MODIFICATION OF TEXTILE FIBER PROPERTIES BY RADIATION-INDUCED GRAFT POLYMERIZATION

by

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Prepared for

Division of Isotopes Development
United States Atomic Energy Commission

October 31, 1962

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Funds for this work were also made available by
Burlington Industries, Cone Mills Corporation,
Reeves Bros., Inc., and J. P. Stevens and Company, Inc.

NCSC-2477-10
Category No. UC-23

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Contract No. AT-(40-1)-2477

Annual Report November 1, 1961 - October 31, 1962

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Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

SUMMARY

Investigations of vapor-phase graft polymerization to textile fibers by means of gamma radiation were conducted in the following areas: (1) variables affecting the rate of grafting; (2) modification of fiber properties by grafting; and (3) the kinetics of vapor-phase graft polymerization.

The effect of the addition of various non-monomeric compounds to the system on the graft polymerization of acrylonitrile, butadiene, vinyl chloride, ethylene, and propylene to various textile fibers was determined. The compounds investigated were water, methanol, ethanol, acetone, ethyl acetate, acetic acid, acetic anhydride, formaldehyde, carbon tetrachloride, and benzene. In general, water, methanol, and acetic acid were the best sensitizers for grafting to cotton, rayon, nylon and wool. The effect of different concentrations of water, methanol, and acetic acid in the vapor-phase on the grafting of acrylonitrile to the various fibers was investigated. The largest additions were obtained for cotton, rayon, wool, and nylon using water as the sensitizer. It was shown by post-irradiation experiments that water was not essential during irradiation, but was necessary during the polymerization reaction.

An increase in graft polymerization was obtained by the use of intermittent irradiation. This was shown to be caused by the additional time between irradiation intervals that was available for monomer diffusion.

The effect of oxygen concentration on grafting of acrylonitrile to the various fibers was determined. Generally, oxygen had a slight effect below a given concentration, but above this level it inhibited grafting markedly.

Increases in temperature had mixed effects on the grafting of butadiene and acrylonitrile to these fibers, but decreased grafting was the general result.

Polypropylene has been modified by grafting methyl acrylate, ethyl acrylate, and vinyl acetate to the fiber using gamma radiation. The modified fiber may be dyed with dispersed dyes by conventional dyeing procedures. Good depth of shade and uniformity of dyeing was obtained, but slight bleeding during wash tests was observed.

The physical properties of acetate, nylon, and polypropylene fibers that had been grafted with various amounts of methyl acrylate, ethyl acrylate, acrylonitrile and butadiene were determined. No marked changes in strength, elongation, modulus, or proportional limit were found. The addition of small amounts of acrylonitrile caused a sharp increase in the melting point of polypropylene, but did not affect the softening point. Moisture regains and solubilities were also determined for these grafts.

The grafting of styrene gave nylon and polypropylene increased weathering resistance but did not affect the weathering of cotton.

The rate of diffusion of monomer and the kinetics of the reaction both play a very significant part in the vapor-phase technique. Since the rate of graft polymerization and the location of the graft polymer both affect the properties of the copolymer formed, accurate diffusion data and kinetic data are necessary for the optimum design of graft polymerization processes. Experiments were initiated to determine the effect of kinetics and the rate of diffusion of monomer on the graft polymerization process. Data are given on the kinetics of graft polymerization of acrylonitrile to filament yarns of cellulose acetate, nylon, polypropylene, and polyester. The effect of oxygen on the rate of graft polymerization for each system was determined.

Post irradiation grafting experiments showed that oxygen decreased the number of available radicals in acetate yarn, but had little effect on those in nylon, polypropylene and polyester. Studies of the build-up of radicals during irradiation indicated that oxygen decreases the rate of formation of radicals as well as increasing the rate of radical decay. In diffusion experiments, it was found that film coefficients controlled the diffusion of acrylonitrile into acetate and nylon yarns, while in polyester, both the diffusivity and film coefficient were significant.

Three publications appeared in the literature during the year based on the work performed under this contract:

> Armstrong, Arthur A. Jr., and Rutherford, Henry A., "Modification of Textile Fiber Properties by Radiation Induced Graft Polymerization", Proceedings of the International Symposium on Radiation-Induced Polymerization and Graft Copolymerization" Battelle Memorial Institute, November 29-30, 1962, TID-7643, 268-99.
>
> Armstrong, Arthur A. Jr., "Diffusion and Kinetics in Radiation Induced Graft Polymerization", Ibid 300-18.

Another paper has been accepted for publication in the Textile Research Journal:

> Armstrong, Arthur A. Jr., and Rutherford, Henry A., "A Vapor-Phase Technique for Radiation-Induced Grafting of Vinyl Monomers to Fibers."

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MODIFICATION OF TEXTILE FIBER PROPERTIES BY RADIATION-INDUCED GRAFT POLYMERIZATION

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November 1, 1961-October 31, 1962

INTRODUCTION

The experimental work under the present contract involves a continuation of the development of techniques related to the modification of properties of textile fibers by gamma radiation-induced graft-polymerization. Studies were directed specifically toward the effect of various parameters on the rate of grafting, the improvement of physical properties of textile fibers, and the kinetics of graft-polymerization.

The following represents the results obtained during the contractual period.

PART I. PARAMETERS AFFECTING GRAFT POLYMERIZATION

The rate of graft polymerization is highly important to both the economics and the design of equipment for a grafting process. The effect of variables on the rate must be determined before proper assessment of a system can be made. Accordingly, the following parameters were investigated: the effect of sensitizers, or the addition of non-monomeric substances to the system; the effect of intermittent irradiation; the concentration of oxygen in the system.

Effect of Sensitizers on the Rate of Graft-Polymerization

The vapor-phase technique has been very successful in the graft-polymerization of the volatile vinyl-monomers to various fibers. In these studies it was found that the presence of water was necessary for the addition of acrylonitrile to cotton. The effect of the water on the reaction has not been explained, but the results suggested that other compounds may exhibit a similar effect. Thus, the work was extended to include methanol, ethanol, acetone, ethyl acetate, acetic acid, acetic anhydride, formaldehyde, benzene, and carbon tetrachloride. Selection of a particular compound as a "sensitizer" was made primarily on the basis of volatility so that an appreciable amount could be obtained in the vapor. Monomers chosen for the experiments, in addition to acrylonitrile, were butadiene, vinyl chloride, ethylene, and propylene. The effect of the sensitizer on the grafting to cotton, polypropylene, rayon, acetate, nylon, polyester, acrylic and wool was determined.

For the gaseous monomers, the following experimental procedure was used:

1. Approximately one-gram skeins of yarn of each material were suspended on a rack and placed inside the stainless-steel beaker used as the reaction vessel. The beaker was attached to the inlet and outlet access ports in the Gammacell sample chamber.

2. The container was flushed for two hours with a mixture of 200 cm.^{3}/min. of gaseous monomer and 200 cm.^{3}/min. of prepurified nitrogen. The gaseous monomer was passed through two bubble towers in series: the first contained 10% sodium hydroxide solution to remove inhibitor and the second contained water to remove any caustic entrainment.

   The prepurified nitrogen was passed through one bubble tower containing the sensitizer. Figure 1 is a sketch of this apparatus.

3. The sample chamber was lowered to the irradiation position and the flushing continued for two hours.

4. The samples were removed from the apparatus, dried overnight at 105-110°C., and the monomer addition determined by the gain in weight of the sample.

A similar procedure was used with acrylonitrile except that the flushing procedure was changed; 500 cm.^{3}/min. of prepurified nitrogen was passed through two bubble towers in series containing distilled acrylonitrile and another 500 cm.^{3}/min. of prepurified nitrogen was passed through one bubble tower containing the sensitizer. A sketch of this apparatus is shown in Figure 2. All experimental runs were made at 75°F., and one atmosphere pressure.

The data showing the effect of each sensitizer on the addition of acrylonitrile to each fiber are given in Table I. The data for butadiene, vinyl chloride, propylene, and ethylene are given in Tables II, III, IV, and V, respectively. An inspection of the data shows the following significant results.

1. The acrylic fiber failed to undergo the addition of any of the monomers. This behavior is believed to be associated with the stability of the acrylic fiber toward radiation.

2. In the presence of nitrogen alone, acrylonitrile, butadiene, and vinyl chloride were added to polypropylene, acetate, and nylon, but there was no appreciable addition to cotton, rayon, wool and the polyester.

3. All of the substances except carbon tetrachloride and benzene increased the rate of addition of acrylonitrile, butadiene, and vinyl chloride to cotton, rayon, acetate, nylon and wool. In general, water, methanol, and acetic acid were the best sensitizers.

4. Polypropylene appeared to add the same amount of polymer with any given monomer regardless of the conditions.

5. Ethylene and propylene failed to add to any of the fibers in significant amounts, although there seemed to be a slight increase in the addition of these two monomers to cotton, rayon, acetate and wool in the presence of both methanol and acetic acid.

In general, water, methanol, and acetic acid appeared to be the best sensitizers. Experiments were next conducted to show the effects of different concentrations of these in the vapor on the addition of acrylonitrile to the various fibers. The experimental procedure was the same as before with one exception: a by-pass line with a rotameter was placed around the bubble tower containing the sensitizer. In this way the sensitizer content of the vapor could be varied by changing the ratio of nitrogen flow between the bubble tower and the by-pass. For methanol and acetic acid the nitrogen flow-rates through the bubble tower were set at 500, 400, 300, 100 or 0 cm.^{3}/min. and the flow-rate through the by-pass at 0, 100, 200, 300, 400 or 500 cm.^{3}/min., respectively. The nitrogen flow-rate was 500 cm.^{3}/min. through the bubble towers containing acrylonitrile for all runs so that the acrylonitrile content of the vapor was constant.

With water it was possible to get a wider range of water vapor concentrations because of the two-phase characteristics of the liquid acrylonitrile-water system. The nitrogen flow-rates were set at 500, 300, 100, or 0 cm.^{3}/min. through the bubble tower containing water and 0, 200, 400, or 500 cm.^{3}/min. through the by-pass. To get the higher water contents the monomer bubble towers contained the two-phase system acrylonitrile-water. Nitrogen flow-rate through the monomer-water bubble towers was maintained at 500 cm.^{3}/min. The nitrogen flow-rates were set at 500 or 250 cm.^{3}/min. through the bubble tower containing water and 0 or 250 cm.^{3}/min. through the by-pass.

The data on the effect of sensitizer content of the vapor for methanol, water, and acetic acid are given in Tables VI, VII, and VIII, respectively. These data are also presented in Figures 3, 4, and 5 as a log-log plot of the acrylonitrile addition versus the sensitizer content of the vapor. Inspection of Figures 3, 4, and 5 shows the following:

1. The addition of acrylonitrile to polypropylene is independent of the sensitizer.

2. Water, methanol, and acetic acid have relatively the same small effect on increasing the addition to acetate.

3. An increase in water, methanol, or acetic acid content of the vapor produces very large increases in acrylonitrile addition to cotton, nylon, and wool. The curves are linear on the log-log scale over the concentration ranges investigated with the exception of water and nylon. This appears to curve upward as the water concentration increases.

4. The largest effects were obtained with water on cotton and wool. The slope of the curve is on the order of 3. The curve for rayon (not plotted) showed the same effect as cotton.

Several investigators have noticed the necessity of water in grafting acrylonitrile to cellulose but have not explained the mechanism. It has been suggested by one investigator that the effect is due primarily to swelling of the cellulose fiber by water so that the sites are accessible to the acrylonitrile. This may play an important part in the vapor-phase process because, as indicated by preliminary work, the rate of grafting is diffusion controlled. However, methanol is not considered a good swelling agent for cellulose and yet good grafting is obtained when this is used.

Some preliminary studies were made on the adsorption of water and acrylonitrile from the vapor-phase on cotton. These experiments showed that approximately 13% water was adsorbed from nitrogen containing approximately 2% water vapor at 70°F. and 1 atmosphere pressure. Approximately 4% acrylonitrile was adsorbed by cotton from nitrogen containing about 10% acrylonitrile vapor while approximately 10% mixture of water and acrylonitrile was adsorbed from nitrogen containing a mixture of about 2% water vapor and 10% acrylonitrile vapor.

In all the experiments in grafting acrylonitrile to cotton, no addition was found in the absence of water (or other sensitizer). Since acrylonitrile is adsorbed very readily by cotton, it appears that the interpretation of this effect by swelling alone does not fully explain the phenomenon. It would appear that the acrylonitrile adsorbed on the fiber surface should add by the vapor-phase technique regardless of swelling.

In order to determine if the presence of water was necessary during the irradiation, a post-irradiation experiment was used. In one case there was no water present either during or after irradiation. In the second case there was no water present during irradiation but the nitrogen was saturated with both water and acrylonitrile during the polymerization period. In the third case water was present during irradiation and during the polymerization period.

The experimental procedure was to place the samples in the stainless steel beaker and flush for two hours with nitrogen or nitrogen saturated with water at a flow-rate of 1000 cm.^{3}/min. Then the samples were irradiated for two hours while the flushing was continued. After irradiation flushing was changed to nitrogen saturated with acrylonitrile or acrylonitrile-water at a flow-rate of 1000 cm.^{3}/min. This flushing was stopped after two hours and the polyacrylonitrile added was determined by the weight gain of the sample. The atmospheres present during each stage of the experiments for the three cases are listed below:

	Preflushing	During Irradiation	After Irradiation (grafting step)
Case I	N_2	N_2	AN-N_2
Case II	N_2	N_2	AN-H_2O-N_2
Case III	N_2-H_2O	N_2-H_2O	AN-H_2O-N_2

The data for the addition of polyacrylonitrile to each fiber sample are listed below for the three cases:

	Polyacrylonitrile Addition in Percent		
	Case I	Case II	Case III
Cotton	0.0	1.1	1.6
Polypropylene	1.0	1.3	1.5
Rayon	0.0	0.8	1.4
Acetate	8.8	11.8	12.0
Nylon	0.7	2.6	3.5
Polyester	0.0	0.2	0.2
Acrylic	0.0	0.0	0.0
Wool	0.0	1.6	3.0

These results do not answer the questions of whether the increase is caused by swelling or the participation of the water in the polymerization reaction. But the data do show that the presence of water is not necessary during irradiation to produce a significant increase in the rate of polymerization. This phenomenon will be investigated further.

Effect of Intermittent Irradiation on Graft-Polymerization

It has been reported that increased yields of graft polymers could be obtained by intermittent irradiation as compared with a continuous irradiation using the same total dose for liquid-phase systems. This point was investigated for the vapor-phase system using the acrylonitrile-water system with the various fibers.

As a control experiment the regular vapor-phase technique was used in which the yarn samples were flushed for two hours with prepurified nitrogen saturated with acrylonitrile-water at a flow-rate of 1000 cm.^{3}/min. Then the samples were irradiated for two hours while the flushing was continued. This procedure was modified by flushing and irradiating in 15 minute intervals followed by flushing for 15 minute intervals until a total irradiation time of two hours was obtained. As a control for checking the effect of the two hours additional flushing time another experimental run was made in which the samples were flushed two hours, flushed and irradiated two hours and then flushed for an additional two hours. The data on these experimental runs are listed below:

	Acrylonitrile Addition in Percent		
	flushed 2 hrs. flushed and irradiated 2 hrs.	flushed 2 hrs. alternate 15 min. flush-irrad. and flushed 4 hrs.	flushed 2 hrs. flushed and irrad. 2 hrs. flushed 2 hrs.
Cotton	3.7	5.7	5.0
Polypropylene	4.6	6.3	6.0
Rayon	3.7	6.7	6.3
Acetate	37.2	43.8	43.7
Nylon	6.6	9.2	8.1
Polyester	0.8	1.1	1.1
Acrylic	0.0	0.0	0.0
Wool	6.2	9.1	9.1

These data show an increase in polyacrylonitrile addition by the intermittent irradiation over the regular vapor-phase procedure; but if additional flushing time is added to the control, then there is no significant difference in the amount of polyacrylonitrile added. Therefore, the increase in acrylonitrile addition by intermittent irradiation over the regular procedure, is caused by the additional time for monomer diffusion into the fiber between the irradiation intervals.

Effect of Oxygen on Graft Polymerization

Although the products of the reaction between oxygen and polymeric free radicals are not known with certainty, it is generally known that a reaction takes place readily, and that it does affect grafting. The following experiment was performed to find out how oxygen affects the grafting of acrylonitrile to all of the fibers under consideration. It was carried out both with and without the use of water as a sensitizer.

The usual vapor-phase technique was used in which the samples were flushed for two hours with 1000 cm.^{3}/min. of nitrogen and oxygen that was saturated with acrylonitrile or with a two-phase solution of acrylonitrile and water. The samples were then irradiated for two hours while flushing continued. The concentration of oxygen in the nitrogen was held at four different levels; 0.002%, 0.024%, 1.0% and 10.0%. The first two concentrations were achieved by using prepurified nitrogen and oil-pumped nitrogen, respectively. Two gas streams, one carrying 10 cm.^{3}/min. of oxygen and the other 990 cm.^{3}/min. of prepurified nitrogen, were mixed to give 1000 cm.^{3}/min. at a 1.0% oxygen content. Similarly, 100 cm.^{3}/min. of oxygen and 900 cm.^{3}/min. of nitrogen formed the 10.0% oxygen mixture. The results are tabulated in Table IX and shown graphically in Figures 6, 7, and 8.

Some definite trends can be seen in these results. In all the cases except acetate and polyester the inhibiting effect of the oxygen shows a rapid increase above a threshold level. This change takes place most markedly in polypropylene between 0.02% and 1.0% oxygen. Cotton, rayon, nylon, and wool do not show the effect until the oxygen concentration exceeds 1.0%, with nylon and wool even showing a slight increase in grafting below this level. Grafting to acetate is seen to be approximately proportional to the minus one-half power of the oxygen concentration, in agreement with data reported previously.[1] Polyester grafting takes place at such low levels that it is difficult to say which trend it follows.

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[1] NCSC-2477-6 Annual Report, January 1, 1962

The Effect of Temperature on Grafting

The possible effects of temperature on vapor-phase grafting are numerous, and, in many cases, oppose each other. Some of the likely results of an increase in temperature are as follows:

A. A decrease in the equilibrium absorption of monomer by the fiber. This should decrease grafting.

B. A decrease in the approach to saturation of monomer in the vapor. This would only happen when the carrier gas was saturated with monomer at room temperature and then heated to the grafting temperature. This should decrease grafting.

C. An increase in mobility of the fiber molecules. This would speed up both the decay of free radicals and the diffusion of monomer to the radicals, giving opposite effects. If a transition temperature or softening temperature were exceeded, the effects would be especially noticeable.

D. A change in the rate of polymerization. In the case where diffusion is not controlling, the polymerization rate depends on $(k_p/k_t^{1/2})$, where k_p and k_t are the reaction velocity constants for propagation and termination respectively.

E. The rate of polymerization also depends on the factor $f^{1/2}$, where f is the initiation efficiency* or the fraction of the radicals produced that react with monomer before they decay or are deactivated. Although this is an important parameter, it is very complex, and it is difficult to predict how it will vary with temperature.

Without knowledge of the magnitudes of these effects it is impossible to predict the overall effect and some tentative experiments were carried out at elevated temperatures. The first experiments were done in the usual manner, except the beaker containing the samples was heated above room temperature. The sample chamber was heated by a glass fabric-insulated heating tape controlled by a variable transformer. The temperature was measured by a thermocouple in an oil-filled thermo-well in the beaker and was recorded continuously. Runs were made at 30, 50, 75, 100 and 125°C. Nitrogen, saturated at room temperature with the two-phase acrylonitrile-water solution was used to flush the heated sample chamber at 1000 $cm.^3$/min. for two hours. The samples were then irradiated for two hours while flushing and heating continued.

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* Flory, P. J., "Principles of Polymer Chemistry" Cornell University Press, Ithaca, New York (1953).

This procedure was duplicated using butadiene as the monomer. The sample chamber was flushed for two hours with a total of 1000 $cm.^3/min.$ of gas; 500 $cm.^3/min.$ of butadiene bubbled through 10% NaOH solution and 500 $cm.^3/min.$ of nitrogen saturated with ethanol. The irradiation period was two hours and fifteen minutes. (See Figure 1.) The results for both experiments are shown in Tables X and XI. Acetate is the only fiber that exhibits a straightforward relationship between grafting and temperature. The other fibers exhibit various maxima and minima as different effects become predominant. Nylon and the polyester had higher grafting rates at 125°C. than at 30°C. in the case of butadiene, but not in the case of acrylonitrile. The overall result, however, is that an increase in temperature is detrimental to vapor-phase grafting.

TABLE I

Effect of Sensitizers on Addition of Acrylonitrile to Textile Fibers by Vapor-Phase Technique

Acrylonitrile Addition in Percent

Fiber / Sensitizer	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
Nitrogen alone	0.0	2.7	0.0	14.0	1.1	0.2	0.0	0.0
Water	0.2	2.7	0.0	15.1	1.6	0.2	0.0	0.1
Methanol	1.6	2.9	0.2	20.1	4.9	0.4	0.0	1.1
Ethanol	0.2	2.8	0.0	18.4	2.0	0.2	0.0	0.2
Acetone	0.0	2.7	0.0	18.9	0.9	0.1	0.0	0.0
Ethyl Acetate	0.1	3.1	0.1	16.1	1.0	0.2	0.0	0.3
Acetic Acid	0.5	2.7	0.3	23.0	4.0	0.3	0.1	1.1
Acetic Anhydride	0.7	2.9	0.3	20.2	3.0	0.2	0.0	1.2
Carbon Tetrachloride	0.0	3.1	0.0	14.9	1.0	0.1	0.0	0.0
Formaldehyde	0.2	2.7	0.0	16.6	1.8	0.2	0.0	0.3
Benzene	0.0	3.1	0.0	13.8	0.9	0.1	0.0	0.0

Flush 2 hr. and flush and irradiate 2 hr., 3.5×10^5 r./hr.
500 cm.^{3}/min. N_2 - Sensitizer
500 cm.^{3}/min. N_2 - Acrylonitrile
75°F. and 1 atm.

TABLE II

Effect of Sensitizers on Addition of Butadiene to Textile Fibers by Vapor-Phase Technique

Butadiene Addition in Percent

Sensitizer \ Fiber	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
Nitrogen alone	0. 0	5. 3	0. 0	10. 4	0. 8	0. 0	0. 0	0. 0
Water	0. 0	5. 2	0. 1	13. 1	0. 9	0. 2	0. 0	0. 0
Methanol	0. 1	5. 2	1. 2	17. 9	2. 3	0. 2	0. 0	0. 6
Ethanol	0. 9	5. 0	1. 9	14. 1	2. 7	0. 4	0. 1	2. 1
Acetone	0. 5	5. 0	0. 8	5. 0	0. 8	0. 2	0. 0	0. 6
Ethyl Acetate	0. 2	4. 8	0. 2	13. 1	0. 7	0. 4	0. 0	0. 1
Acetic Acid	3. 0	4. 8	2. 3	6. 9	4. 7	0. 2	0. 0	2. 8
Acetic Anhydride	0. 4	5. 1	0. 2	12. 7	0. 7	0. 3	0. 0	0. 0
Carbon Tetrachloride	1. 9	2. 2	1. 2	9. 8	2. 0	0. 2	0. 0	1. 9
Formaldehyde	0. 0	5. 3	0. 0	11. 1	0. 9	0. 2	0. 0	0. 0
Benzene	0. 3	4. 5	0. 1	8. 7	0. 7	0. 3	0. 0	0. 2

Flush 2 hr. and flush and irradiate 2 hr., 3.5×10^5 r./hr.
200 cm.^{3}/min. Butadiene - NaOH-H_2O
200 cm.^{3}/min. N_2 - Sensitizer
75°F. and 1 atm.

TABLE III

Effect of Sensitizers on Addition of Vinyl Chloride to Textile Fibers by Vapor-Phase Technique

Vinyl Chloride Addition in Percent

Fiber Sensitizer	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
Nitrogen alone	0.0	1.9	0.0	2.5	0.8	0.1	0.0	0.0
Water	0.0	1.8	0.0	2.9	1.5	0.0	0.0	0.0
Methanol	0.3	1.5	0.1	3.4	3.5	0.1	0.0	0.0
Ethanol	0.5	1.6	0.0	4.4	2.1	0.0	0.0	0.0
Acetone	0.5	1.5	0.2	3.3	1.5	0.2	0.0	0.3
Ethyl Acetate	0.3	0.4	0.2	1.4	0.9	0.0	0.0	0.4
Acetic Acid	1.6	2.5	0.8	5.3	3.8	0.3	0.0	1.7
Acetic Anhydride	1.5	2.1	0.7	5.4	3.0	0.4	0.0	0.9
Carbon Tetrachloride	0.0	1.1	0.0	2.1	0.7	0.1	0.0	0.0
Formaldehyde	0.8	2.0	0.8	2.7	1.6	0.3	0.1	0.8
Benzene	0.0	1.3	0.0	2.6	0.8	0.2	0.0	0.0

flush 2 hr. and flush and irradiate 2 hrs., 3.5×10^5 r./hr.
200 cm.^{3}/min. vinyl chloride - $NaOH-H_2O$
200 cm.^{3}/min. N_2 - Sensitizer
75°F. and 1 atm.

TABLE IV

Effect of Sensitizers on Addition of Ethylene to Textile Fibers by Vapor - Phase Technique

Ethylene Addition in Percent

Fiber Sensitizer	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
Nitrogen alone	0.1	0.1	0.1	0.2	0.3	0.1	0.0	0.0
Water	0.1	0.0	0.2	0.1	0.2	0.0	0.0	0.1
Methanol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ethanol	0.7	0.0	0.7	0.0	0.0	0.0	0.0	0.0
Acetone	0.6	0.0	0.3	0.1	0.2	0.0	0.0	0.2
Ethyl Acetate	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
Acetic Acid	1.4	0.0	0.5	0.0	0.0	0.0	0.0	0.8
Acetic Anhydride	1.3	0.0	0.6	0.0	0.1	0.0	0.0	0.3
Carbon Tetrachloride	0.2	0.0	0.7	0.3	0.3	0.0	0.0	0.2
Formaldehyde	0.5	0.0	0.6	0.0	0.1	0.0	0.0	0.2
Benzene	0.3	0.0	0.2	0.1	0.1	0.0	0.0	0.0

flush 2 hr. and flush and irradiate 2 hr., 3.5×10^{5} r./hr.
200 cm.^{3}/min. Ethylene - $NaOH$-H_2O
200 cm.^{3}/min. N_2 - Sensitizer
75°F. and 1 atm.

TABLE V

Effect of Sensitizers on Addition of Propylene to Textile Fibers by Vapor-Phase Technique

	Propylene Addition in Percent							
Fiber Sensitizer	Cotton	Propylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
Nitrogen alone	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Water	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Methanol	0.1	0.0	0.5	0.0	0.2	0.0	0.0	0.0
Ethanol	0.9	0.0	1.3	0.0	0.0	0.0	0.0	0.5
Acetone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ethyl Acetate	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Acetic Acid	2.1	0.0	1.3	1.5	0.4	0.0	0.0	3.0
Acetic Anhydride	0.2	0.0	0.1	0.2	0.1	0.0	0.0	0.1
Carbon Tetrachloride	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Formaldehyde	0.8	0.0	1.1	0.3	0.5	0.0	0.0	0.7
Benzene	0.3	0.0	0.3	0.3	0.7	0.1	0.0	0.0

flush 2 hr. and flush and irradiate 2 hr., 3.5x10^5 r. /hr.
200 cm.^{3}/min. Propylene - $NaOH$-H_2O
200 cm.^{3}/min. N_2 - Sensitizer
75°F. and 1 atm.

TABLE VI

Effect of Methanol Content of Vapor on Addition of Acrylonitrile to Textile Fibers by Vapor-Phase Technique

Acrylonitrile Addition in Percent

Fiber / Methanol Content in Percent	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
0	0.1	2.7	0.1	14.6	1.0	0.2	0.0	0.0
1.5	0.2	2.6	0.0	14.6	1.7	0.2	0.0	0.0
3.1	0.9	2.7	0.5	14.4	2.5	0.4	0.0	0.6
4.6	0.6	2.2	0.0	15.1	3.1	0.2	0.0	0.7
6.2	0.9	2.7	0.0	18.1	3.9	0.2	0.0	0.3
7.7	1.6	2.9	0.2	20.1	4.9	0.4	0.0	1.1

flush 2 hr. and flush and irradiate 2 hr., 3.5×10^5 r./hr.
500 cm.^{3}/min. N_2 - Acrylonitrile
500 cm.^{3}/min. N_2 and N_2 - Methanol
75°F. and 1 atm.
Acrylonitrile Content of Vapor 6.6%

TABLE VII

Effect of Water Content of Vapor on Addition of Acrylonitrile to Textile Fibers by Vapor-Phase Technique

	Acrylonitrile Addition in Percent							
Fiber / Water Content in Percent	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
0	0.0	2.7	0.0	14.0	1.1	0.2	0.0	0.0
0.3	0.0	2.5	0.0	13.6	1.0	0.1	0.0	0.0
0.9	0.1	2.7	0.0	14.5	1.4	0.2	0.0	0.0
1.5	0.2	2.7	0.0	15.1	1.6	0.2	0.0	0.1
2.25	1.9	2.7	1.9	16.6	2.7	0.2	0.0	1.8
3.0	3.1	2.6	3.3	19.0	4.0	0.2	0.0	3.2

flush 2 hr. and flush and irradiate 2 hr., $3.5x10^5$ r./hr.
500 cm.^{3}/min. N_2 - Acrylonitrile or N_2 - H_2O - Acrylonitrile
500 cm.^{3}/min. N_2 and N_2 - water
75°F. and 1 atm.
Acrylonitrile Content of Vapor 6.6%

TABLE VIII

Effect of Acetic Acid Content of Vapor on Addition of Acrylonitrile to Textile Fibers by Vapor-Phase Technique

Acrylonitrile Addition in Percent

Fiber / Acetic Acid Content in Percent	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
0	0.0	2.7	0.0	14.0	1.1	0.2	0.0	0.0
0.2	0.2	2.5	0.4	15.1	1.4	0.1	0.0	0.5
0.4	0.5	2.8	0.4	17.7	2.3	0.4	0.1	0.6
0.6	0.4	2.9	0.2	19.2	3.0	0.3	0.0	0.8
0.8	0.3	2.5	0.1	19.6	2.9	0.1	0.0	0.7
1.0	0.5	2.7	0.3	23.0	4.0	0.3	0.1	1.1

flush 2 hr. and flush and irradiate 2 hr., 3.5×10^5 r./hr.
500 cm.^{3}/min. N_2 - Acrylonitrile
500 cm.^{3}/min. N_2 - Acetic Acid
75°F. and 1 atm.
Acrylonitrile Content of Vapor 6.6%

TABLE IX

Effect of Oxygen on Graft Polymerization

	Acrylonitrile Addition in Percent			
	No Water Present			
	0.002%	0.024%	1.0%	10.0% O_2
Cotton	0.0	0.0	0.0	0.0
Polypropylene	4.2	3.2	0.0	0.0
Rayon	0.0	0.0	0.0	0.0
Acetate	21.1	9.8	0.6	0.1
Nylon	1.8	1.9	1.3	0.2
Polyester	0.6	0.2	0.1	0.0
Acrylic	0.0	0.0	0.0	0.0
Wool	0.3	0.0	0.0	0.0
	Vapor Saturated with Water			
Cotton	3.4	3.5	3.6	1.9
Polypropylene	4.1	3.3	0.0	0.0
Rayon	36.0	4.5	4.2	2.3
Acetate	26.5	13.8	0.6	0.4
Nylon	5.5	5.5	5.0	2.4
Polyester	0.6	0.3	0.2	0.2
Acrylic	0.0	0.0	0.0	0.0
Wool	4.5	5.6	4.5	1.5

TABLE X

Effect of Temperature on Addition of Acrylonitrile to Textile Fibers by Vapor-Phase Technique

Fiber Temp. °C.	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
30	4.22	6.57	4.27	25.81	6.52	0.56	0	6.08
50	0	3.46	0	9.69	2.91	0.03	0	0.71
75	0.09	0.23	0	3.22	3.50	0.12	0	0.96
100	0.36	0	0.18	1.36	4.09	0.22	0.14	1.41
125	0	0	0	0.54	1.43	0.10	0.33	1.07

flush 2 hr. and flush and irradiate 2 hr., 3.12×10^5 r./hr.
1000 cm.^{3}/min. N_2-Acrylonitrile-water

TABLE XI

Effect of Temperature on Addition of Butadiene to Textile Fibers by Vapor-Phase Technique

Fiber / Temp. °C.	Cotton	Polypropylene	Rayon	Acetate	Nylon	Polyester	Acrylic	Wool
30	1.1	4.2	1.1	11.3	2.4	0.3	0	1.0
50	0	4.0	0	7.4	0.9	0.4	0	0.2
75	0	1.6	0	5.6	1.3	0.5	0	0.3
100	0	0.2	0	6.3	3.0	1.3	0	0.5
125	0	0	0	5.1	4.3	1.6	0.2	0.1

flush 2 hr. and flush and irradiate 2-1/4 hr. 3.12×10^5 r./hr.
500 cm.^{3}/min. Butadiene-NaOH-H_2O
500 cm.^{3}/min. Ethanol-N_2

