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RADIOLYTIC GRAFTING OF MONOMERS ON POLYMERIC FILMS

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I. Introduction

A letter from Mr. Ballentine received on May 15, 1970 indicated that NASA is seeking economical films having improved strength, heat sealability, and barrier properties toward oxygen and water vapor for space applications in food packaging.

The writer proposed to accomplish desirable modifications of film properties by radiolytic grafting of various monomers on suitable substrate films. A product comprising a surface layer grafted on a base film would not have the undesirable delamination tendencies of present products made up of several plastic film layers.

Mr. Ballentine mentioned the interest of NASA in polyvinylalcohol, Aclar, and Teflon films. At the start of the present research project, it was decided to use polyvinylalcohol film as a substrate for the radiolytic grafting of various vinyl monomers. Polyvinylalcohol (PVA) film is a remarkably good oxygen barrier, but it has poor water resistance and poor heat

sealing properties. Hence, the objective of the present research is to improve the water resistance and heat sealing properties by grafting a suitable monomer on the PVA film.

The experimental results to date are preliminary and exploratory in nature. Some difficulty was encountered from the start in obtaining reproducible grafting rates. In the technique used, a small sample of PVA film is immersed in styrene solution in a glass tube, sealed shut, and the complete assembly irradiated with gamma rays from a cobalt 60 source. The preliminary work has disclosed that in order to obtain reproducible grafting rates it is necessary to (1) control the water content of the film sample, and (2) control the water content of the styrene solution in which the film is immersed.

II. Experimental Procedure

The 0.5 curie source was arranged and employed as described earlier (1). Before use, each monomer was distilled and stored over Drierite at refrigerator temperature. Just prior to making a grafting run, oxygen was removed from the monomer in a high vacuum system as described previously.

In each run, a sample of PVA film about 0.5 cm by 2.0 cm was used. The film as received was found to vary in thickness, and a micrometer was used to check a portion of film and select a section of 0.0060 inch in thickness. Prior to making a run, the film was stored for several days at room temperature in a desiccator over a saturated aqueous solution of sodium bromide, which was found to yield a film having a reproducible water content of 9.5 percent.

After completion of the grafting run, each grafted film sample was extracted by stirring in warm acetone for 48 hours, then dried in a desiccator and weighed. The purpose of this technique was to remove homopolymer in or on the film. The procedure has been found rather successful in this regard by other investigators. A separate experiment with ungrafted PVA film showed that no correction was needed for weight loss by PVA during acetone extraction.

All runs to date on PVA have carried out at room temperature, 23 $\pm$ 1°C. Percent grafting was computed in the usual way from film weight (P_o) prior to grafting, and weight after grafting (P_g) as follows:

$$\text{Percent Grafting} = \left[\frac{P_g - P_o}{P_o}\right] \times 100 \qquad (1)$$

Immediately after grafting, the swollen film was quickly dried and weighed to obtain the swollen film weight (P_s), and percent swelling uncorrected for grafting was computed as follows:

$$\text{Percent Swelling} = \left[\frac{P_s - P_o}{P_o}\right] \times 100 \qquad (2)$$

After trying several monomer solutions, a solution of styrene/methanol at a volume ratio of 20/5 was selected for the preliminary work. Prior to mixing the methanol with the

styrene, a known amount of water was added to the methanol, so that the volume percent water in the grafting solution for each run could readily be computed.

III. Results and Discussion

A. Comparison of Monomers

One of the early goals of the work is the comparison of the grafting rates for various monomers on polyvinylalcohol, but only styrene has been tried so far. Percent by weight of styrene grafted versus time is shown in Figure 1. As usual for grafting versus time in monomer/polymer systems, this initial stage of the curve is linear in shape. The 20/5 solution of styrene/methanol was used for obtaining the data of Figure 1 and water content by volume in the monomer solution was held constant at 0.5 percent. The films used in Figure 1 had a water content of 9.5 percent at the start of the runs, which resulted from film conditioning for several days as described above.

While methyl methacrylate has not yet been tried in the present research, the grafting of methyl methacrylate on PVA is more efficient than that of styrene according to Sakurada (2), and grafting of methyl methacrylate up to 4,000 percent of original film weight was obtained.

Grafting of liquid methyl acrylate, acrylonitrile, and vinyl acetate on wet PVA film has also been reported by Sakurada (3). The grafting of vapor phase acrylonitrile on wet films and fibers of PVA has been described (4). Acrylamide, vinylpyridine, and acrylic acid have been grafted on PVA films, but with low efficiency (3). Methylvinylpyridine, vinylpyridine, and acrylamide were grafted on PVA fibers to improve

their dyeability (5).

