faculty of the Department of Paper Technology  
in partial fulfillment  
of the  
Degree of Bachelor of Science

Western Michigan University  
Kalamazoo, Michigan  
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### ABSTRACT

The effect of molecular weight on the rate of retrogradation of amylose was studied by monitoring turbidity (corrected for molecule shape) with a light scattering photometer. The results obtained showed that by acid modification of the amylose fraction of starch, the chain length of amylose molecules were reduced. The rate of retrogradation increased with decreasing molecular weight until a maximum was reached at  $1\frac{1}{2}$  hours of hydrolysis. The rate of retrogradation then decreased with further decreasing molecular weight until retrogradation began to lessen.

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## INTRODUCTION

Generally, the paper industry uses starch because starch pastes possess unusual viscosity characteristics and they are effective film formers. Starch is also used in coating operations as a pigment adhesive. These starches normally contain various percentages of both amylose (approx. 27% of corn) and amylopectin.

Since such common starch problems of skinning over, retention, and viscosity changes upon storage are related to the retrogradation characteristics of starch, it is desirable to study the process of retrogradation. Because retrogradation occurs almost exclusively with the amylose fraction of starch, amylose was chosen for this study. While this study is not immediately applicable to industry because of the many other factors affecting retrogradation, it should be viewed as another entry to the collection of information gathered about the retrogradation of amylose. Eventually this body of information gathered about the retrogradation of amylose may enable us to prevent the problems now encountered with starch usage.

## HISTORICAL BACKGROUND

### A Description of Starch

Starch is a white granular polymer synthesized by plants from simple dextrose units. The dextrose units may be combined by the plant into two different distinct fractions. The linear carbohydrate chain fraction (amylose) is composed of approximately 6000 chemically united glucose units. The second fraction (amylopectin) is a highly branched molecule consisting of about 50,000 glucose units. While these two starch fractions behave similarly in many chemical reactions, the physical and colloidal properties are widely different.

### The Amylopectin Fraction of Starch

Attempts to determine the molecular structure of amylopectin suggest that it is extremely heterogeneous with respect to molecular weight and degree or extent of branching. Molecular weights obtained from osmotic pressure measurements by Meyer (1) and Potter and Hassid (2) give values in the range of  $10^5$  to  $10^6$ . Molecular weight measurements obtained from light scattering methods by Zimm and Thurmond (3) and by Witnauer, Senti, and Stern (4) average approximately  $10^7$ . Part of this discrepancy can be explained by the fact that the light scattering method measures the weight-average molecular weight which is always greater than the number-average molecular weight by osmotic pressure methods. Amylopectin also forms relatively stable solutions in water. It will not normally return to its previous solid state by lowering the temperature of the solution and allowing it to stand for a given duration of time.

### The Amylose Fraction of Starch

Amylose, on the other hand, is insoluble in cold water and, at best, only partially soluble under more suitable conditions.

By dissolving amylose in water at 140°C. under pressure and allowing it to cool, a process of "retrogradation" occurs in which the amylose reverts to an insoluble form. Foster (5) feels that retrogradation is the result of hydrogen bonding between starch molecules that have both hydroxyl groups and hydrogen acceptor sites. The extended linear molecules of amylose are more free to orient themselves with respect to other amylose molecules in solution than are the larger, more compacted, branched molecules of amylopectin. Therefore, retrogradation is associated almost exclusively with the amylose fraction. The amylose structure permits the formation of many hydrogen bonding between adjoining molecules so that a solution of amylose is highly unstable. He further states that at amylose concentrations above two percent, extensive hydrogen bonding occurs between adjoining molecules and a gel is formed. At lower concentrations or under controlled temperature conditions, the molecules orient themselves in a manner that permits the formation of numerous crystallites. When the aggregates of crystallites exceed colloidal dimensions, a granular precipitate separates. Doppert and Stoverman (6) suggest that the mechanism of retrogradation is based on von Smoluchowski's theory of coagulation\*. They concluded that from the rate of retrogradation only a small fraction of collisions between amylose aggregates lead to permanent coagulation because there must be a mutual orientation of colliding aggregates.

Therefore amylose must be able to assume several configurations in solution. Studies conducted by Rao and Foster (7), Everett and Foster (8), and Holló Szejtli and Gantner (9) agree that amylose in solution exists as nearly Gaussian, but

\* von Smoluchowski's theory of coagulation is that of spherical particles diffusing into each other's sphere of influence and then sticking together.

relatively stiff coils, the backbone of which is essentially helical. A gel results when the helical or partly uncoiled helical molecules form hydrogen bonds between each other. Retrogradation occurs when the molecules uncoil and align themselves to permit the formation of crystallites which ultimately grow into large aggregates. Greenwood (10) suggests an equilibrium solution exists in the following manner:

Aggregated helices  $\rightleftharpoons$  helical configuration  $\rightleftharpoons$  linear configuration  $\rightleftharpoons$  aggregated linear chains.

#### Factors Affecting the Retrogradation of Amylose

There are several factors that may affect the rate of retrogradation. Foster and Sturman (11) suggest a dependence of retrogradation on the prior physical state of amylose (i.e., the conditions of precipitation and drying). They concluded that retrogradation is retarded by increased perfection of the helical crystalline form. They further suggest that the rate of retrogradation is governed by the rate of disruption of the intramolecularly hydrogen bonded helical form of amylose.

Another important factor is the molecular weight of amylose. Loewus and Briggs (12) found that doubling the molecular weight of the amylose increased the time required to reach a particular stage of retrogradation by a factor of six to eight. Whistler and Johnson (13) noted that on acid hydrolysis, the rate of retrogradation increased to a maximum and then continuously decreased as the molecular magnitude was decreased. In other words, at larger or smaller molecular weights than the retrogradation size, the rate of retrogradation is slower. Loewus and Briggs (12) confirmed this observation by also noting that the rate gradually accelerated to a



maximum and then decayed as complete retrogradation was approached. Lansky, Kooi, and Schoch (14) determined from turbidimetric measurements that the chain length was inversely proportional to the retrogradation rate until a certain critical value was reached, below which the molecules were too small to crystallize.

Time, temperature, and amylose concentration in solution are also important factors determining the rate of retrogradation. With any particular amylose preparation the rate of retrogradation inversely on the approximate square of the amylose concentration.

From turbidimetric studies on corn amylose as a function of pH and time, Paschall and Foster (15) found that at pH 4.0 the turbidity was constant for at least thirty days. In 1 N. KOH, there was a slow reduction of turbidity. They also found that at pH 6.5 to 7.0 there was a much more rapid decrease in turbidity. Kalb and Sterling (16) measured retrogradation by crystallinity and found that maximum retrogradation occurred at pH 5 when gelled after pH adjustments, while the maximum retrogradation occurred at pH 1 to 2 when gelled before pH adjustment.

The rate of retrogradation of amylose may also be altered by chemical reaction with other substances to form acetylated or ethylated starches for example. Whistler (17) also suggests that the presence of foreign ions also affects the rate of retrogradation.