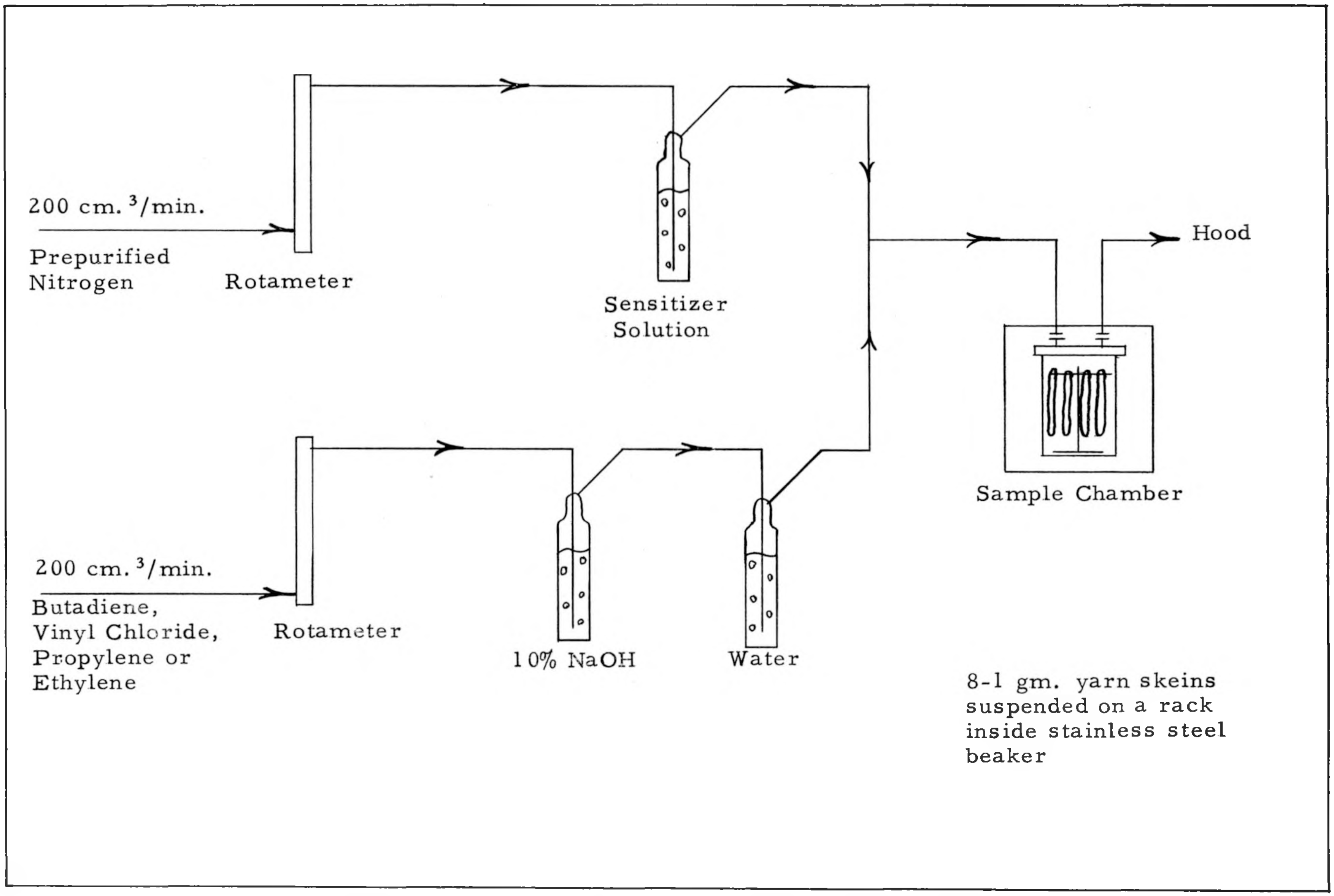

Figure 1. Diagrammatic Sketch of Vapor-Phase Apparatus

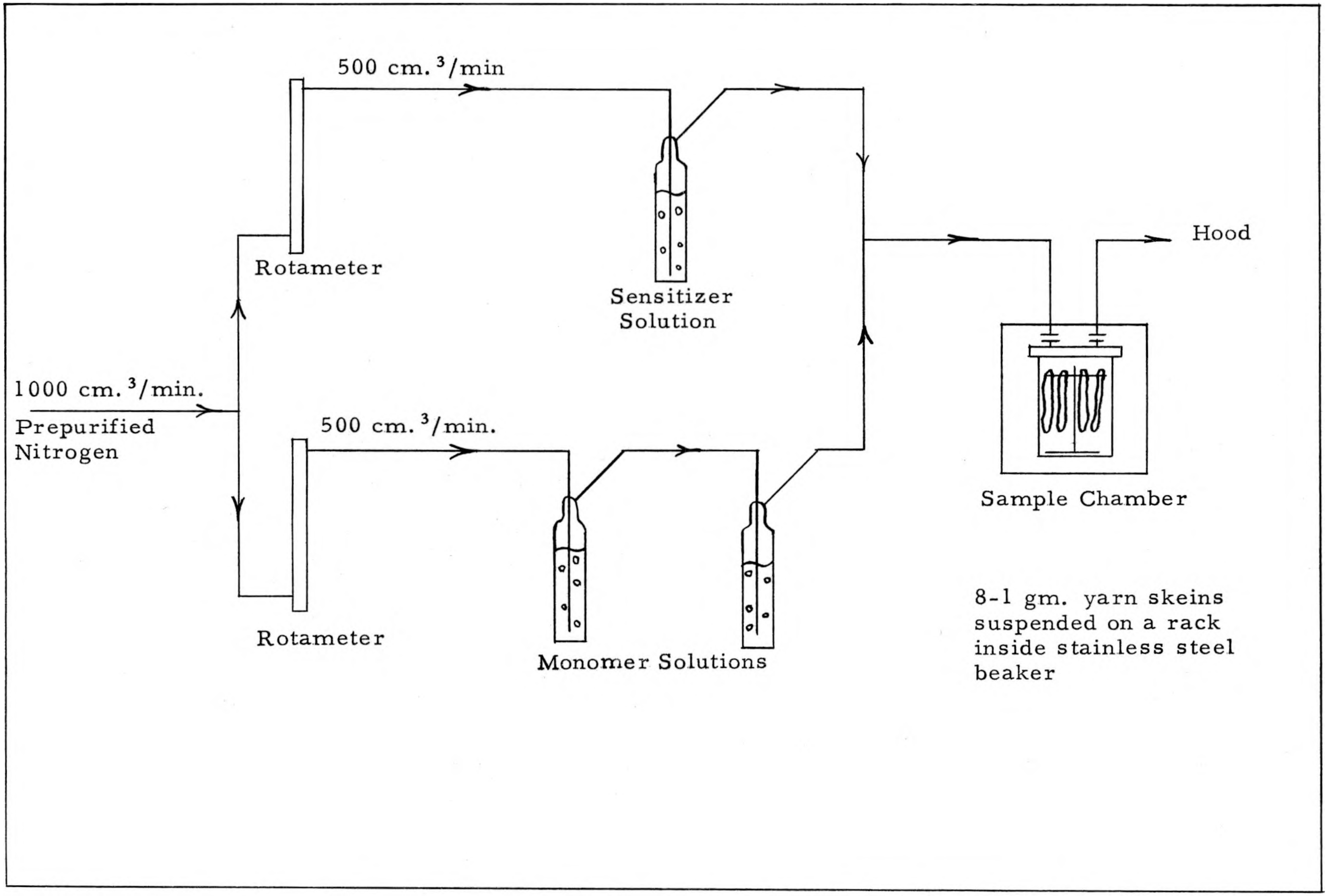

Figure 2. Diagrammatic Sketch of Vapor-Phase Apparatus

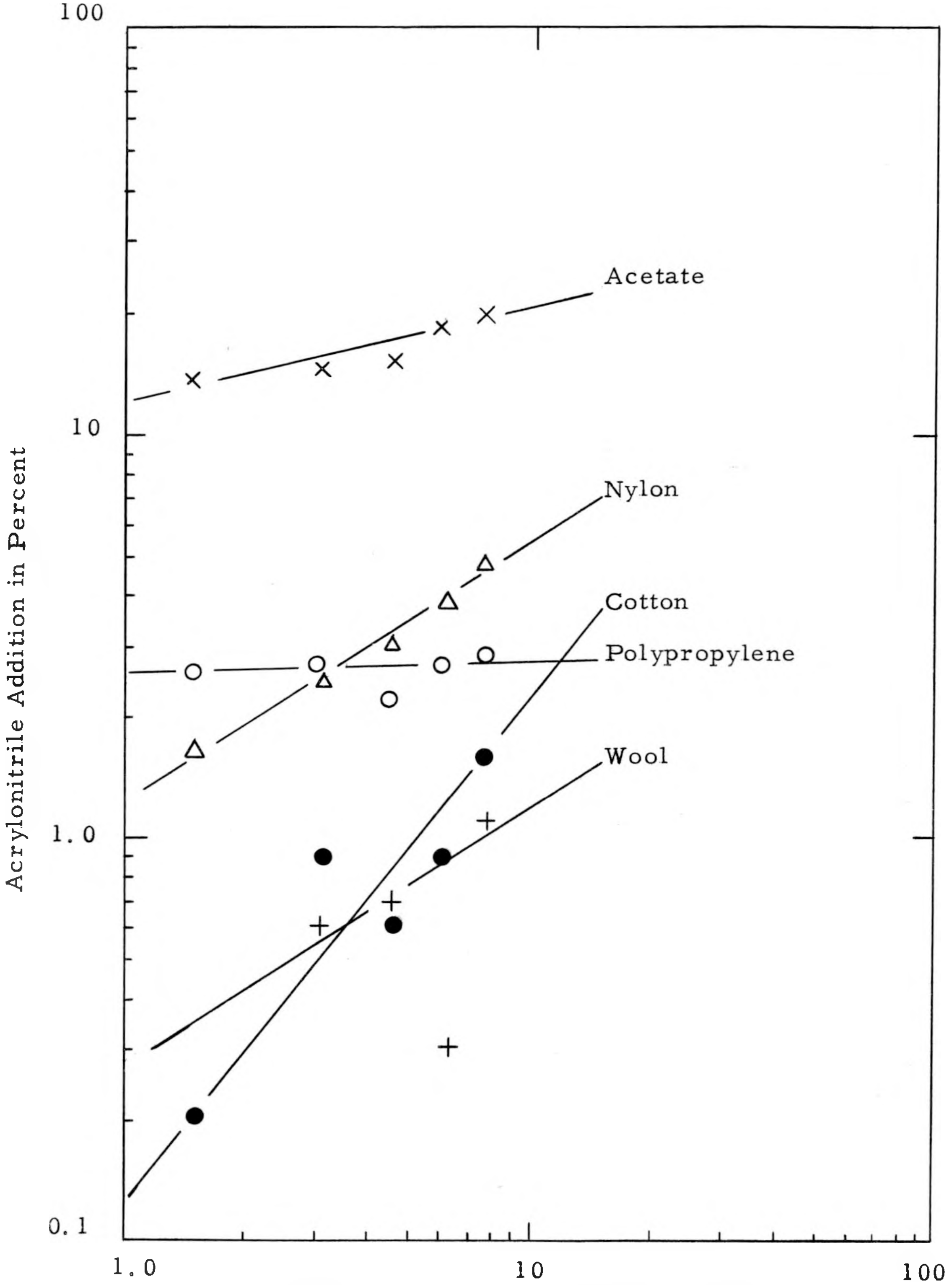

Figure 3

Effect of Methanol Content of Vapor on Acrylonitrile Addition to Textile Fibers

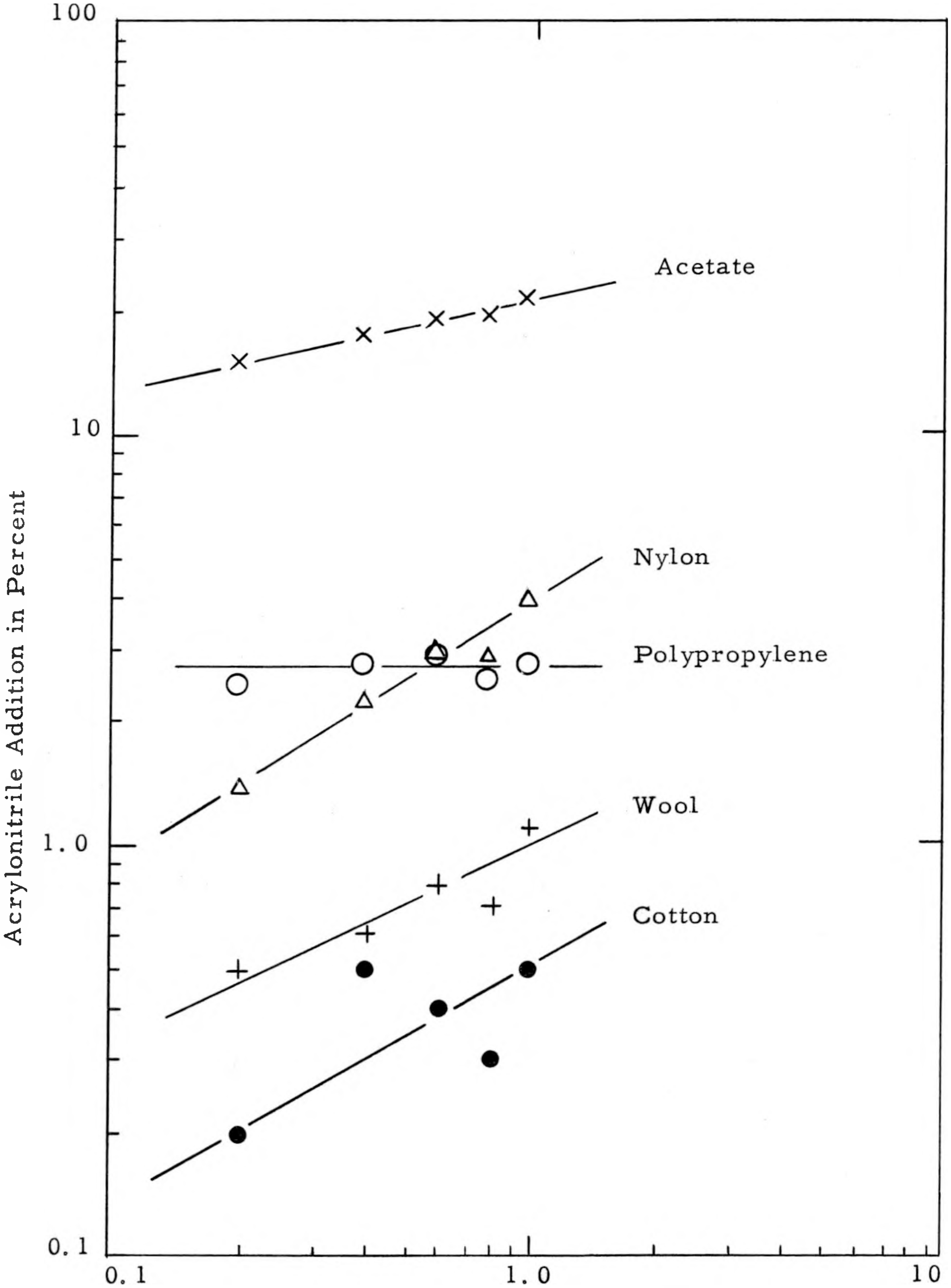

Figure 4

Effect of Acetic Acid Content of Vapor on Acrylonitrile Addition to Textile Fibers

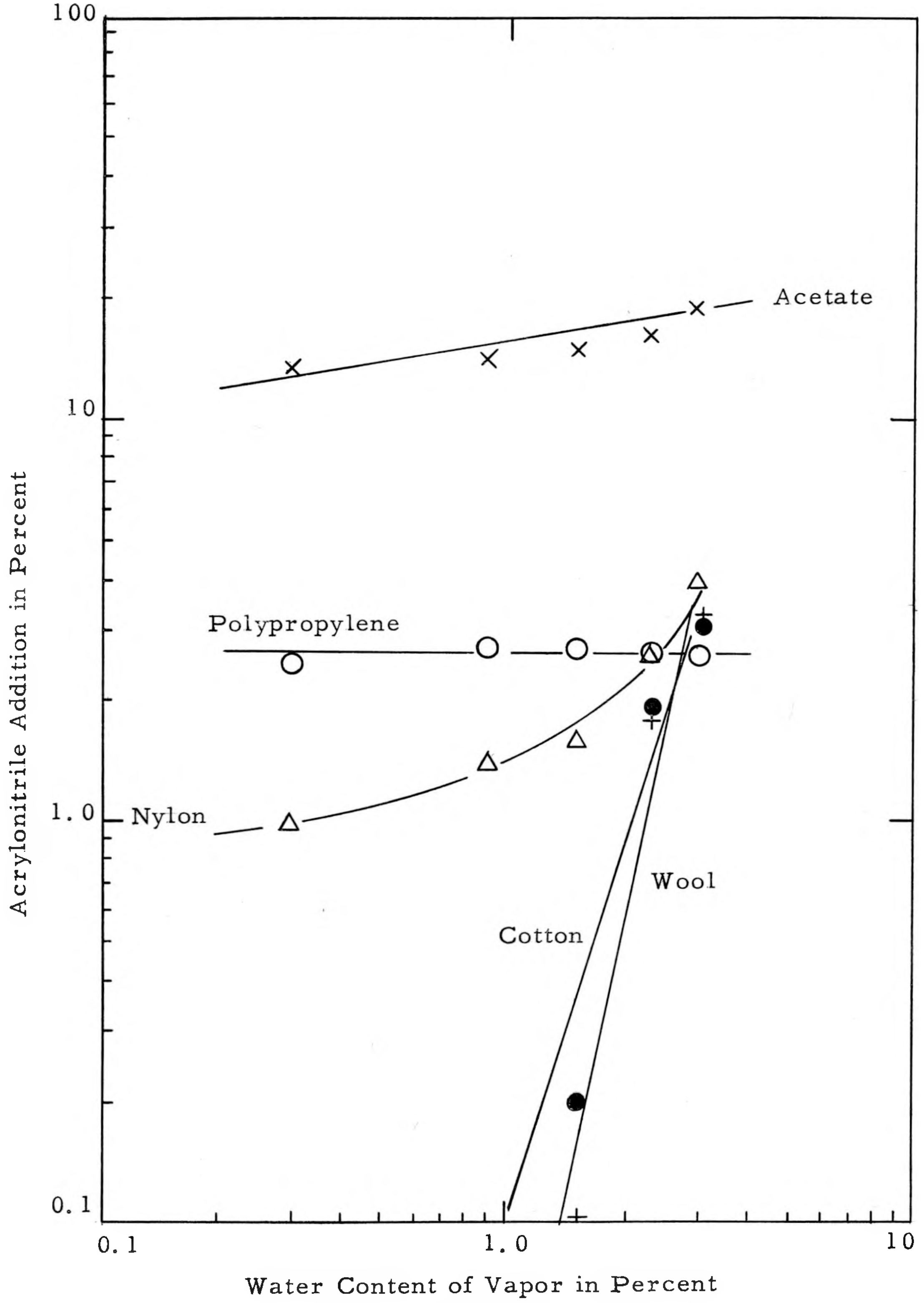

Figure 5

Effect of Water Content of Vapor on Acrylonitrile Addition to Textile Fibers

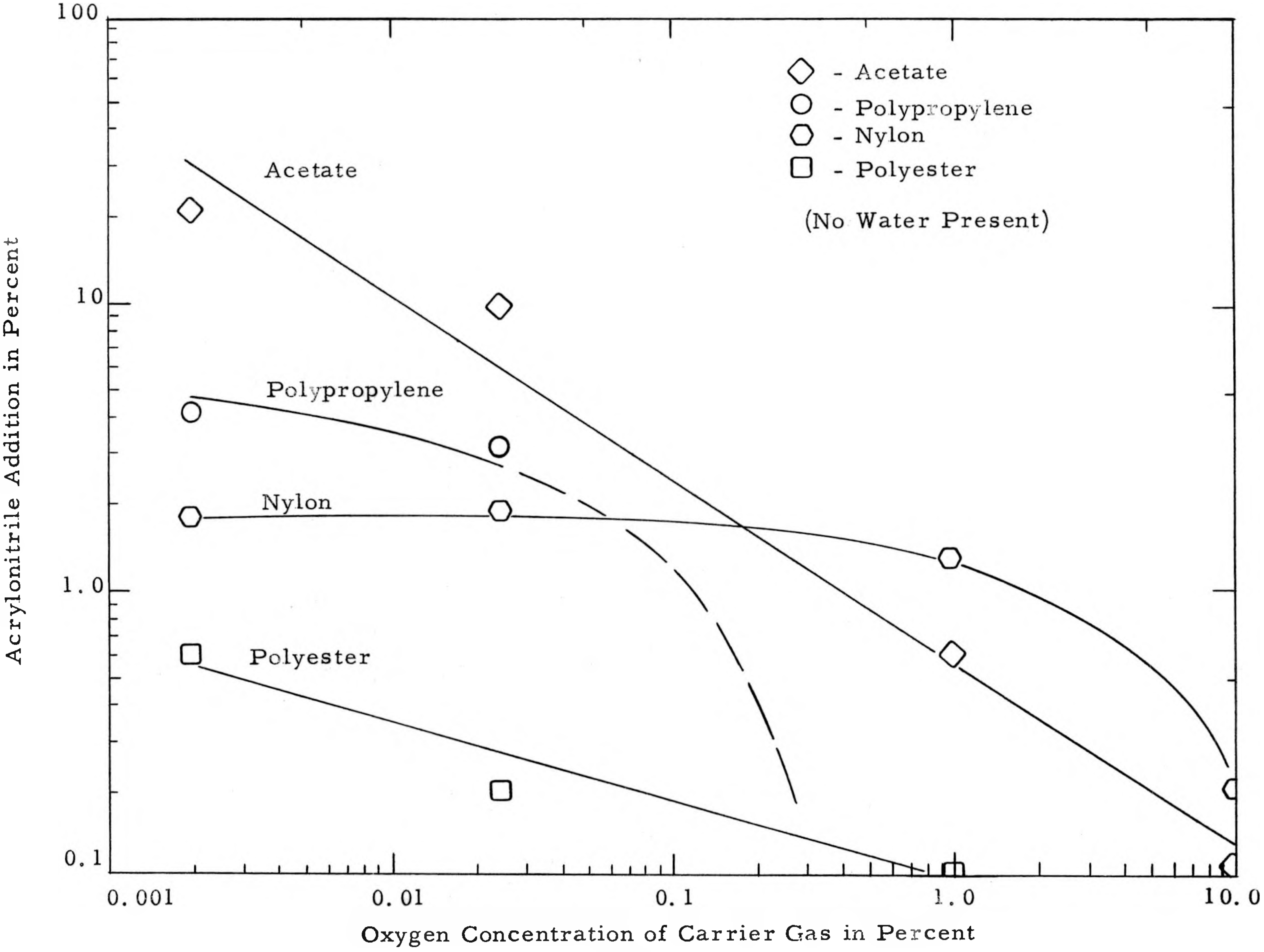

Figure 6.

Effect of Oxygen on Acrylonitrile Addition to Textile Fibers

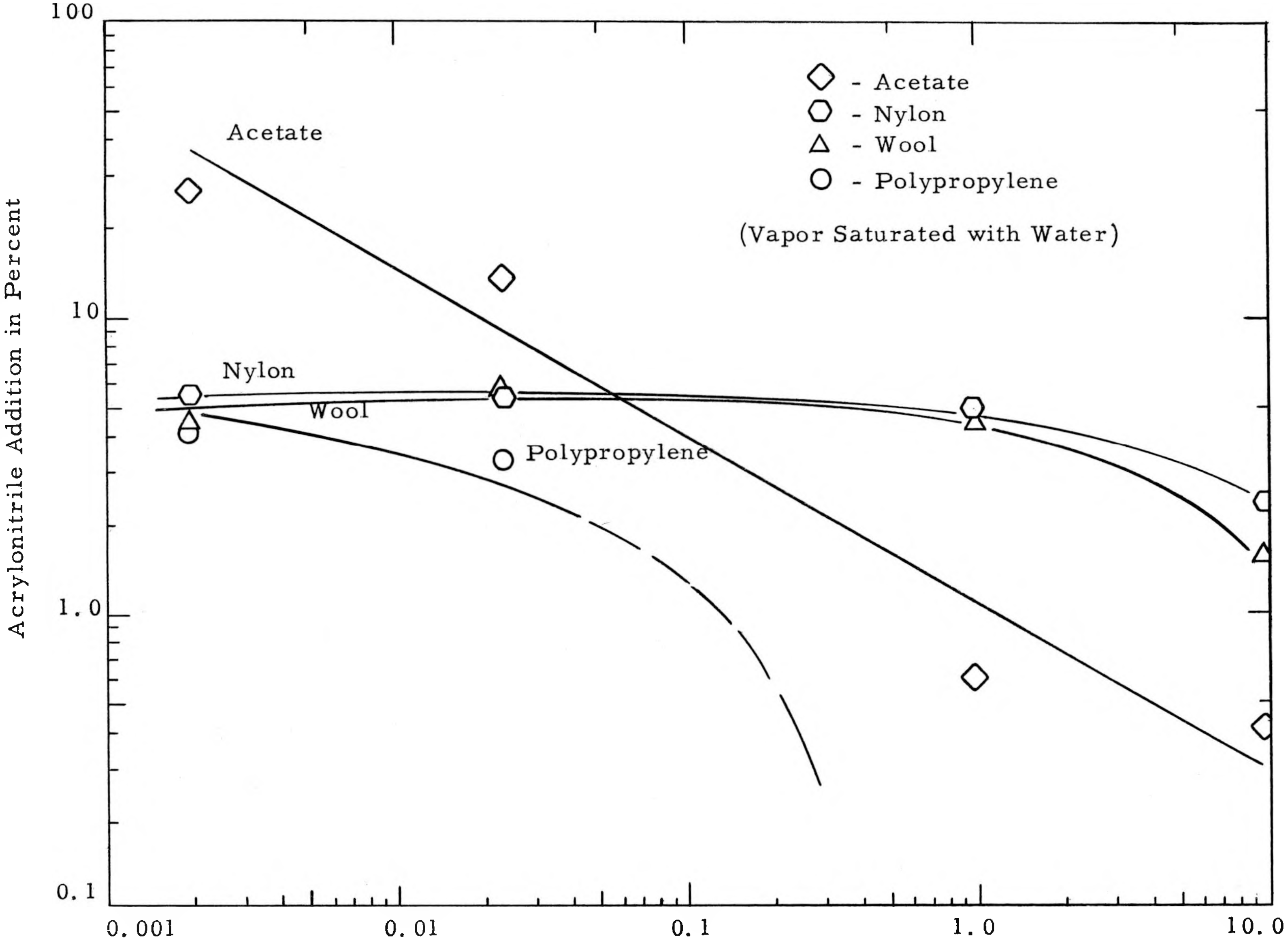

Figure 7.

Effect of Oxygen on Acrylonitrile Addition to Textile Fibers

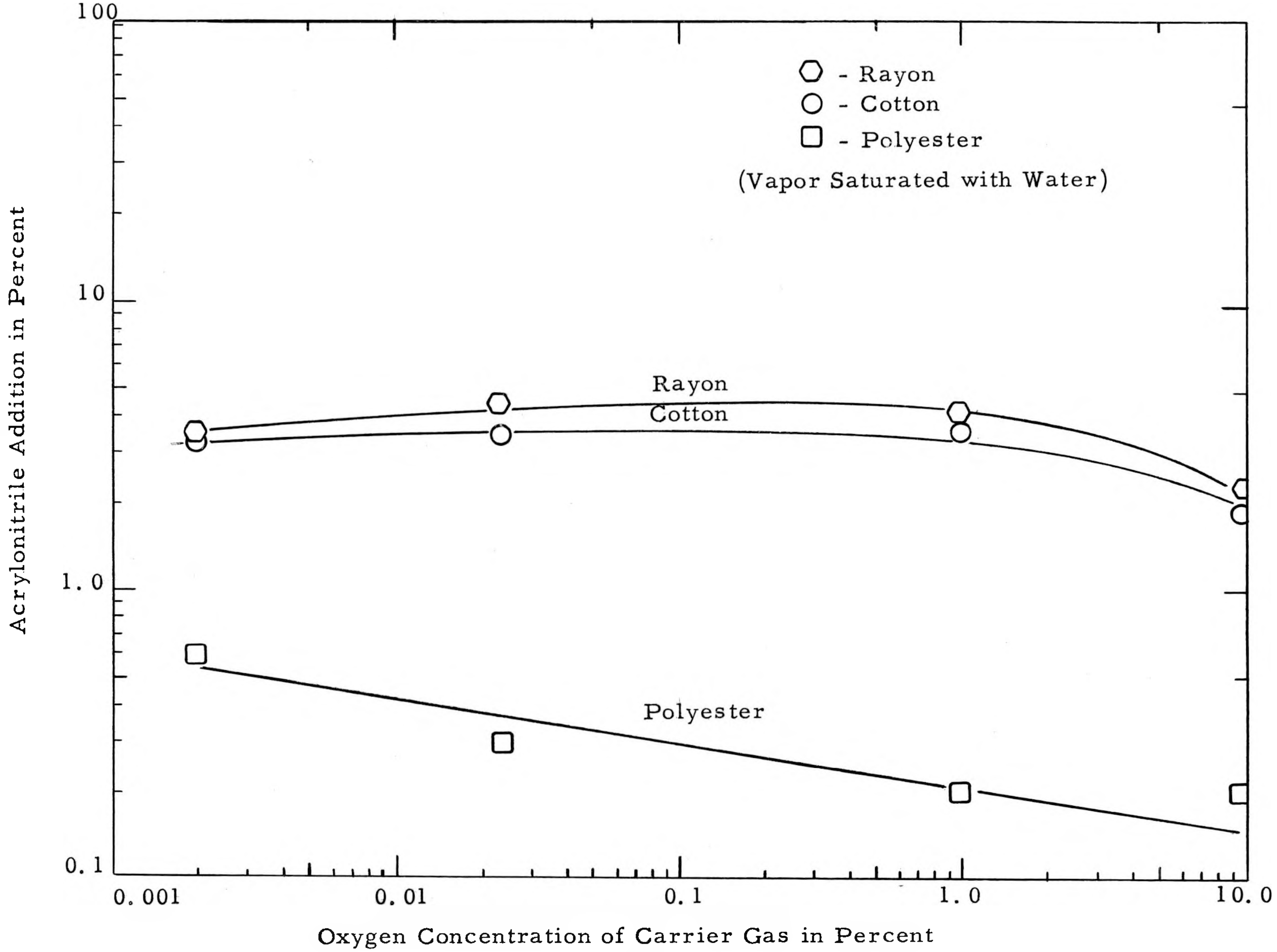

Figure 8

Effect of Oxygen on Acrylonitrile Addition to Textile Fibers

PART II. MODIFICATION OF TEXTILE FIBER PROPERTIES

Dyeing of Polypropylene

The usefulness of polypropylene fibers to the textile industry is limited because of several properties; one of these is the inability to dye the fiber using the conventional dyeing process, and at the same time obtain good fastness properties. Considerable effort is being expended to improve dyeability because the fiber is attractive from a number of points of view, one of which is low cost.

To improve the dyeability of the fiber it has been suggested that dye-receptive groups such as carboxyl, amino, ester, or amide, be attached to the fiber by graft-polymerization. The low volatility of vinyl monomers containing acidic and basic groups eliminated these from use in the vapor-phase process. Three volatile monomers were available which contained ester groups: vinyl acetate, methyl acrylate, and ethyl acrylate. These were grafted in different amounts to polypropylene yarn. All of the samples then dyed satisfactorily with dispersed dyes using standard dyeing techniques.

Because methyl acrylate grafted more readily than the other monomers, it was chosen for further study. Ten grams of the staple fiber were packed loosely in the irradiation chamber. The container was flushed for two hours with prepurified nitrogen saturated by a two-phase methyl acrylate-water solution. Then the samples were irradiated with the flushing continued. Irradiation was carried out for various periods of time in order to obtain different quantities of polymer grafted to the fibers, the amount of which was determined by weight gain.

The grafted polypropylene staple fiber was dyed by the standard disperse dye technique using 4 percent (based on fiber) of the following dyes: Latyl Blue FLW, Latyl Yellow 3G, Latyl Cerise B, and a mixture of 1 part Latyl Blue FLW and 1 part Latyl Yellow 3G. All of the dyes gave very deep shades and completely uniform dyeings of all the fibers. The dye baths were practically exhausted in all cases. The depth of shade increased with increase in polymethyl acrylate content and 10 percent add-on was sufficient to give a deep shade. At this level the "hand" of the fiber was not appreciably changed.

Polypropylene fabric was also grafted with different amounts of polymethyl acrylate using the vapor-phase technique. Fabric samples containing 5, 10, 20, 50 and 100 percent polymethyl acrylate based on original fabric were made. These samples were dyed using 3 percent (based on fiber) of Latyl Blue FLW, Latyl Green, and Latyl Cerise B. The dyed fabric samples gave the same depth of shade and dye uniformity as the staple fiber samples. The samples with 50 and 100 percent add-on had a very harsh hand because of the large amount of grafted polymer.

Standard wash tests (AATCC) made on the dyed samples showed bleeding of the dye to acetate fabric included in the wash test solution. The bleeding was not sufficient to detect a decrease in shade of the dyed sample and was no worse than that experienced with other types of fiber dyed with the same dyes. Thus, commercial acceptance of the grafted polypropylene appears possible.

Attempts were made to improve the color fastness of the dyed polypropylene staple to the wash tests. Dyeings were carried out both under pressure (15 psig and 45 psig) to increase the temperature, and in the presence of several carriers which have been used to achieve better dyeing of polyester fiber. Also dyeings were carried out both under pressure and in the presence of carriers. All procedures resulted in slight reductions in bleeding during washing, but there appeared to be no significant advantage in using any of them in preference to the low-temperature or non-carrier systems.

Because of recent developments by several manufacturers, interest in using radiation to accomplish the dyeing of polypropylene has understandably waned.[1] In spite of this, it is believed that grafting procedures, such as used here, are not by any means impractical. The vapor-phase technique (as well as other that might be developed) provides a fiber that exhibits good dyeing qualities with respect to color yield, penetration, and uniformity without sacrifice in other properties. This, it is felt, has been adequately demonstrated, and in view of other approaches to the problem by the several manufacturers cited above, work on this phase of the project has been terminated.

Physical Properties of Grafted Fibers

With the improvements in grafting that have been made recently (described in earlier reports), a study of the physical properties of some of the grafted fibers now seems advisable. Cellulose acetate, nylon, and polypropylene, because of their relatively high grafting rates, were chosen for the study. Four monomers; acrylonitrile, butadiene, methyl acrylate, and ethyl acrylate were grafted to each of these fibers, using the vapor-phase process.

The experimental procedure was as follows: (1) Scoured skeins of 75-24 bright acetate, 840-136 bright nylon, and 6 dpf polypropylene were suspended on a rack inside the stainless steel beaker

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[1] Brief news releases have appeared in the "Chementator" section of Chemical Engineering for February 5, 1962, page 38; April 2, 1962, page 40: and June 25, 1962, page 55. Reference is also made to Chemical Week for January 27, 1962, page 25 and June 9, 1962, page 67.

in the gammacell sample chamber; (2) the beaker was flushed two hours at a flow rate of 1000 cm.^{3}/min. with prepurified nitrogen saturated with two-phase solutions of acrylonitrile-water, methyl acrylate-water, or ethyl acrylate-water; (3) the yarn samples were irradiated for 1/2, 1, 2, or 4 hours while flushing continued. In the case of butadiene the beaker was first purged for 30 minutes with prepurified nitrogen at a flow-rate of 1000 cm.^{3}/min. Then the beaker was flushed for two hours with the gaseous monomer saturated with water at a flow-rate of 200 cm.^{3}/min. (Inhibitor was removed from the butadiene by bubbling though a 10% aqueous NaOH solution.) The same rate of flushing was used during irradiation.

To show the effect of radiation alone on the physical properties of these yarns, the experiments were repeated using prepurified nitrogen alone for flushing. These experiments were also made using prepurified nitrogen saturated with water. (As an unirradiated control, yarn samples were flushed 2 hours with prepurified nitrogen at a flow-rate of 1000 cm.^{3}/min.)

The polymer addition to the grafted samples was determined by weight gain. Stress-strain curves were made under standard laboratory conditions on 20 single filaments from each sample using an Instron. The amounts of monomer added as a function of radiation dose are shown in Figures, 1, 2, and 3. Figures 4 through 18 show representative stress-strain curves for the controls and grafted filaments. A visual inspection of the stress-strain curves shows the following effects as the graft-polymer content increases:

Acetate Yarn

Methyl Acrylate
1. slight increase in breaking strength
2. slight increase in elongation
3. increase in proportional limit
4. slight increase in modulus

Ethyl Acrylate
1. practically no change in properties

Butadiene
1. decrease in breaking strength
2. decrease in elongation
3. slight increase in modulus
4. increase in proportional limit
5. development of a yield point

Acrylonitrile
1. large increase in breaking strength
2. decrease in elongation
3. increase in modulus
4. increase in proportional limit

Nylon Yarn

Methyl Acrylate - Ethyl Acrylate
1. very little change in physical properties

Butadiene
1. strength passes through a minimum
2. elongation passes through a maximum
3. little change in modulus or proportional limit

Acrylonitrile
1. decrease in strength and elongation
2. little change in modulus or proportional limit

Polypropylene Yarn

Methyl Acrylate - Ethyl Acrylate
1. strength passes through maximum
2. elongation increases
3. modulus decreases
4. little change in proportional limit

Butadiene
1. increases in strength and elongation
2. no change in modulus or proportional limit

Acrylonitrile
1. strength and elongation pass through a maximum
2. modulus and proportional limit decrease slightly

When the values for breaking strength, modulus, and proportional limit were corrected for the increase in denier of the grafted samples, the data in Figures 19, 20, and 21 were obtained. Data for the control and the irradiated samples are given in Tables I, III, and V and for the grafted samples in Tables II, IV, and VI. Inspection of Figure 19 shows that acrylonitrile is the only monomer of the group that significantly improves the physical properties of acetate yarn. The breaking strength of the fiber is unaffected by acrylonitrile addition when corrected for increase in denier, but the modulus and proportional limit are both increased by acrylonitrile addition. In Figure 20, it can be seen that grafting to nylon produces slight decreases in strength and that addition of small amounts of polymer causes increases in modulus and proportional limit. Table III shows, however, that this effect is also produced by radiation with no monomer present. Figure 21 indicates that the only significant change in physical properties of grafted polypropylene is a decrease in modulus.

The melting points of all the preceding combinations of grafted fibers were measured using a Fisher-Johns melting point apparatus, and are shown in Figures 22, 23, and 24. Grafting to acetate decreased its melting point, except in the case of acrylonitrile addition of more than twenty percent, where the acetate charred and did not melt. The melting point of nylon was not significantly changed by grafting any of the monomers used. While the softening point of polypropylene fiber was unaffected by any amount of grafting, the addition of relatively large amounts of methyl acrylate increased its melting point significantly. The acrylonitrile-polypropylene graft, however, showed a marked increase in melting point at acrylonitrile additions of over four percent (see Figure 24). The graft is located on the surface of the fiber and it appears that the polypropylene in the center of the fiber melts, while the grafted "shell" on the surface holds it together. This could also explain the fact that the softening point is unchanged.

Moisture regains were also measured on these fibers. One-gram samples were dried to constant weight in a 105°C. circulating oven, conditioned at 70°F. and 65 percent relative humidity, and reweighed. The percent weight gains, based on the weight of the graft copolymer and on the weight of the ungrafted sample, are shown in Tables VII, VIII, and IX. Grafted acetate shows a marked decrease in regain, calculated on both bases. The regains of nylon and polypropylene, however, based on the ungrafted weight, were not significantly changed.

Increasing amounts of grafting caused a decrease in solubility of these fibers in their respective solvents. A summary of the changes in solubility with grafting is given in Tables X, XI, and XII. The results are not quantitative, and only show the general trend indicated above.