B. Effect of Film Water Content on Grafting Rate

Earlier published work had indicated that water in the PVA film has an accelerating effect on the grafting of various vinyl monomers.

In the present work, it was found convenient to obtain various water contents by placing PVA film in a desiccator over distilled water for various lengths of time. Grafting rates of styrene were then measured as a function of water content, with the results shown in Figure 2. Each point on the graph was computed from a run of approximately 24 hours duration. Figure 2 demonstrates that the rate of grafting is an approximately linear function of the water content of the film. For all runs in Figure 2, the water content of the styrene/methanol grafting solution was held constant at 0.2 percent by volume.

Numerous references to the effect of PVA film water content on grafting are found in the literature. Sakurada (2) stated that the grafting of styrene on PVA film proceeded smoothly when the film contained 5 percent water or more. Stannett (6) and Sakurada (3) found that styrene, methylmethacrylate, methyl acrylate, acrylontrile, and vinyl acetate grafted readily on wet PVA films, but showed little or no radiolytic grafting on dry PVA films. Sakurada (3) found little grafting of styrene on PVA film containing less than 4 percent water. For higher water contents, the importance of the grafting process gradually increased, and proceeded extremely quickly when the film contained as much as 20 percent

water.

Chapiro (7) pointed out that the lack of grafting when using dry monomer resulted from the inability of most common monomers to diffuse into the PVA. He further stated that when the packing of the polymer chain is loosened through the action of a swelling agent (water), the monomer can penetrate more readily into the film and grafting is favored. This behavior of PVA emphasizes the importance of diffusion effects in graft copolymerization.

C. Effect of Monomer Water Content on Grafting Rate.

The grafting solution in the present work consisted of a 20/5 volume ratio of styrene/methanol, containing a known amount of water which was dissolved in the methanol prior to mixing. Figure 3 shows the rate of styrene grafting as a function of percent water by volume in the styrene/methanol grafting solution. The plot of rate versus percent water exhibits a linear curve. For each run shown in Figure 3, the initial water content of the PVA film was 9.5 percent.

After the PVA film (containing water) is placed in the monomer solution (containing water) prior to the grafting run, there may be some exchange of water to an unknown extent between the film and the solution. This may account for some of the difficulty that still persists in obtaining reproducible grafting rates.

The accelerating effect of water in the monomer solution has been observed by other investigators. Sakurada (2) stated that the presence of water in the monomer solutions (styrene

and methyl methacrylate) increased considerably the amount of monomer grafted on the PVA film. Stannett (6) found it helpful to incorporate water in the grafting solution when irradiating PVA in solutions of styrene/acetone or styrene/dioxane.

D. Grafting Rate as a Function of Swelling.

According to the reports of Chapiro and others, the amount of grafting on PVA is closely related to the amount of swelling that takes place. The writer (1) had also observed a linear relation between percent grafting and uncorrected swelling in the grafting of styrene on polymethylpentene film.

Hence, it seemed logical to plot grafting versus swelling for styrene/PVA, using all data collected so far. This plot is presented in Figure 4, which contains the results of all runs at various film water contents and monomer water contents, except those in which a known error was made in measuring swelling or grafting. The data fit very well on a straight line, indicating a strong correlation between grafting and swelling. The line intersects the swelling axis at about 10 percent swelling, indicating that no grafting can be expected for swelling (uncorrected) less than 10 percent.

These results make it clear that the percent grafting depends strongly on the percent swelling, and that such swelling can be promoted by water in the film, water in the monomer solution, or water in both. The following relations would be expected between percent of swelling produced in a 24 hour irradiation run and the relative water content of film and monomer solution:

1. High swelling: High water content in film;

high water content in monomer.

2. Medium swelling: High water content in film; low water content in monomer.

3. Medium swelling: Low water content in film; high water content in monomer.

4. Low swelling: Low water content in film; low water content in monomer.

Based on this reasoning, a plot of the 24 hour swelling using film water content and monomer water content as coordinates should result in a series of contour lines, each contour line representing the amount of swelling taking place in 24 hours of irradiation. (See rough sketch, Figure 5.) Each contour would probably be roughly hyperbolic in shape, as shown by the dotted lines in the sketch. Where possible, each contour line is made to pass through an experimental point corresponding to an experimental grafting run. Evidently a single point cannot establish a curve, but the total picture is logical, and contour lines similar to those in Figure 5 may perhaps be established by further experimentation.

E. Water Vapor Absorption of Grafted Films.

One of the goals of the present research is to improve the water resistance of the PVA film. One method of assessing water resistance is to place dry film in a desiccator at controlled 58 percent relative humidity, and observe how fast film weight increases due to water absorption.