#### The Light Scattering Method as Applied to Dilute Solutions

The rate of retrogradation of standard amylose solutions (prepared by 1-butanol fractionations) at varying concentrations was monitored by light scattering. the study was conducted under standard conditions of pH, temperature, and time.

To fully appreciate this investigation, it is necessary to possess a basic understanding of the light scattering method as applied to dilute solutions (18-22). Light scattering occurs whenever light encounters matter. Light incident on matter causes the electrons of the atoms and molecules to undergo induced vibrations in phase with the incident light wave. The particle then becomes a source of scattered light.

The atom or molecule involved determines the amplitude and the intensity of the scattered light. Figure 1 shows a light wave traveling in the  $xz$  plane incident upon a particle located at the origin.

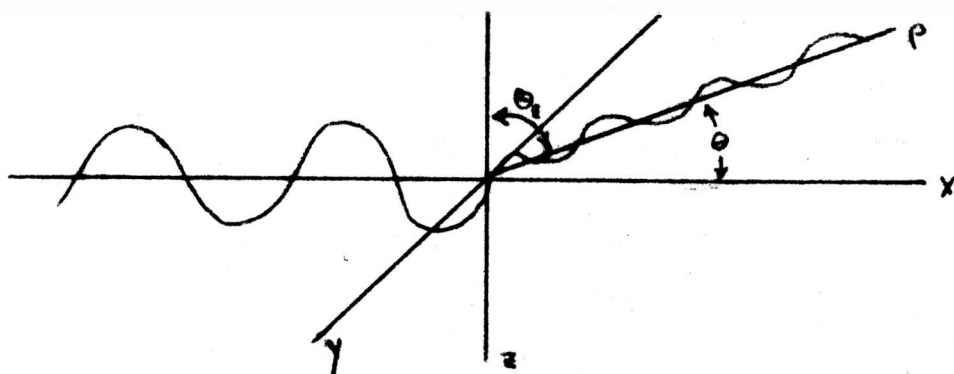


Figure 1. The path of a light wave striking a particle at the origin.

The equation developments will be made by first assuming the light is plane polarized and that the particle is isotropically polarizable. This particle will then scatter light equally at any angle  $\theta_z$  (assuming its size is less than one-twentieth of the wavelength of the incident light) from the  $xz$  plane.

The electrical intensity of the incident light  $E$ , can be expressed by the following equation

$$E = \frac{A_0 z \cos^2 \pi c t}{\lambda} \quad (1)$$

where

$c$  = the velocity of light

$A_{0z}$  = the amplitude of the incident beam which is plane polarized in the  $xz$  plane  
 $t$  = time  
 $\lambda$  = the wavelength of light

The wave will induce an electric moment in the particle, the strength of this moment is proportional to the electric field intensity.

$$m = \epsilon E = \frac{\epsilon A_{0z} \cos \pi^2 ct}{\lambda} \quad (2)$$

where

$m$  = the induced electric moment  
 $\epsilon$  = the molecular polarizability

The electrical intensity of the scattered wave depends upon the acceleration of the induced moment which is equal to  $d^2m/dt^2$ . If equation (2) is solved for the acceleration of the induced moment it is found that the amplitude of the scattered wave will be

$$A_{sc} = \left( \frac{\epsilon A_{0z}}{r} \right) \left( \frac{2\pi}{\lambda} \right)^2 \sin \theta_z \quad (3)$$

where

$A_{sc}$  = the amplitude of the scattered light  
 $r$  = distance of observation from the origin of scatter  
 $\theta_z$  = the angle of observation from the  $xz$  plane

The intensity of the scattered wave equals the square of the amplitude

$$i_z = \frac{16\pi^4 I_{0z} \epsilon^2 \sin^2 \theta_z}{r^2 \lambda^4} \quad (4)$$

where

$I_{0z} = A_{0z}^2$  = intensity of incident beam  
 $i_z$  = the intensity of the scattered beam

This is scattering due to a single particle when the incident beam is plane polarized.

However, most light scattering instruments use unpolarized light and the solution of many particles. So the combined intensity of scattered light at a distance  $r$  and in a direction specified by  $\theta$  due to all particles in a unit volume  $N/V$  of a dilute solution becomes

$$i_{\theta} = \frac{I_0 N}{V} \frac{8\pi^4 \alpha^2}{\lambda^4} \frac{1 + \cos^2 \theta}{r^2} \quad (5)$$

where

$i_{\theta}$  = combined intensity of scattered light at a distance  $r$  and in a direction specified by  $\theta$  due to all particles

$N$  = number of particles

$V$  = unit volume

For practical use the polarizability must be replaced by observable quantities; in particular the optical dielectric constants  $\xi$  and  $\xi_0$ . The excess polarizability  $\alpha$ , is related to the dielectric constants in the following manner

$$\alpha = (\xi - \xi_0) \left( \frac{V}{4\pi N} \right) \quad (6)$$

The dielectric constants are equal to the squares of their respective refractive indexes providing both of these quantities are measured at the same frequency. Therefore

$$\alpha = \left( \frac{V}{4\pi N} \right) (n^2 - n_0^2) \quad (7)$$

where

$n$  = refractive index of the solution

$n_0$  = refractive index of solvent

When the refractive index is substituted for dielectric constant, the refractive index increment is used because it is an intrinsic constant of most dilute solutions:

$$\epsilon - \epsilon_0 = \frac{n^2 - n_0^2}{c}$$

$$\frac{(n - n_0)(n + n_0)}{c} \approx \frac{2n_0(n - n_0)}{c} = 2n_0 \left( \frac{dn}{dc} \right) \quad (8)$$

where

$$\frac{n - n_0}{c} = \frac{dn}{dc} \quad \text{refractive index increment}$$

Through algebraic manipulation (separation of terms and division by  $c$ ) it can be shown that equation (7) may be expressed as

$$= \left( \frac{V}{N} \right) \left( \frac{1}{4} \right) (c) \left( \frac{n - n_0}{c} \right) (2n_0) \quad (9)$$

for dilute solutions. Substitution of equation (9) into equation (5) and subsequent combining of terms yields

$$\frac{i_{\theta} r^2}{I_0} = \frac{(2\pi^2 n_0^2)(n - n_0)^2}{\lambda^4 N_0 c} (Mc) (1 + \cos^2 \theta) \quad (10)$$

where

$\frac{N}{V}$  = number of molecules

$V$  = volume in which they are contained

$c$  = concentration in grams per milliliter

Instead of measuring the intensity of the light scattered from the incident beam, often the diminution of the incident beam, due to scattering upon transversing a distance,  $l$ , is measured. The turbidity is known as the natural log of the decrease in the transmitted intensity,  $I$ . The turbidity is equal to the extinction coefficient for absorbing systems.

$$I = I_0 e^{-\tau l}$$

The turbidity equals the total scattering integrated over all

angles.

$$\tau = \int \theta^i d\theta$$

Therefore,

$$R_{90} = \frac{8\pi}{3} \frac{i_{90} r^2}{I_0} = \frac{16\pi}{3} R_{90}$$

where

$$R_{90} = 2i_{\theta} r^2 \quad \text{and} \quad \tau = \frac{32\pi^3 n^2 (n - n_0) M c}{3N_0 \lambda^4} \quad (11)$$

This is a basic development of the relationship between scattered light and the molecular weight of a dissolved molecule.