Weather Resistance of Fabrics Grafted with Styrene

Polystyrene is noted for its resistance to degradation by all types of radiation, and an experiment was designed to see whether the weathering of fabrics could be retarded by grafting them with styrene. Fabric strips of cotton, nylon, and polypropylene were grafted with various amounts of styrene, using methanol as a sensitizer. The strips of fabric were placed in the irradiation chamber, flushed with nitrogen saturated with a 50 percent methanol-styrene solution, and irradiated for various times. In each run, two 5"x12" strips were prepared for testing, and four 1"x6" strips were included for measurement of the polymer addition. One 5"x12" strip from each run, plus irradiated and unirradiated controls, were placed on a weathering rack and left exposed for ten weeks, according to Technical Manual AATCC (1960) p. 73. The results are given in Tables XIII, XIV and XV, and in

Figure 25. The breaking strengths are averages of eight breaks made on 1"x6" strips cut from each sample. All breaks were made in the warp direction. Inspection of Figure 25 reveals that styrene addition up to about 6 percent does not affect the weathering of cotton. The nylon and polypropylene were significantly improved, however. The addition of 12 percent styrene cut the strength loss in nylon by about one-third. Not enough styrene was added to polypropylene to produce a large effect, but the slope of the curve indicates that the rate of improvement is about equal to that of nylon.

TABLE I. Physical Properties of Acetate Yarn

Dose in Rads	Weight Gain in Percent	Strength in Gm/Denier	Elongation in Percent	Modulus in Gm/Denier/ Unit Elong.	Proportional Limit in Gm/Denier
Control - Unirradiated, Flushed 2 hr. with N_2-1000 cm.^{3}/min.					
0	0	1.40	32.6	30.1	0.66
Control-Irradiated in N_2-1000 cm.^{3}/min.					
1.56×10^5	0	1.30	30.7	31.3	0.59
3.12×10^5	0	1.31	29.0	33.5	0.54
6.24×10^5	0	1.29	29.4	31.8	0.56
1.25×10^6	0	1.27	29.0	33.4	0.59
Control-Irradiated in N_2-H_2O-1000 cm.^{3}/min.					
1.56×10^5	0	1.32	28.7	34.1	0.55
3.12×10^5	0	1.28	29.9	32.7	0.57
6.24×10^5	0	1.27	28.5	33.8	0.54
1.25×10^6	0	1.26	27.4	34.1	0.60

TABLE II. Physical Properties of Grafted Acetate Yarn

Dose in Rads	Weight Gain in Percent	Strength in Gm/Denier	Elongation in Percent	Modulus in Gm/Denier/ Unit Elong.	Proportional Limit in Gm/Denier
	Sample - Irradiated in Acrylonitrile-N_2-H_2O-1000 cm.^{3}min.				
1.56×10^5	9.4	1.34	31.1	31.3	0.66
3.12×10^5	16.5	1.41	28.1	33.9	0.72
6.24×10^5	24.2	1.40	26.0	34.6	0.75
1.25×10^6	43.3	1.41	22.9	39.9	0.81
	Sample - Irradiated in Ethyl Acrylate-N_2-H_2O-1000 cm.^{3}/min.				
1.56×10^5	10.9	1.35	29.4	33.9	0.64
3.12×10^5	23.1	1.21	28.5	32.6	0.58
6.24×10^5	47.4	0.99	29.0	24.4	0.56
1.25×10^6	107.3	0.71	28.9	16.1	0.37
	Sample - Irradiated in Methyl Acrylate -N_2-H_2O-1000 cm.^{3}/min.				
1.56×10^5	23.2	1.22	26.5	33.8	0.66
3.12×10^5	36.3	1.20	25.5	34.7	0.79
6.24×10^5	59.3	1.09	23.9	31.8	0.79
1.25×10^6	106.1	0.82	26.3	22.6	0.52
	Sample - Irradiated in Butadiene -H_2O-200 cm.^{3}/min.				
1.56×10^5	3.6	1.26	29.0	32.6	0.58
3.12×10^5	11.1	1.14	25.8	31.5	0.57
6.24×10^5	22.6	0.88	24.7	30.1	0.66
1.25×10^6	33.3	0.84	16.6	31.8	0.75

TABLE III. Physical Properties of Nylon Yarn

Dose in Rads	Weight Gain in Percent	Strength in Gm/Denier	Elongation in Percent	Modulus in Gm/Denier/ Unit Elong.	Proportional Limit in Gm/Denier
Control - Unirradiated					
0	0	8.04	26.9	30.5	0.49
Control - Irradiated in N_2-1000 cm.^{3}/min.					
1.56×10^5	0	7.44	27.7	26.7	0.46
3.12×10^5	0	7.45	27.8	33.2	0.50
6.24×10^5	0	7.71	27.2	33.5	0.60
1.25×10^6	0	7.33	26.8	31.8	0.58
Control - Irradiated in N_2-H_2O 1000 cm.^{3}/min.					
1.56×10^5	0	7.73	28.1	33.7	0.55
3.12×10^5	0	7.77	25.7	34.7	0.55
6.24×10^5	0	6.88	21.7	37.9	0.61
1.25×10^6	0	7.24	23.0	35.0	0.60

TABLE IV. Physical Properties of Grafted Nylon Yarn

Dose in Rads	Weight Gain in Percent	Strength in Gm/Denier	Elongation in Percent	Modulus in Gm/Denier/ Unit Elong.	Proportional Limit in Gm/Denier
Sample - Irradiated in Acrylonitrile-N_2-H_2O- 1000 cm.^{3}/min.					
$1.56x10^5$	2.7	7.46	24.2	34.2	0.56
$3.12x10^5$	4.0	7.28	25.0	34.9	0.65
$6.24x10^5$	5.4	6.73	23.3	35.9	0.60
$1.25x10^6$	7.4	6.45	22.3	35.4	0.60
Sample - Irradiated in Ethyl Acrylate-N_2H_2O-1000 cm.^{3}/min.					
$1.56x10^5$	0.5	7.50	26.3	30.6	0.57
$3.12x10^5$	1.0	7.48	23.9	33.7	0.60
$6.24x10^5$	9.5	6.57	25.8	24.7	0.45
$1.25x10^6$	44.7	unable to run			
Sample - Irradiated in Methyl Acrylate-N_2H_2O-1000 cm.^{3}/min.					
$1.56x10^5$	1.2	7.64	26.2	34.0	0.60
$3.12x10^5$	5.3	7.23	26.2	34.6	0.58
$6.24x10^5$	26.2	5.83	26.9	27.1	0.44
$1.25x10^6$	104.9	unable to run			
Sample Irradiated in Butadiene-H_2O-200 cm.^{3}/min.					
$1.56x10^5$	0.6	7.26	25.2	31.2	0.59
$3.12x10^5$	1.7	7.33	26.7	35.5	0.59
$6.24x10^5$	3.4	6.77	25.3	32.4	0.56
$1.25x10^6$	6.6	6.99	24.1	31.0	0.52

TABLE V. Physical Properties of Polypropylene Yarn

Dose in Rads	Weight Gain in Percent	Strength in Gm/Denier	Elongation in Percent	Modulus in Gm/Denier/ Unit Elong.	Proportional Limit in Gm/Denier
Control - Unirradiated					
0	0	6.95	26.2	42.8	3.68
Control - Irradiated in N_2-1000 cm.^{3}/min.					
1.56×10^5	0	7.13	23.5	43.7	4.00
3.12×10^5	0	6.05	20.6	39.5	3.63
6.24×10^5	0	5.81	20.3	38.2	3.48
1.25×10^6	0	6.42	20.8	40.2	3.79
Control - Irradiated in N_2-H_2O-1000 cm.^{3}/min.					
1.56×10^5	0	6.07	25.9	36.0	3.35
3.12×10^5	0	7.14	24.4	41.8	4.33
6.24×10^5	0	6.13	22.0	37.6	3.79
1.25×10^6	0	5.68	19.2	39.9	3.74

TABLE VI. Physical Properties of Grafted Polypropylene

Dose in Rads	Weight Gain in Percent	Strength in Gm/Denier	Elongation in Percent	Modulus in Gm/Denier/ Unit Elong.	Proportional Limit in Gm/Denier
Sample - Irradiated in Acrylonitrile N_2-H_2O 1000 cm.^{3}/min.					
1.56x10^5	1.1	6.75	22.8	42.5	3.74
3.12x10^5	2.3	7.21	26.8	42.0	3.81
6.24x10^5	4.0	6.30	23.4	37.1	3.54
1.25x10^6	7.4	4.88	18.8	33.9	2.86
Sample - Irradiated in Ethyl Acrylate -N_2-H_2O-1000 cm.^{3}/min.					
1.56x10^5	2.5	6.61	22.9	40.5	3.98
3.12x10^5	4.5	6.83	26.2	38.4	4.07
6.24x10^5	17.7	5.97	27.5	30.2	3.80
1.25x10^6	63.2	unable to run			
Sample - Irradiated in Methyl Acrylate-N_2-H_2O-1000 cm.^{3}/min.					
1.56x10^5	4.3	6.55	25.3	38.5	3.95
3.12x10^5	11.1	6.97	27.8	37.2	4.22
6.24x10^5	54.5	5.10	29.8	22.9	3.46
1.25x10^6	182.2	unable to run			
Sample - Irradiated in Butadiene-H_2O-200 Cm.^{3}/min.					
1.56x10^5	1.5	6.18	20.7	41.2	3.93
3.12x10^5	3.0	6.25	21.4	38.3	4.30
6.24x10^5	5.0	6.65	23.7	37.3	4.73
1.25x10^6	7.4	6.64	26.0	34.5	4.80

TABLE VII. Moisture Regain of Grafted Acetate Yarn

Sample	Radiation Time	Percent Regain	Percent Regain Based on Ungrafted Sample
Control	0	5.8	5.8
Irradiated in N_2-H_2O-1000 cc/min.	1/2 hour	6.2	6.2
	1	5.9	5.9
	2	5.9	5.9
	4	5.0	5.0
	Polymer Content		
Grafted with Acrylonitrile	9.4 percent	4.4	4.8
	16.5	4.1	4.8
	24.2	3.8	4.7
	43.3	3.3	4.7
Graded with Ethyl Acrylate	10.9 percent	3.6	4.0
	23.1	2.8	3.4
	47.4	2.3	3.4
	107.3	1.7	3.5
Grafted with Methyl Acrylate	23.2 percent	2.9	3.6
	36.3	2.4	3.3
	59.3	2.0	3.2
	106.1	1.6	3.3
Grafted with Butadiene	3.6 percent	4.0	4.1
	11.1	3.4	3.8
	22.6	3.1	3.8
	33.3	3.0	4.0

TABLE VIII. Moisture Regain of Grafted Nylon Yarn

Sample	Radiation Time	Percent Regain	Percent Regain Based on Ungrafted Sample
Control	0	3.8	3.8
Irradiated in N_2-H_2O	1/2 hour	3.8	3.8
	1	4.4	4.4
	2	3.7	3.7
	4	3.8	3.8
	Polymer Content		
Grafted with Acrylonitrile	2.7 percent	3.1	3.2
	4.0	3.5	3.6
	5.4	3.3	3.5
	7.4	3.4	3.7
Grafted with Ethyl Acrylate	0.5 percent	3.5	3.5
	1.0	3.7	3.7
	9.5	3.3	3.6
	44.7	2.7	3.9
Grafted with Methyl Acrylate	1.2 percent	3.8	3.8
	5.3	3.7	3.9
	26.2	3.1	3.9
	104.9	2.3	4.7
Grafted with Butadiene	0.6 percent	3.4	3.4
	1.7	3.5	3.6
	3.4	3.3	3.4
	6.6	3.4	3.6

TABLE IX. Moisture Regain of Grafted Polypropylene Yarn

Sample	Radiation Time	Percent Regain	Percent Regain Based on Ungrafted Sample
Control	0	0.1	0.1
Irradiated in N_2-H_2O-1000 cc/min.	1/2 hour	0.1	0.1
	1	0.2	0.2
	2	0.2	0.2
	4	0.2	0.2
	Polymer Content		
Grafted with Acrylonitrile	1.1 percent	0.1	0.1
	2.3	0.1	0.1
	4.0	0.1	0.1
	7.4	0.1	0.1
Grafted with Ethyl Acrylate	2.5 percent	0.2	0.2
	4.5	0.1	0.1
	17.7	0.2	0.2
	63.2	0.3	0.5
Grafted with Methyl Acrylate	4.3 percent	0.0	0.0
	11.1	0.1	0.1
	54.5	0.2	0.3
	182.2	0.6	1.7
Grafted with Butadiene	1.5	0.4	0.4
	3.0	0.3	0.3
	5.0	0.2	0.2
	7.4	0.1	0.1

TABLE X. Solubility of Grafted Acetate Yarn in Acetone

Sample	Polymer Content	Solubility (Room Temperature)
Acrylonitrile	9.4 percent	Slowly soluble
	16.5	Insoluble overnight
	20.2	Insoluble overnight - swells
	43.3	Insoluble overnight - swells
Ethyl Acrylate	10.9 percent	Soluble
	23.1	Soluble
	47.4	Slowly soluble
	107.3	Slowly soluble
Methyl Acrylate	23.2 percent	Soluble
	36.3	Slowly soluble
	59.3	Slowly soluble
	106.1	Insoluble overnight - swells
Butadiene	3.6 percent	Soluble
	11.1	Soluble
	22.6	Partially soluble overnight - swells
	33.3	Partially soluble overnight - swells

TABLE XI. Solubility of Grafted Nylon Yarn in Formic Acid

Sample	Polymer Content	Solubility (Room Temperature)
Acrylonitrile	2.7 percent	Soluble
	4.0	Soluble when heated
	5.4	Soluble when heated
	7.4	Soluble when heated
Ethyl Acrylate	0.5 percent	Soluble
	1.0	Soluble
	9.5	Slowly soluble
	44.7	Partially soluble when heated
Methyl Acrylate	1.2 percent	Soluble
	5.3	Soluble
	26.2	Partially soluble when heated
	104.9	Partially soluble when heated
Butadiene	0.6	Soluble
	1.7	Soluble
	3.4	Partially soluble when heated
	6.6	Partially soluble when heated

TABLE XII. Solubility of Grafted Polypropylene Yarn in Boiling Xylene

Sample	Polymer Content	Solubility
Acrylonitrile	1.1 percent	Partially soluble
	2.3	Partially soluble
	4.0	Partially soluble
	7.4	Partially soluble
Ethyl Acrylate	2.5 percent	Soluble
	4.5	Soluble
	17.7	Soluble
	63.2	Partially soluble
Methyl Acrylate	4.3 percent	Partially soluble
	11.1	Partially soluble
	54.5	Partially soluble
	182.2	Slightly soluble
Butadiene	1.5 percent	Soluble
	3.0	Partially soluble
	5.0	Partially soluble
	7.4	Slightly soluble

TABLE XIII. Weather Resistance of Cotton Grafted with Styrene

Sample	Styrene Added-Weight Percent	Unweathered		Weathered		Percent Strength Loss
		Breaking Strength-Pounds	Standard Deviation	Breaking Strength-Pounds	Standard Deviation	
1. Control	-	39.9	2.3	27.7	1.2	30.5
2. Control	-	-	-	25.5	1.5	37.3
3. Irradiated 4 hours in N_2	-	37.9	2.3	23.9	2.3	36.9
4. Irradiated 1 hour with Styrene	1.6	41.3	2.0	22.8	3.6	44.7
5. Irradiated 2 hours with Styrene	2.3	42.1	2.3	24.6	1.4	41.7
6. Irradiated 3 hours with Styrene	5.0	40.7	2.9	26.1	1.9	35.9
7. Irradiated 4 hours with Styrene	5.9	39.9	2.1	22.6	2.6	43.4

TABLE XIV. Weather Resistance of Nylon Grafted with Styrene

Sample	Styrene Added-Weight Percent	Unweathered Breaking Strength-Pounds	Unweathered Standard Deviation	Weathered Breaking Strength-Pounds	Weathered Standard Deviation	Percent Strength Loss
1. Control	-	44.5	2.0	2.9	0.6	93.5
2. Control	-	-	-	1.8	0.5	96.0
3. Irradiated 4 hours in N_2	-	40.3	1.1	1.5	0.3	96.4
4. Irradiated 1 hours with Styrene	4.6	43.3	2.3	9.5	1.7	78.1
5. Irradiated 2 hours with Styrene	7.2	42.8	4.0	10.3	0.9	76.0
6. Irradiated 3 hours with Styrene	8.3	41.4	2.3	12.4	1.7	70.0
7. Irradiated 4 hours with Styrene	11.7	45.6	1.3	15.7	1.1	65.6

TABLE XV. Weather Resistance of Polypropylene Grafted with Styrene

Sample	Styrene Added-Weight Percent	Unweathered		Weathered		Percent Strength Loss
		Breaking Strength-Pounds	Standard Deviation	Breaking Strength-Pounds	Standard Deviation	
1. Control	-	108.4	3.7	4.7	0.2	95.7
2. Irradiated 4 hours in N_2	-	92.0	3.0	1.4	0.6	98.5
3. Irradiated 1 hour in Styrene	0.0	109.1	3.2	3.6	0.2	96.0
4. Irradiated 2 hours in Styrene	0.8	99.0	5.3	4.4	0.4	95.6
5. Irradiated 3 hours in Styrene	0.8	92.9	4.3	4.5	0.2	95.2
6. Irradiated 4 hours in Styrene	1.8	97.1	1.6	6.9	1.6	92.9