This method has given the results shown in Figure 6. The figure compares water absorption of PVA films containing 106 percent grafted styrene, 20 percent grafted styrene, and no grafted styrene. It is evident that the grafted film absorbs water much less rapidly than the control film.

IV. Further Work Planned

Survey of Monomers: Grafting of several other monomers on PVA will be investigated in the attempt to improve water resistance and heat sealability of the PVA. Film monomers to be studied will include methyl methacrylate, vinyl acetate, methyl acrylate, acrylonitrile, etc.

Activation Energy of Grafting: The activation energy of grafting on PVA film will be determined by measuring the rate of grafting at several different temperatures. The same technique and equipment will be employed that were used in the grafting of styrene on polymethylpentene, previously described (8).

Effect of Monomer Concentration: The work to date has involved a grafting solution containing styrene/methanol at a 4/1 volume ratio. The effect of monomer concentration will be assessed in future runs by using 3/2, 2/3, and 1/4 volume ratios of styrene/methanol. The concentration effect of other monomers will be evaluated in a similar way.

Number of Radical Sites Formed: The concentration of free radicals formed in the PVA will be estimated by reaction with a free radical scavenges such as diphenylpicrylhydrazyl (DPPH), followed by determination of combined DPPH using spectrometric analysis. Studies of this type will be started in the near future.

Polymer-Polymer Grafting: Gamma irradiation of PVA

film immersed in a solution of some other polymer should produce corsslinking between the two polymers. An attempt will be made to carry out such reactions as a part of this research.

Study of Accelerators and Inhibitors: The use of a redox system such as ferric acetylacetonate plus benzoin has been found to accelerate the grafting of styrene on polyethylene (9). It is planned to evaluate some accelerators as part of the present research for grafting on PVA film. Grafting inhibitors will also be studied.

Extended Water Resistance Studies: The work on water resistance will be expanded to evaluate the effect of several other grafted monomers, and will include water absorption of grafted samples in high humidity and also when immersed in liquid water.

Evaluation of Heat Sealing: Heat sealing strength of the various monomer/PVA graft combinations will be measured with the Dillon Universal Tester Model M-1, which is now on hand in our laboratory. It can also be used to determine compression or shear strength if desired.

Effect of Film Thickness: In the work on styrene/polymethylpentene, it was found that a critical film thickness exists above which grafting rate is proportional to film surface area rather than film weight. Assessment of similar phenomena will be attempted for the grafting of monomers on PVA film.

Grafting of PVA on Polyethylene: It may be possible to

irradiate an aqueous solution of PVA containing a sample of polyethylene film, and obtain grafting of the PVA on polyethylene. The product might combine some of the advantages of both polymers, and this experiment will be tried to enable examination of such a product.

V. Acknowledgement

The writer would like to express appreciation for the student research assistant, Mr. Donnie Shaw, who assisted in the experimental work and in drawing the figures.

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Figure Captions

Figure 1: Grafting of styrene on 0.006 inch polyvinylalcohol film at room temperature.

Figure 2: Grafting rate of styrene on polyvinylalcohol film versus film water content, holding water content at 0.2 percent in monomer solution.

Figure 3: Grafting rate versus monomer solution water content, holding film water content at 9.5 percent.