However, it was assumed that we had an ideal solution and that isotropic molecules are completely random with respect to one another. Actually, the solutions are non-ideal and the thermal movements of the scattering units are not totally independent. Consequently the total intensity of the scattered light cannot be obtained by the sum intensity of light scattered from the individual molecules. Destructive interference occurs due to "local order" and there is a decrease in the intensity of the scattered light.

Light scattering by non-ideal solutions is considered to depend on the irregular spacing of scattering centers. When molecules are regularly spaced such as in a perfect crystal the scattering from one volume is cancelled by the scattering from a similar volume appropriately located.

The scattering from a solution than should become greater as the system becomes more heterogeneous or, more precisely, as the density and concentration within volume elements fluctuate.

Since the scattering of the solute molecules is of interest, the scattering due to concentration fluctuations must be considered. The scattering resulting from density fluctuations may be eliminated by subtracting the scattering due to the solvent from the scattering due to the solution.

Optically, the concentration fluctuation can be measured by the resulting deviation of the dielectric constant from its mean value. By relating the mean square fluctuation in concentration to the mean square fluctuation in dielectric constant and the effect of fluctuation in the dielectric constant on turbidity, Einstein developed the following equation:

$$\frac{Kc}{R_{90}} = \frac{1}{M} + Bc \quad (11)$$

and

$$\frac{Hc}{\tau} = \frac{1}{M} + Bc$$

where

$$B = \text{interaction constant}$$

$$H = \frac{32\pi^3 n_0^2 (n - n_0/c)^2}{3N_0 \lambda_0^4}$$

$$K = \frac{2\pi^2 n_0^2 (n - n_0/c)^2}{N_0 \lambda_0^4}$$

which allows us to consider scattering due to concentration fluctuation in a non-ideal solution.

Because the amylose particle size is greater than  $1/20$  of the wavelength of light, still another correction must be made in order to determine the molecular weight. Previously, individual molecules could be treated as point sources or scattered light. However, when the particles exceed  $1/20$  of the wavelength of light. Light is scattered from different parts of the same molecule and consequently optical interference will occur. This is of major importance because it leads to decrease in the intensity of the scattered light, the effect increasing as the scattering angle increases. Since the molecular weight relation in equation (12) does not take this interference into account it is obvious that a correction must be applied.

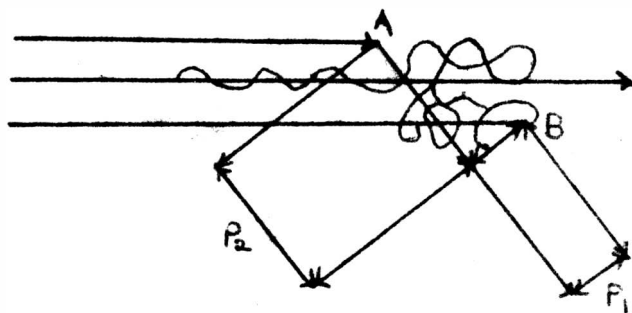


Figure 2. Path difference between forward and backward scattering of light waves.

Figure 2 shows that the path difference is greater for the portions of waves scattered from A to B in the backward or  $P_2$  direction. Destructive interference owing to phase differences between rays scattered by different sections of the same molecule will therefore be greater the larger the scattering angle and will vanish as the scattering angle approaches zero. It is obvious then that the scattering will not be symmetrical about  $90^\circ$ . It will be less at angles greater than  $90^\circ$  than for angles equally smaller than  $90^\circ$ . The observed ratio is the ratio of the light scattered at  $45^\circ$  to the light scattered at  $135^\circ$ .

$$z = \frac{i_{45}}{i_{135}} \quad (13)$$

It is obvious that the dissymmetry ratio can be used as a relative measure of molecular size. It is, in effect, a measure of the radius of gyration.

The intensity,  $i_\theta$ , in the direction  $\theta$ , will be reduced by intra-particle interference at a factor customarily designated by  $P(\theta)$  which depends on the size and shape of the particles as well as on the angle  $\theta$ .

The derivation of an expression for  $P(\theta)$  which may be called the particle scattering factor was first derived by Rayleigh for the case of spheres, by Neugebauer for rod-like particles, and for randomly coiled chain molecules by Zimm, Stein, Debye, and Doty. Tables of  $1/P(\theta)$ ,  $z$ , and  $D/\lambda$  have been calculated for each of these three main types of molecules.



## EXPERIMENTAL PROCEDURES

### Amylose Fractionation

An amylose fraction was prepared by a standard 1-butanol fractionation. The complex consisted of 20% amylose in butanol to be used for acid modification and light scattering measurements.

### Acid Modification of Amylose

Since this thesis is a continuance of work John Bergin began in 1966, the acid modified samples used were those prepared at that time. They were acid modified by using a potassium acid phthalate buffer at a pH of 4.2 to 4.5. The samples were stored at a concentration of about 0.5% amylose. After hydrolysis, the butanol complex was reformed and stored under butanol.

### Preparation of the Solutions for Light Scattering Measurements:

The hydrolyzed amylose fractions were recovered by introducing the butanol complex into distilled water at 100°C. This was done to avoid capsulation of the amylose when distilling off the butanol. The butanol and water form a minimum boiling azeotrope at 93°C. By keeping the volume of the solution constant by adding water it is possible to distill all the butanol off by successive dilutions of water. The dispersions were adjusted to 0.1 to 0.5% concentrations. The amylose dispersions were clarified for light scattering measurements by filtration through 0.22 millipore filters.

Turbidity, Dissymetry, and  $\frac{1}{P(\theta)}$

Acid hydrolysis reduced the chain length of the starch molecules. This enabled the molecules to align them-

selves more easily. Therefore, the rate of retrogradation should increase as the molecular weight decreases, until the chain length is no longer characteristic of a polymer and the property of retrogradation is no longer present.

The amylose dispersions were clarified at 95°C and allowed to cool for  $\frac{1}{2}$  hour to obtain a constant temperature. The molecular weight at the various hydrolysis levels is not obtainable using the above procedure because retrogradation occurred during this initial  $\frac{1}{2}$  hour before the first turbidity and dissymmetry measurements (at time = 0 on Figures 2 through 6). Since turbidity is proportional to the molecular weight, by plotting turbidity ( $\tau$ ) vs. time and correcting the turbidity for the effects of molecule shape and size ( $\frac{1}{P(\theta)}$ ), it was possible to observe the rate of retrogradation by noting the rate of particle growth with time.

After preliminary agitation to effect a constant temperature, the dispersions were not agitated again. The effect obtained was that the molecules would retrograde to a maximum agglomerate size, whereby the particles would begin to precipitate and settle to the bottom of the cell. This procedure was followed to maintain the validity of the light scattering measurements. Because the light scattering application applies to dilute solutions of known shape and size, the scattering of light by precipitating large agglomerates, may thus affect the significance of any measurements made after precipitation has started to occur.