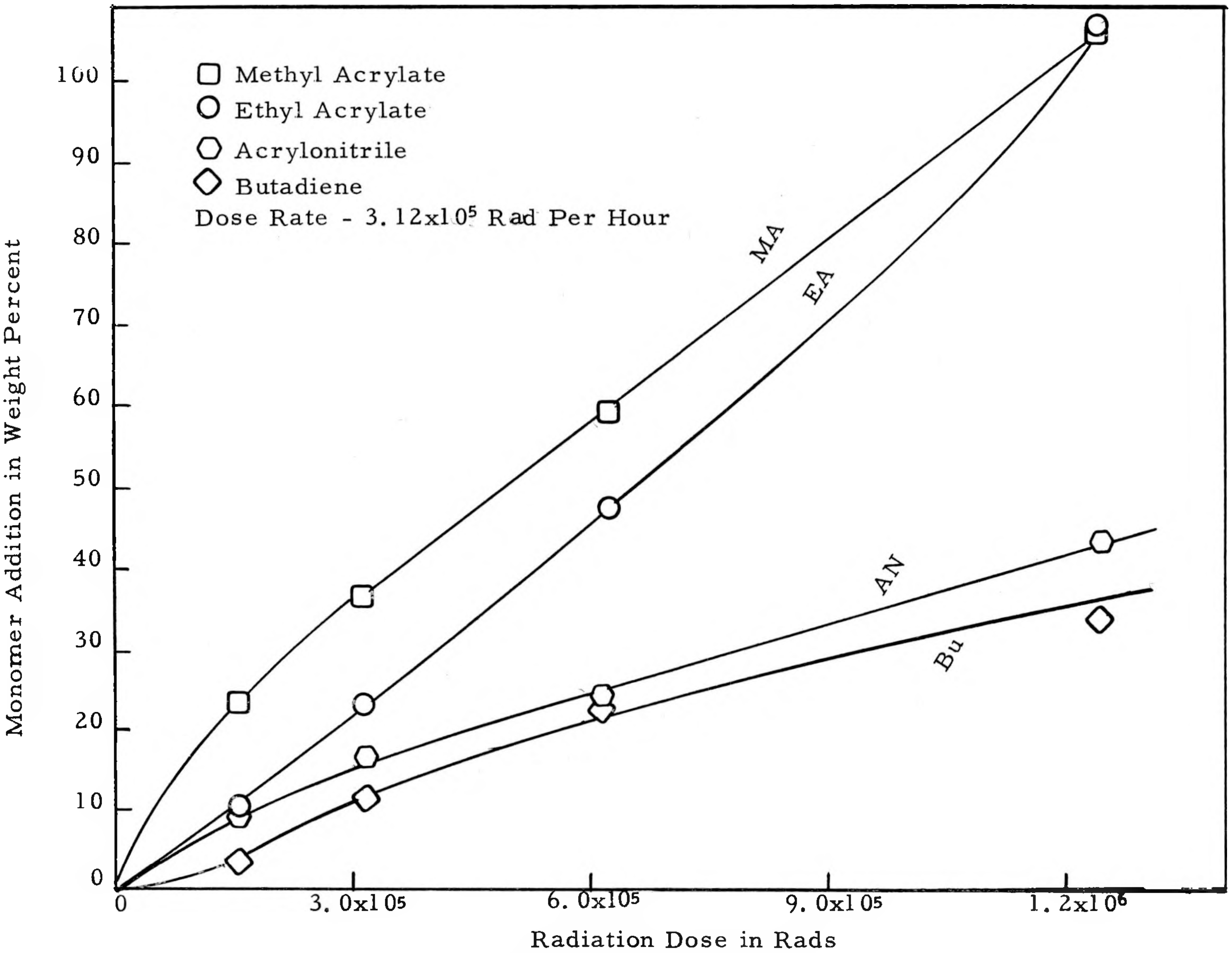


Figure 1. Addition of Monomers to Acetate Yarn

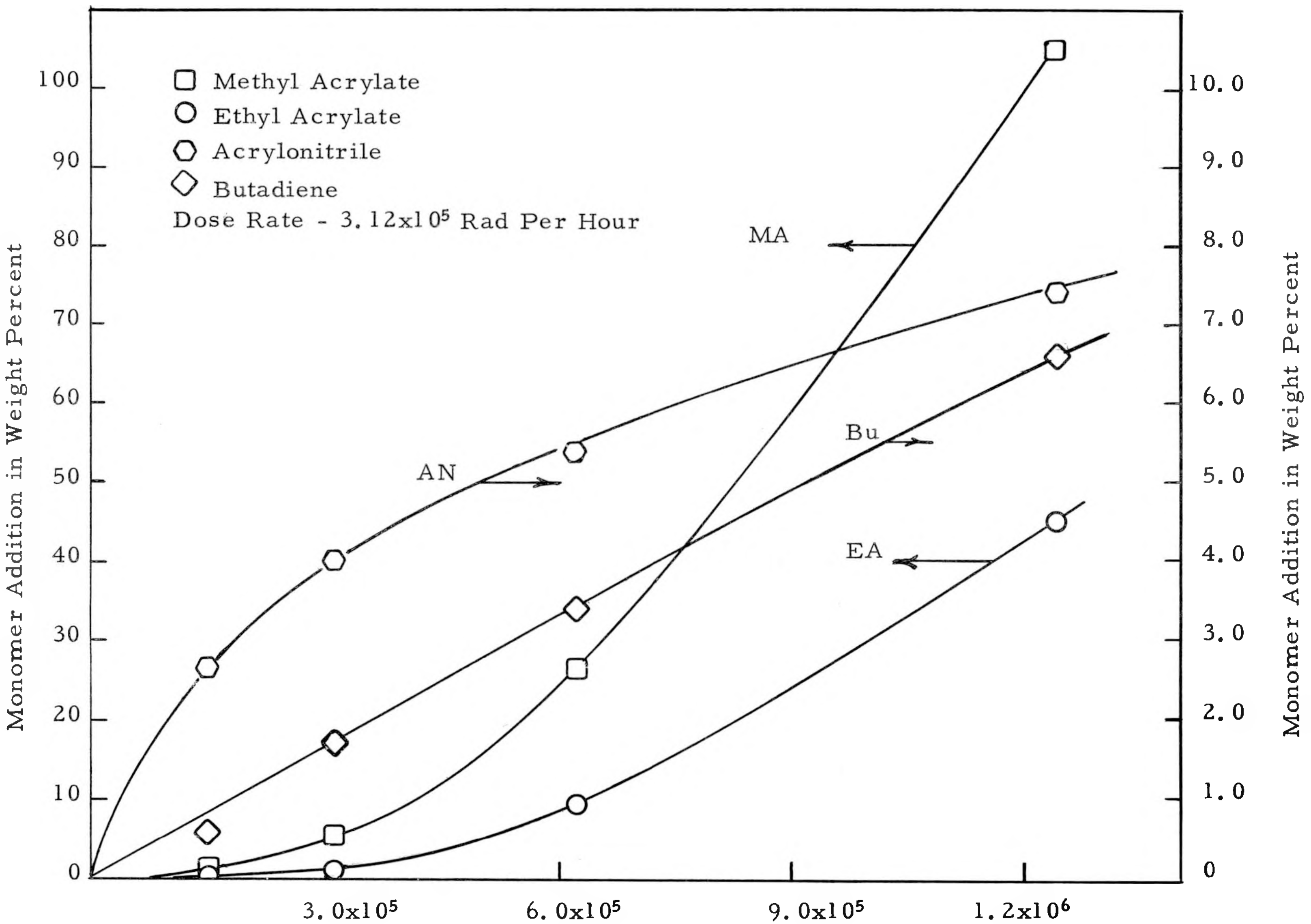


Figure 2. Addition of Monomers to Nylon Yarn

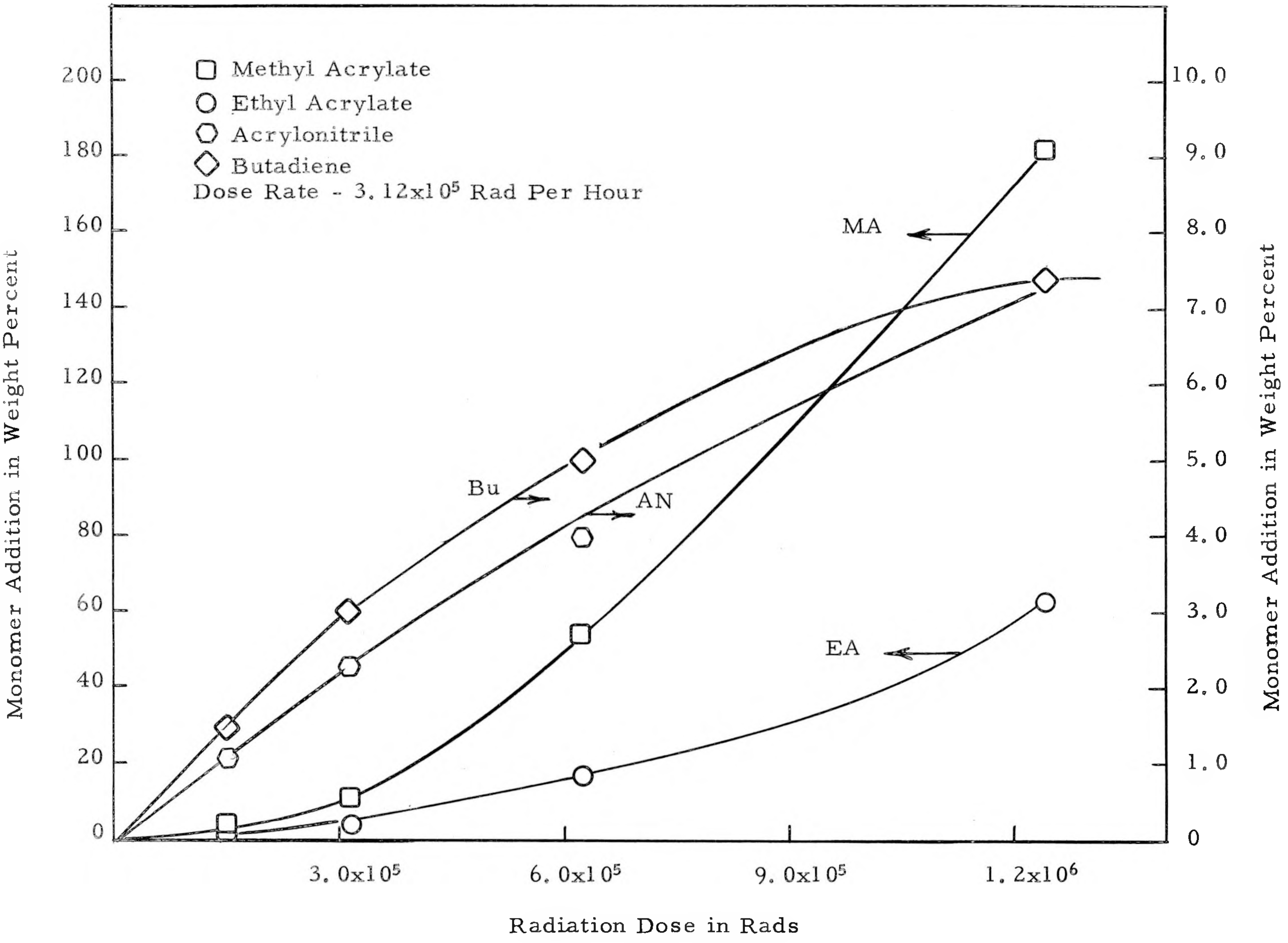


Figure 3. Addition of Monomers to Polypropylene Yarn

Figure 4. Stress-Strain Curve for Acetate Fiber
Unirradiated Control

Arbitrary Units

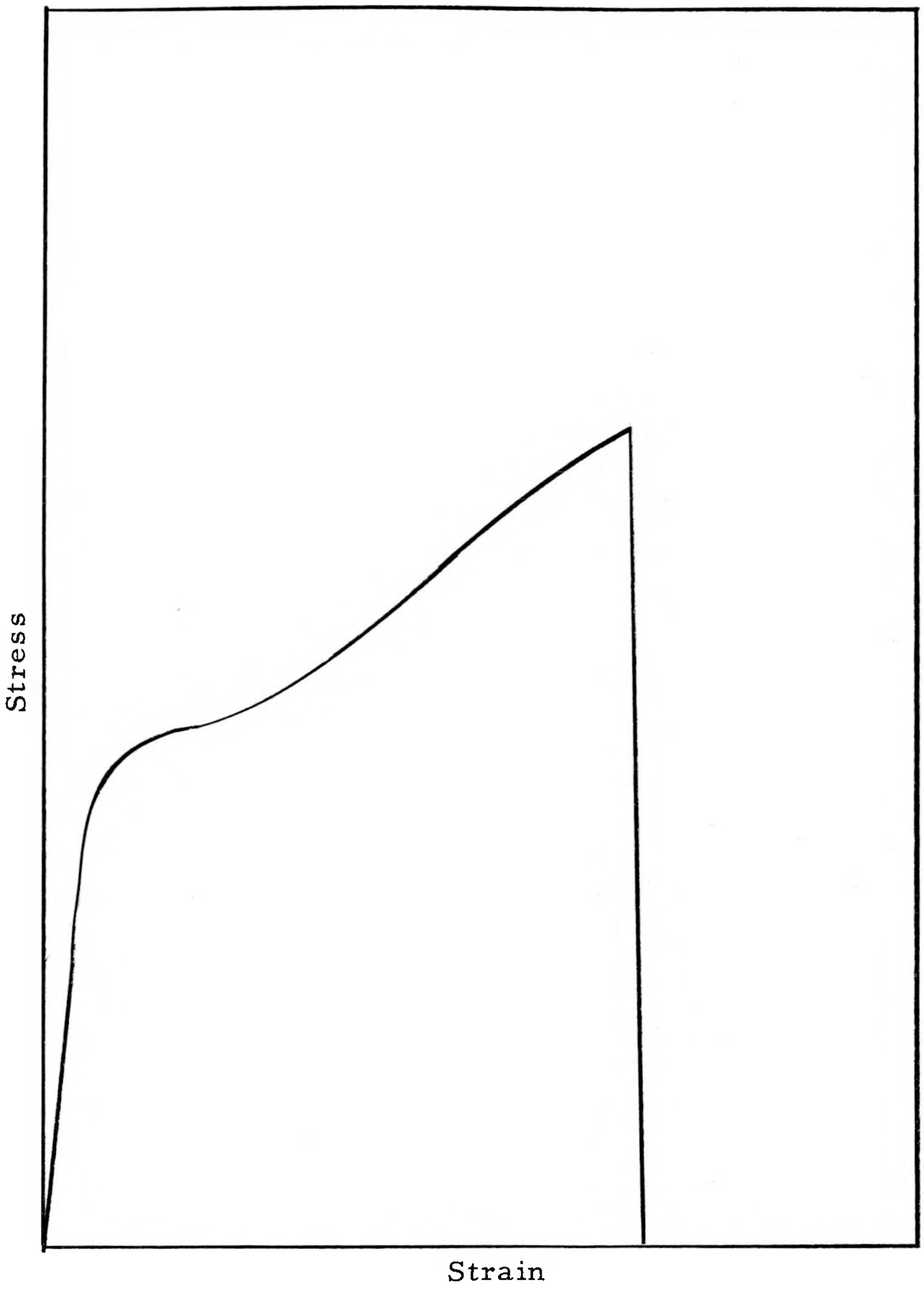


Figure 5. Stress-Strain Curves for Acetate Fiber Grafted with Methyl Acrylate

Arbitrary Units

Curve	Percent Graft
A.	23.2
B.	36.3
C.	59.3
D.	106.1

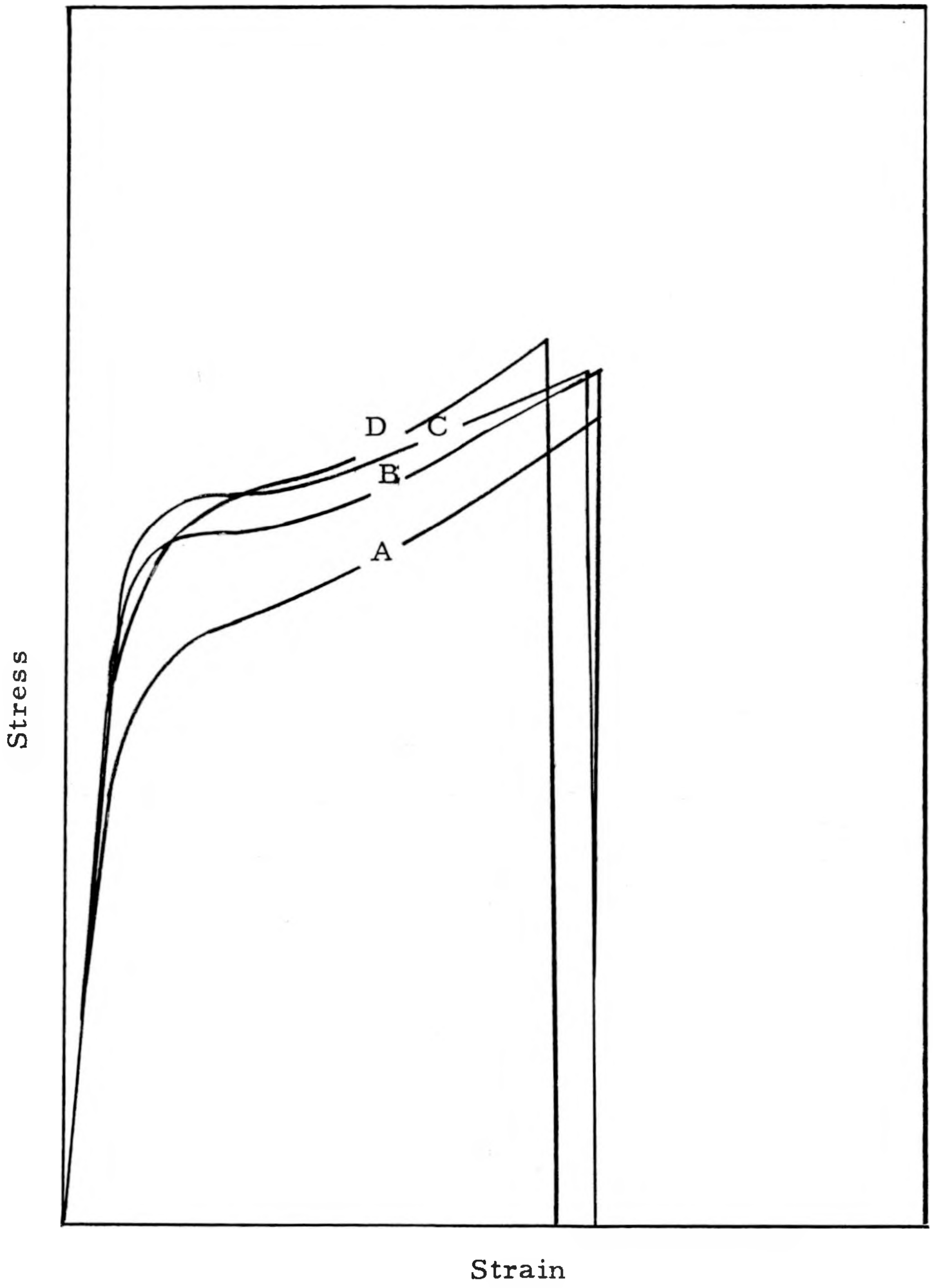


Figure 6. Stress-Strain Curves for Acetate Fiber Grafted with Ethyl Acrylate

Arbitrary Units

Curve	Percent Graft
A.	10.9
B.	23.1
C.	47.4
D.	107.3

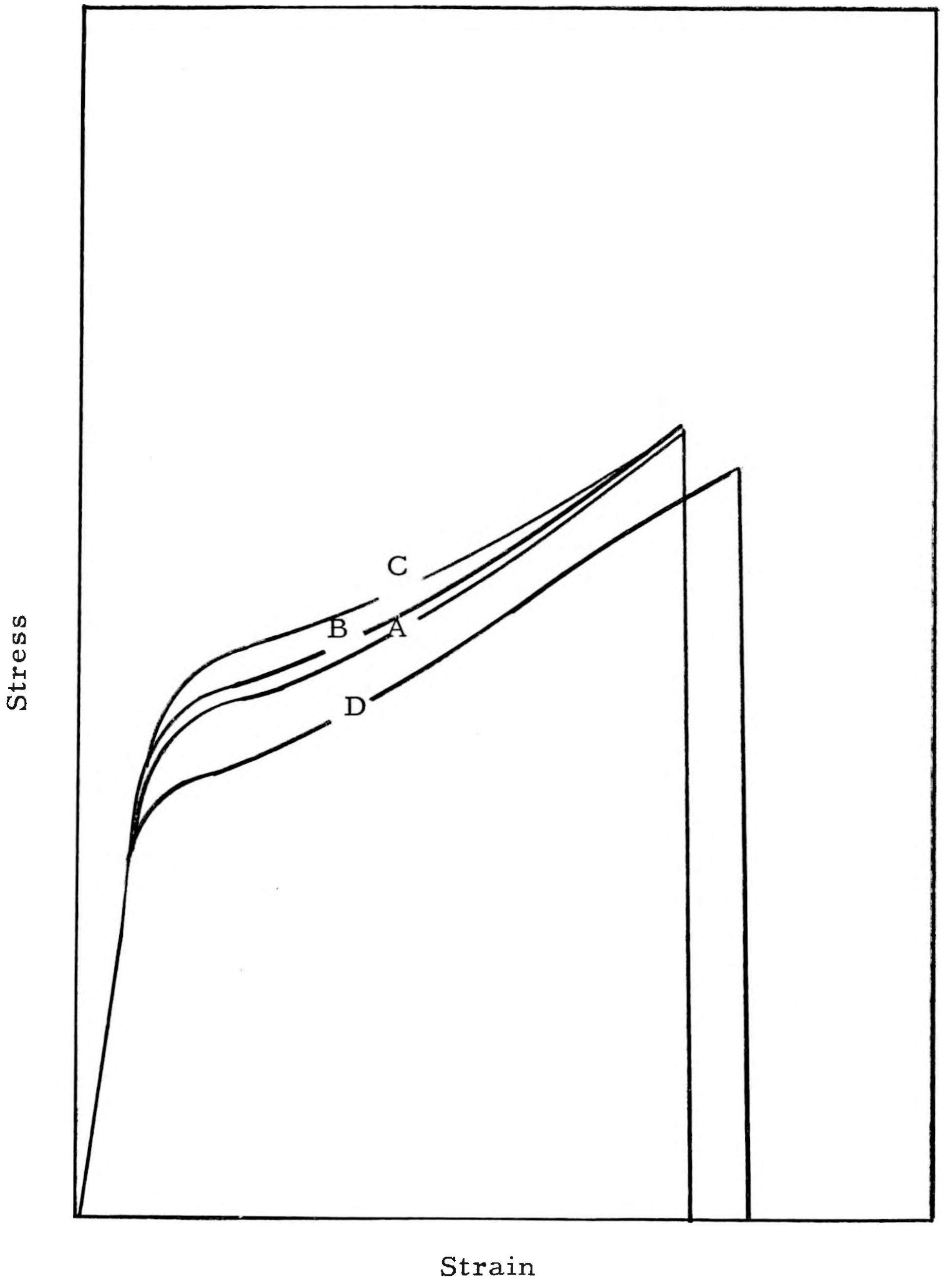


Figure 7. Stress-Strain Curves for Acetate Fiber Grafted with Butadiene

Arbitrary Units

Curve	Percent Graft
A.	3.6
B.	11.1
C.	22.6
D.	33.3

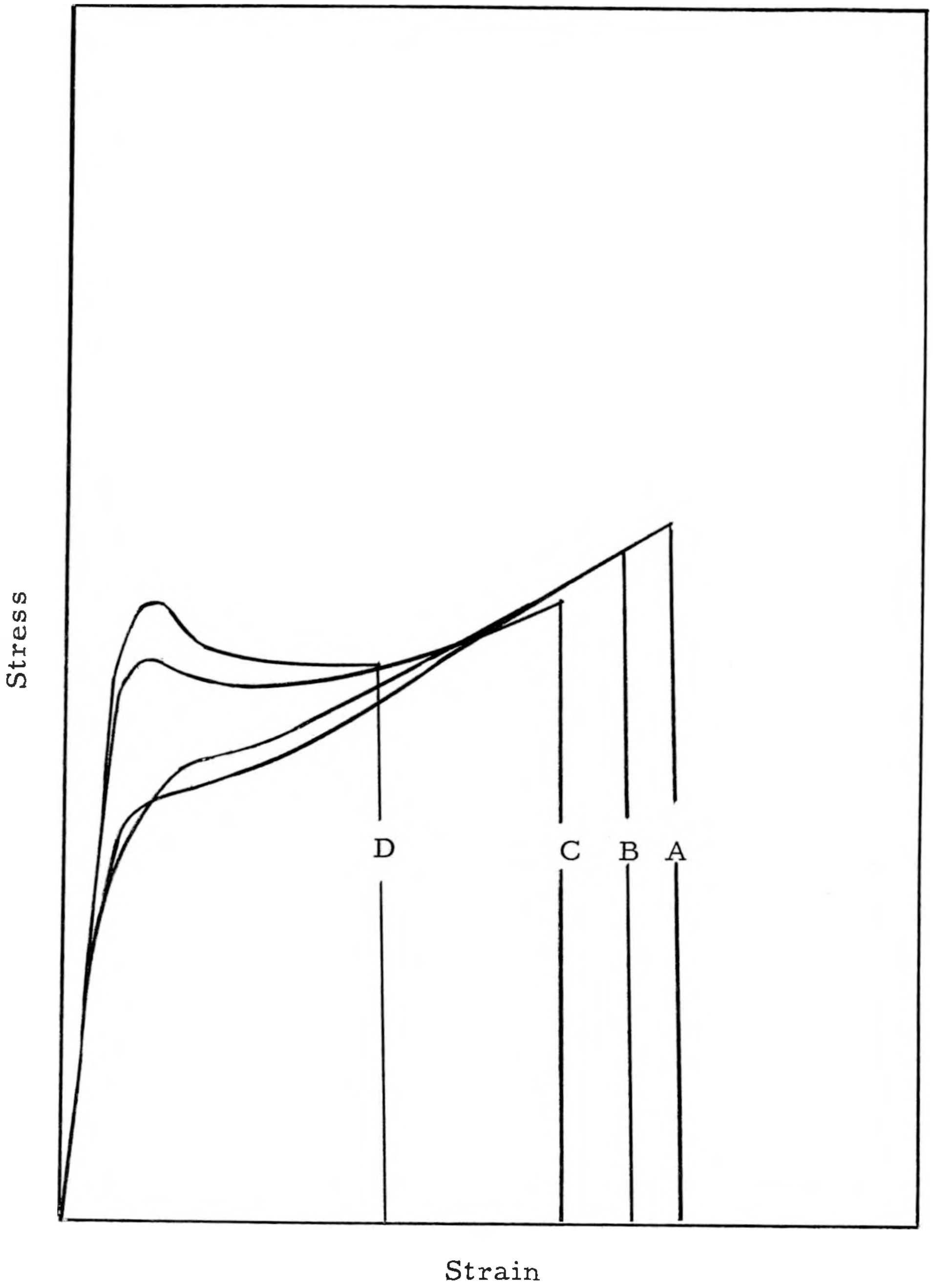


Figure 8. Stress-Strain Curves for Acetate Fiber Grafted with Acrylonitrile

Arbitrary Units

Curve	Percent Graft
A.	9.4
B.	16.5
C.	24.2
D.	43.3

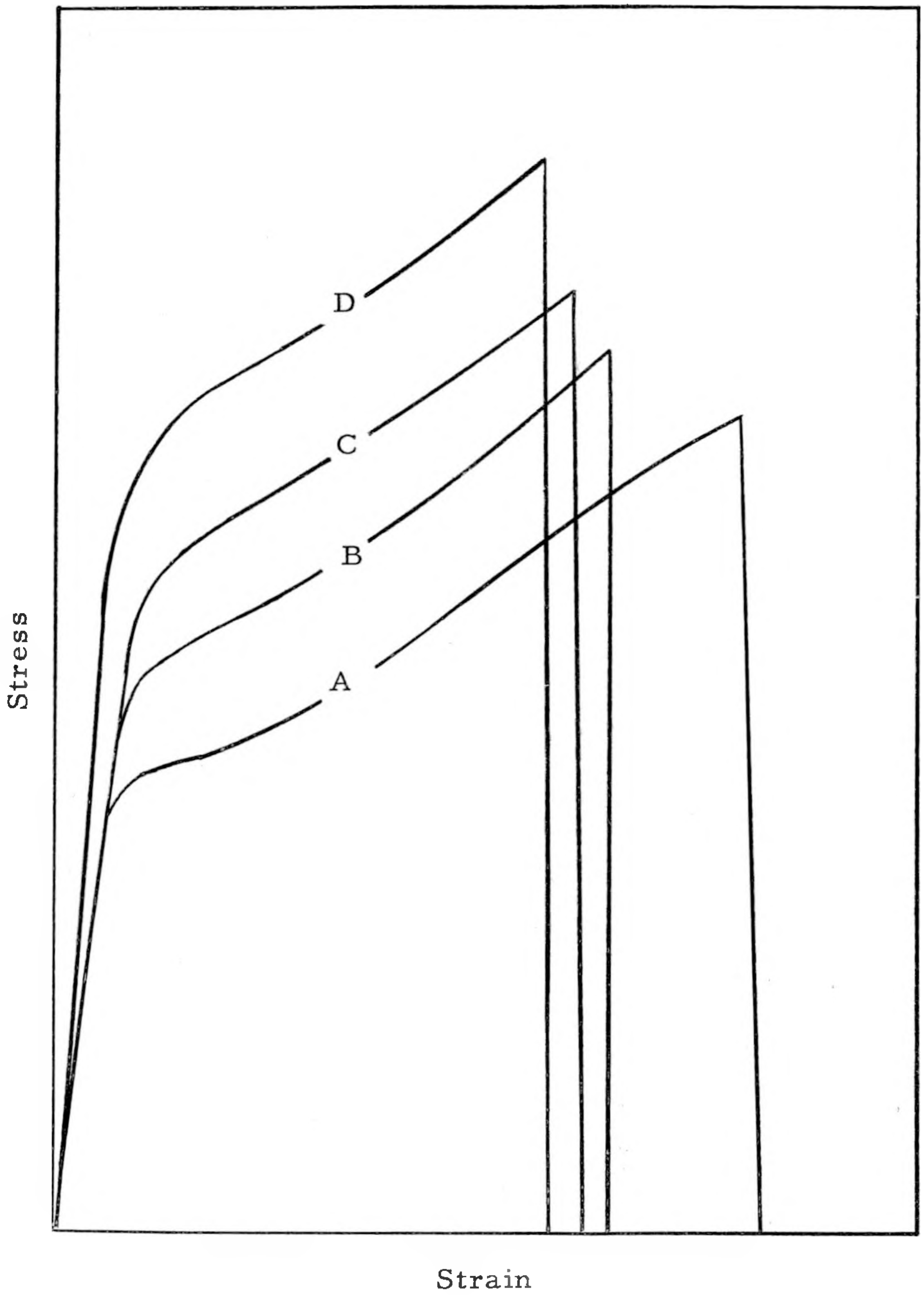


Figure 9. Stress-Strain Curve for Nylon Fiber Unirradiated Control

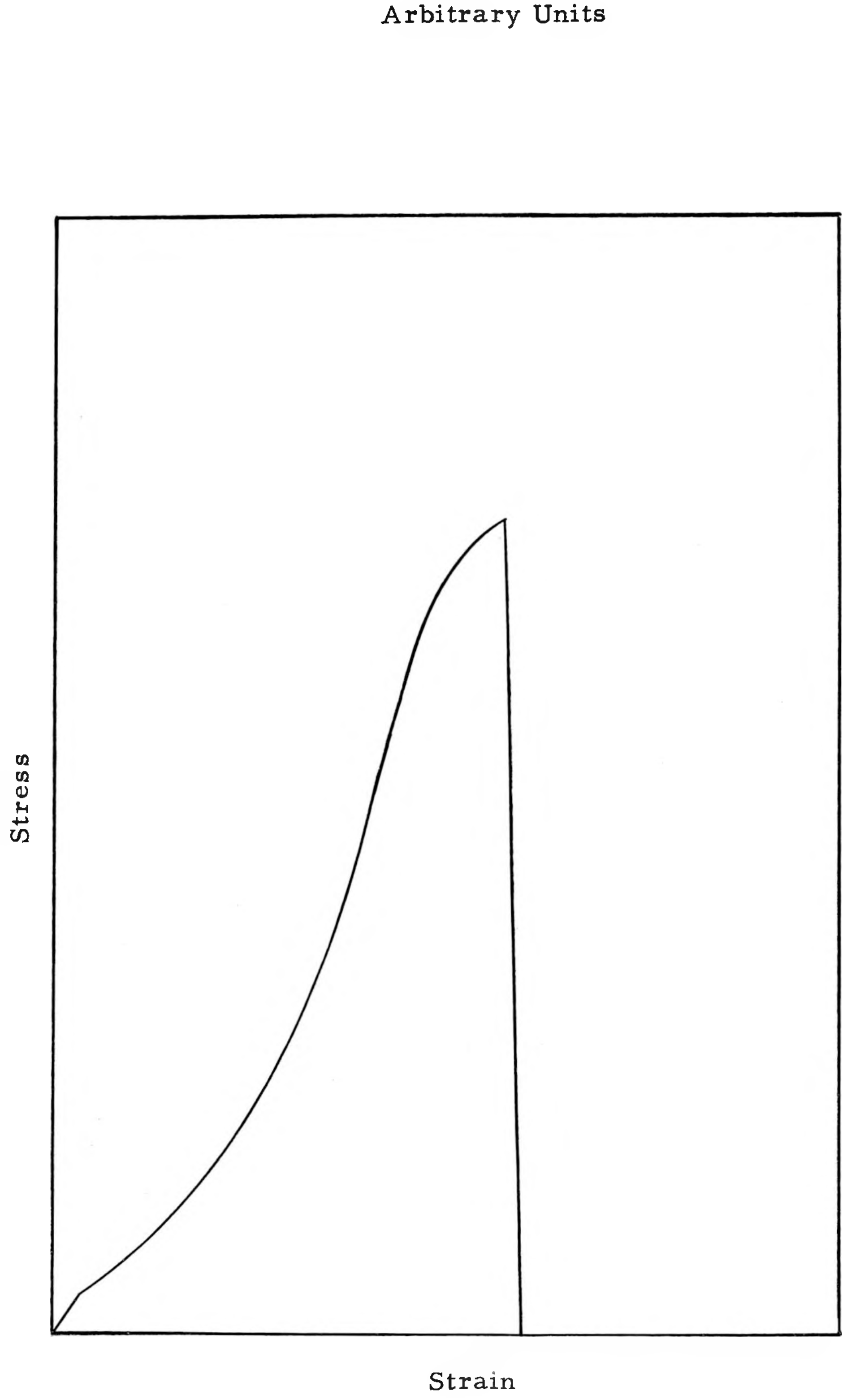


Figure 10. Stress-Strain Curve for Nylon Fiber Grafted with Methyl Acrylate

Arbitrary Units

Curve	Percent Graft
A.	1.2
B.	5.3
C.	26.2

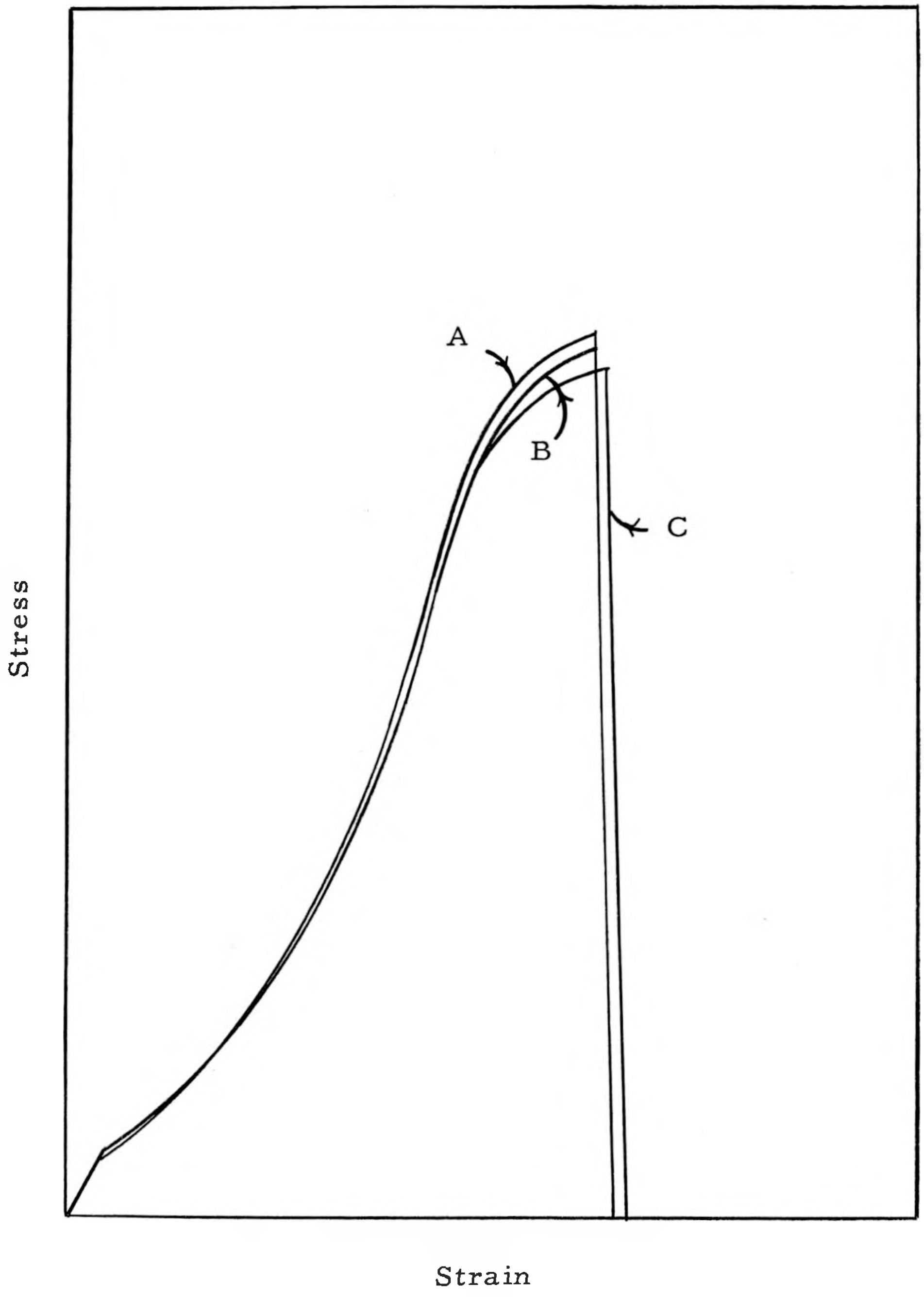


Figure 11. Stress-Strain Curve for Nylon Fiber Grafted with Ethyl Acrylate

Arbitrary Units

Curve	Percent Graft
A.	0.5
B.	1.0
C.	9.5

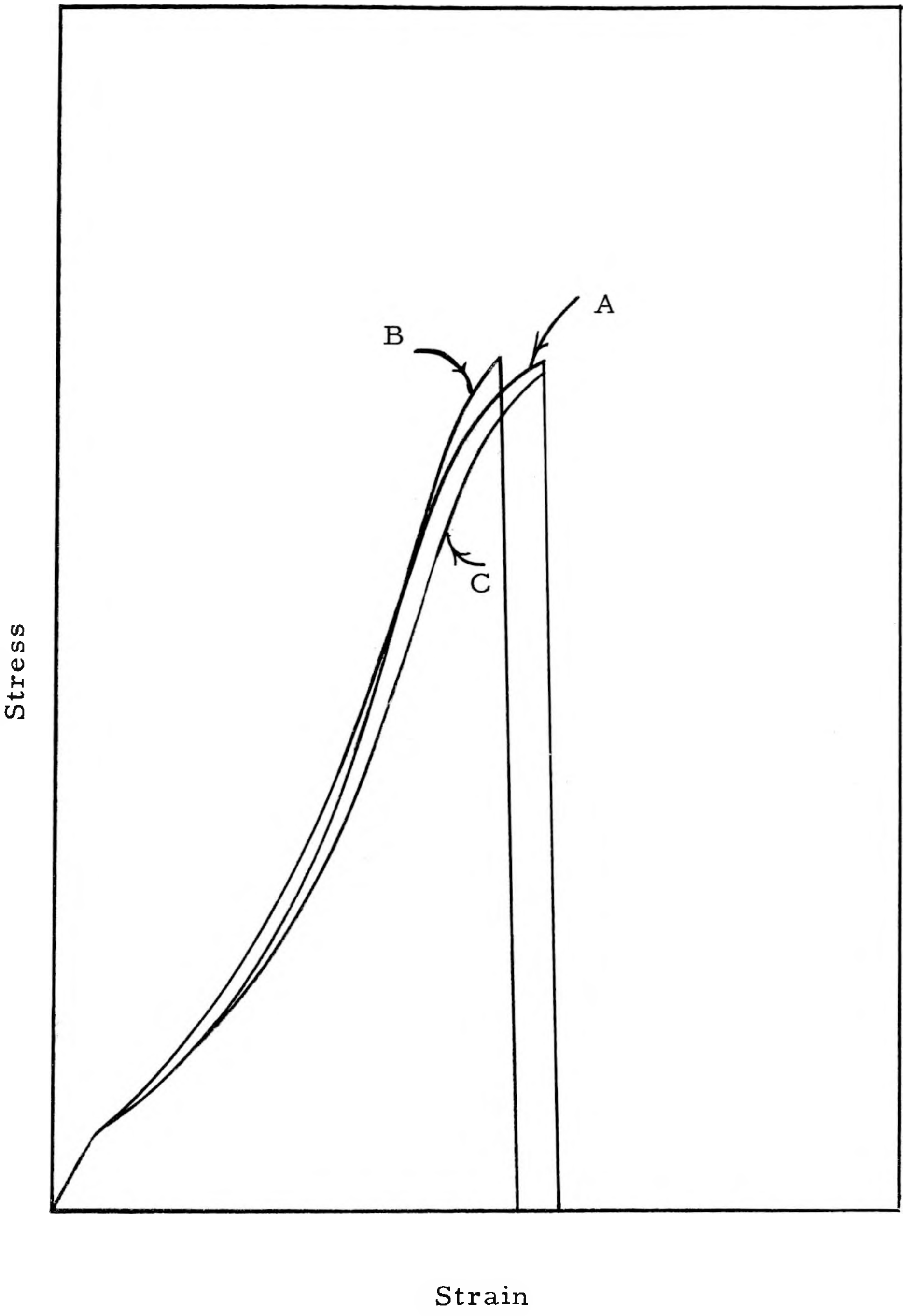


Figure 12. Stress-Strain Curves for Nylon Fiber Grafted with Butadiene

Arbitrary Units

Curve	Percent Graft
A.	0.6
B.	1.7
C.	3.4
D.	6.6

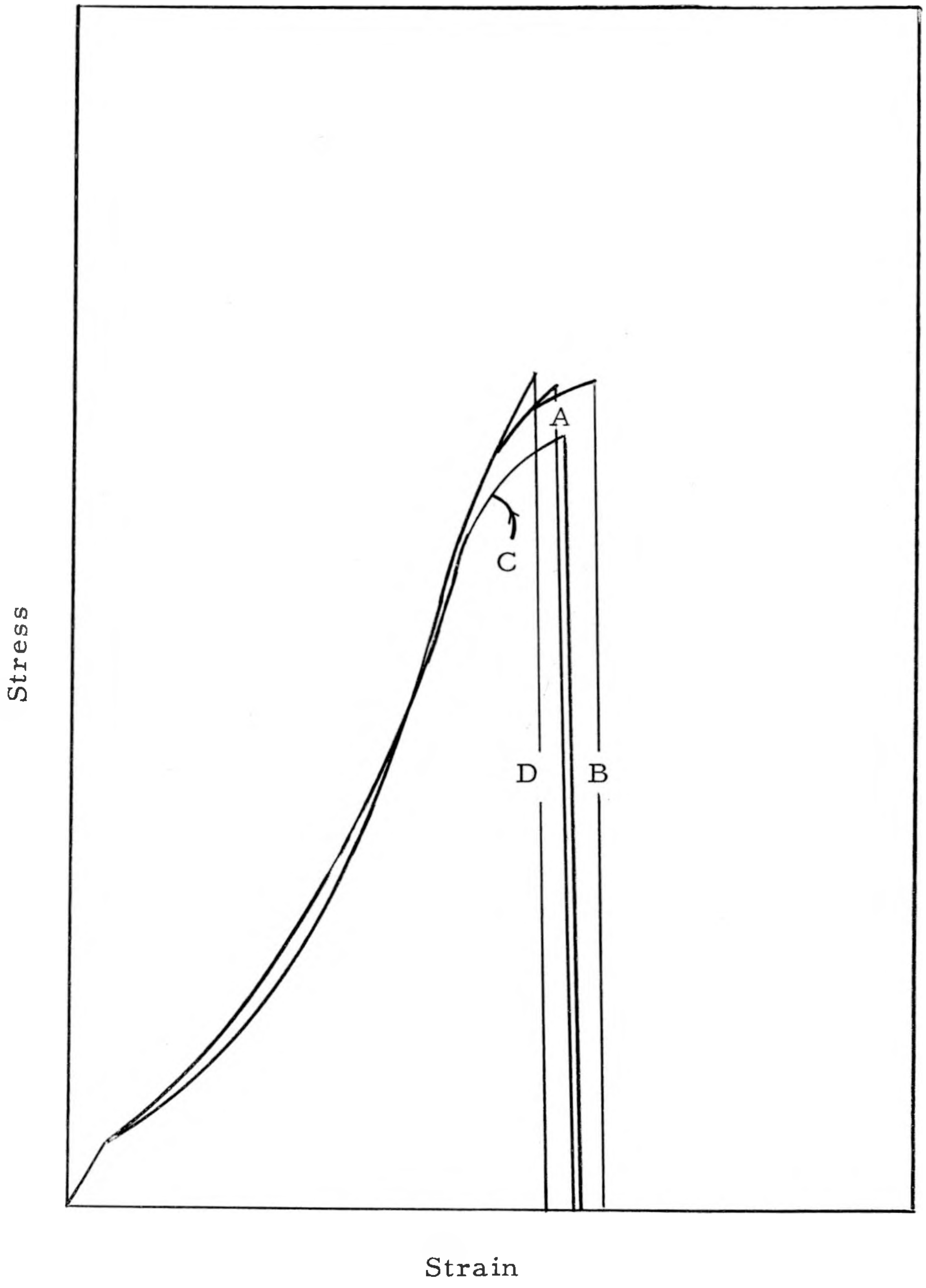


Figure 13. Stress-Strain Curves for Nylon Fiber Grafted with Acrylonitrile

Arbitrary Units

Curve	Percent Graft
A.	2.7
B.	4.0
C.	5.4
D.	7.4

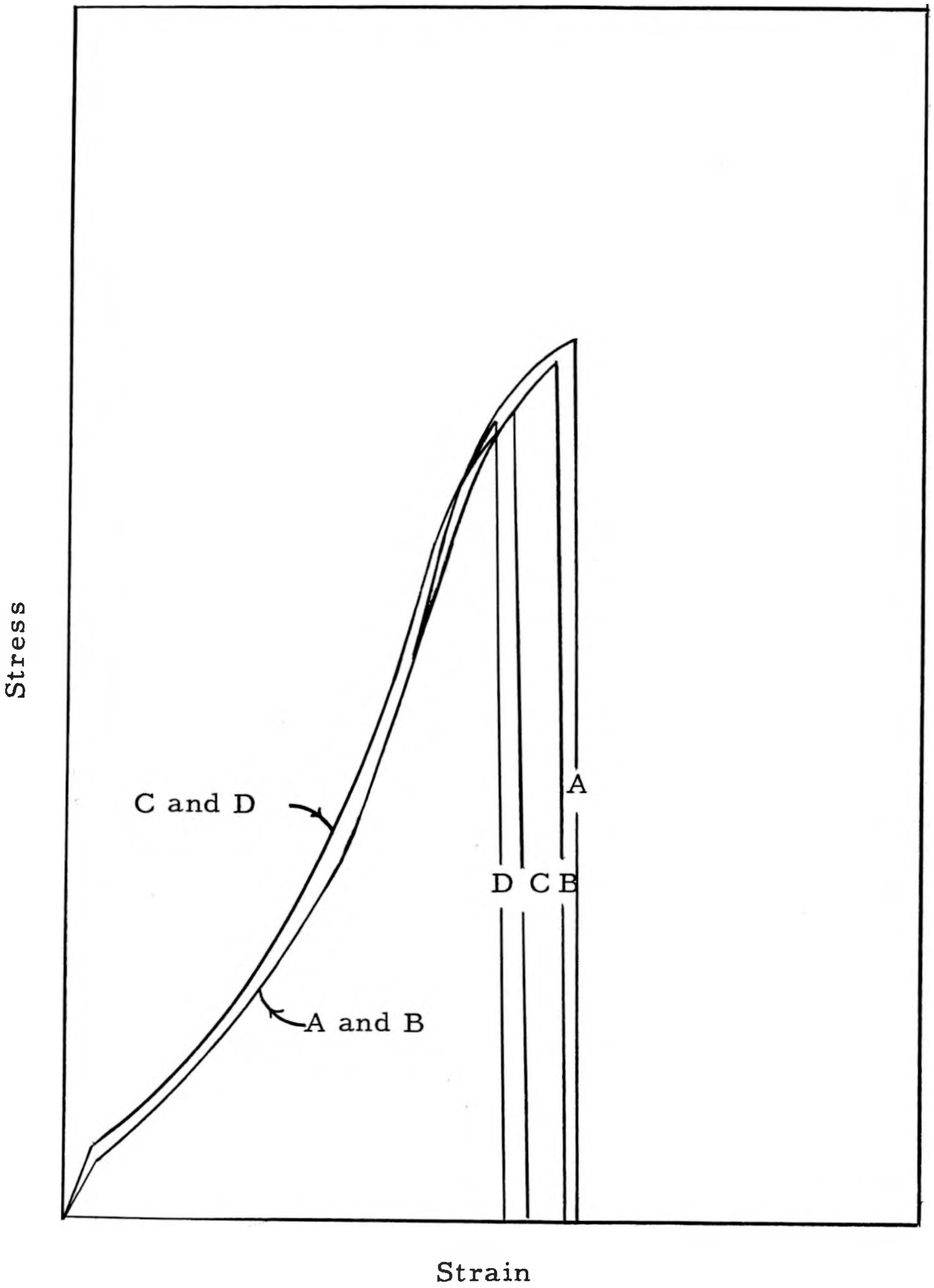


Figure 14. Stress-Strain Curve for Polypropylene Fiber Unirradiated Control

Arbitrary Units

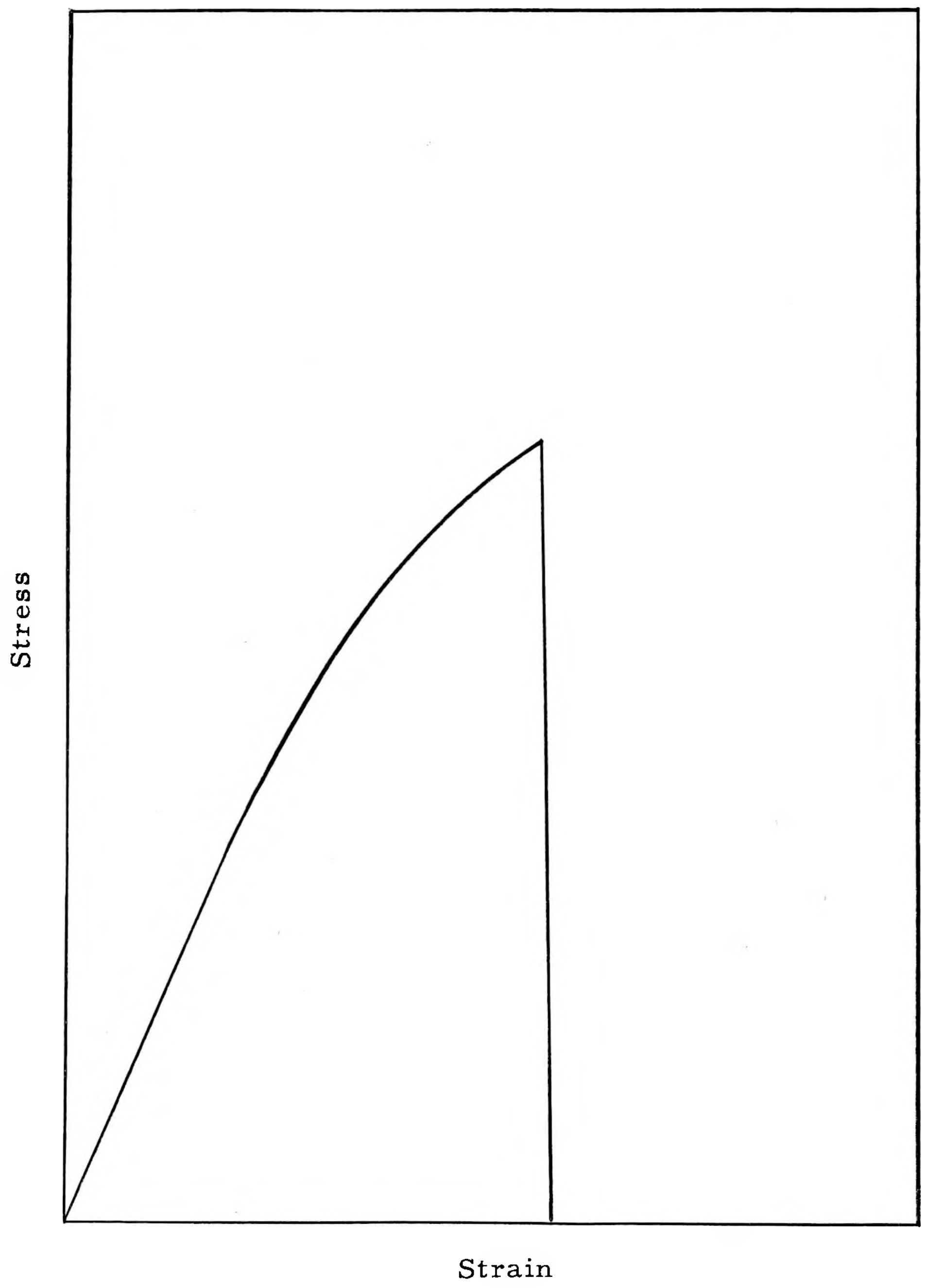


Figure 15. Stress-Strain Curve for Polypropylene Fiber Grafted with Methyl Acrylate