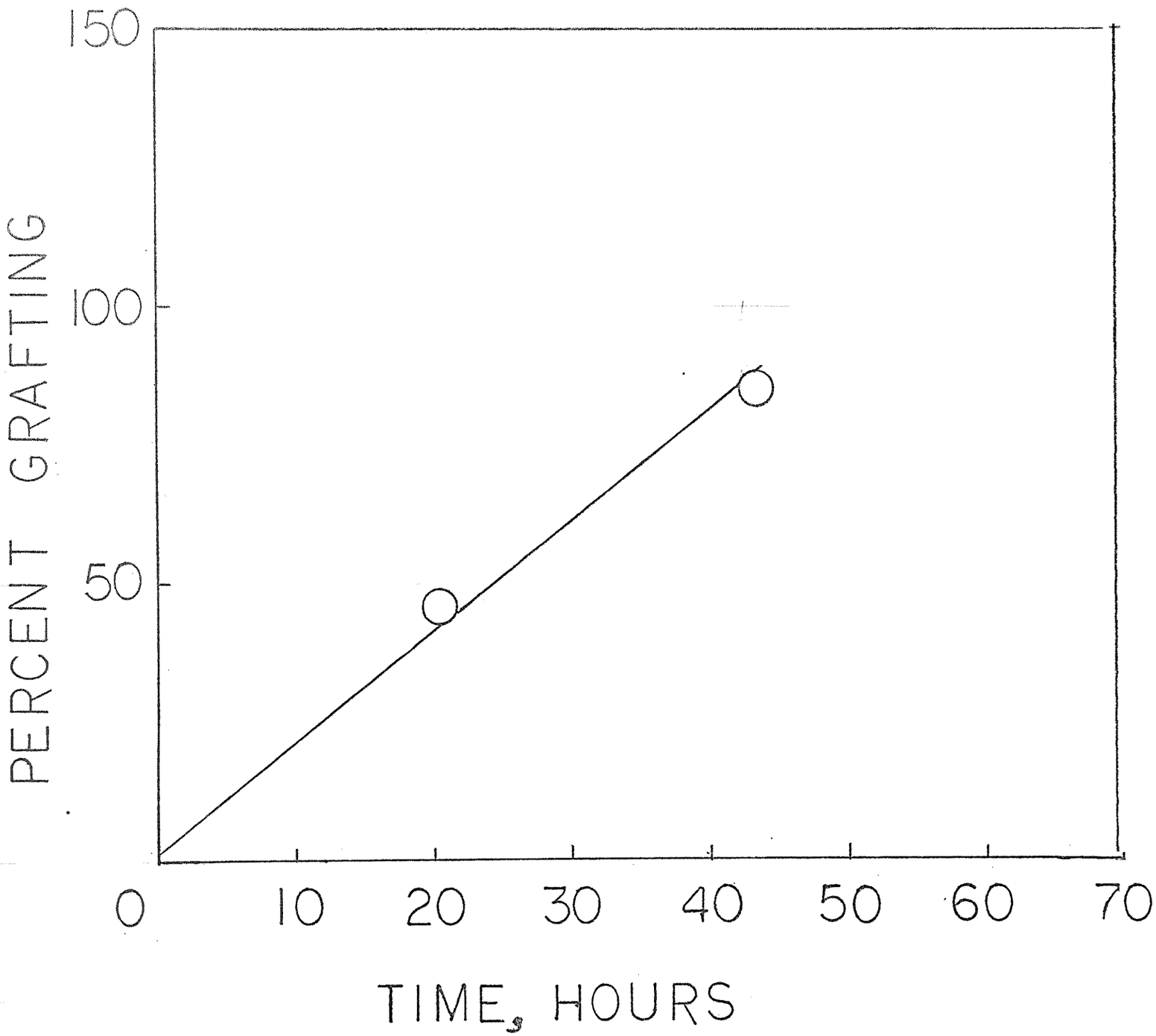
Figure 4: Percent grafting of styrene on polyvinylalcohol film versus uncorrected percent swelling of the film.

Figure 5: Twenty four hour percent swelling contours versus water content of film and monomer solution.

Figure 6: Weight gain at 58% R.H. for:

○ - ungrafted PVA; ● - 106% grafted styrene on PVA;