The initial molecular weight of unhydrolyzed amylose was so high that during the initial  $\frac{1}{2}$  hour cooling period the particle size was large enough to cause precipitation. It can be seen in Figure 3 that the dispersions at 0.352 and 0.306% had precipitated before the first measurements could be taken. The  $\frac{1}{2}$  and 1 hour hydrolyzed samples (Figures 4 and 5) rates of retrogradation. The 1 $\frac{1}{2}$  Hydrolysis (Figure 6) seems to have reduced the chain length of amylose to the point where the molecules are the most mobile and can align

themselves easily, thereby increasing the rate of retrogradation to a maximum. As can be seen from Figure 6, retrogradation has occurred and the particles have almost completely settled out of the dispersion. The 2 $\frac{1}{2}$  hydrolysis (Figure 7) of three different concentrations exhibits quite different curves. It is possible to see the rate of retrogradation decreasing with respect to the previous hydrolysis samples. It is possible that the chain length of the molecules have been reduced to the point where retrogradation is no longer being exhibited.

Table I. Data Compiled From Light Scattering Measurements of Unhydrolyzed Amylose Solutions.

Time (min)	Conc. = 0.306%				Conc. = 0.352%				Conc. = 0.374%			
	$\gamma$ $\times 10^3$	Z	$\frac{1}{P(\theta)}$	$\frac{\gamma}{P(\theta)}$	$\gamma$ $\times 10^3$	Z	$\frac{1}{P(\theta)}$	$\frac{\gamma}{P(\theta)}$	$\gamma$ $\times 10^3$	Z	$\frac{1}{P(\theta)}$	$\frac{\gamma}{P(\theta)}$
0	2.81	4.48	7.0	.0196	3.41	>4.8	10	.0341	4.22	>4.8	10	.0422
90	—	—	—	—	2.90	>4.8	10	.0290	4.43	4.56	7.6	.0375
95	2.69	4.59	8.0	.0215	—	—	—	—	—	—	—	—
175	—	—	—	—	—	—	—	—	8.48	3.60	3.9	.0330
180	2.65	4.59	8.0	.0212	1.58	>4.8	10	.0158	—	—	—	—
235	—	—	—	—	—	—	—	—	14.8	1.53	1.4	.0227
240	2.70	4.65	8.6	.233	—	—	—	—	—	—	—	—
250	—	—	—	—	.222	>4.8	10	.00222	—	—	—	—

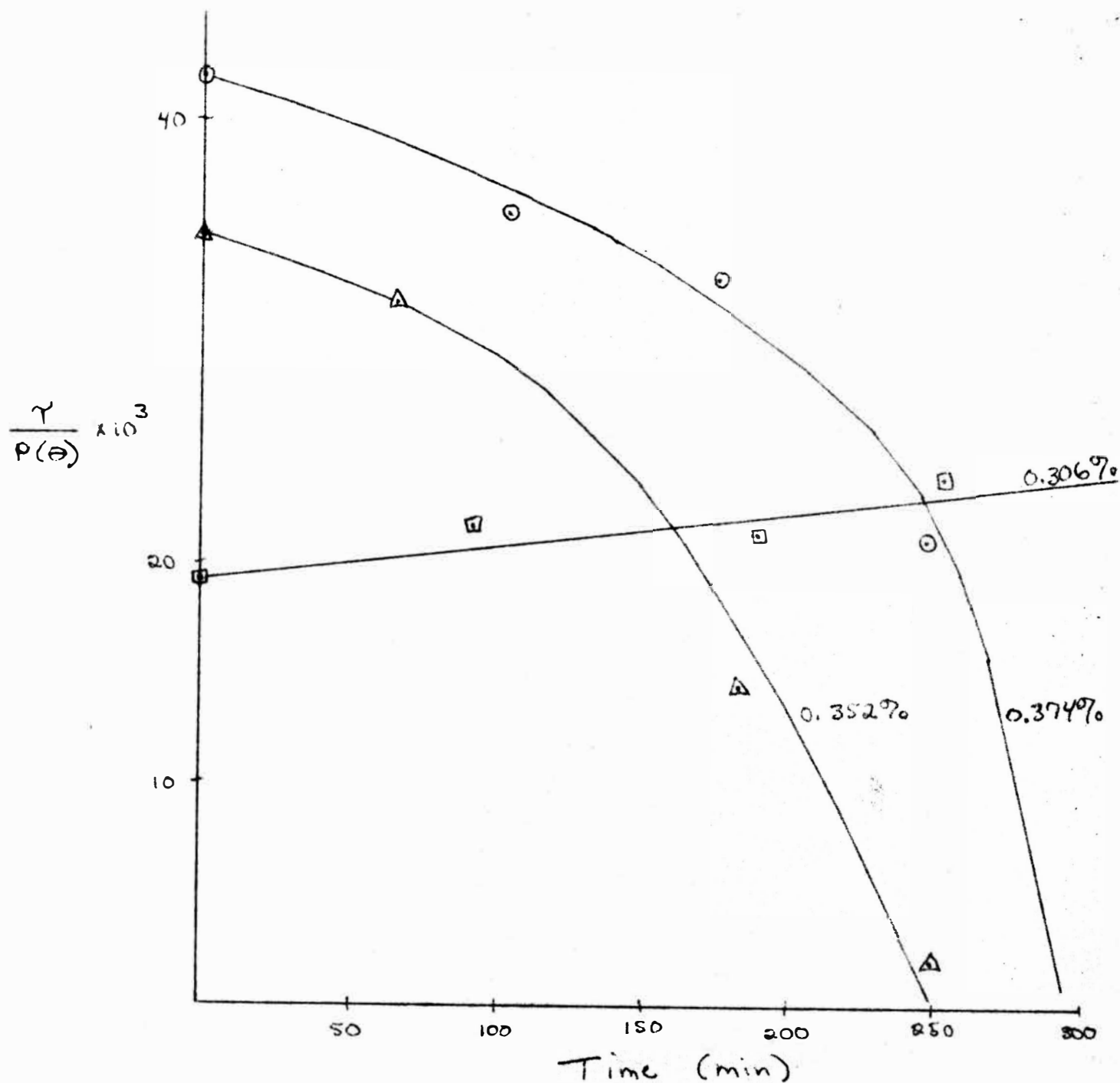


Figure 3. Agglomerate Size Vs. Time for Unhydrolyzed Amylose at Three Concentrations.

Table II. Data Compiled From Light Scattering Measurements of  $\frac{1}{2}$  Hr. Hydrolysis.