Arbitrary Units

Curve	Percent Graft
A.	4.3
B.	11.1
C.	54.5

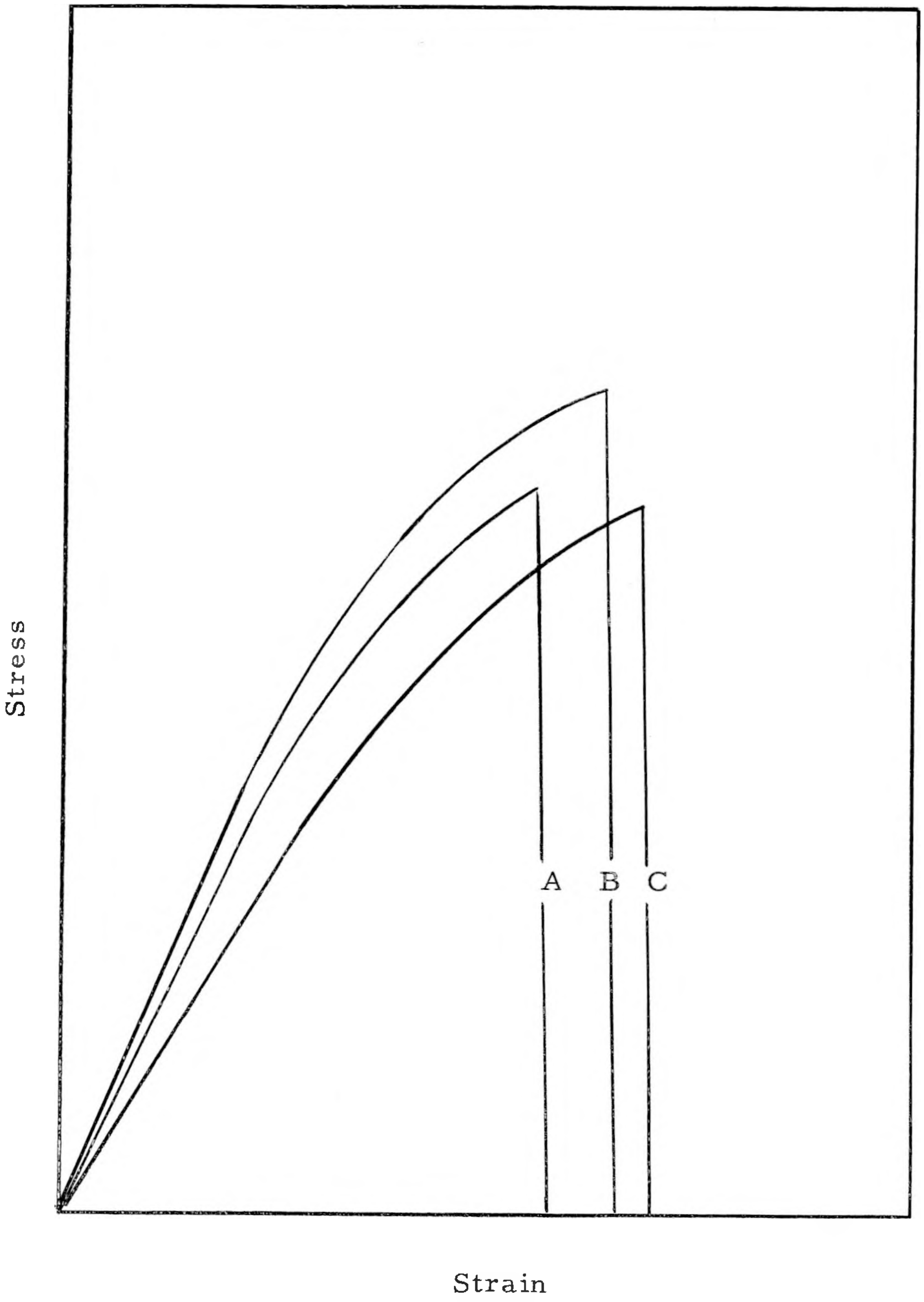


Figure 16. Stress-Strain Curves for Polypropylene Fiber Grafted with Ethyl Acrylate

Arbitrary Units

Curve	Percent Graft
A.	2.5
B.	4.5
C.	17.7

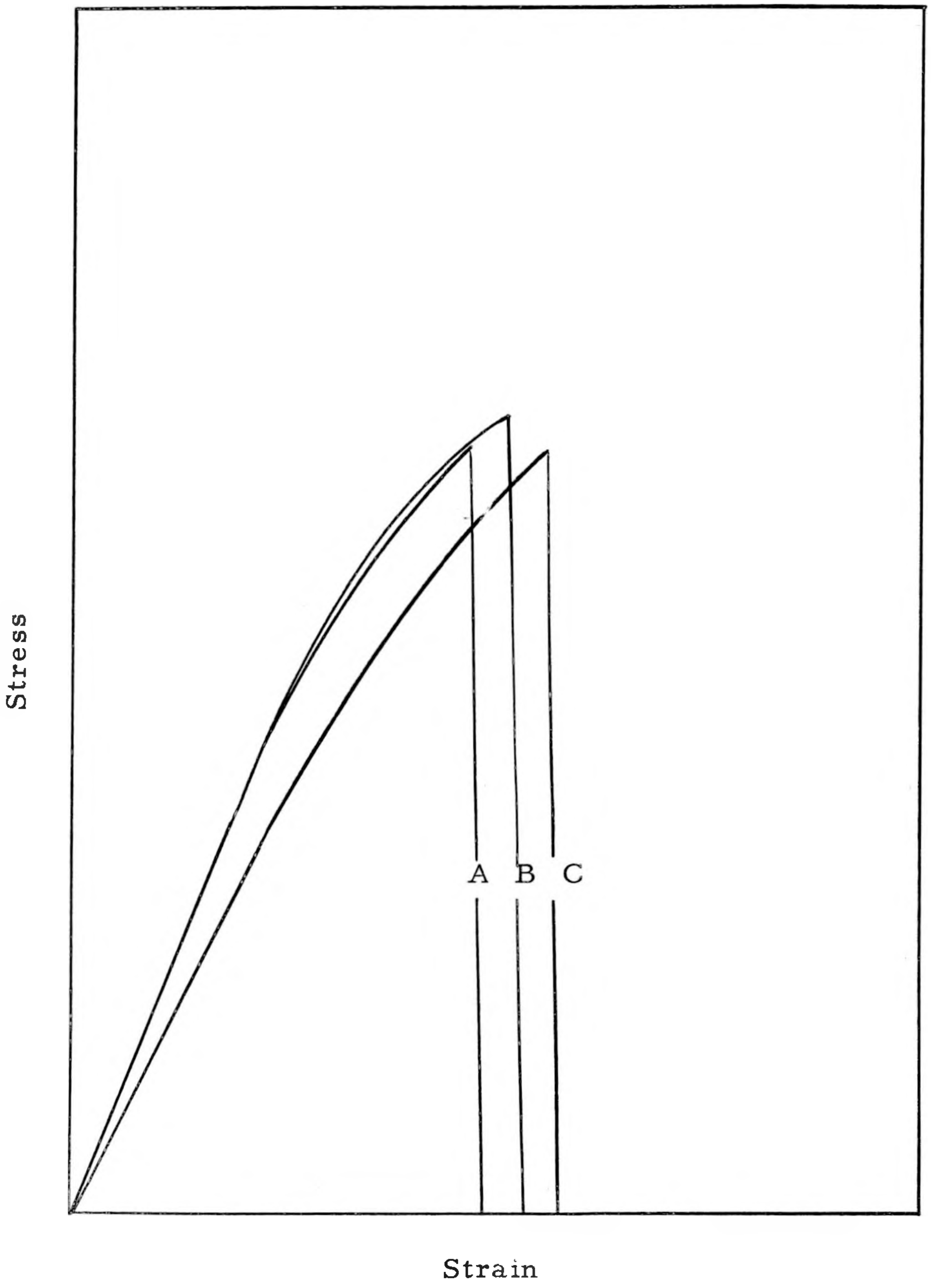


Figure 17. Stress-Strain Curves for Polypropylene Fiber Grafted with Butadiene

Arbitrary Units

Curve	Percent Graft
A.	1. 5
B.	3. 0
C.	5. 0
D.	7. 4

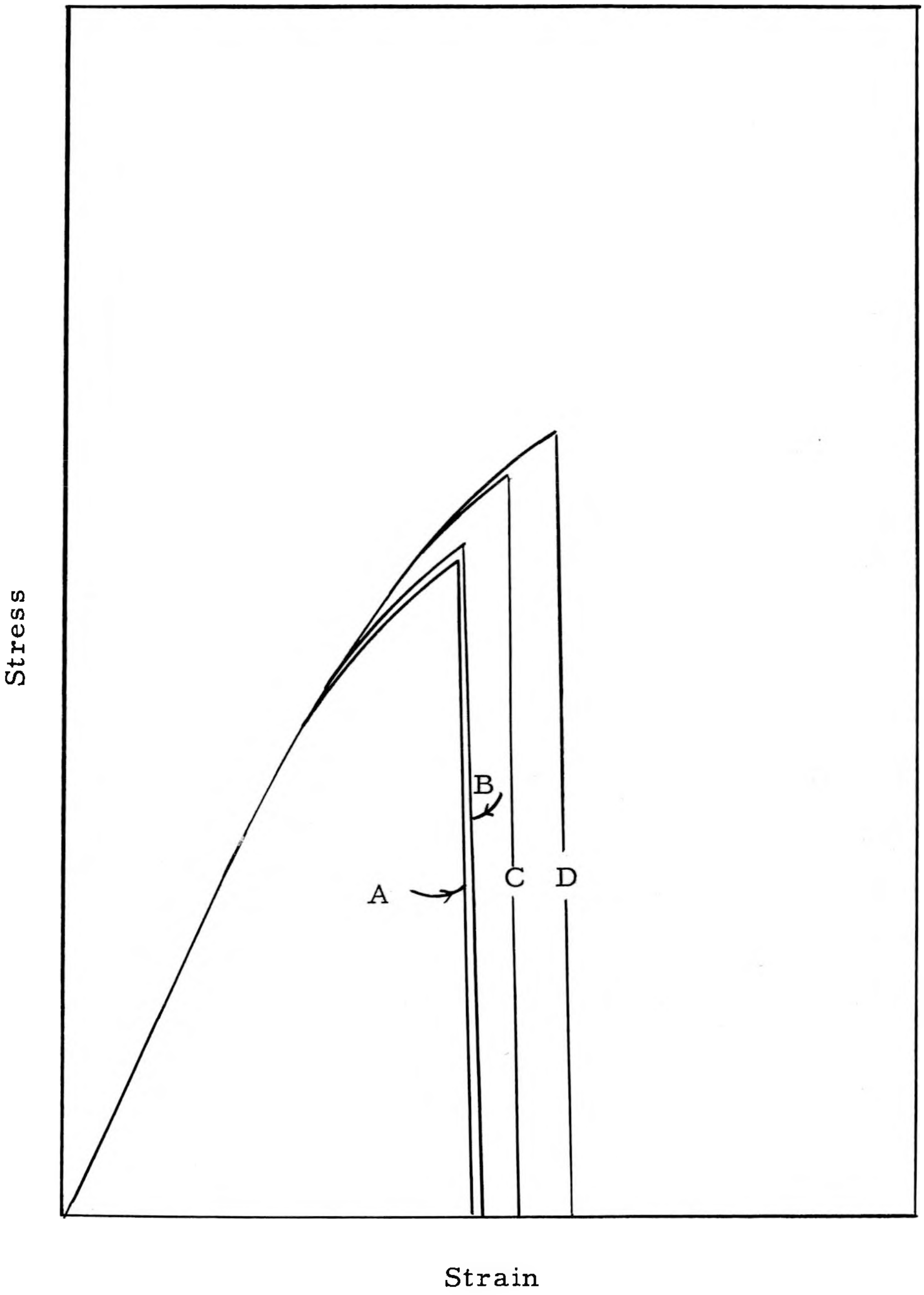
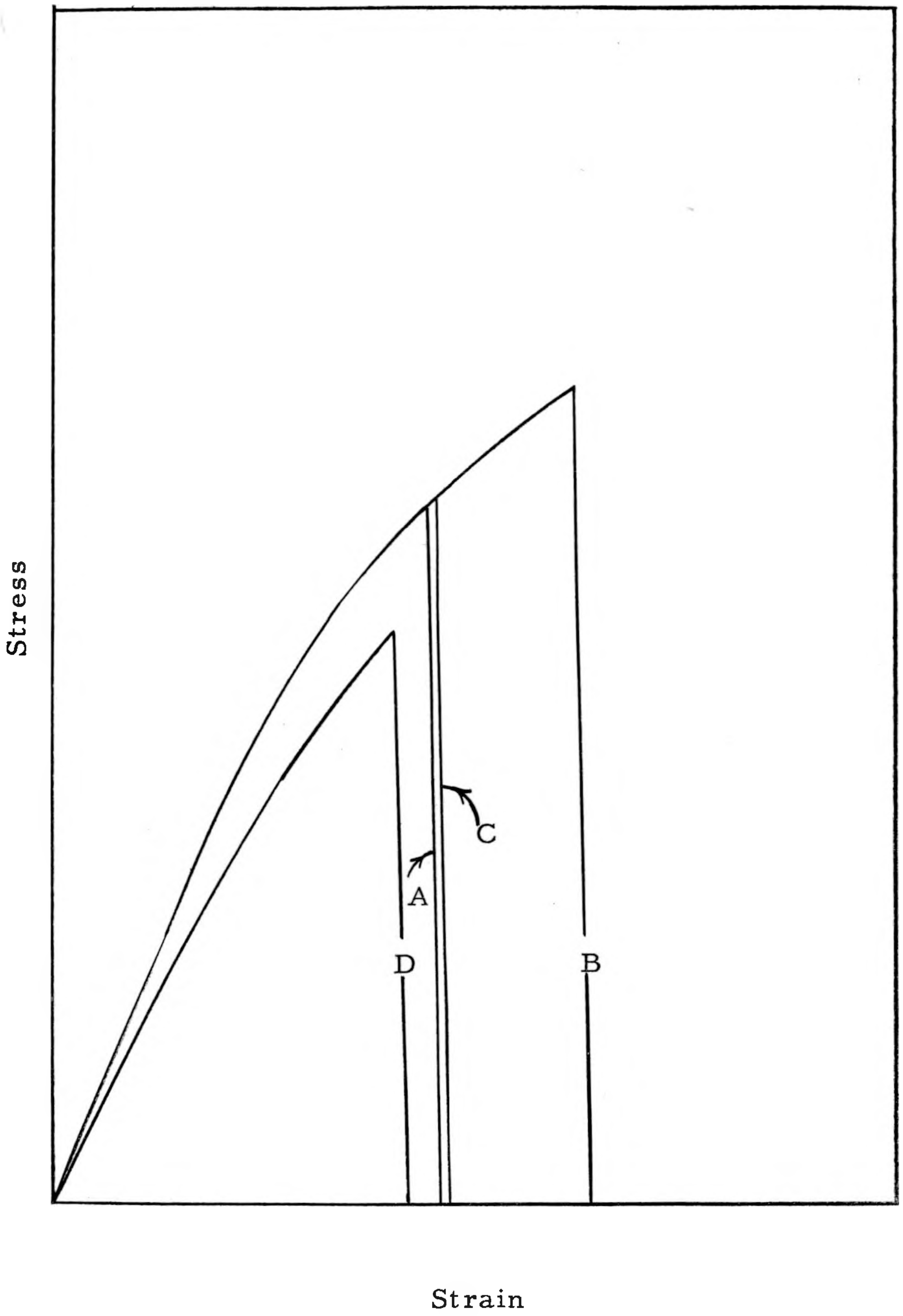


Figure 18. Stress-Strain Curves for Polypropylene Fiber Grafted with Acrylonitrile

Arbitrary Units

Curve	Percent Graft
A.	1.1
B.	2.3
C.	4.0
D.	7.4



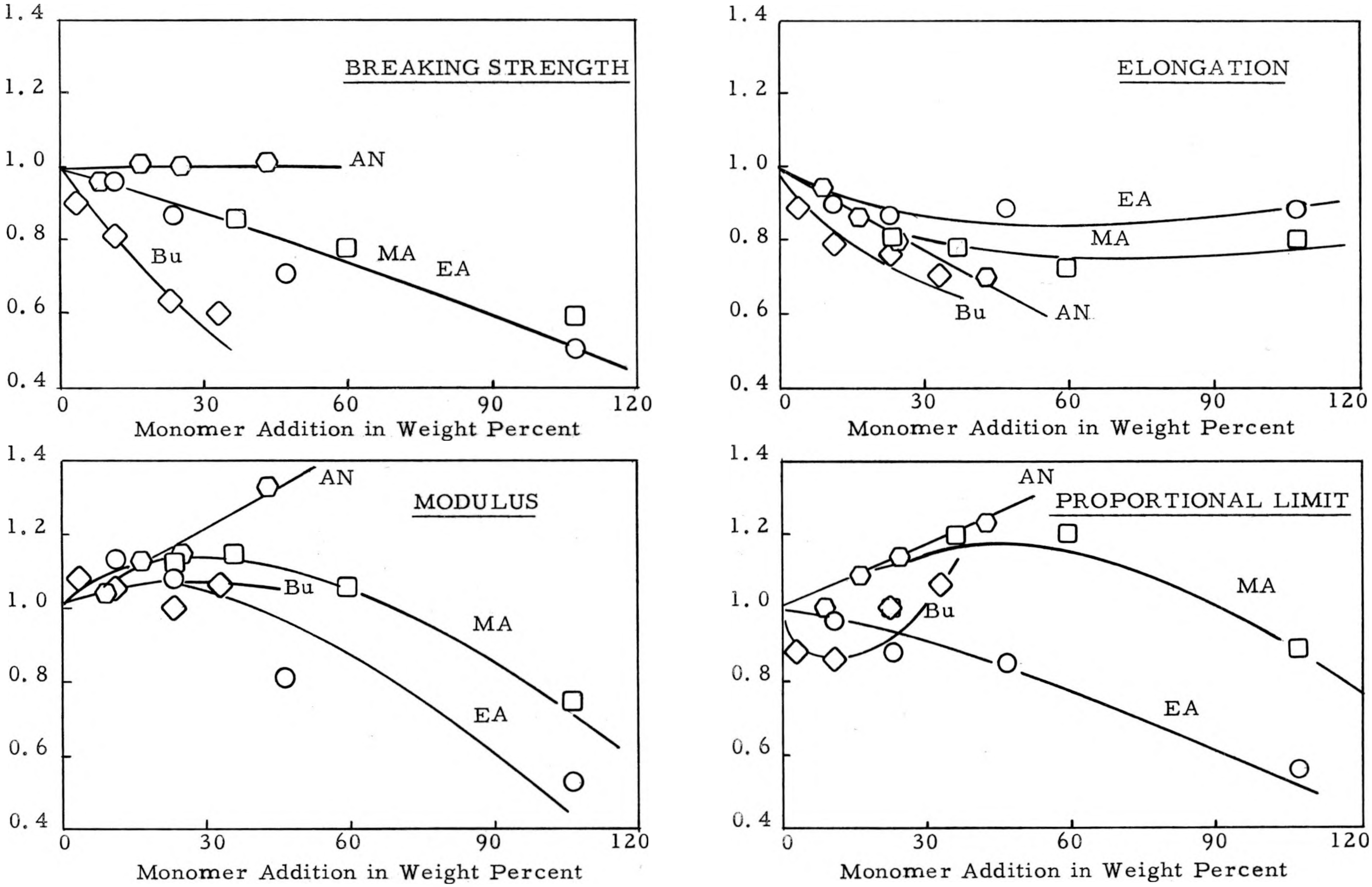


Figure 19. Physical Properties of Grafted Acetate Yarn Relative to Unirradiated Control.

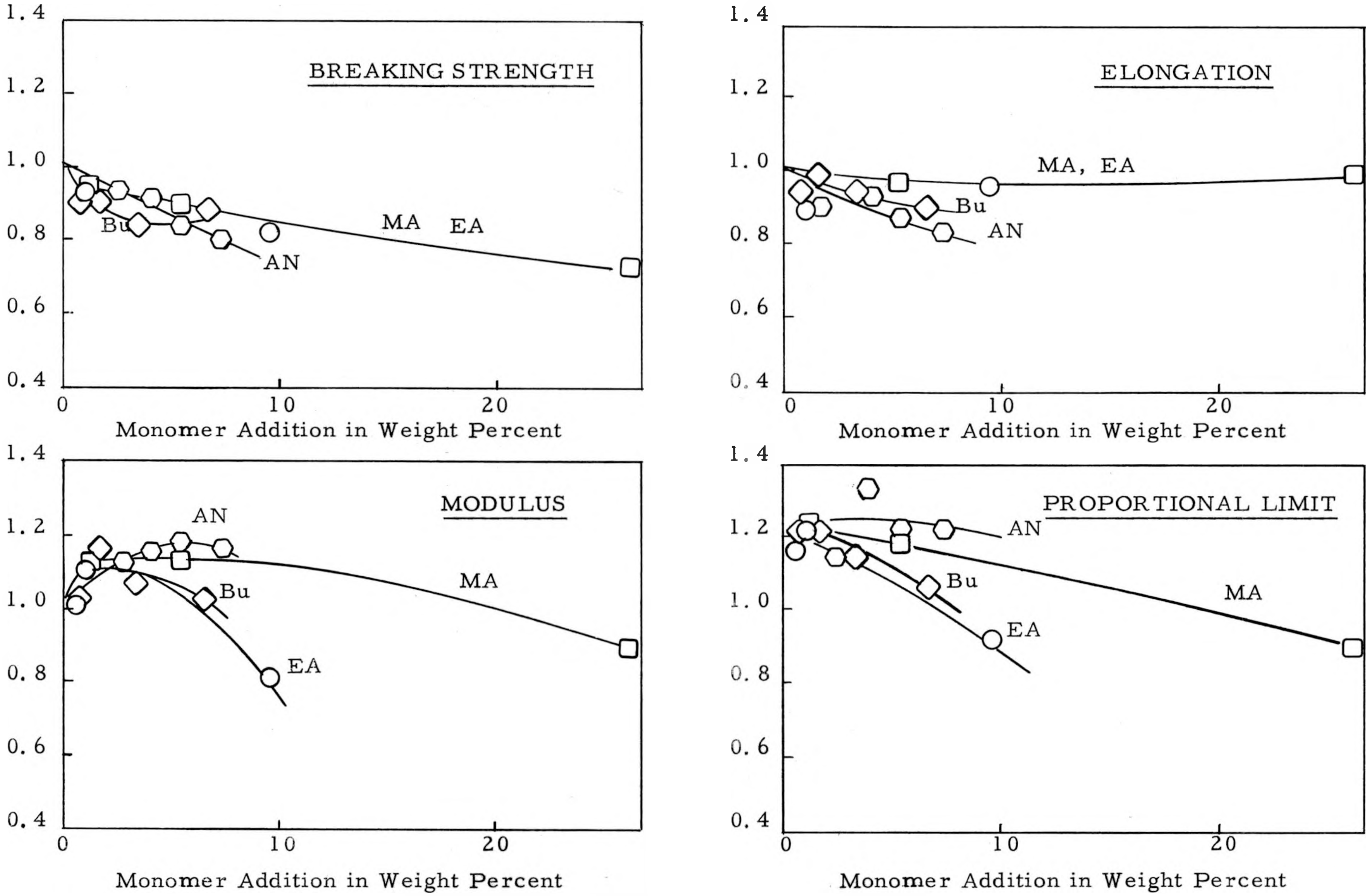


Figure 20. Physical Properties of Grafted Nylon Yarn
Relative to Unirradiated Control

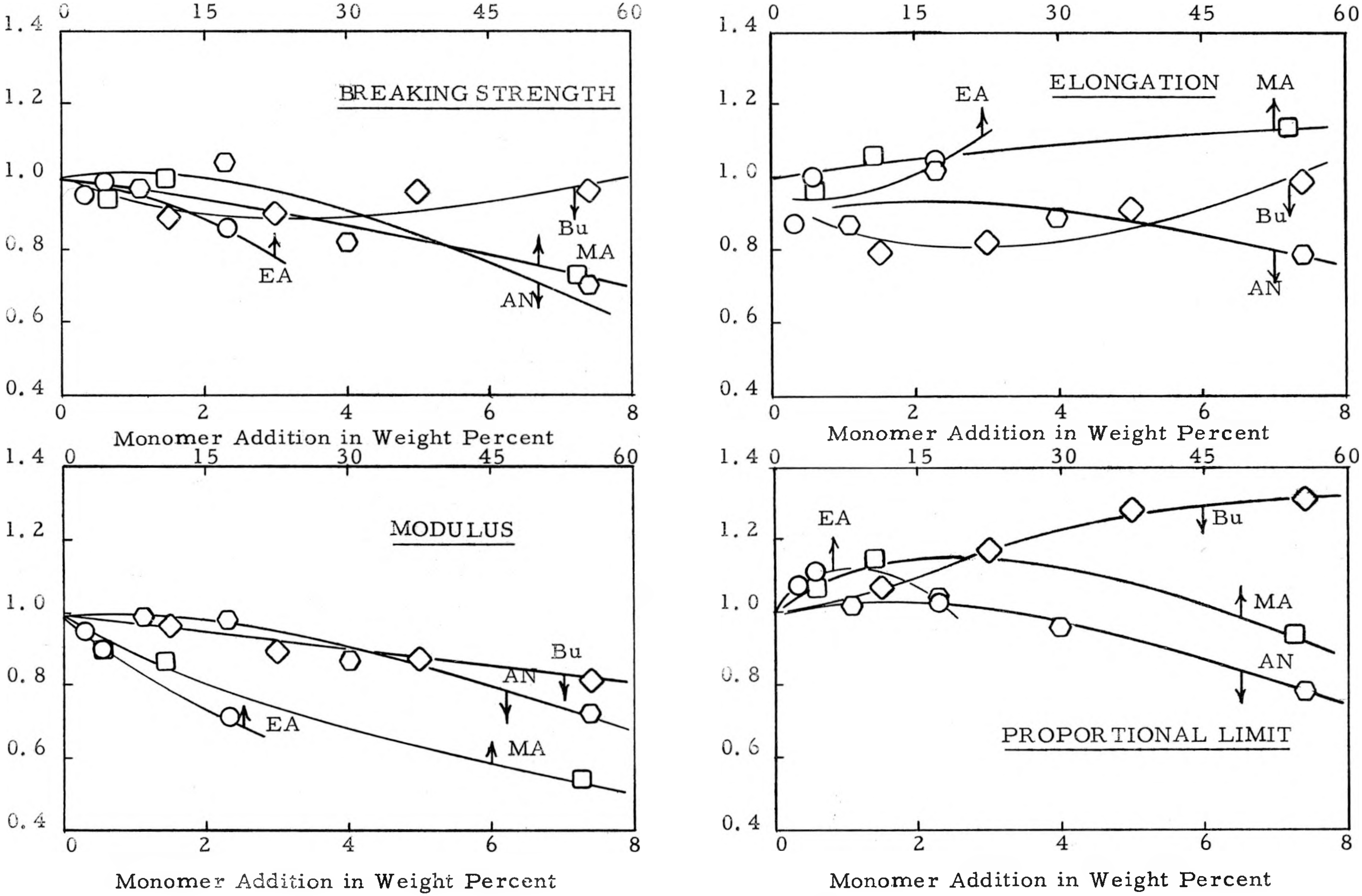


Figure 21. Physical Properties of Grafted Polypropylene Yarn Relative to Unirradiated Control

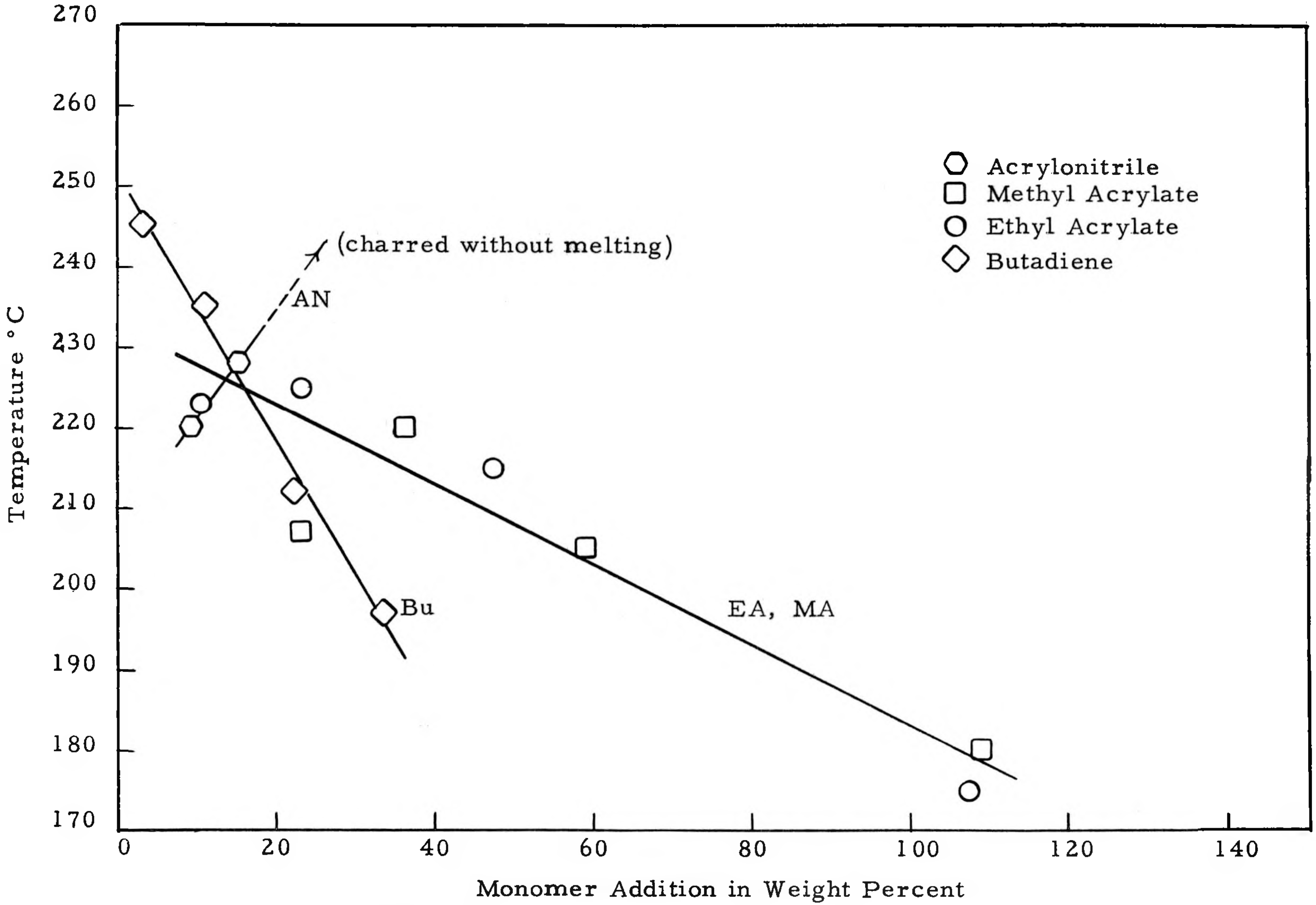


Figure 22. Melting Point of Grafted Acetate Yarn

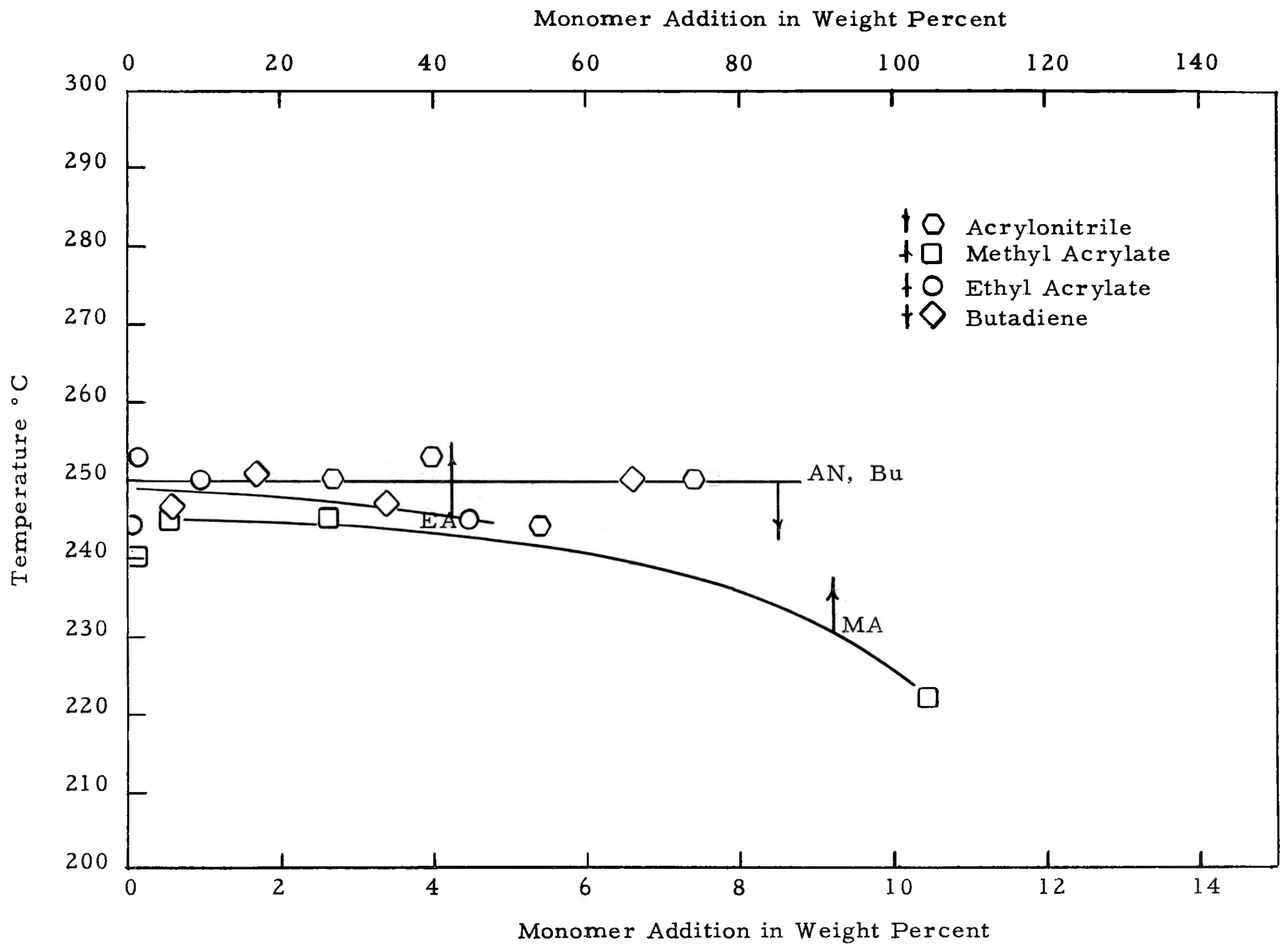


Figure 23. Melting Point of Grafted Nylon Yarn

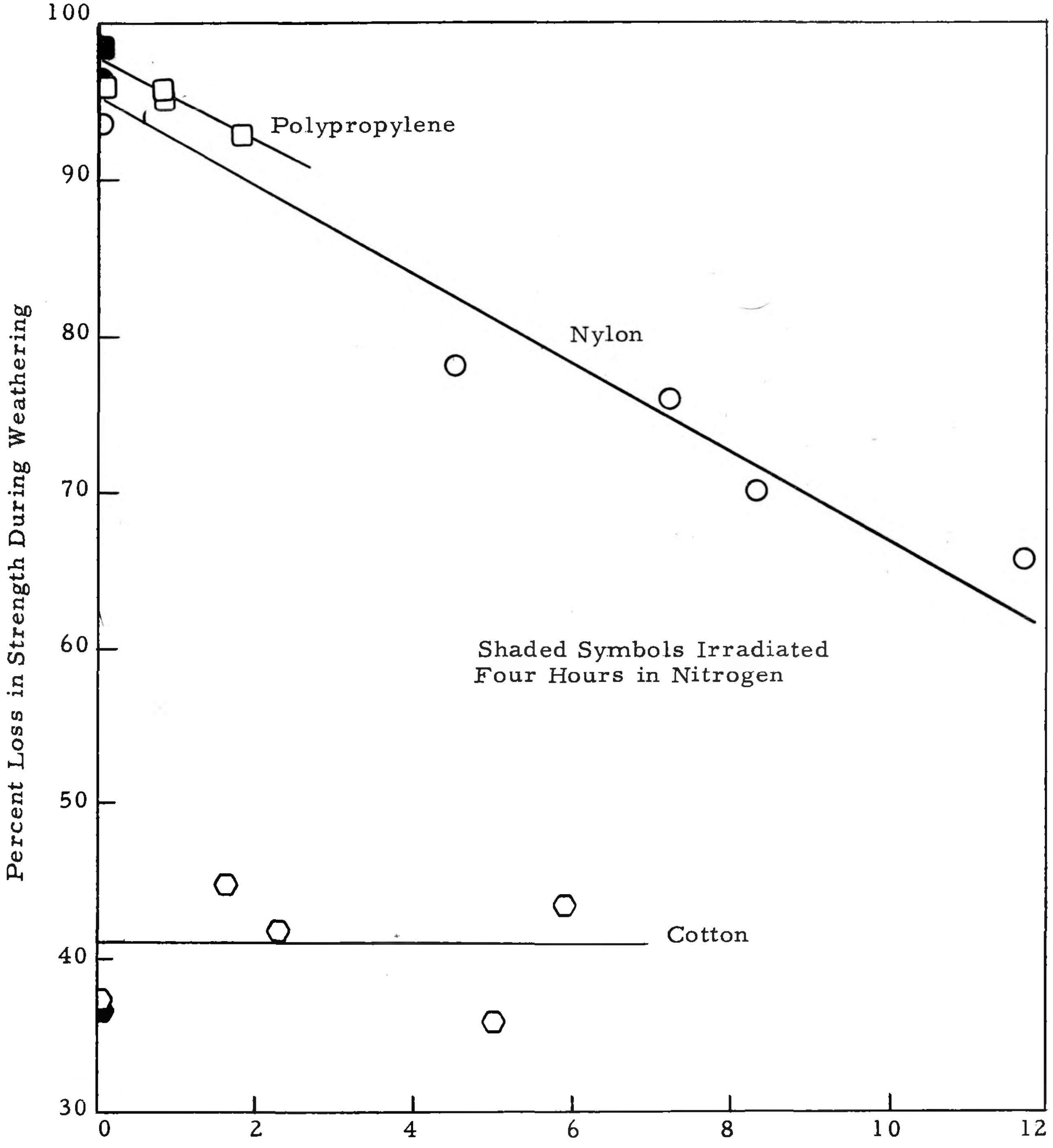


Figure 25. Weather Resistance of Fabrics
Grafted with Styrene

PART III. KINETICS AND DIFFUSION IN RADIATION INDUCED GRAFT POLYMERIZATION

The vapor-phase technique has proved to be a very effective method of uniformily grafting the more volatile vinyl monomers to fiber substrates. In some cases where the rate of diffusion of monomer vapor into the fiber is very rapid (e. g. , the cellulosics), the polymer is uniformily distributed throughout the fiber cross-section. While in the cases where the rate of diffusion is very slow (e. g. , the polyolefins), the polymer is concentrated at the surface of the fiber.