□ - 20% grafted styrene on PVA.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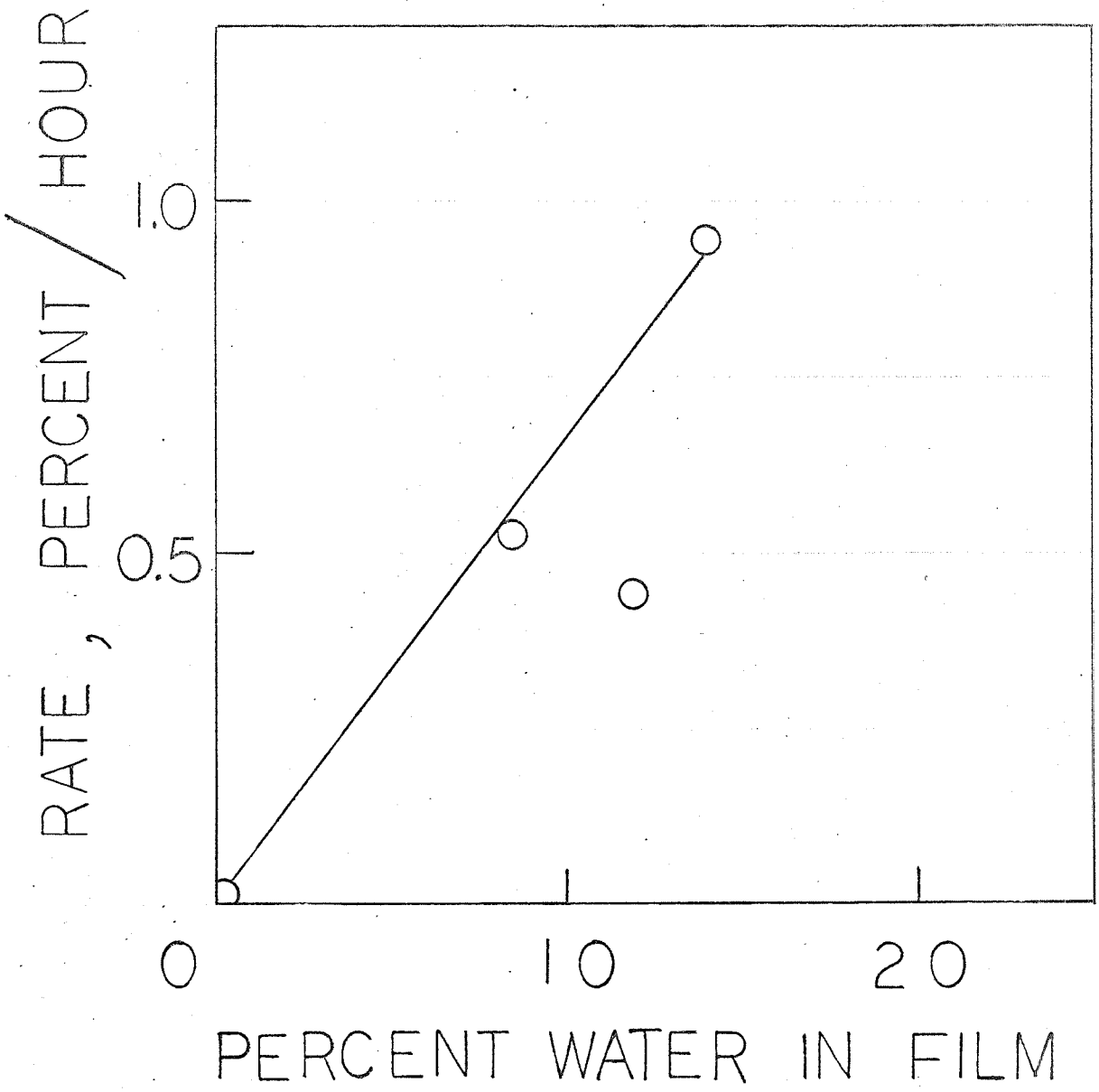
100
50
PERCENT GRAFTING
0
10
20
30
40
50
60
70
TIME, HOURS