Time (min)	Conc. = 0.125%				Conc. = 0.274%			
	$\tau$ $\times 10^3$	$\frac{1}{P(\theta)}$	$z$	$\frac{\tau}{P(\theta)}$	$\tau$ $\times 10^3$	$\frac{1}{P(\theta)}$	$z$	$\frac{\tau}{P(\theta)}$
0	.696	10	74.8	$\frac{6.96}{\times 10^{-3}}$	.915	10	74.8	$\frac{9.15}{\times 10^{-3}}$
12	.753	10	74.8	$\frac{7.53}{\times 10^{-3}}$	—	—	—	—
32	.835	10	74.8	$\frac{8.35}{\times 10^{-3}}$	—	—	—	—
90	—	—	—	—	.675	10	74.8	$\frac{6.75}{\times 10^{-3}}$
147	.958	10	74.8	$\frac{9.58}{\times 10^{-3}}$	—	—	—	—
162	.968	10	74.8	$\frac{9.68}{\times 10^{-3}}$	—	—	—	—
177	.968	10	74.8	$\frac{9.68}{\times 10^{-3}}$	—	—	—	—
180	—	—	—	—	.886	10	74.8	$\frac{8.86}{\times 10^{-3}}$
207	.958	10	74.8	$\frac{9.58}{\times 10^{-3}}$	.740	—	—	—
237	.964	10	74.8	$\frac{9.64}{\times 10^{-3}}$	—	—	—	—
270	—	—	—	—	.749	10	74.8	$\frac{7.49}{\times 10^{-3}}$
997	1.26	2.1	2.28	$\frac{2.66}{\times 10^{-3}}$	—	—	—	—

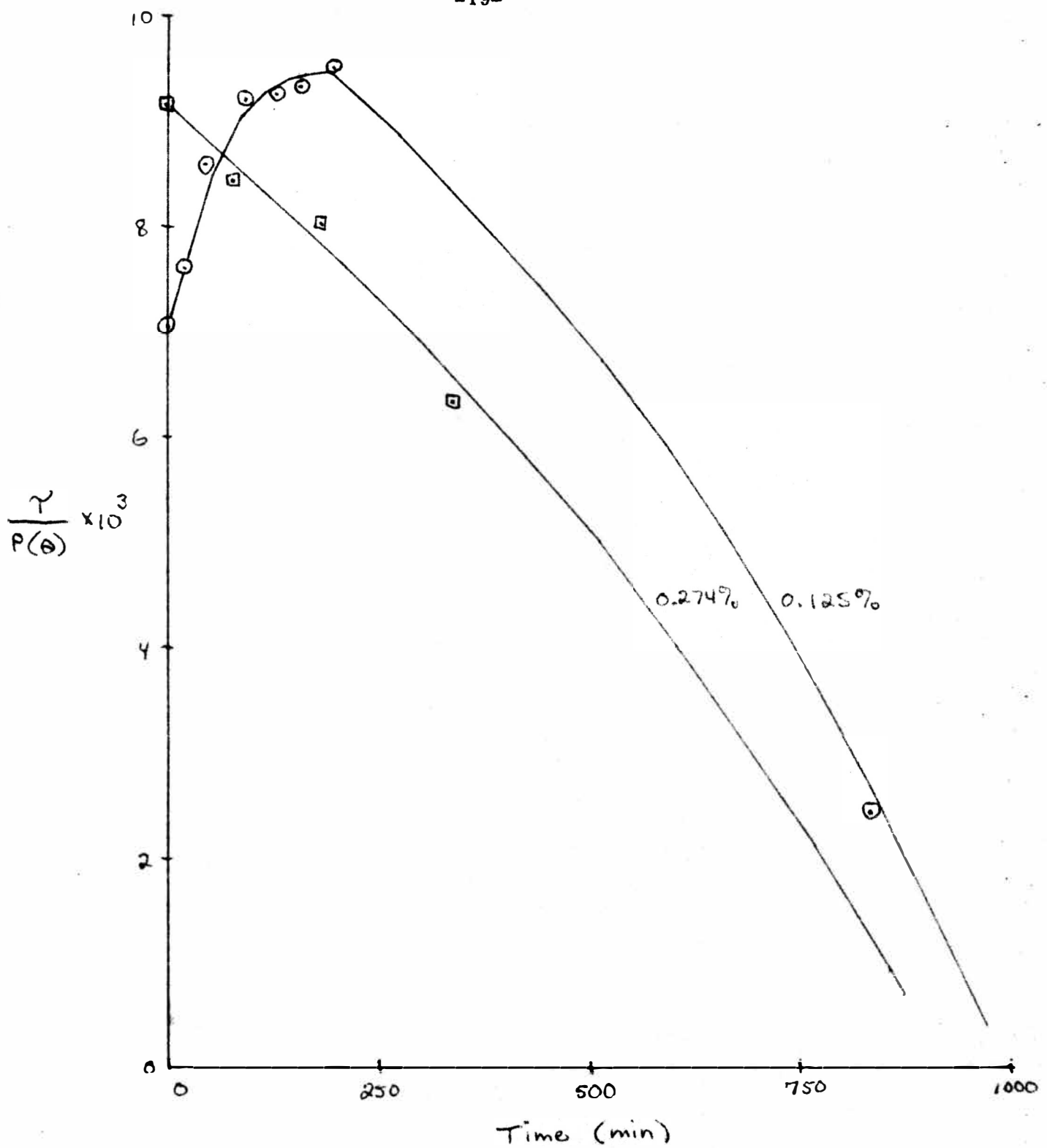


Figure 4. Agglomerate Size vs. Time for  $\frac{1}{2}$  Hr. Hydrolyzed Amylose at Two Concentrations.

Table III. Data Compiled From Light Scattering Measurements of  
1 Hr. Hydrolysis.

Time (min)	Conc. = 0.088%				Conc. = 0.167%				Conc. = 0.177%				Conc. 0.366%			
	$\tau$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\tau}{P(\theta)}$	$\tau$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\tau}{P(\theta)}$	$\tau$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\tau}{P(\theta)}$	$\tau$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\tau}{P(\theta)}$
0	.384	4.30	6.2	$\frac{2.38}{\times 10^{-3}}$	.496	4.12	5.3	$\frac{2.63}{\times 10^{-3}}$	.384	74.8	10	$\frac{3.84}{\times 10^{-3}}$	.969	4.40	6.7	$\frac{6.49}{\times 10^{-3}}$
50	.384	4.30	6.2	$\frac{2.38}{\times 10^{-3}}$	—	—	—	—	—	—	—	—	—	—	—	—
55	—	—	—	—	—	—	—	—	.647	4.42	6.7	$\frac{4.33}{\times 10^{-3}}$	—	—	—	—
85	—	—	—	—	.838	2.45	1.9	$\frac{1.59}{\times 10^{-3}}$	—	—	—	—	1.07	4.65	9.3	$\frac{9.96}{\times 10^{-3}}$
115	—	—	—	—	—	—	—	—	.638	4.48	7.2	$\frac{4.59}{\times 10^{-3}}$	—	—	—	—
120	.390	4.21	5.8	$\frac{2.22}{\times 10^{-3}}$	—	—	—	—	—	—	—	—	—	—	—	—
165	.383	4.42	6.7	$\frac{2.57}{\times 10^{-3}}$	—	—	—	—	—	—	—	—	—	—	—	—
170	—	—	—	—	—	—	—	—	.656	4.19	5.8	$\frac{3.81}{\times 10^{-3}}$	—	—	—	—
245	—	—	—	—	.492	4.43	6.7	$\frac{3.30}{\times 10^{-3}}$	—	—	—	—	—	—	—	—
250	—	—	—	—	—	—	—	—	—	—	—	—	1.14	3.17	3.2	$\frac{3.64}{\times 10^{-3}}$
555	—	—	—	—	.743	4.46	7.2	$\frac{5.26}{\times 10^{-3}}$	—	—	—	—	—	—	—	—
560	—	—	—	—	—	—	—	—	—	—	—	—	1.23	4.66	9.4	$\frac{11.57}{\times 10^{-3}}$
905	.416	5.20	10	$\frac{4.16}{\times 10^{-3}}$	—	—	—	—	—	—	—	—	—	—	—	—
920	—	—	—	—	—	—	—	—	.708	4.30	6.2	$\frac{4.39}{\times 10^{-3}}$	—	—	—	—