The kinetics of polymerization and the rate of diffusion of monomer both play a very significant part in the vapor-phase technique. Since the rate of graft-polymerization and the location of the grafted polymer may both affect the properties of the copolymer formed, accurate kinetic data and diffusion data are necessary for optimum design of graft-polymerization processes. This discussion presents the preliminary phase of an investigation to correlate both the kinetics and diffusion in the vapor-phase technique.

Kinetics of Graft Polymerization

Gamma radiation interacts with matter by the photoelectric effect, Compton scattering, and pair production. For gamma rays from Co-60 the predominant effect in organic materials is Compton scattering. In the Compton effect the incident gamma ray interacts with an orbital electron ejecting the electron from its orbit and producing another photon of lower energy. Both the electron and photon subsequently interact with the material or the surroundings. The electrons interact with orbital electrons to form ions (ionization) if the orbital electron is ejected from the atom or to form excited molecules (excitation) if the orbital electron is moved to an orbit of higher energy. It is believed that excitation and ionization produced by radiation account for the major changes observed in irradiated organic materials, (1,2). The ions and excited molecules are very reactive. They either react with other materials present or decompose into radicals and atoms or molecules. The free radicals produced may be used to initiate graft-polymerization.

In the vapor-phase technique it is practically impossible to separate the kinetics from the effect of diffusion. As a first approximation the effect of diffusion is neglected and the average values of polymer and monomer content in the fiber are used to study the kinetics. This may be a good assumption where the rate of diffusion is rapid and may be erroneous if the rate of diffusion is slow compared to the rate of polymerization.

For this study a post irradiation process was chosen and the following mechanism was proposed:

$$R\cdot + M \xrightarrow{k_p} RM\cdot \tag{1}$$

$$R\cdot + R\cdot \xrightarrow{k_2} RR \text{ or } R+R \tag{2}$$

$$R\cdot + O_2 \xrightarrow{k_1} \left[R\cdot + O_2\right] \tag{3}$$

Then
$$\frac{dP}{dt} = -\frac{dM}{dt} = k_p \quad RM \tag{4}$$

where
P = polymer concentration
M = monomer concentration
R = radical concentration
k_p = polymerization velocity constant
k_2 = termination velocity constant
k_1 = velocity constant for radical-oxygen reaction which includes oxygen concentration
t = time

The rate of radical decay is

$$\frac{dR}{dt} = - k_1 R - k_2 R^2 \tag{5}$$

$$R = R_0 \text{ at } t = 0$$

The solution of this differential equation is

$$R = \frac{k_1 R_0}{\left[k_1 + k_2 R_0\right] e^{k_1 t} - k_2 R_0} \tag{6}$$

Multiplying both sides of this equation by k_p and rearranging

$$\left[\frac{1}{k_p R} + \frac{k_2}{k_1 k_p}\right] = \left[\frac{k_1 + k_2 R_0}{k_1 k_p R_0}\right] e^{k_1 t} \tag{7}$$

Taking the logarithm of both sides of the equation

$$\log \left[\frac{1}{k_p R} + \frac{k_2}{k_1 k_p}\right] = \frac{k_1}{2.303} t + \log \left[\frac{k_1 + k_2 R_0}{k_1 k_p R_0}\right] \tag{8}$$

If the $\log \left[\frac{1}{k_p R} + \frac{k_2}{k_1 k_p}\right]$ is plotted versus t a straight line will be formed if the proposed model is correct. The slope of the line will be $(k_1/2.303)$ and the intercept at t = 0 will be

$$\log \frac{k_1 + k_2R_0}{k_1k_p\ R_0}$$

The equation for the rate of polymerization can be rearranged in this form:

$$\frac{1}{k_pR} = \frac{M}{dP/dt}$$

The value of M and (dP/dt) may be determined at a number of points and values of $(1/k_pR)$ calculated. A plot of log $(1/k_pR)$ versus t will be a curved line. If a constant value "A" can be added to $(1/k_pR)$ so that log $[(1/k_pR) + A]$ versus t is a straight line, then the data obey the proposed model. "A" will be (k_2/k_1k_p) as given in equation 7.

Post irradiation experiments were made to determine the reaction velocity constants for graft polymerization of acrylonitrile to acetate, nylon, polypropylene, and polyester yarns. The experimental procedure was to suspend a one-gram skein of each yarn on a rack in a stainless steel beaker as shown in Figure 1. The beaker was purged for two hours with nitrogen at a flow-rate of 1000 $cm.^3/min$. Then the samples were irradiated for two hours with the nitrogen flushing continuing. Immediately after irradiation the beaker was flushed for various time intervals (1/2, 1, 2, 4 and 8 hours) with nitrogen saturated with acrylonitrile. These experiments were made at an exposure dose rate of 3.4×10^5 roentgens per hour from a Co-60 source at 75°F. and 1 atmosphere total pressure. In order to show the effect of oxygen on the polymerization these experiments were made using prepurified nitrogen containing 0.002% oxygen and oil-pumped nitrogen containing 0.024% oxygen. (In each experimental run one-gram skeins of each of the following yarns were used: cotton, rayon, acetate, nylon, polypropylene, acrylic, polyester and wool. There was no polymer addition in any of the experimental runs for cotton, rayon, acrylic or wool.)

Each sample was weighed immediately after the experiment to determine the total weight gain (monomer plus polymer) and after drying to obtain the polymer addition. The data for monomer content and polymer content of each yarn using prepurified nitrogen are shown in Figures 2-5. For oil-pumped nitrogen the data are shown in Figures 6-9.

From Figures 2-9 the slope of the polymer curve (dP/dt) was determined at several points and the value M/(dP/dt) calculated. These values are equal to $(1/k_pR)$ and the log $(1/k_pR)$ is plotted versus time in Figures 10-13 for prepurified nitrogen and in Figures 14-17 for oil-pumped nitrogen (acrylonitrile in both cases). A constant value "A" was determined by trial and error which gave a straight line when log $[(1/k_pR) + A]$ was plotted versus time. Then the value of the intercept and slope of the straight line were determined. From these values k_1, k_2R_0 and k_pR_0 were calculated and are given in Table I.

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Inspection of these data show that the reaction velocity constants for nylon, polypropylene and polyester yarns are affected very little by the different oxygen contents of the two nitrogens used. In the case of acetate the reaction velocity constant k_1 is four times as large for oil-pumped nitrogen which indicates that the oxygen is terminating the free radicals present. The reaction velocity constants k_pR_0 and k_2R_0 are six times and four times the values for the oil-pumped nitrogen. Since the constants k_p and k_2 should be the same in both cases, then the initial value of free radical concentration R_0 is different for the two cases.

In order to determine the effect of the oxygen content on the formation of free radicals, a post irradiation procedure was used to measure the radical build-up. The procedure was the same as the previous experiment with the exception that various times of irradiation (1/2, 1, 2, 4 and 8 hours) and a constant time of flushing after irradiation with acrylonitrile vapor of two hours were used.

The experimental procedure was as follows: One-gram skeins of acetate, nylon, polypropylene and polyester yarn were placed on a rack in a stainless steel beaker in the Gammacell sample chamber. The beaker was purged for two hours with nitrogen at a flow-rate of 1000 cm.^{3}/min. Then the samples were irradiated for various time intervals (1/2, 1, 2, 4 and 8 hours) with the nitrogen purging continuing. Immediately after irradiation the beaker was flushed for two hours with nitrogen saturated with acrylonitrile at 75°F. and 1 atmosphere pressure. The radiation exposure dose rate was 3.4×10^5 roentgens per hour. The acrylonitrile addition was determined by the weight gain of the sample. (In each experimental run one-gram skeins of each of the following yarns were used: cotton, rayon, acetate, nylon, polypropylene, acrylic, polyester and wool. There was no polymer addition in any of the experimental runs for cotton, rayon, acrylic or wool.)

By making the assumption that the molecular weight of the grafted copolymer is the same in both cases, then the polymer addition is a measure of the free radicals present. (This was shown to be a good approximation by measuring the molecular weight of homopolymer formed.) The data for polymer addition to each yarn as a function of irradiation time are shown in Figures 18-21 for both prepurified and oil-pumped nitrogen.

Inspection of the two curves in Figure 18 for acetate reveals two interesting results:

1. The asymptotic value for radical concentration is less for oil-pumped nitrogen.

2. The rate of formation of free radicals is much smaller for oil-pumped nitrogen. The slope of the curve at time zero is a measure of the rate of formation of free radicals.

Therefore the conclusion was drawn that oxygen affects both the rate of formation and the rate of termination of free radicals.

In an attempt to explain this mechanism it is assumed that oxygen is entering the reaction before the formation of free radicals that initiate polymerization. It is proposed that radiation produces excited sites or precursor radicals which decompose into the free radicals which initiate graft polymerization. Also these activated sites or precursor radicals may react with oxygen to form inactive sites as well as forming free radical sites.

The following kinetic model is proposed for the process:

$$A \overset{k^*I}{\rightsquigarrow} A^* \tag{9}$$

$$A^* \xrightarrow{k} A\cdot \ + B \tag{10}$$

$$A^* + O_2 \xrightarrow{k_0} \left[A^* + O_2\right] \tag{11}$$

$$A\cdot \ + O_2 \xrightarrow{k_1} \left[A\cdot \ + O_2\right] \tag{12}$$

$$A\cdot \ + A\cdot \xrightarrow{k_2} AA \text{ or } A + A \tag{13}$$

The gamma radiation forms activated molecules or sites A* in the polymer A. The activated sites decompose to form free radical sites or react with oxygen to form unreactive sites. (The products formed from the decomposition and the reaction with oxygen are not specified.) The rate of formation of activated sites is

$$\frac{dA^*}{dt} = k^*I - kA^* - k_0\ (O_2)A^* \tag{14}$$

$A^* = 0$ for $t = 0$

A^* = number of activated sites per unit of polymer

k^* = reaction velocity constant for formation of sites

I = intensity of radiation

k = reaction velocity constant for radical formation

k_0 = reaction velocity constant for reaction of activated site with oxygen

(O_2) = oxygen concentration

The solution of this differential equation is

$$A^* = \frac{k^*I}{k + k_0(O_2)} \left[1 - e^{-\left[k + k_0(O_2)\right] t}\right] \tag{15}$$

Since the reactions of the activated sites are very rapid, it is assumed that a steady-state activated site concentration is maintained during irradiation:

$$A^{*} = \frac{k^{*}I}{k+k_0\ (O_2)} \tag{16}$$

The rate of formation of radical sites is

$$\frac{dR}{dt} = kA^{*} - k_1R - k_2R^2 \tag{17}$$

$R = 0$ for $t = 0$

R = concentration of radical sites

Simplify the equation by placing

$$kA^{*} = \frac{k\ k^{*}I}{k+k_0\ (O_2)} = KI \tag{18}$$

then $$\frac{dR}{dt} = KI - k_1R - k_2R^2 \tag{19}$$

The solution of this differential equation is

$$R = -\frac{k_1}{2k_2} + \frac{\sqrt{k_1^2 + 4KIk_2}}{2k_2} \bullet \left[\frac{1 + \dfrac{k_1 - \sqrt{k_1^2 + 4KIk_2}}{k_1 + \sqrt{k_1^2 + 4KIk_2}}\ e^{-\sqrt{k_1^2 + 4KIk_2}\ t}}{1 - \dfrac{k_1 - \sqrt{k_1^2 + 4KIk_2}}{k_1 + \sqrt{k_1^2 + 4KIk_2}}\ e^{-\sqrt{k_1^2 + 4KIk_2}\ t}} \right] \tag{20}$$

This equation gives the radical content for the proposed model as a function of time and reaction velocity constants. For the simple case in which there is no oxygen present the differential equation redcues to:

$$\frac{dR}{dt} = KI - k_2R^2 \quad \text{where} \quad K = k^{*} \tag{21}$$

and $$R = \sqrt{\frac{KI}{k_2}}\ \tanh\ \sqrt{kIk_2}\ t \cdot \tag{22}$$

The radical concentration R in both equations is linear for small values of time. The slope (dR /dt) of both equations 20 and 22 at t = 0 is equal to KI. From the experimental data the slope of the curve at t = 0 determines KI. From the asymptotic value a relationship between k_1 and k_2 is obtained:

$$\left[\frac{-k_1 + \sqrt{k_1^2 + 4KIk_2}}{2k_2}\right] = \text{asymptotic value}$$

Then by trial and error values of k_1 and k_2 are found which best fit the data using equation 20 and 22. The values obtained for the experiment are given in Table II.

The data for acetate are more significant and will be used for discussion. Using equation (18) the values for the rate of production of free radicals are:

$$\frac{k\ k^*\ I}{k+k_0\ (O_2)} = 5.20 \text{ for prepurified nitrogen and}$$

$$\frac{k\ k^*\ I}{k+k_0\ (O_2)} = 0.90 \text{ for oil-pumped nitrogen}$$

Since k*, I and k should be the same in both cases, then k_0 (O_2) must be different and should be a function of the oxygen content of the nitrogen used for the experiment.

The proposed model fits the data but this does not necessarily mean that the model is correct. Several assumptions have been made which must be justified and more precise experimental techniques will be necessary to explain the exact mechanism.

The initial radical concentration R_0 must be known in order to calculate values for the reaction velocity constants. Estimates were made for the values of R_0 using the number average molecular weight M_n determined from viscosity measurements on homopolymer of polyacrylonitrile extracted from grafted yarn. For acetate yarn the number average molecular weights were 12,000 for the case using prepurified nitrogen and 18,000 for oil-pumped nitrogen. For nylon, 4200 and 3800 and for polypropylene, 6000 and 2900. There was not enough homopolymer on polyester for a viscosity measurement for the determination of molecular weight. Calculated values of the reaction velocity constants are given in Tables III, IV, and V.

Diffusion

Values for the diffusivity of monomer in the various fibers and for the diffusion coefficients between the vapor and fiber surfaces must be known in order to correlate the effect of diffusion in the graft-polymerization process. Consider the individual fiber as a semi-infinite circular cylinder with radius "a". The initial monomer concentration in the fiber is zero. At time zero the fiber is placed in a vapor with constant monomer concentration M_0. There is a resistance to monomer diffusion between the vapor and fiber surface. The differential equation and boundary conditions for this case are:

$$\frac{1}{D}\frac{\partial M}{\partial t} = \frac{\partial^2 M}{\partial r^2} + \frac{1}{r}\frac{\partial M}{\partial r} \qquad (23)$$

$M\,(r, t)$ is finite at $r = 0$

$M\,(r, 0) = 0$

$$h\left[M_0 - M(a,t)\right] = D\left[\frac{\partial M}{\partial r}\right]_{r=a} \quad \text{for} \quad t > 0$$

The solution for the case is

$$\frac{M_0 - M}{M_0} = \sum_p \frac{2\,Ha \qquad J_0(pr)}{(p^2a^2 + H^2a^2)\,J_0(pa)}\, e^{-Dp^2t} \qquad (24)$$

where $\left[pa\ J_1\,(pa) = HaJ_0\,(pa)\right]$

$$H = \frac{h}{D}$$

D = diffusivity of fiber for monomer

M = monomer concentration in fiber

M_0 = asymptotic monomer concentration in fiber

r = radial dimension

a = radius of fiber

t = time

h = diffusion film coefficient at fiber surface

The solution may also be obtained for the average monomer concentration.

$$\frac{M_0 - M_{av}}{M_0} = \sum_p \frac{4\,H^2a^2}{p^2a^2\,(p^2a^2 + H^2a^2)}\, e^{-Dp^2t} \qquad (25)$$

numerical values for this solution are given by Newman (3). To obtain values for the diffusivity and the diffusion coefficient, it is necessary to obtain data on fibers of two different radii. Then by trial and error values of D and h are obtained which satisfy both sets of data.

The rate of diffusion of acrylonitrile vapor into acetate, nylon, polypropylene and polyester yarn was measured. The experimental procedure was to place dried one-gram skeins of each yarn on a rack in a stainless steel beaker and flush the beaker for two hours with nitrogen at a flow-rate of 1000 cm.^{3} /min. Then the beaker was flushed for various time intervals (1/4, 1/2, 1, 2, 4 and 8 hours) with nitrogen saturated with acrylonitrile at 75°F. and 1 atmosphere pressure. The average monomer content of the yarn was determined by the weight gain of the sample.

The experimental data for the various fibers are shown in Figure 22. The polyester fiber obeys the mathematical equation. Acetate and nylon obey the equation for short periods of time but tend to swell for long periods of time as the monomer content increases. Polypropylene adsorbs approximately 0.3% monomer in 15 minutes and does not adsorb any more up to 8 hours exposure. For polypropylene the initial adsorption is probably on the surface with no diffusion into the fiber.

The diffusion experiments were repeated using yarn skeins with different denier filaments. For acetate 3 dpf and 20 dpf filament yarns were used; for nylon, 2 dpf and 6 dpf filament yarns; and for polyester, 2 dpf and 5 dpf filament yarns. For acetate and nylon yarns the film coefficients for diffusion were so small compared to the diffusivity that the film coefficients were completely controlling. In the case of polyester yarn the following values for diffusivity and film coefficient for diffusion were obtained:

$$D = 6 \times 10^{-11} \text{ cm.}^2/\text{sec.}$$

$$h = 1 \times 10^{-7} \text{ moles/cm.}^2 \text{ sec. } (\text{moles/cm.}^3).$$

The accuracy of this determination is poor because of the small difference between the two yarn filament diameters (1.4×10^{-3} cm. and 2.3×10^{-3} cm.).

A better approach for determining design data on diffusion would be to use a steady-state method similar to Vanderkooi, Long and Mock (4) for determining average values of diffusivity. Then set up an experimental diffusion process to simulate the actual large scale process and determine the rate of diffusion. From the values of diffusivity and rate of diffusion, a value for the film coefficient of diffusion may be determined which would be suitable for design purposes.

Kinetics and Diffusion

A modification may be made to the general diffusion differential equation to take into account the effect of kinetics. Mock and Vanderkooi (5) illustrate this method for mutual radiation grafting in film. Consider the simultaneous diffusion and grafting in the post-irradiation technique. The initial monomer content of the fiber is zero. At time zero the fiber is placed in a vapor of constant monomer concentration M_0. There is a resistance to monomer diffusion between the vapor and fiber surface. The initial radical concentration in the fiber is R_0 and the radical decay is second order. The differential equation and boundary conditions for this case are:

$$\frac{\partial M}{\partial t} = D \left[\frac{\partial^2 M}{\partial r^2} + \frac{1}{r} \frac{\partial M}{\partial r} \right] - kpRM \tag{26}$$

M (r, t) is finite at r = 0

M (r, t) = 0 at t = 0

$$h \left[M_0 - M(a,t) \right] = D \left[\frac{\partial M}{\partial r} \right]_{r=a} \quad \text{for} \quad t = 0$$

R (t) = R_0 at t = 0

$$\frac{dR}{dt} = - k_2 R^2 \tag{27}$$

Work has been initiated to obtain mathematical solutions for this differential equation. If satisfactory solutions can not be obtained then it is planned to use computer techniques to study the effect of different variables on the graft polymerization technique.

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TABLE I. Post Irradiation Graft Polymerization of Acrylonitrile to Textile Yarns

Prepurified Nitrogen

Yarn	k_1	k_pR_0	k_2R_0
Acetate	9.1×10^{-5} sec. $^{-1}$	1.0×10^{-3} sec. $^{-1}$	4.6×10^{-3} sec. $^{-1}$
Nylon	6.1×10^{-6}	1.0×10^{-3}	1.2×10^{-3}
Polypropylene	5.8×10^{-5}	5.9×10^{-4}	----
Polyester	3.0×10^{-6}	5.0×10^{-5}	3.0×10^{-4}

Oil-Pumped Nitrogen

Yarn	k_1	k_pR_0	k_2R_0
Acetate	3.5×10^{-4} sec. $^{-1}$	1.7×10^{-4} sec. $^{-1}$	1.2×10^{-3} sec. $^{-1}$
Nylon	7.2×10^{-6}	1.0×10^{-3}	1.4×10^{-3}
Polypropylene	1.9×10^{-4}	4.0×10^{-4}	----
Polyester	3.3×10^{-6}	5.0×10^{-5}	3.2×10^{-4}

TABLE II. Radical Buildup in Textile Yarns

Prepurified Nitrogen

Yarn	Asymptotic Value	KI	k_1	k_2
Acetate	$12.0 \frac{\text{gm.}}{100\ \text{gm.}}$	$5.2 \frac{\text{gm.}}{100\ \text{gm. hr.}}$	0	$3.6 \times 10^{-2} \frac{100\ \text{gm.}}{\text{gm. hr.}}$
Nylon	1.0	0.7	0	5.8×10^{-1}
Polypropylene	1.7	0.8	0	2.8×10^{-2}
Polyester	-	0.03	-	----

Oil-Pumped Nitrogen

Yarn	Asymptotic Value	KI	k_1	k_2
Acetate	$3.0 \frac{\text{gm.}}{100\ \text{gm.}}$	$0.9 \frac{\text{gm.}}{100\ \text{gm. hr.}}$	$5.3 \times 10^{-5}\ \text{sec.}^{-1}$	$3.6 \times 10^{-2} \frac{100\ \text{gm.}}{\text{gm. hr.}}$
Nylon	0.9	0.5	0	6.2×10^{-1}
Polypropylene	0.95	0.25	$5.0 \times 10^{-7}\ \text{sec.}^{-1}$	2.8×10^{-2}
Polyester	-	0.008	----	----

TABLE III. Reaction Velocity Constants for Acrylonitrile and Acetate Yarn

Radical Buildup

	Prepurified Nitrogen	Oil-Pumped Nitrogen
KI	1.6×10^{-6} moles/liter sec.	1.8×10^{-7} moles/liter sec.
G	12 radicals/100 eV	1.4 radicals/100 eV
k_1	0	5.3×10^{-5} sec.$^{-1}$
k_2	9.1×10^{-3} liters/mole sec.	1.4×10^{-2} liters/mole sec.

Post Irradiation Graft Polymerization

	Prepurified Nitrogen	Oil-Pumped Nitrogen
Mn	12,000	18,000
R_0	9.1×10^{-3} moles/liter	9.5×10^{-4} moles/liter
k_1	9.1×10^{-5} sec.$^{-1}$	3.5×10^{-4} sec.$^{-1}$
k_2	0.51 liters/mole sec.	1.3 liters/mole sec.
k_p	0.11 liters/mole sec.	0.18 liters/mole sec.

TABLE IV. Reaction Velocity Constants for Acrylonitrile and Nylon Yarn

Radical Buildup

	Prepurified Nitrogen	Oil-Pumped Nitrogen
KI	5.3 x 10^{-7} moles/liter sec.	4.2 moles/liter sec.
G	4.7 radicals/100 eV	3.7 radicals/100 eV
k_1	0	0
k_2	5.9 x 10^{-2} liters/mole sec.	5.6 x 10^{-2} liters/mole sec.

Post Irradiation Graft Polymerization

M_n	4200	3800
R_0	2.2 x 10^{-3} moles/liter	2.1 x 10^{-3} moles/liter
k_1	6.1 x 10^{-6} sec. $^{-1}$	7.2 x 10^{-6} sec. $^{-1}$
k_2	0.55 liters/mole sec.	0.67 liters/mole sec.
k_p	0.45 liters/mole sec.	0.48 liters/mole sec.

TABLE V. Reaction Velocity Constants for Acrylonitrile and Polypropylene Yarn

Radical Buildup

	Prepurified Nitrogen	Oil Pumped Nitrogen
KI	3.4×10^{-7} moles/liter sec.	2.2×10^{-7} moles/liter sec.
G	3.8 radicals/100 eV	2.4 radicals/100 eV
k_1	0	5.0×10^{-7} sec.$^{-1}$
k_2	5.2×10^{-3} liters/mole sec.	$2.4 \times 10^{-}{}_{3}$ liters/mole sec.
	Post Irradiation Graft Polymerization	
M_n	6000	2900
R_0	1.8×10^{-3} moles/liter	1.5×10^{-3} moles/liter
k_1	5.8×10^{-5} sec.$^{-1}$	1.9×10^{-4}
k_2	--------	--------
k_p	0.33 liters/mole sec.	0.27 liters/mole sec.

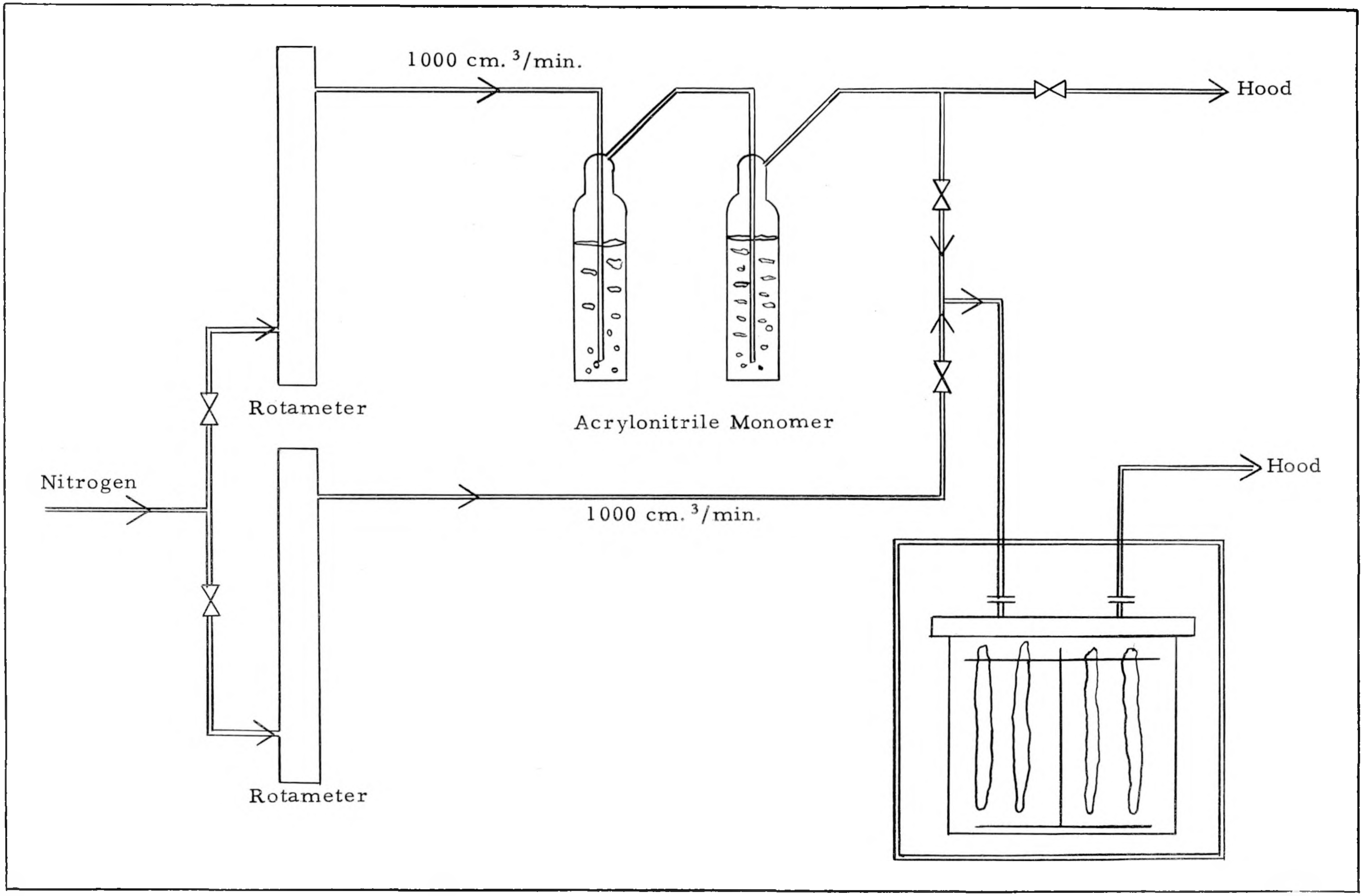


Figure 1. Sketch of Vapor Phase Process

Figure 2.

Post Irradiation Graft Polymerization of Acrylonitrile to Acetate Yarn

Prepurified Nitrogen

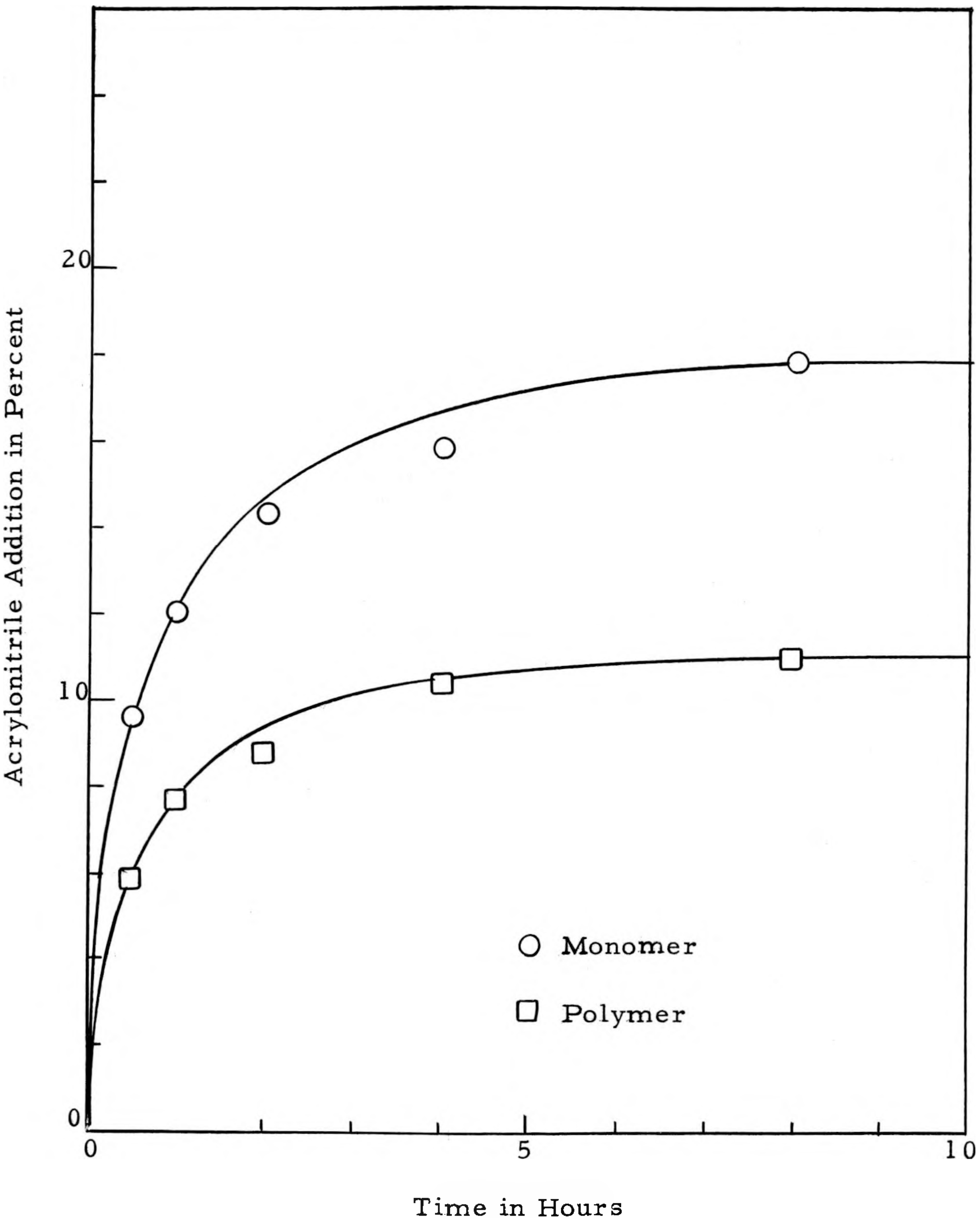


Figure 3.

Post Irradiation Graft Polymerization of Acrylonitrile to Nylon Yarn

Prepurified Nitrogen

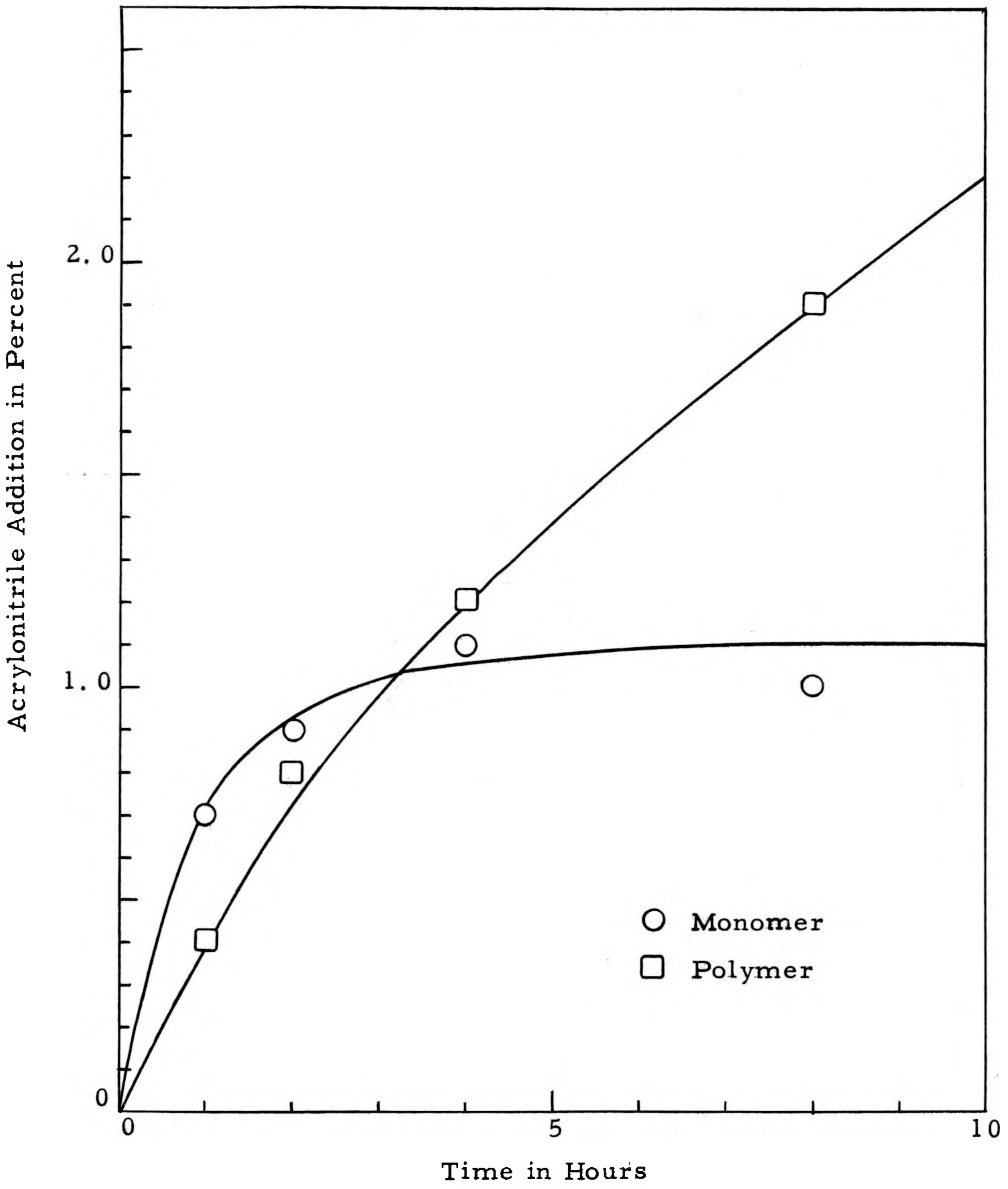


Figure 4.