RATE, PERCENT / HOUR
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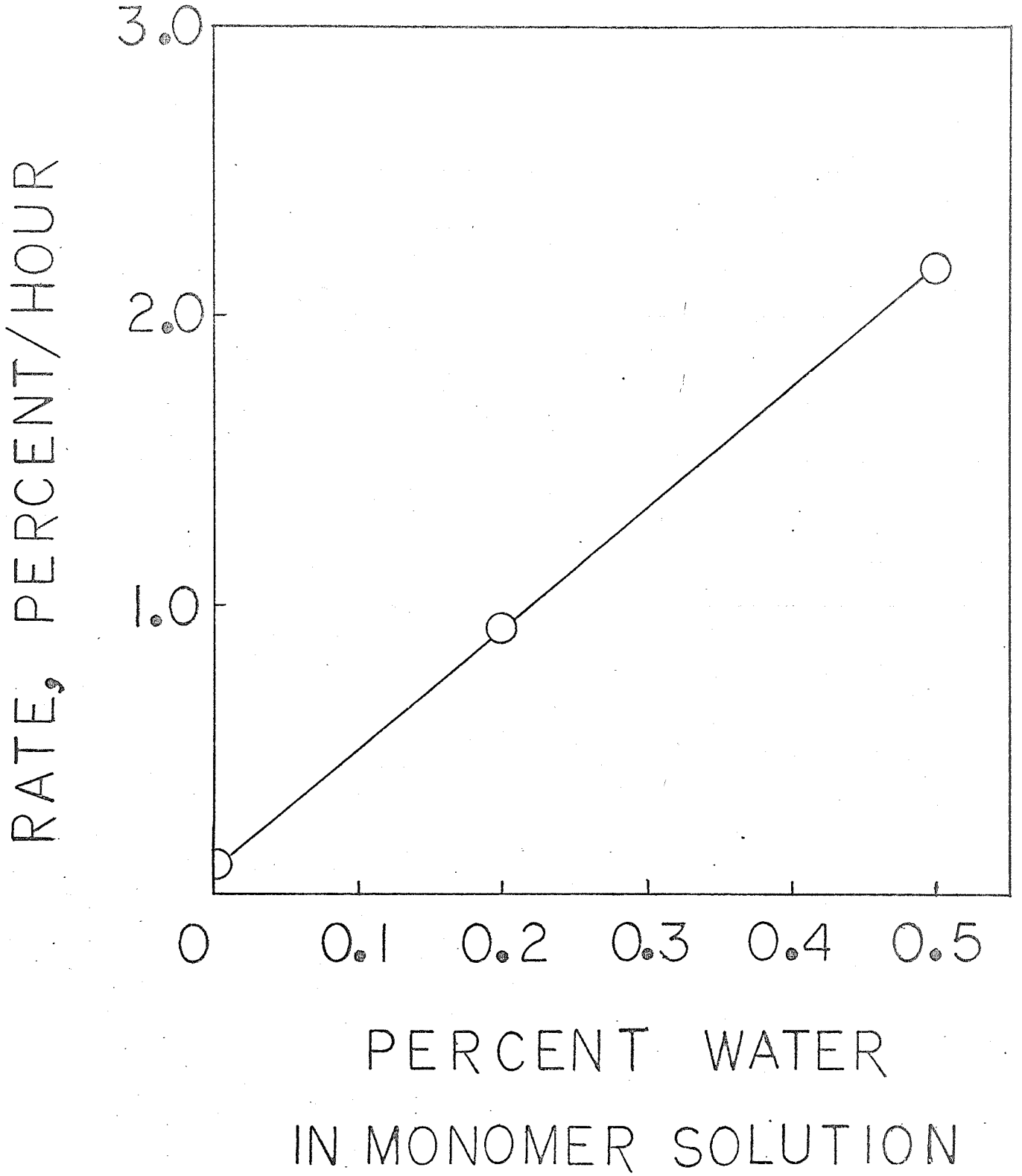
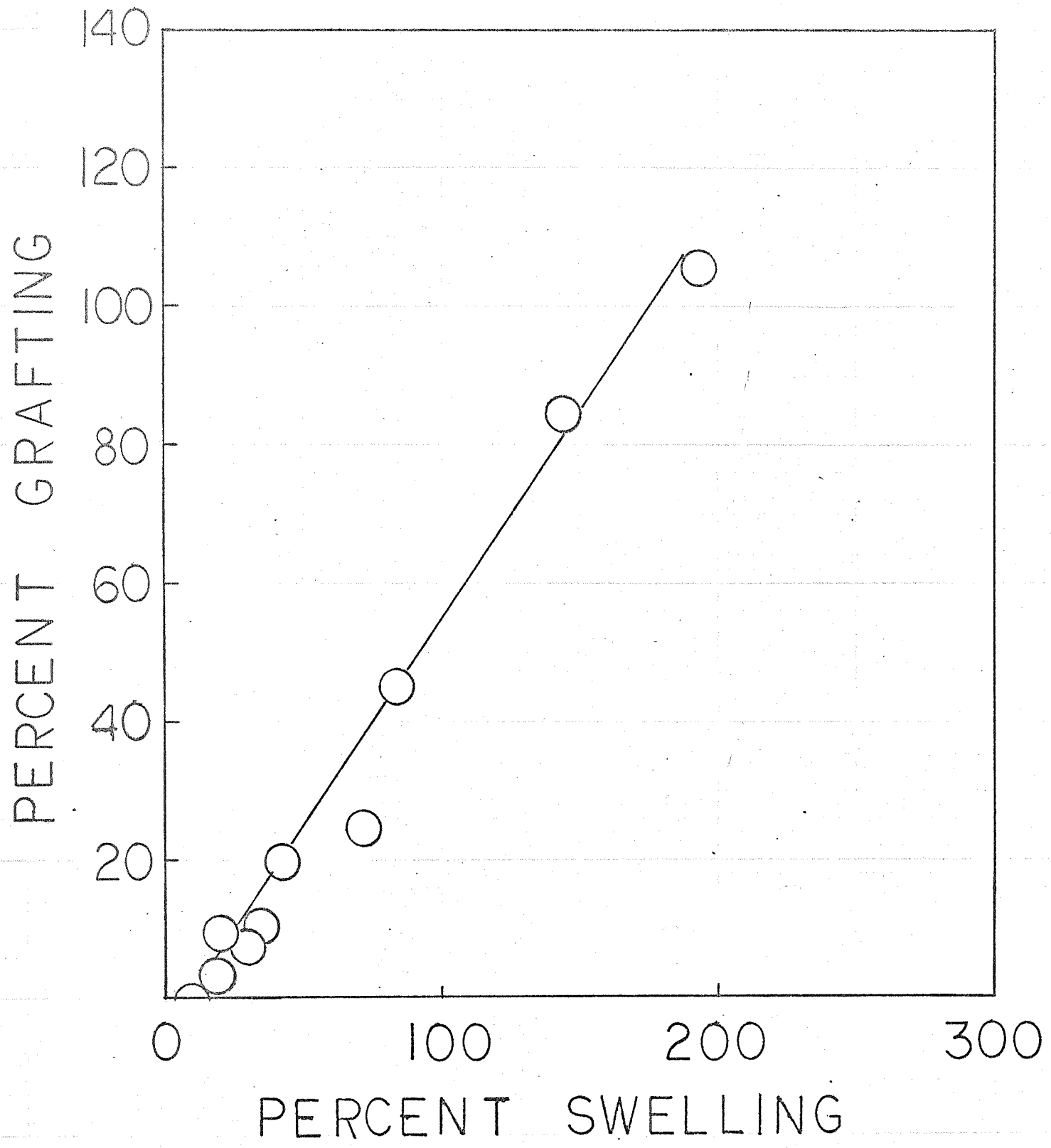
0.5
0
10
20
PERCENT WATER IN FILM