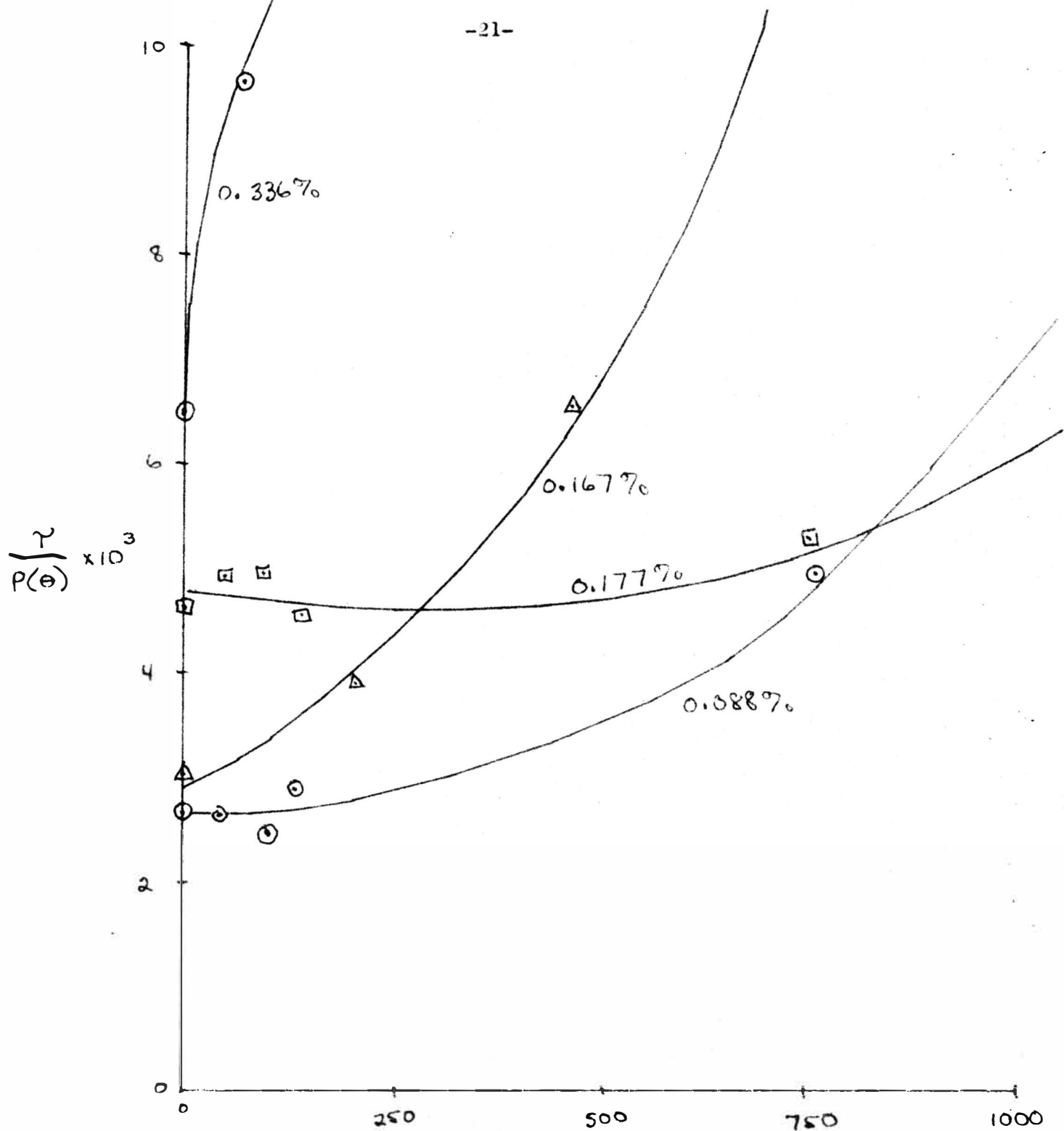


Figure 5. Agglomerate Size vs. Time for 1 Hr. Hydrolyzed Amylose at Four Concentrations.

Table IV. Data Compiled From Light Scattering Measurements of  
1½ Hr. Hydrolysis.

Time (min)	Conc. = 0.275%				Conc. = 0.283%			
	$\gamma$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\gamma}{P(\theta)}$	$\gamma$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\gamma}{P(\theta)}$
0	.920	>4.8	10	$\frac{9.20}{\times 10^{-3}}$	.820	>4.8	10	$\frac{8.20}{\times 10^{-3}}$
35	1.82	>4.8	10	$\frac{18.21}{\times 10^{-3}}$	.798	>4.8	10	$\frac{7.98}{\times 10^{-3}}$
60	1.82	>4.8	10	$\frac{18.21}{\times 10^{-3}}$	—	>4.8	10	—
75	—	>4.8	10	—	.798	>4.8	10	$\frac{7.98}{\times 10^{-3}}$
90	.715	>4.8	10	$\frac{7.15}{\times 10^{-3}}$	—	>4.8	10	—
145	—	>4.8	10	—	.791	>4.8	10	$\frac{7.91}{\times 10^{-3}}$
155	.910	>4.8	10	$\frac{9.10}{\times 10^{-3}}$	—	>4.8	10	—
210	.929	>4.8	10	$\frac{9.29}{\times 10^{-3}}$	—	>4.8	10	—
250	—	>4.8	10	—	.784	>4.8	10	$\frac{7.84}{\times 10^{-3}}$
365	.894	>4.8	10	$\frac{8.94}{\times 10^{-3}}$	—	>4.8	10	—
430	—	>4.8	10	—	.751	>4.8	10	$\frac{7.51}{\times 10^{-3}}$
1165	—	>4.8	10	—	.732	>4.8	10	$\frac{7.32}{\times 10^{-3}}$
1565	1.70	>4.8	10	$\frac{17.0}{\times 10^{-3}}$	—	>4.8	10	—