Post Irradiation Graft Polymerization of Acrylonitrile to Polypropylene Yarn

Prepurified Nitrogen

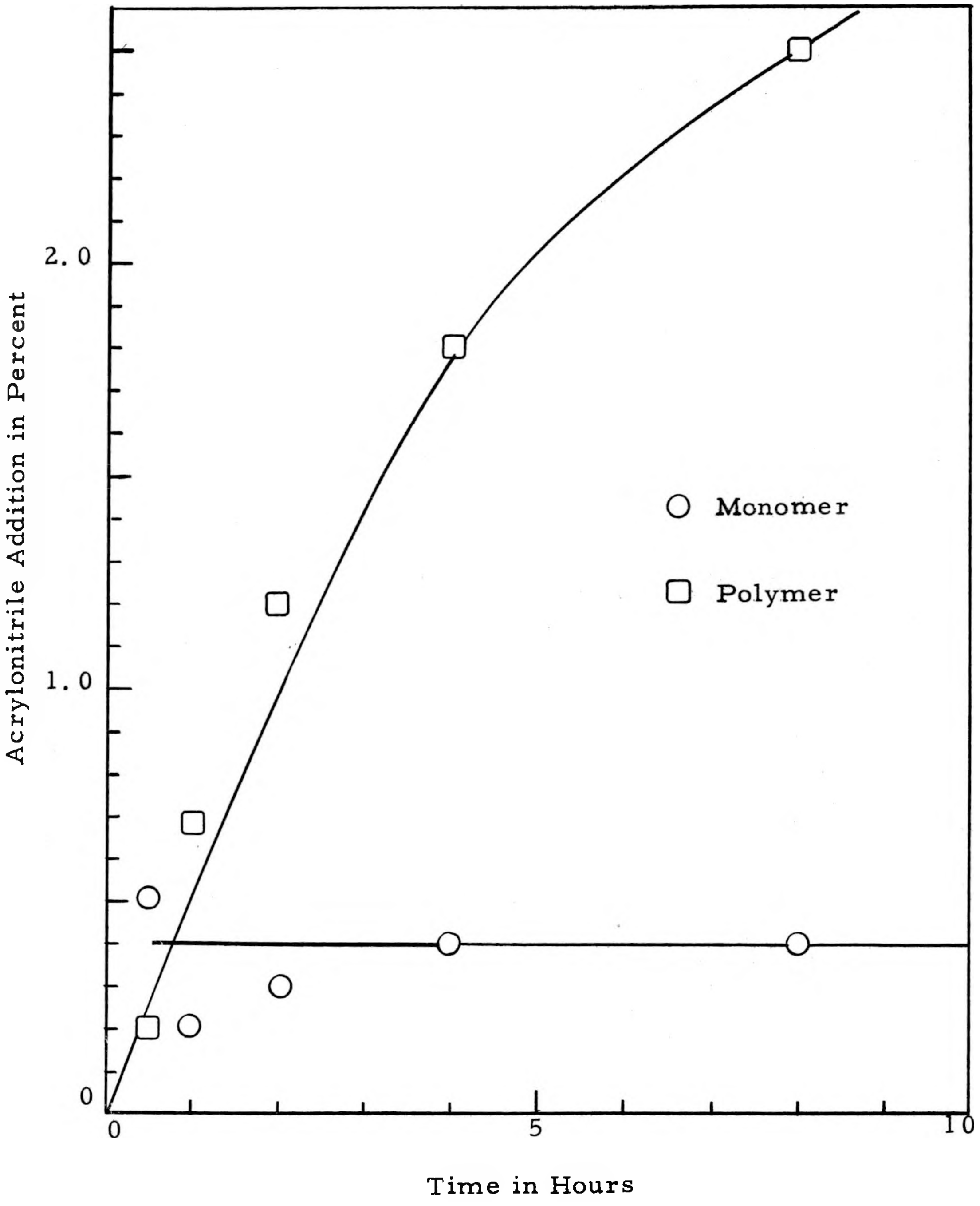


Figure 5.

Post Irradiation Graft Polymerization of Acrylonitrile to Polyester Yarn

Prepurified Nitrogen

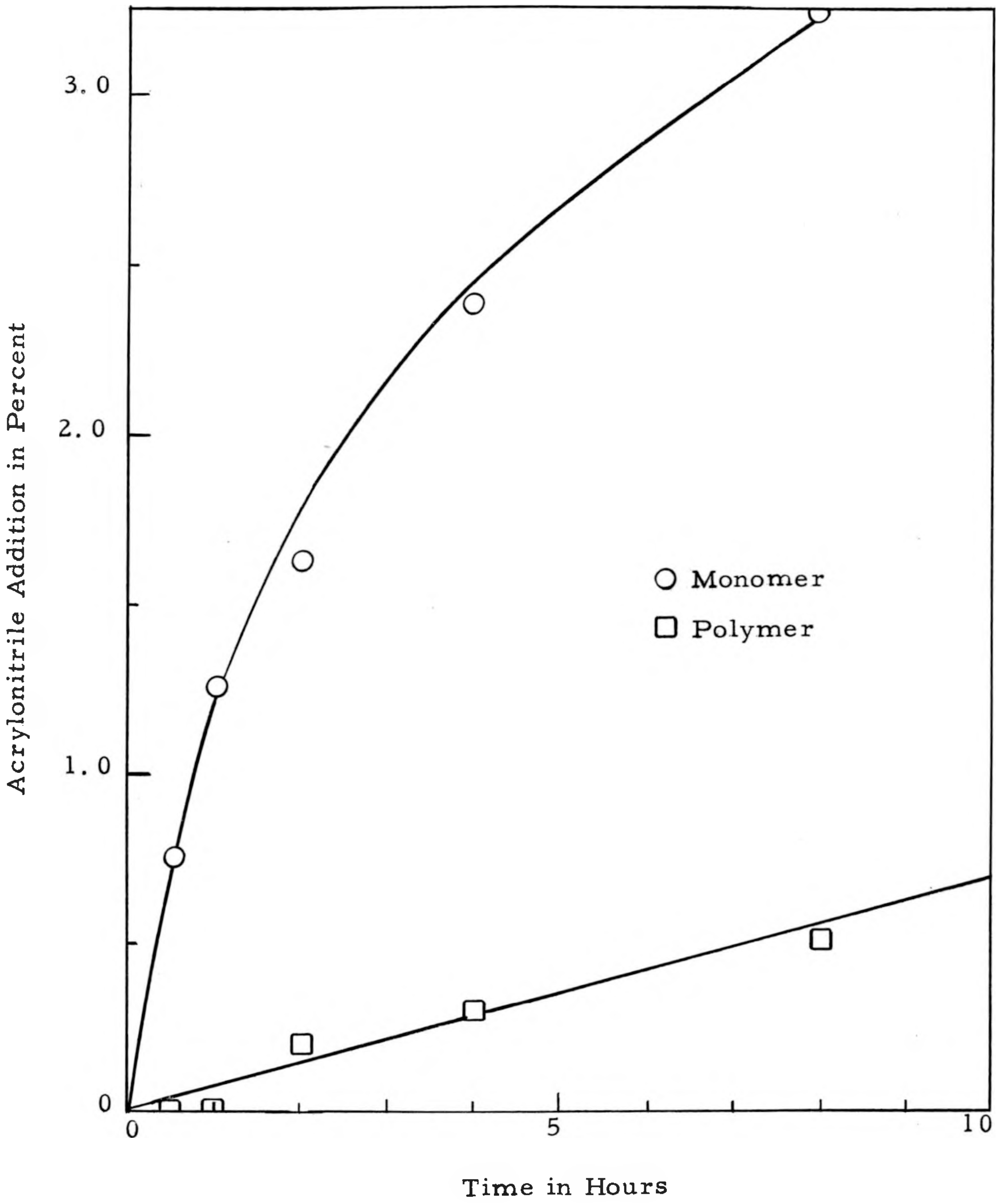


Figure 6.

Post Irradiation Graft Polymerization of Acrylonitrile to Acetate Yarn

Oil-Pumped Nitrogen

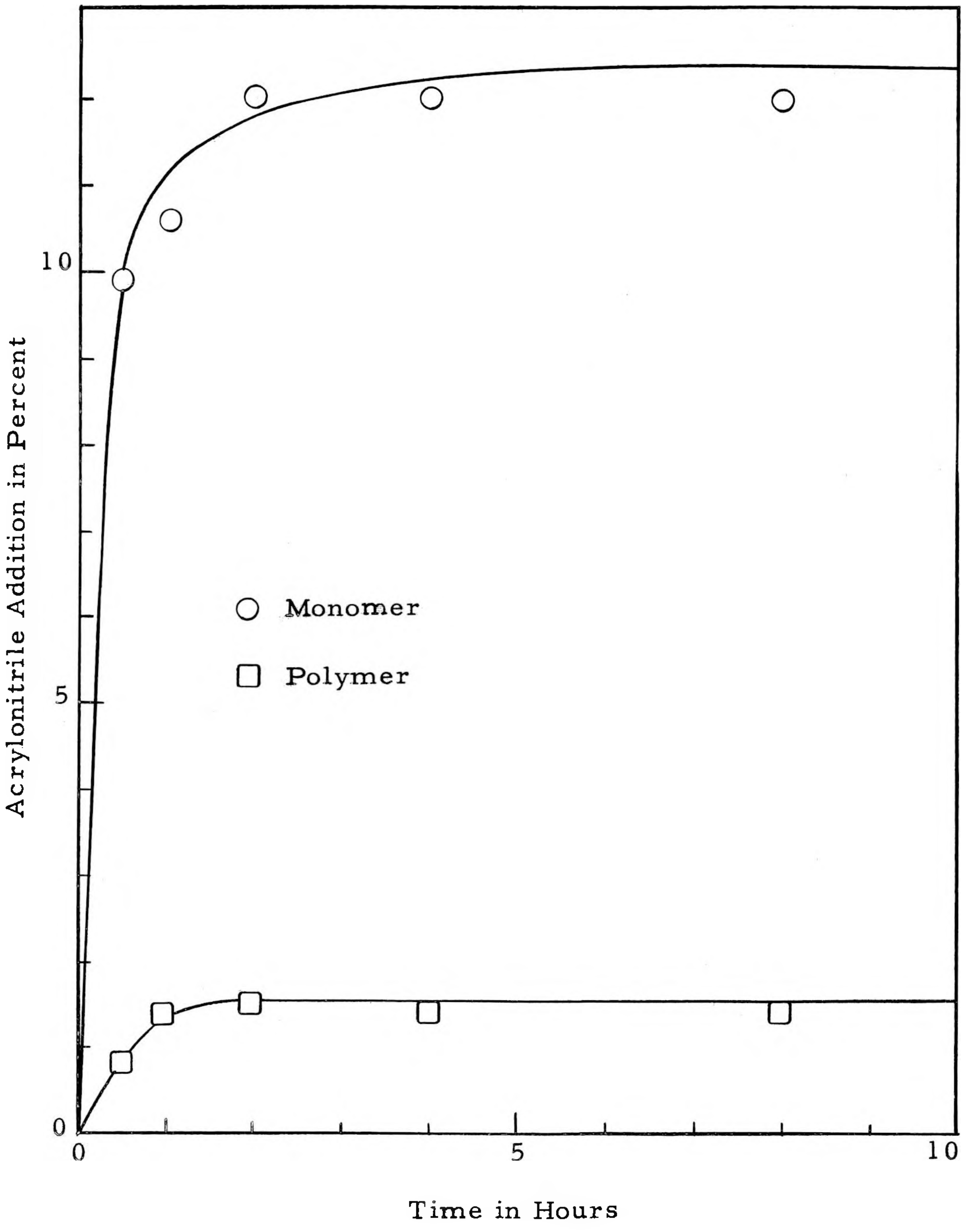


Figure 7.

Post Irradiation Graft Polymerization of Acrylonitrile to Nylon Yarn

Oil-Pumped Nitrogen

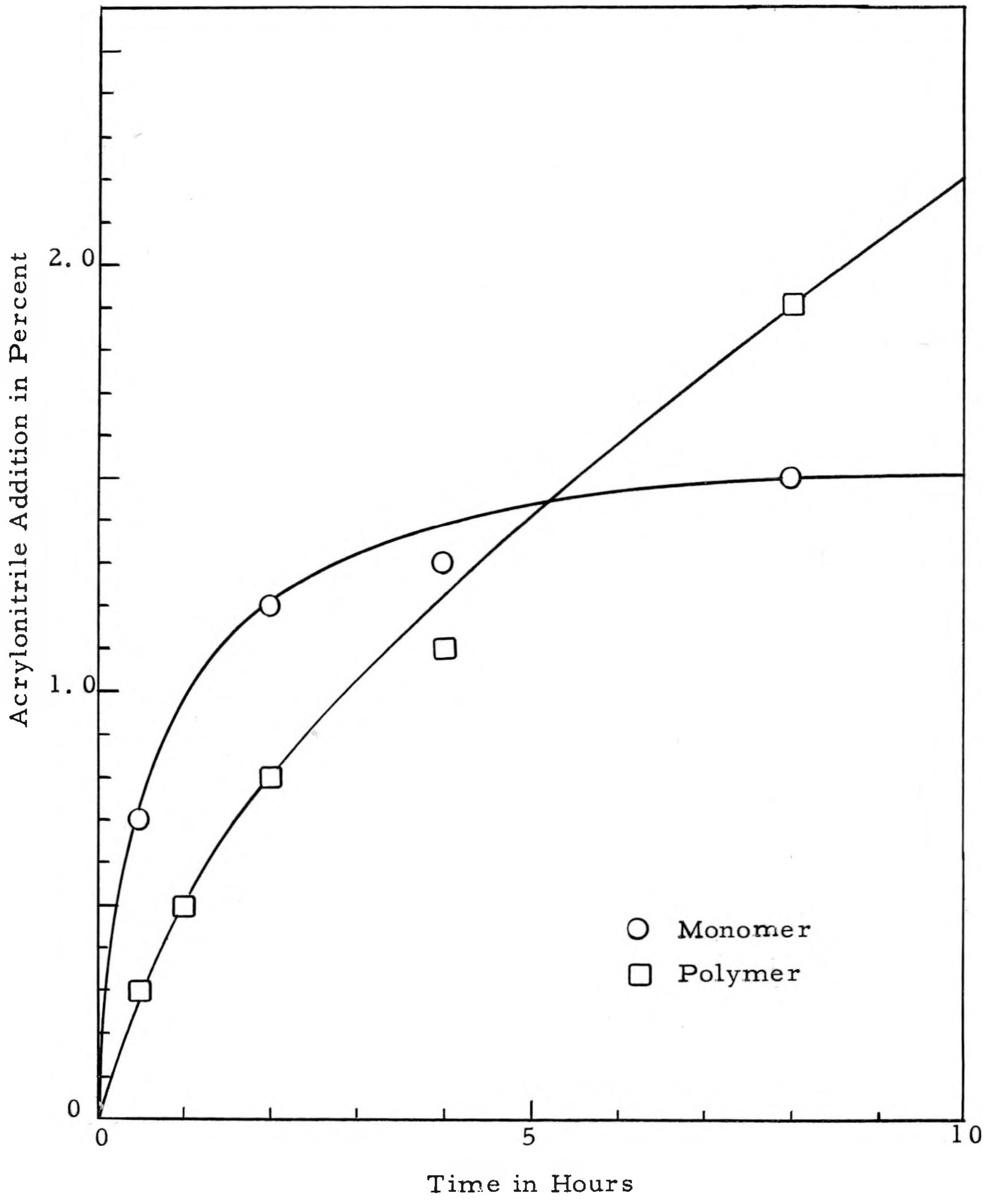


Figure 8.

Post Irradiation Graft Polymerization of Acrylonitrile to Polypropylene Yarn

Oil-Pumped Nitrogen

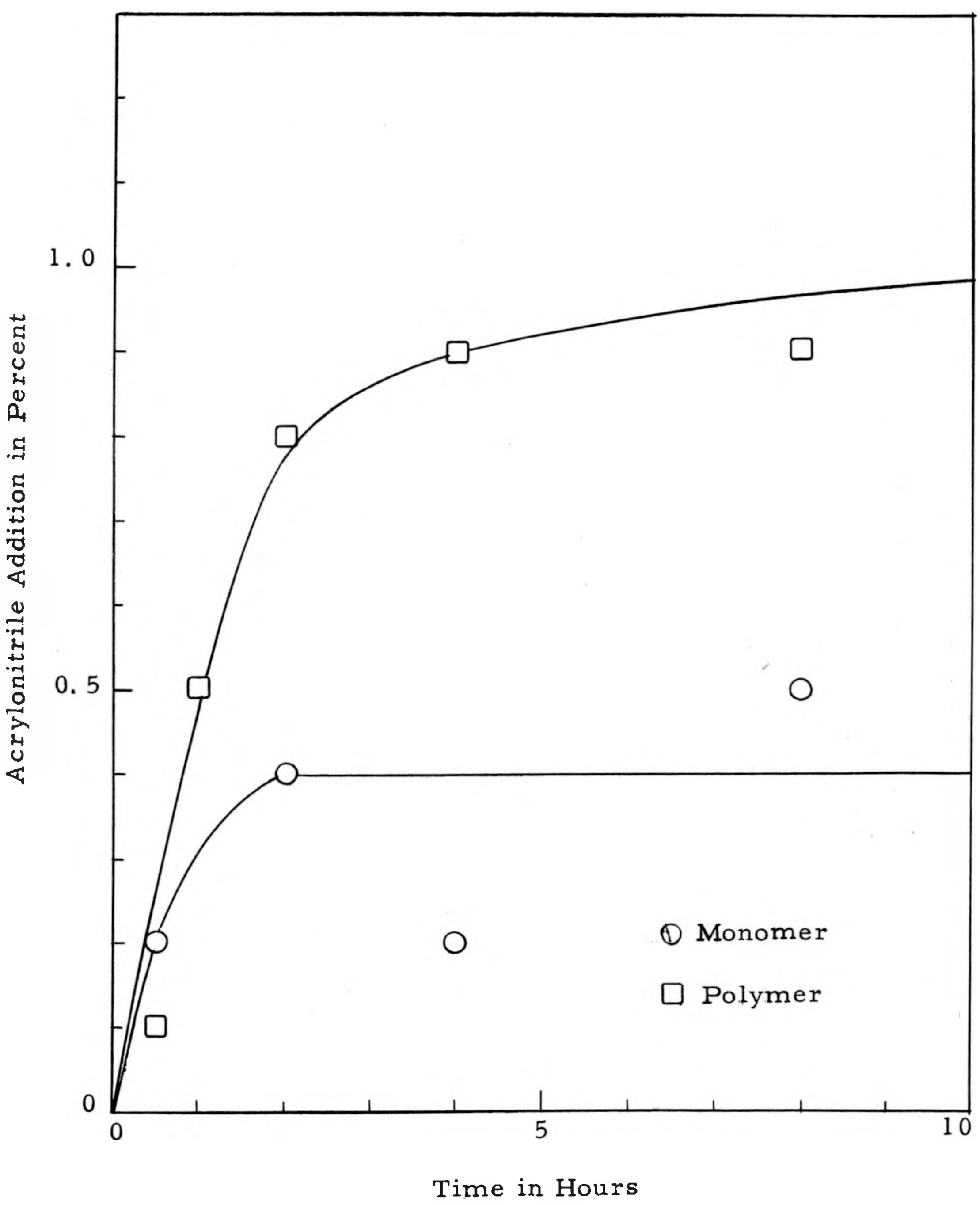
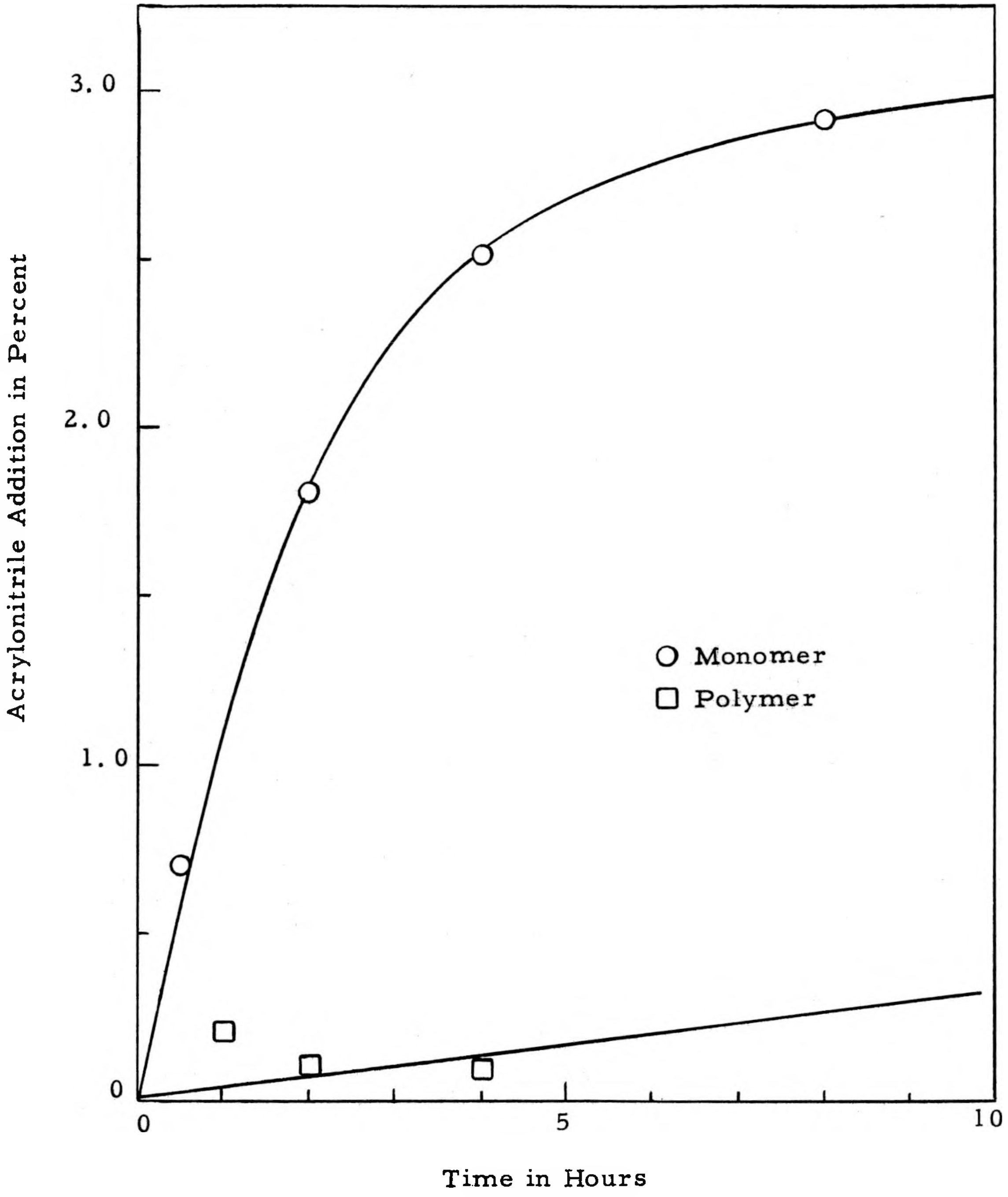


Figure 9.

Post Irradiation Graft Polymerization of Acrylonitrile to Polyester Yarn

Oil-Pumped Nitrogen



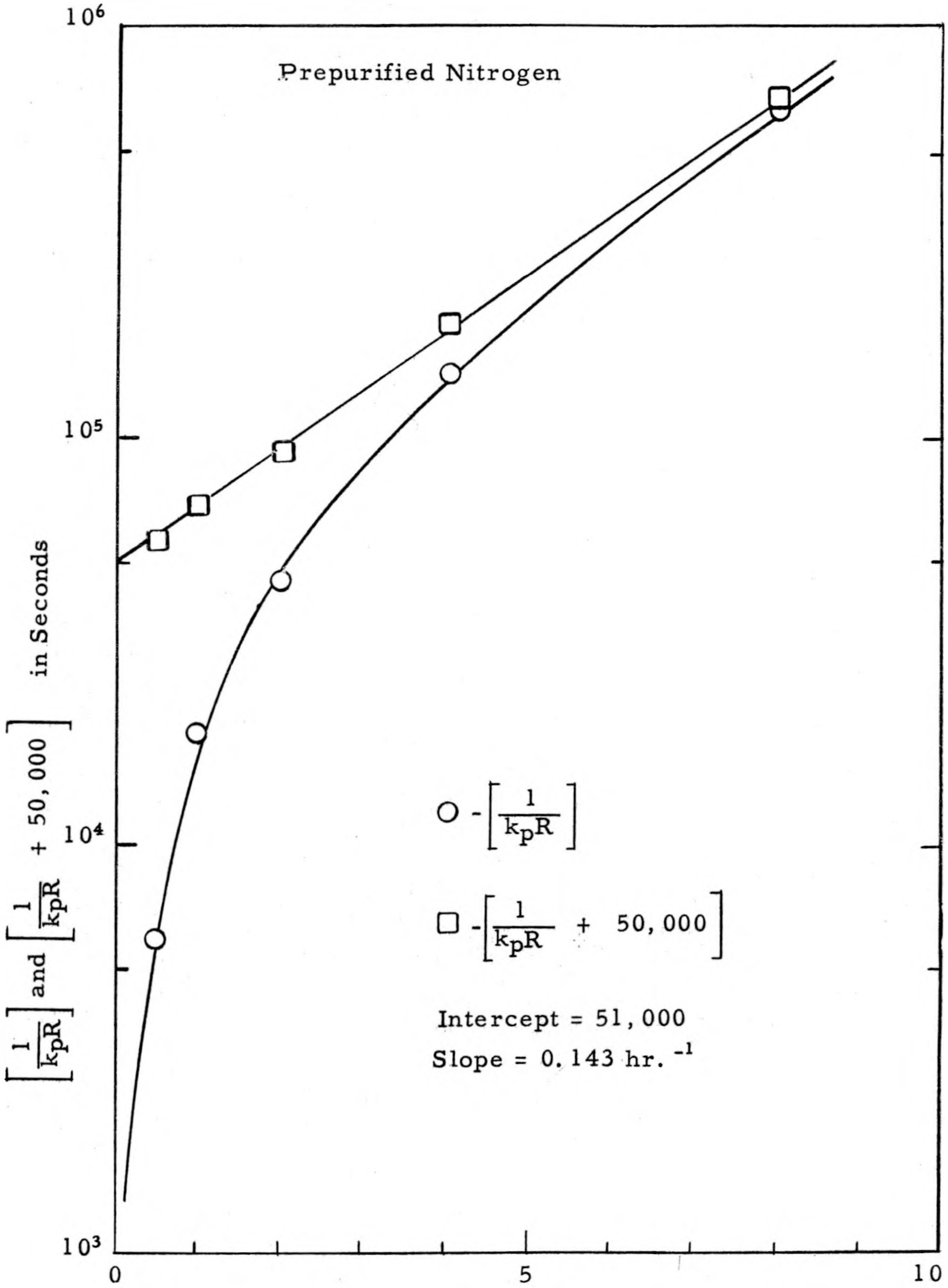


Figure 10. Post Irradiation Graft Polymerization of Acrylonitrile to Acetate Yarn

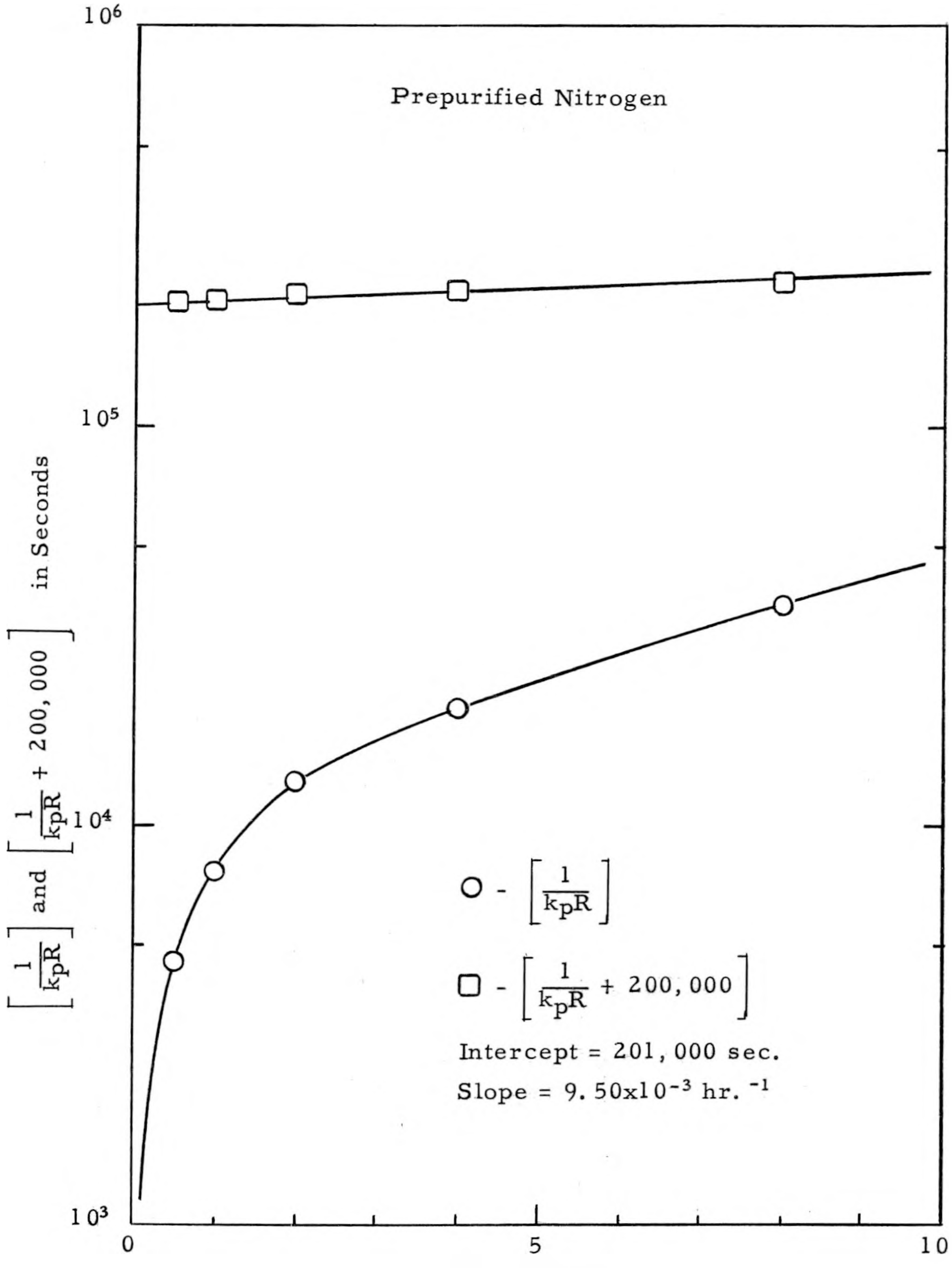


Figure 11. Post Irradiation Graft Polymerization of Acrylonitrile to Nylon Yarn

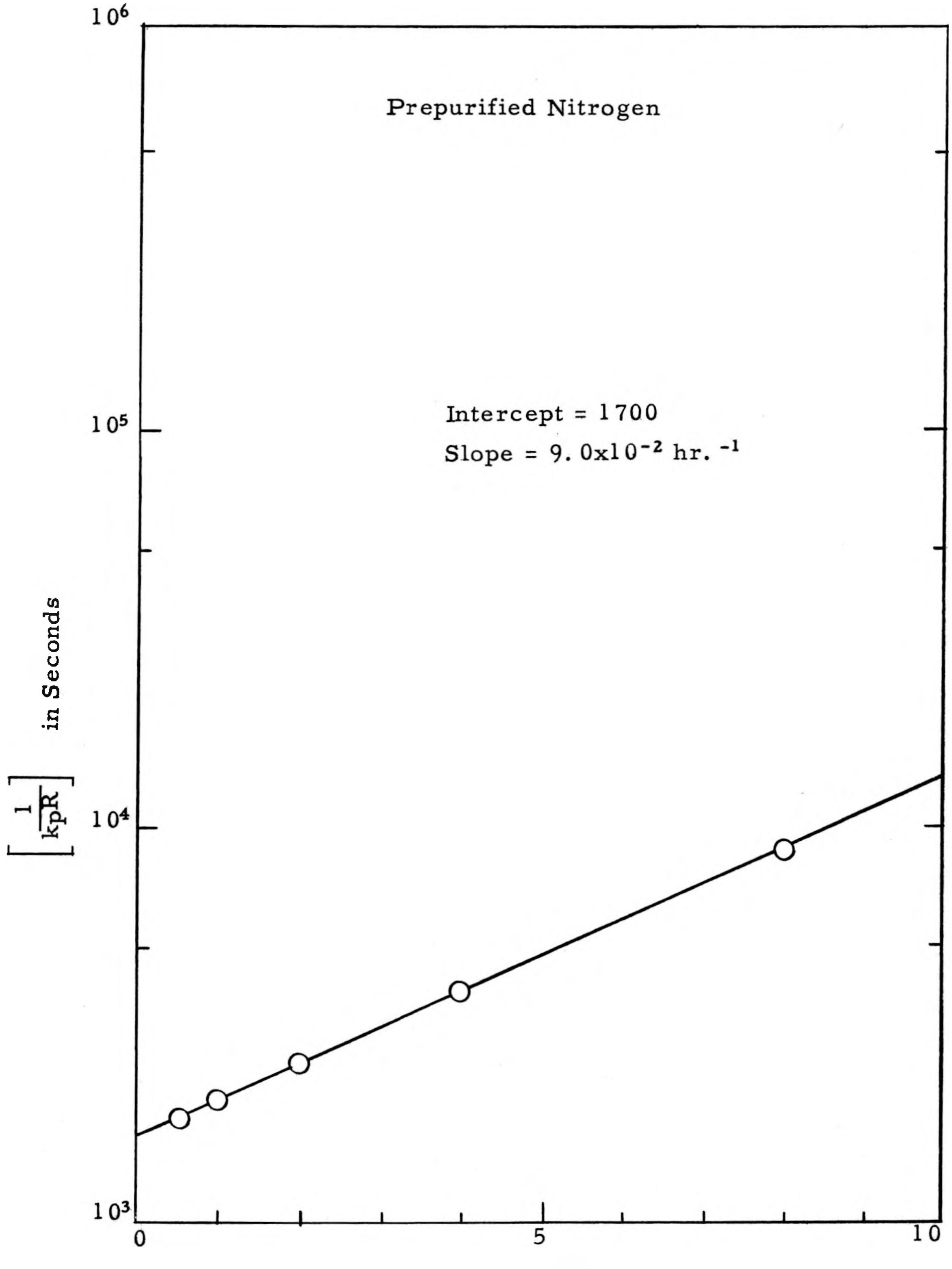


Figure 12. Post Irradiation Graft Polymerization of Acrylonitrile to Polypropylene Yarn