3.0
2.0
1.0
RATE, PERCENT/HOUR
0
0.1
0.2
0.3
0.4
0.5
PERCENT WATER
IN MONOMER SOLUTION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120
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40
20
PERCENT GRAFTING
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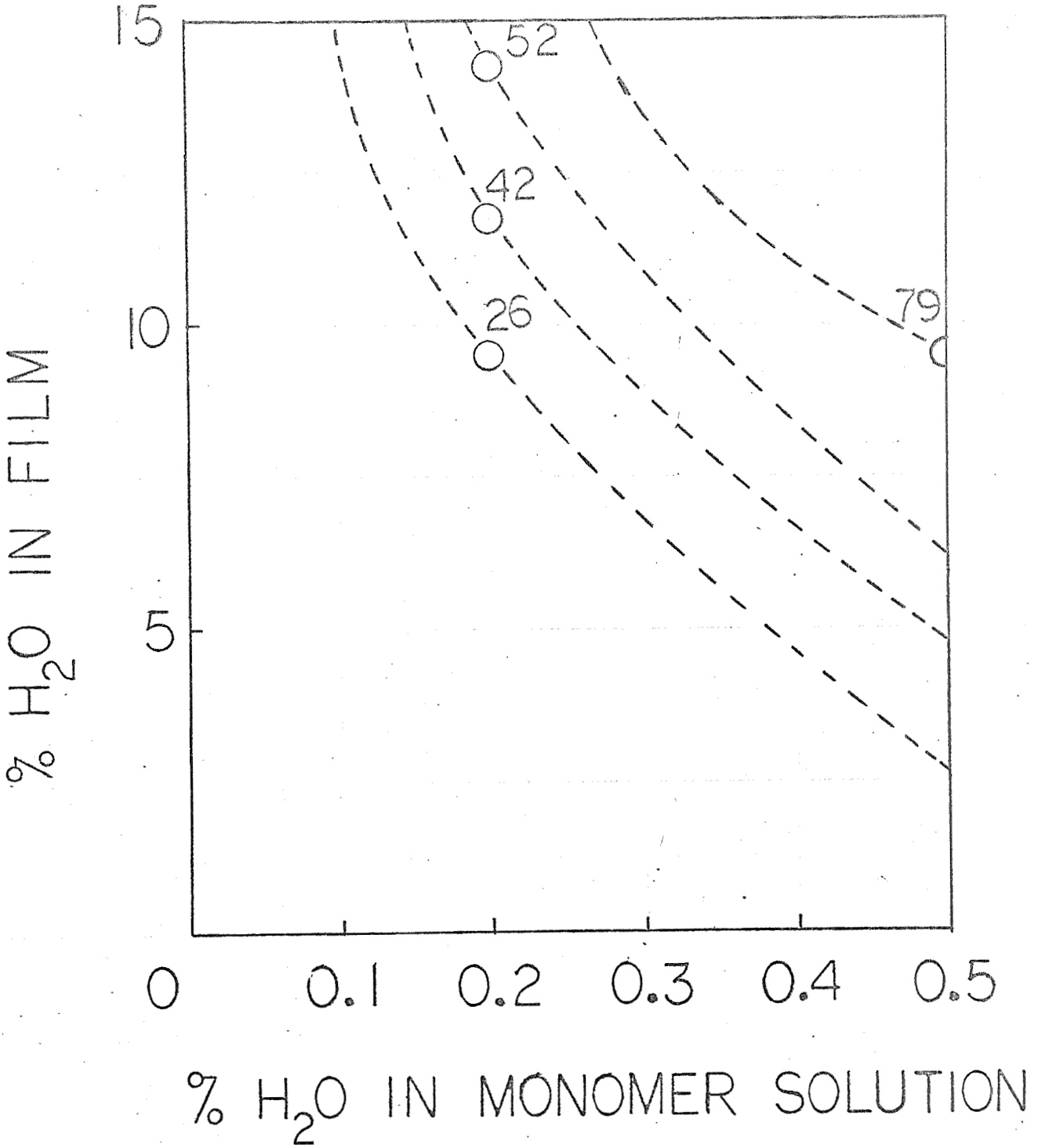
100
200
300
PERCENT SWELLING