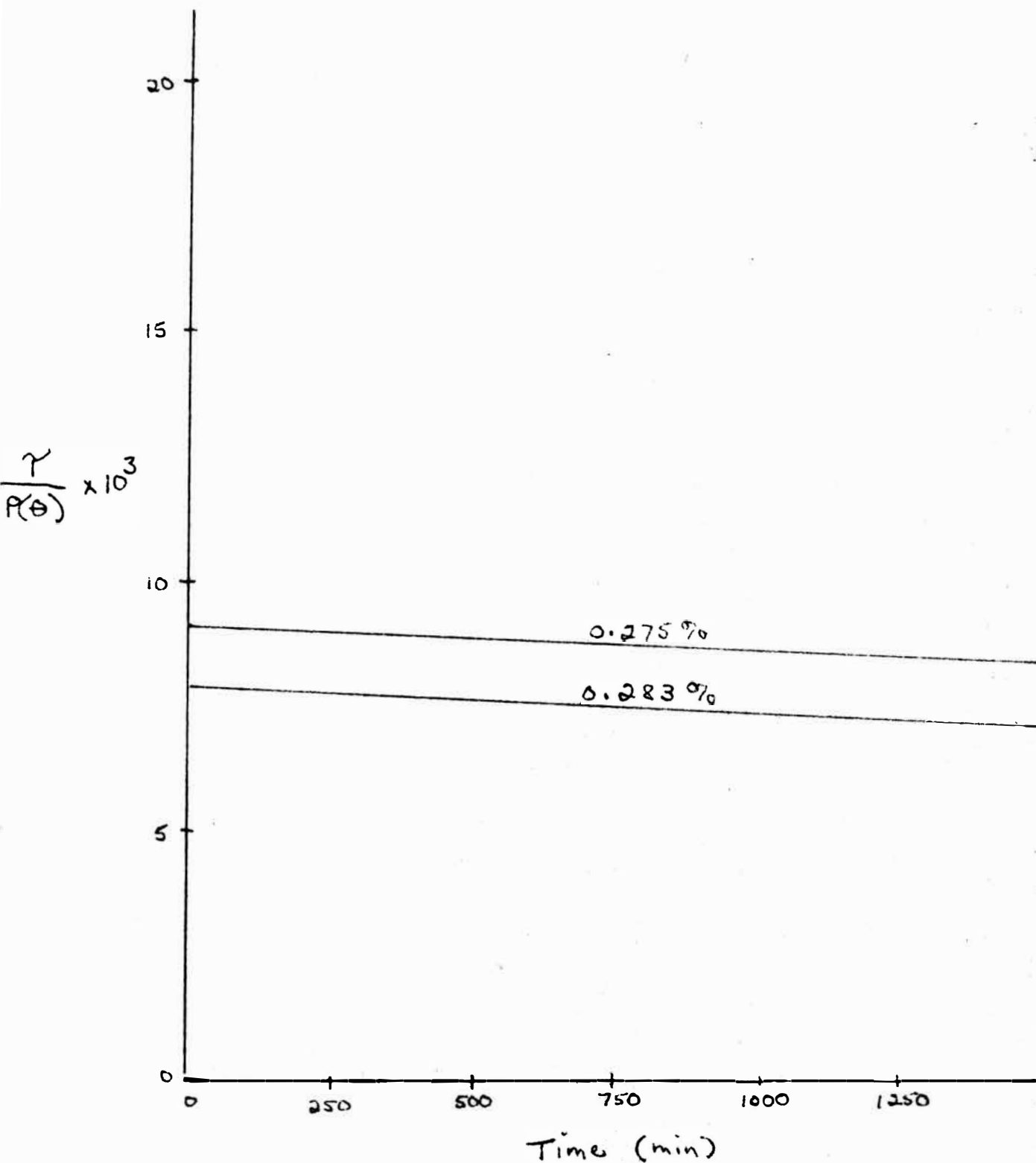


Figure 6. Agglomerate Size vs. Time for 1 1/2 Hr. Hydrolyzed Amylose at Two Concentrations.

Table V. Data Compiled From Light Scattering Measurements of  
2½ Hr. Hydrolysis.

Time (min)	Conc. = 0.186%				Conc. = 0.197%				Conc. = 0.283%			
	$\gamma$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\gamma}{P(\theta)}$	$\gamma$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\gamma}{P(\theta)}$	$\gamma$ $\times 10^3$	$z$	$\frac{1}{P(\theta)}$	$\frac{\gamma}{P(\theta)}$
0	.530	74.8	10	5.30 $\times 10^{-3}$	.757	4.52	7.4	5.61 $\times 10^{-3}$	.650	74.8	10	6.50 $\times 10^{-3}$
25	—	—	—	—	.771	4.73	9.6	7.40 $\times 10^{-3}$	—	—	—	—
30	.532	74.8	10	5.32 $\times 10^{-3}$	—	—	—	—	—	—	—	—
60	—	—	—	—	.757	4.59	8.0	6.16 $\times 10^{-3}$	—	—	—	—
90	—	—	—	—	—	—	—	—	.626	74.8	10	6.26 $\times 10^{-3}$
110	.549	74.8	10	5.49 $\times 10^{-3}$	—	—	—	—	—	—	—	—
120	—	—	—	—	.745	74.8	10	7.45 $\times 10^{-3}$	—	—	—	—
180	—	—	—	—	—	—	—	—	.563	74.8	10	5.63 $\times 10^{-3}$
210	.520	74.8	10	5.20 $\times 10^{-3}$	—	—	—	—	—	—	—	—
260	—	—	—	—	—	—	—	—	.532	74.8	10	5.32 $\times 10^{-3}$
280	—	—	—	—	.741	4.50	5.0	3.70 $\times 10^{-3}$	—	—	—	—
1165	.552	74.8	10	5.52 $\times 10^{-3}$	—	—	—	—	—	—	—	—
1200	—	—	—	—	1.46	74.8	10	14.6 $\times 10^{-3}$	—	—	—	—