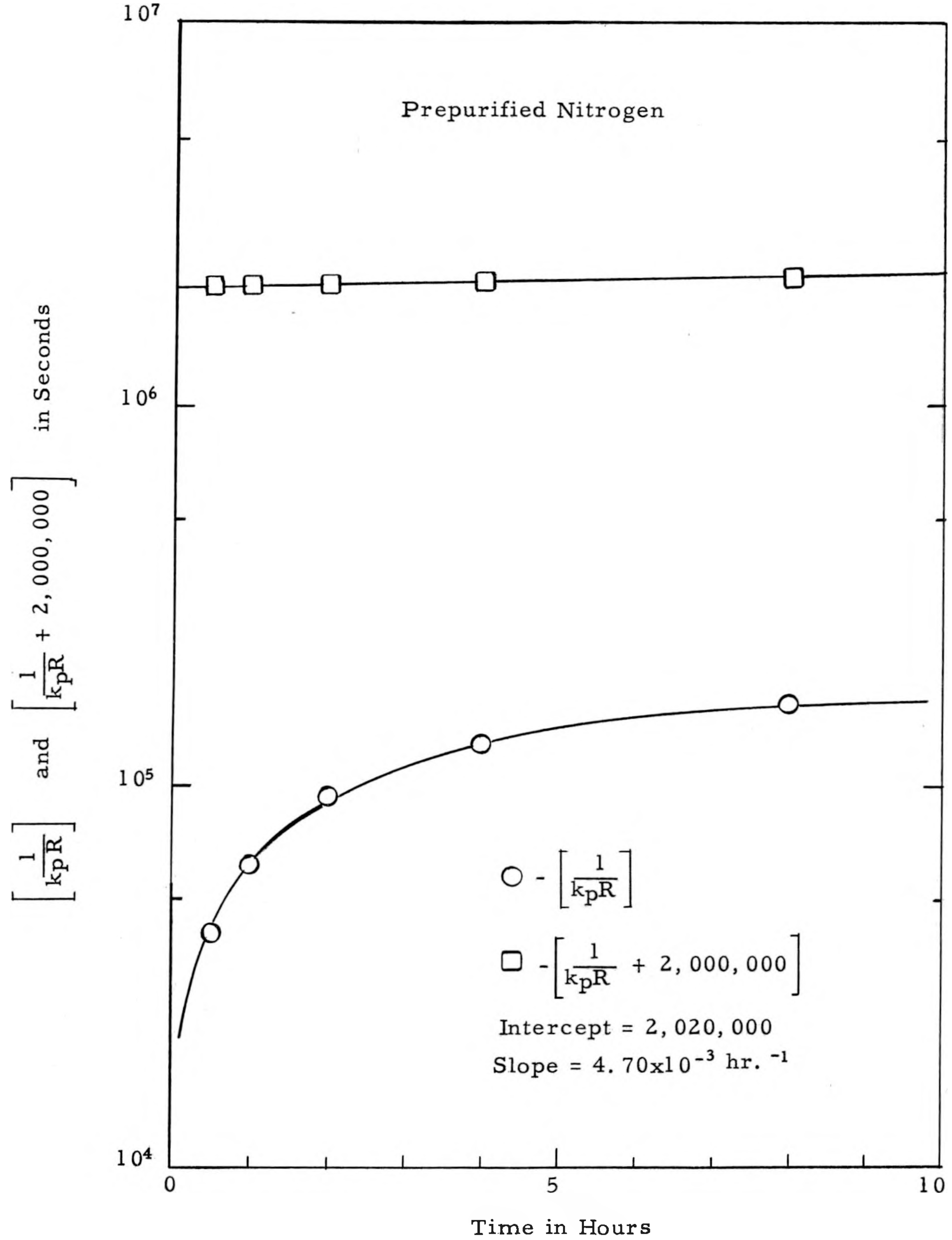


Figure 13. Post Irradiation Graft Polymerization of Acrylonitrile to Polyester Yarn

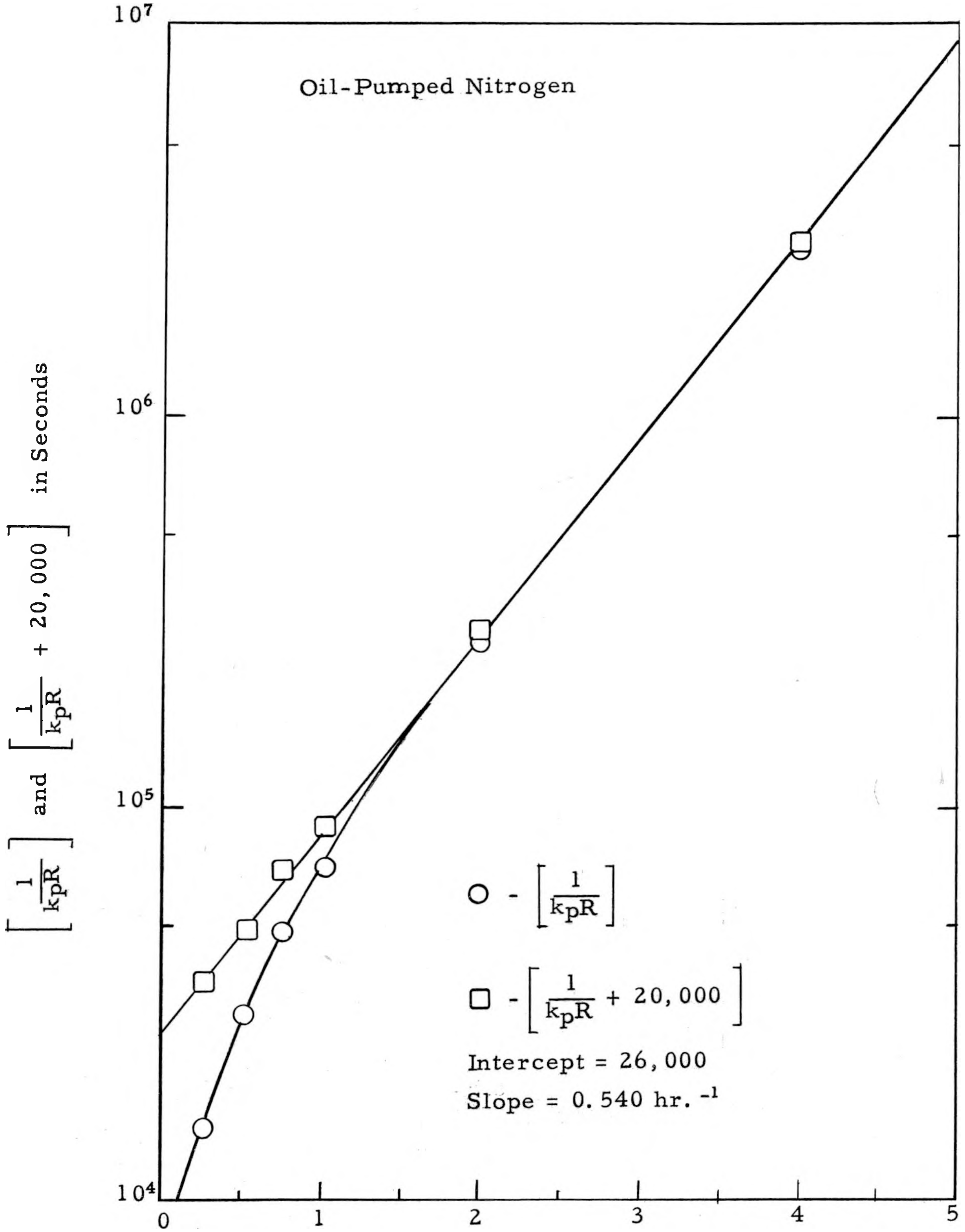


Figure 14. Post Irradiation Graft Polymerization of Acrylonitrile to Acetate Yarn

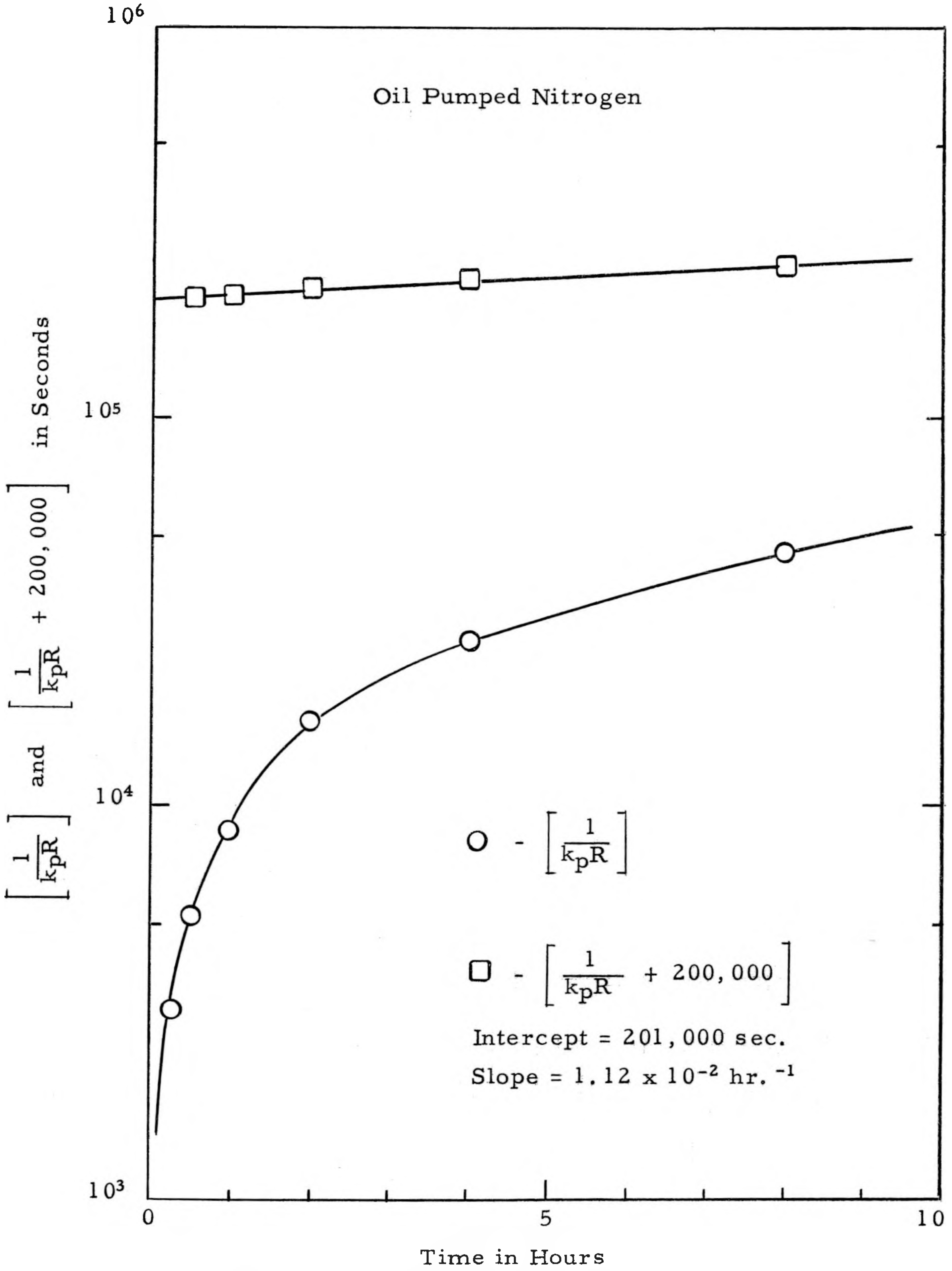


Figure 15. Post Irradiation Graft Polymerization of Acrylonitrile to Nylon Yarn

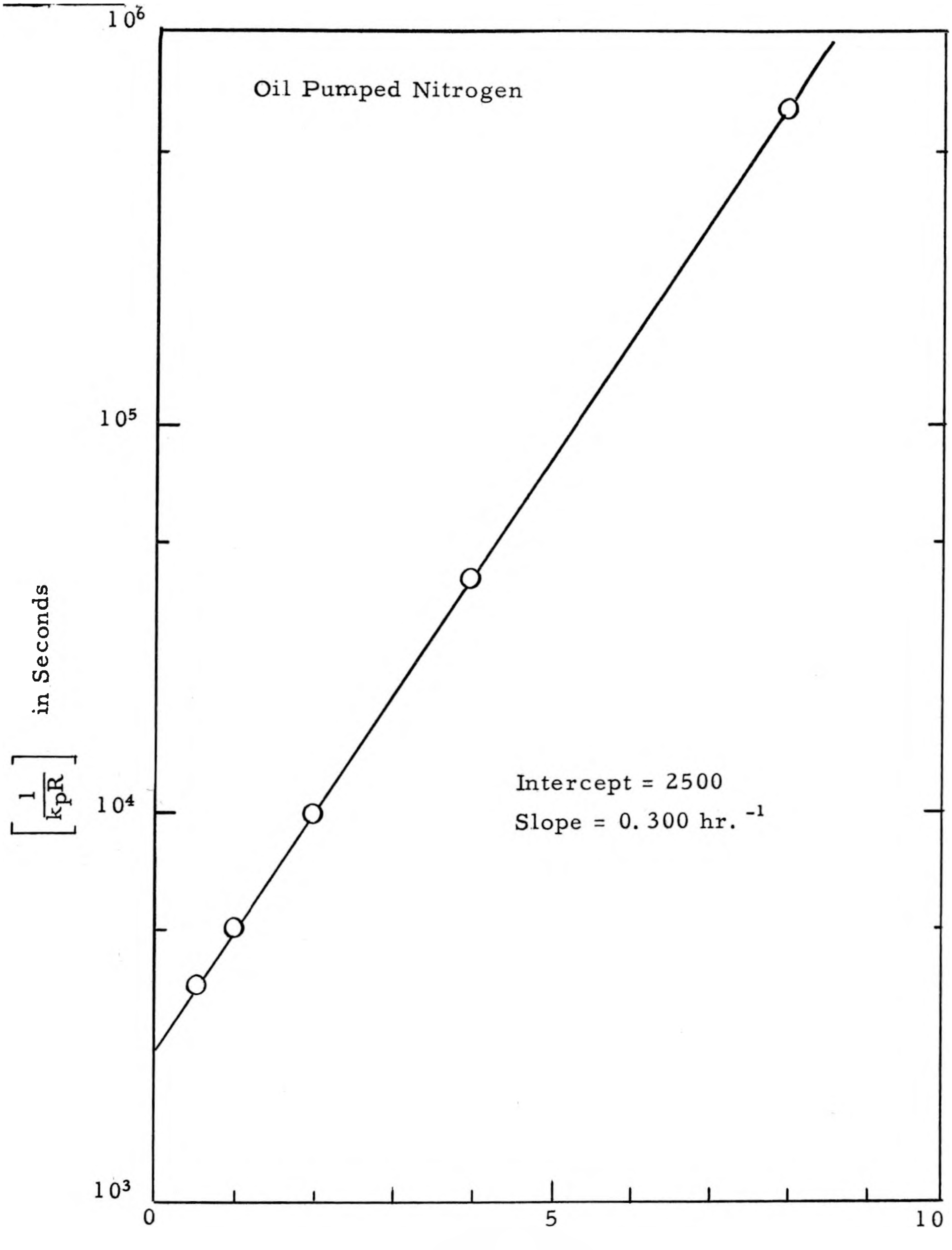


Figure 16. Post Irradiation Graft Polymerization of Acrylonitrile to Polypropylene Yarn

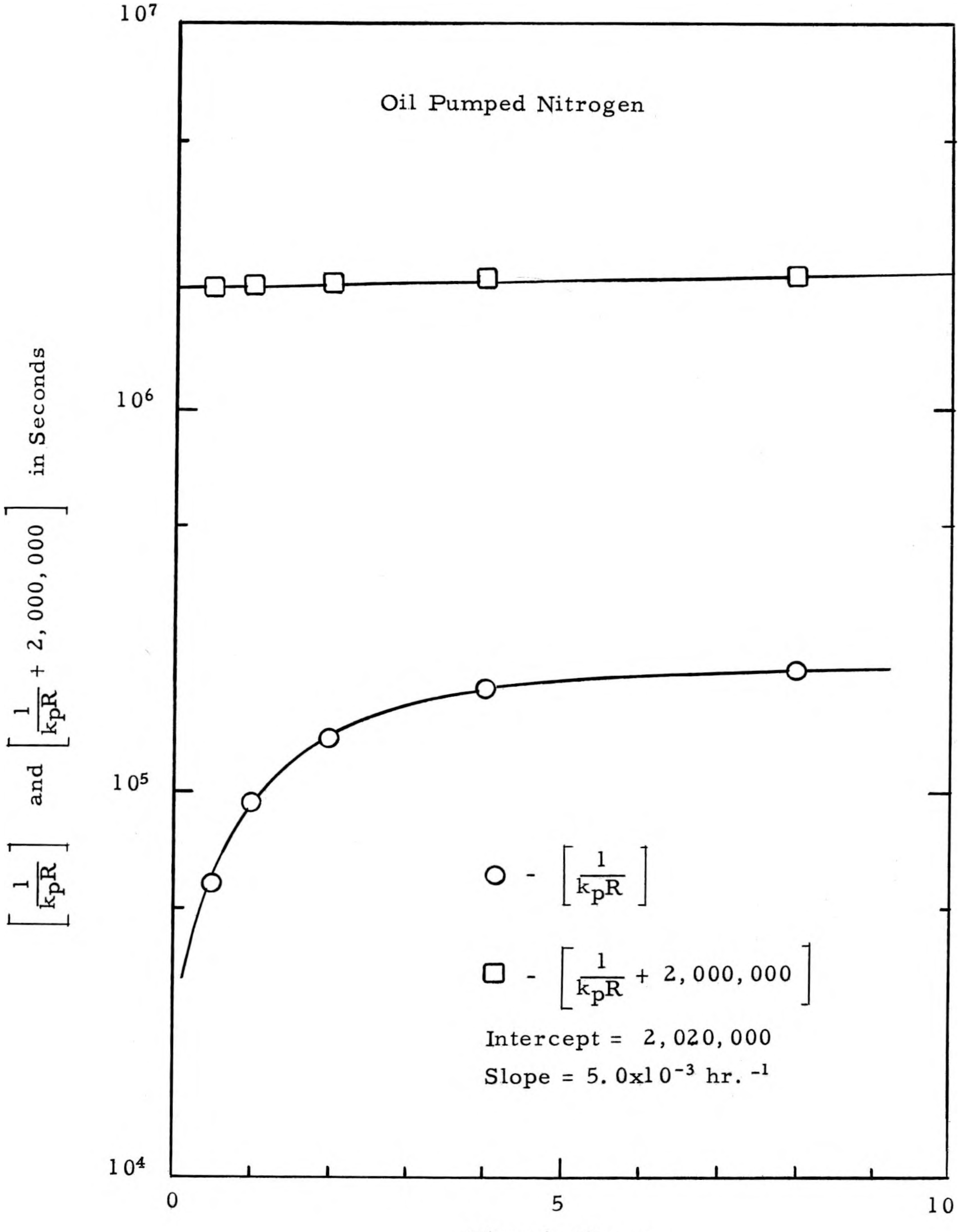


Figure 17. Post Irradiation Graft Polymerization of Acrylonitrile to Polyester Yarn

Figure 18.

Radical Buildup in Acetate Yarn

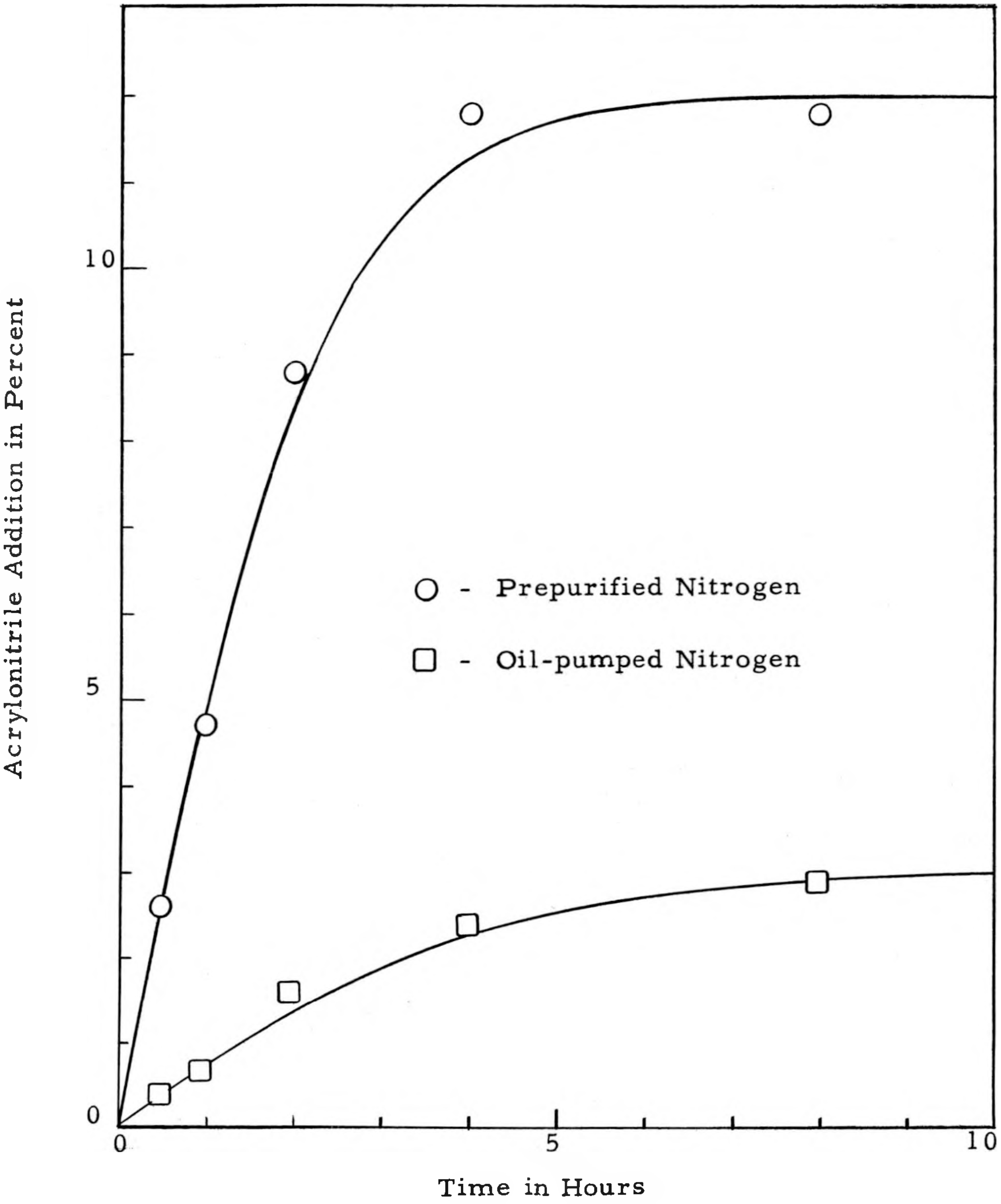


Figure 19.

Radical Buildup in Polypropylene Yarn

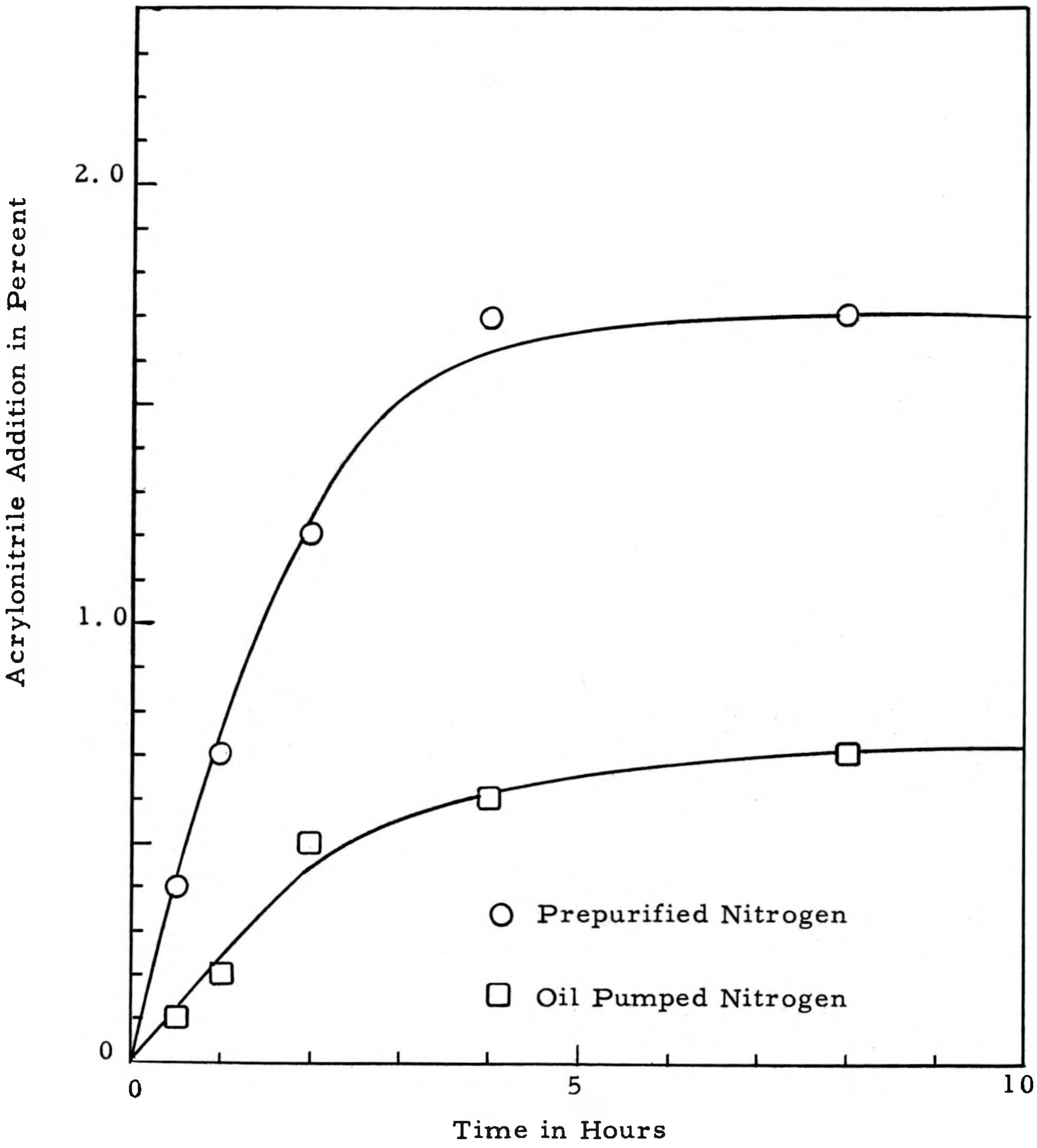


Figure 20.

Radical Buildup in Nylon Yarn

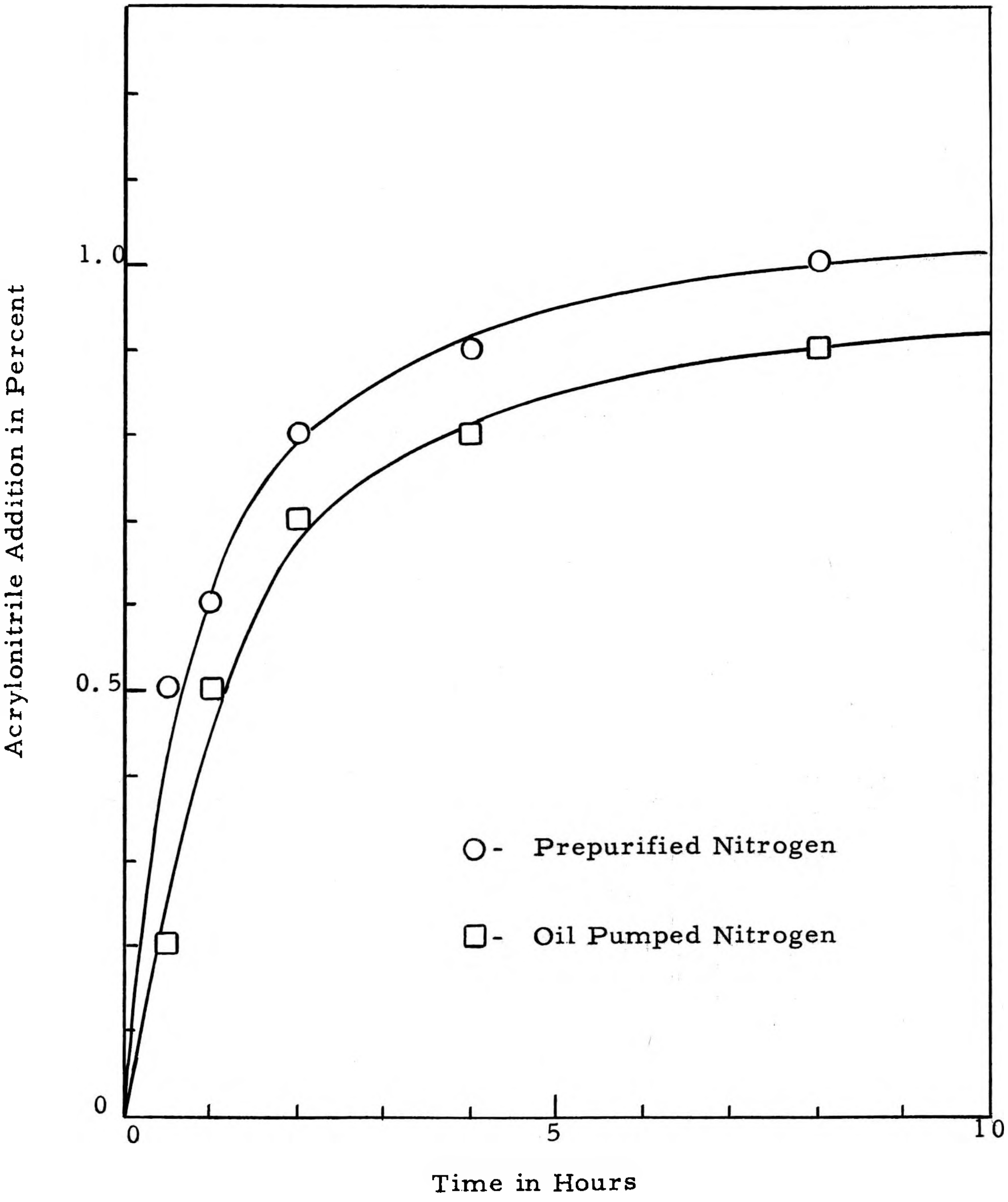
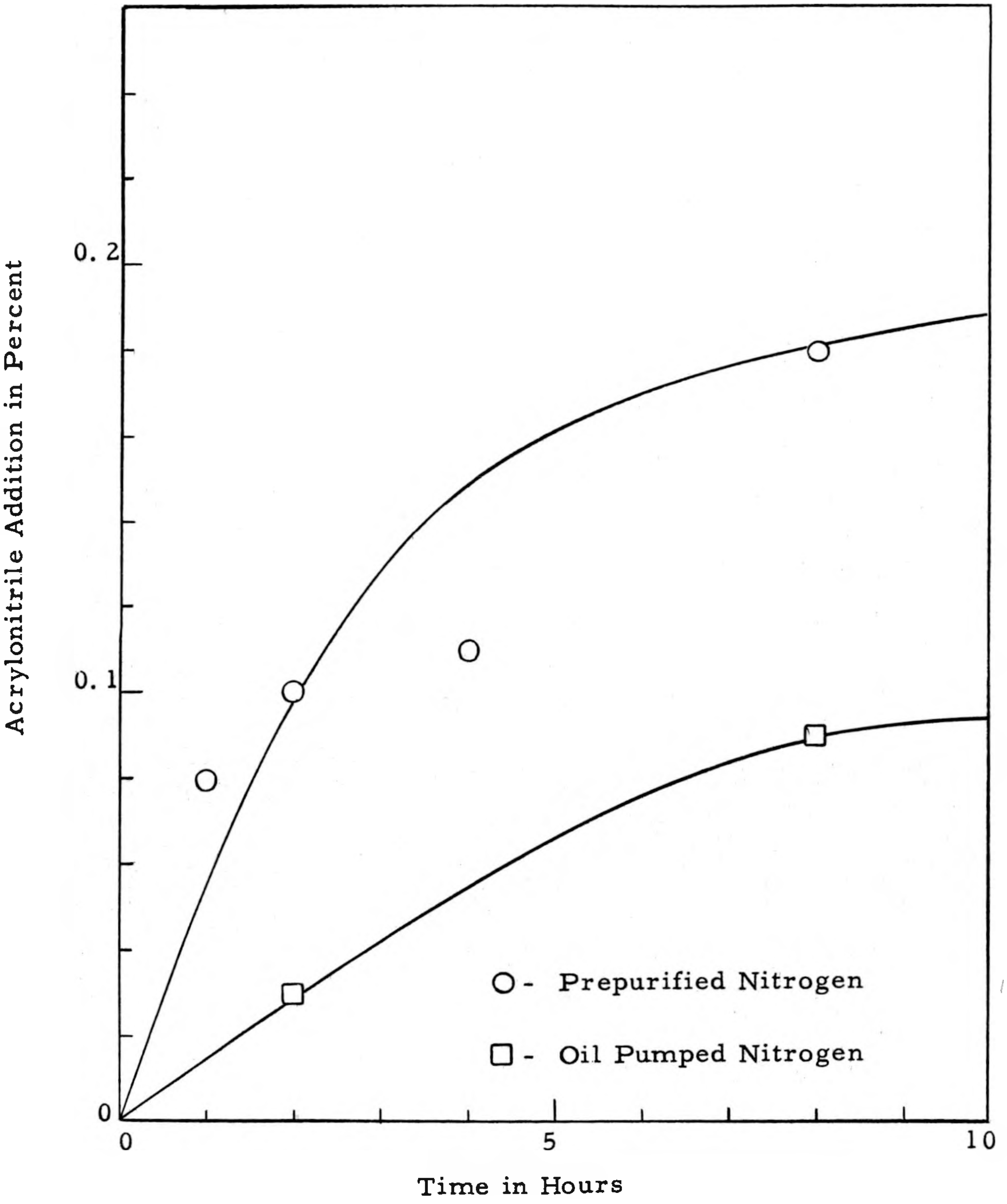


Figure 21.
Radical Buildup in Polyester Yarn



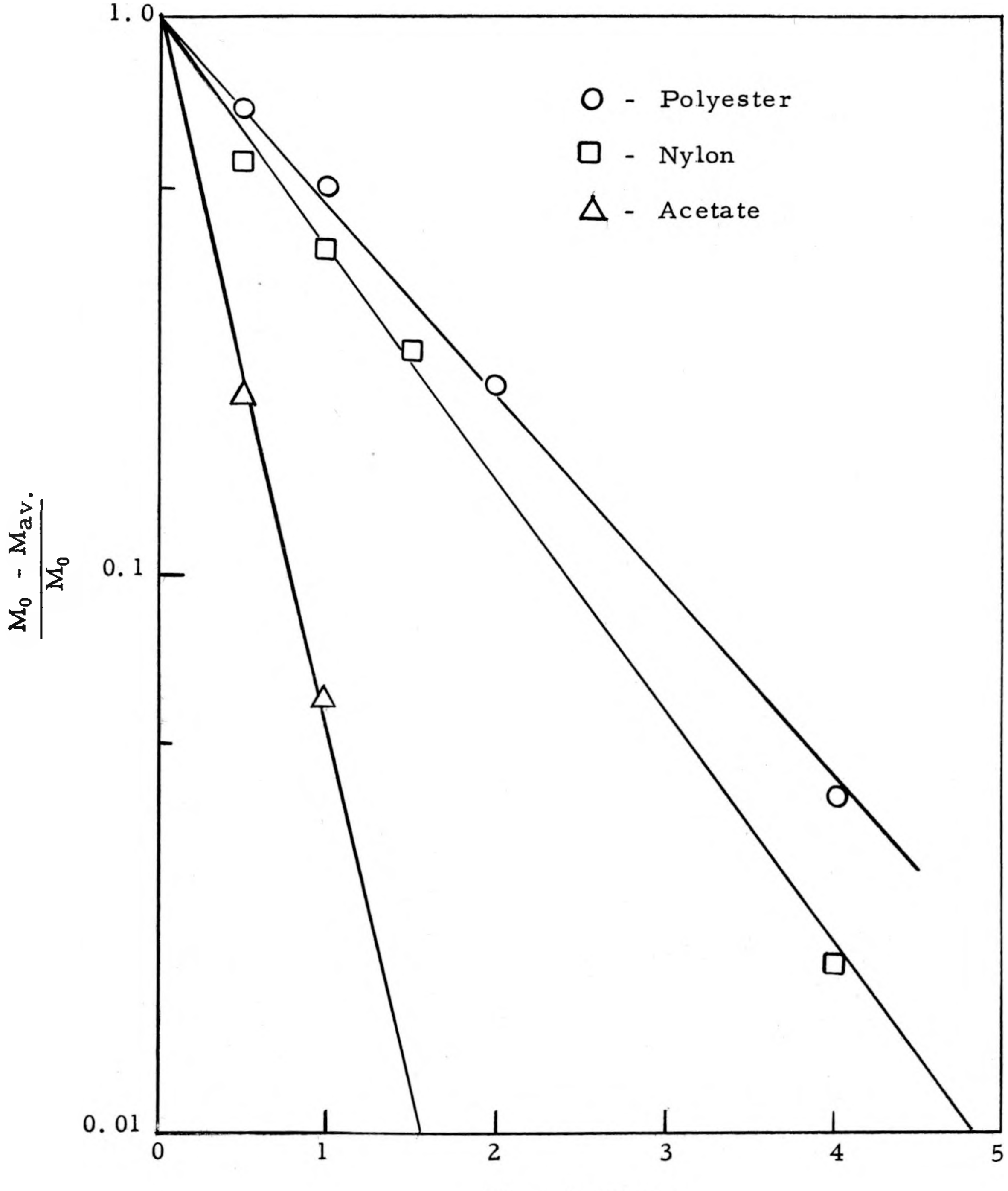


Figure 22. Diffusion of Acrylonitrile Vapor into Yarns