15
10
5
0
0.1
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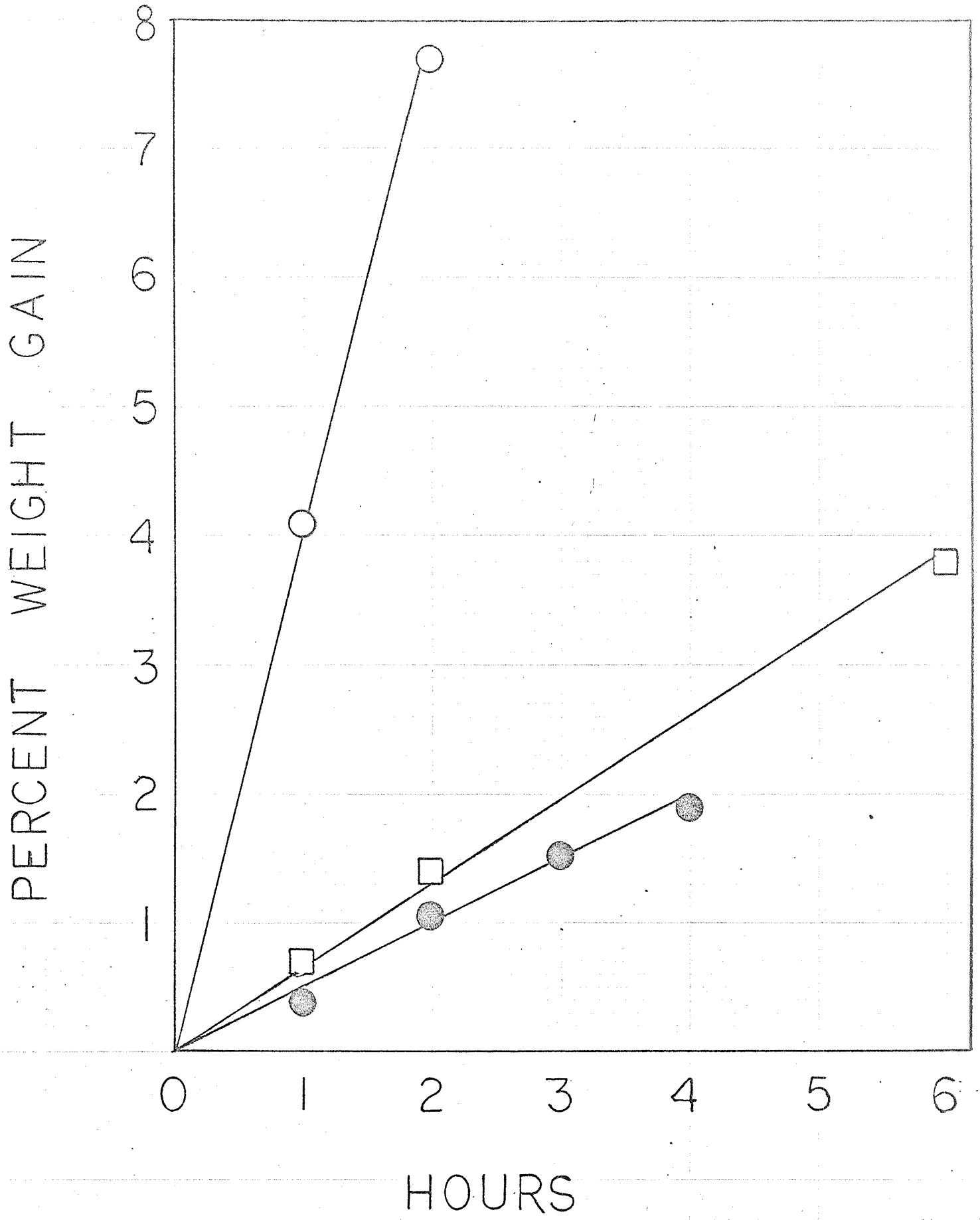
52
42
26
79
% H_2O IN FILM
% H_2O IN MONOMER SOLUTION


PERCENT WEIGHT GAIN
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HOURS