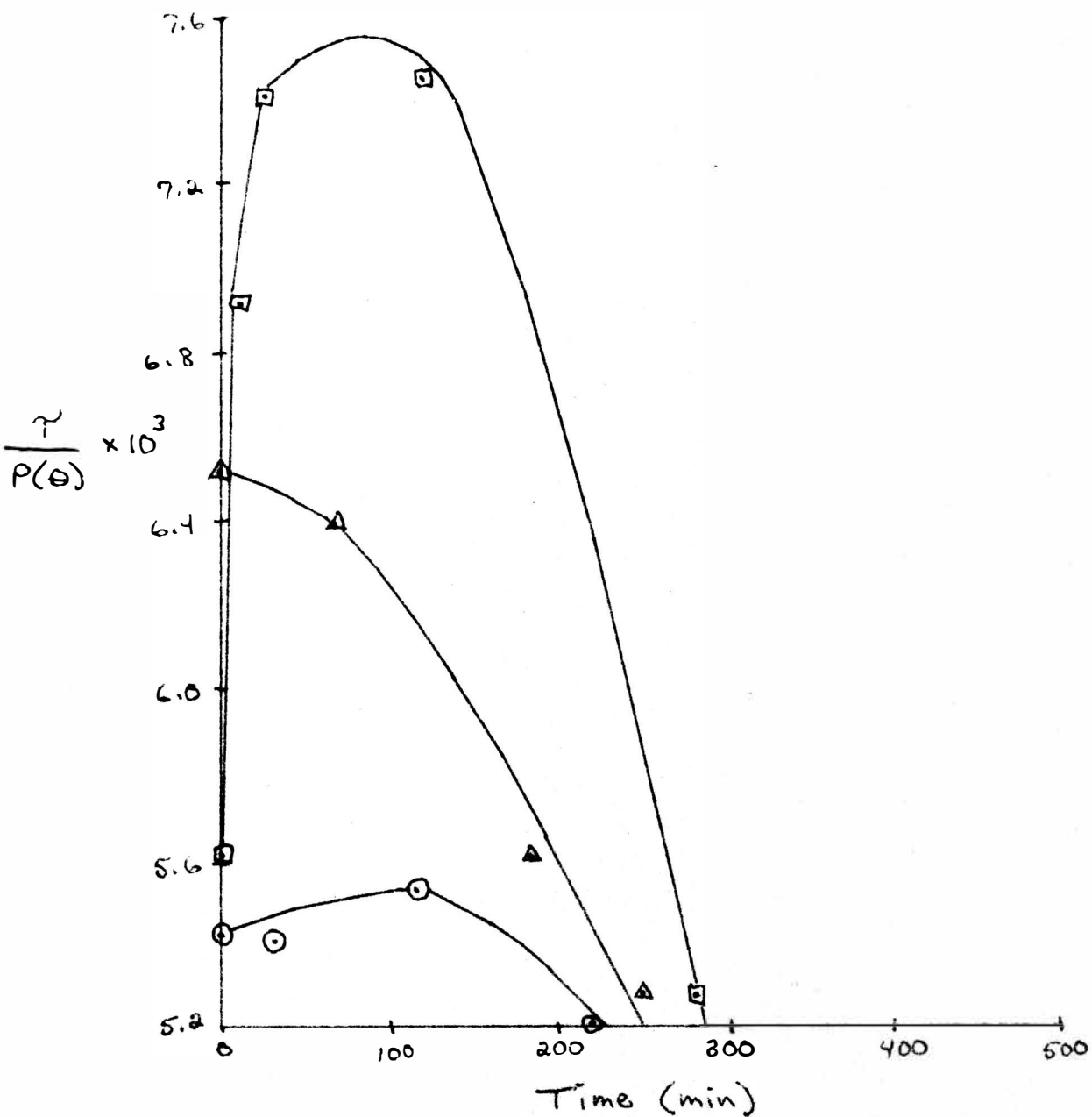


Figure 7. Agglomerate Size vs. Time for  $2\frac{1}{2}$  Hr. Hydrolyzed Amylose at Two Concentrations.

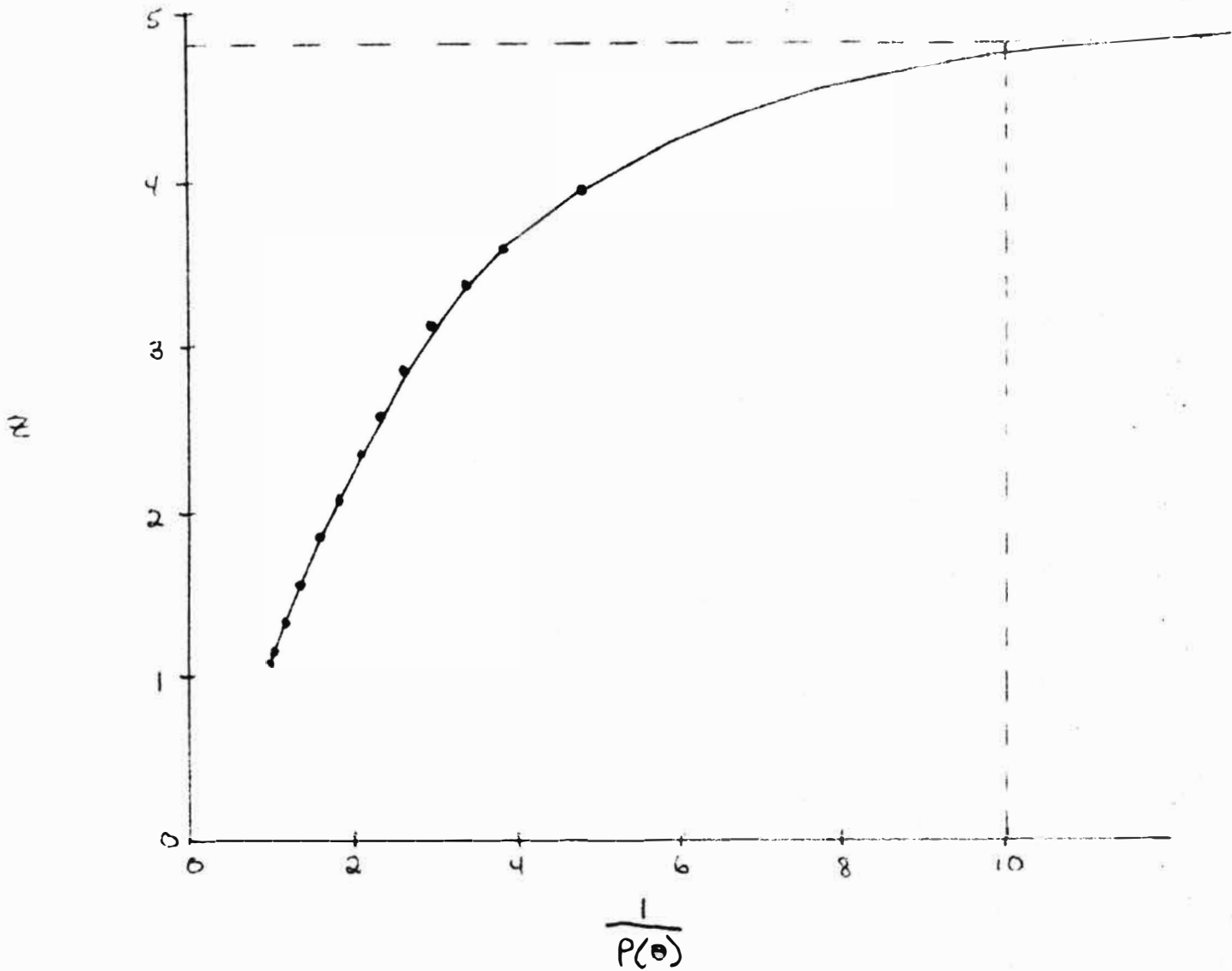


Figure 8. Bissymmetry vs.  $1/P(\theta)$  for monodisperse coils with the graph extrapolated from  $z=4$  and  $1/P(\theta)=3$ .

### CONCLUSIONS

The results obtained generally followed the expected. By acid modifying, the chain length of amylose molecules were reduced. The rate of retrogradation increased with decreasing molecular weight until a maximum was reached at  $1\frac{1}{2}$  hours of hydrolysis. The rate of retrogradation then decreased with further decreasing molecular weight until retrogradation began to lessen.

While the rate of retrogradation of the unhydrolyzed amylose dispersion could not be observed, the  $\frac{1}{2}$  and 1 hour hydrolyzed dispersions generally exhibited an increasing rate at  $1\frac{1}{2}$  hours of hydrolysis. At  $2\frac{1}{2}$  hours of hydrolysis the rate of retrogradation seemed transient, i.e., the rate decreased with respect to the  $\frac{1}{2}$ , 1, and  $1\frac{1}{2}$  hour samples and also seemed to lose the properties of retrogradation, which possibly is due to decreased chain length.

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