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RADIATION CHEMISTRY LABORATORY SERIES  
RESEARCH REPORT NO. 3

IRRADIATION "FACTOR-DEPENDENCY"  
Styrene With Additives

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NOVEMBER 1960

NATICK, MASSACHUSETTS

## FOREWORD

This is Research Report No. 3 of the Radiation Chemistry Laboratory Series on the general topic of Irradiation "Factor-Dependency." Some effects of parameters such as additives, dose rate, and dose level are reported for the irradiation-induced polymerization of styrene on a forty-five minute cycle at 75°C.

Research Report No. 1, Styrene, considered factors such as (1) atmosphere, (2) degassing, (3) diluent, (4) dose, (5) dose rate, (6) moisture, and (7) temperature. A statistical study of the significance of atmosphere, dose rate, and temperature for the irradiation-induced polymerization of styrene was included.

Research Report No. 2, Some Vinyl Monomers, presented data which indicate that under the conditions of these studies: (1) polymerization rate is not equal to  $kI^{\frac{1}{2}}$ , (2) the E-value (modified "G<sub>e</sub>"-value) increases in general with a decrease in dose rate, (3) there is a non-additivity of dose, and (4) unless parameters are critically defined, irradiation-induced polymerization rate has no apparent significance.

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Irradiation "Factor-Dependency": Styrene with Additives

By Ed. F. Degering, G. J. Caldarella, Flora E. Evans,  
Stephen Grib, and Throop Smith

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A. Introduction

Experimental results presented in these reports represent relative rather than absolute values. This is a consequence of certain slight uncontrollable variations in parameters such as: (1) source of the monomer, (2) moisture content and other impurities, (3) wall thickness of irradiation tubes, (4) uniformity of the flame-out of the glass tubes, (5) uniformity of the degassing procedure from tube to tube on the manifold, (6) preparation of the samples, (7) fluctuations in the beam current and deviations in its distribution, (8) temperature, (9) refrigeration time between irradiation and processing, and (10) processing procedure.

To minimize experimental error, a meticulous routine procedure is used in the preparation, irradiation, and processing of the samples. In this particular study on the effect of certain additives, triplicate samples were used. About eight hundred samples were prepared, irradiated on the same day, and processed in order to determine the effect of: (1) additive, (2) flaming out the tubes, (3) degassing of the monomer, (4) dose rate, and (5) dose level on both the amount and the molecular weight of the polymer.

B. Preparation of Samples

The procedure developed in this laboratory is as follows: The monomer (styrene) is vacuum distilled, dried several days over anhydrous potassium carbonate, and siphoned as used into a 250 ml. glass stoppered graduate, which is connected in turn

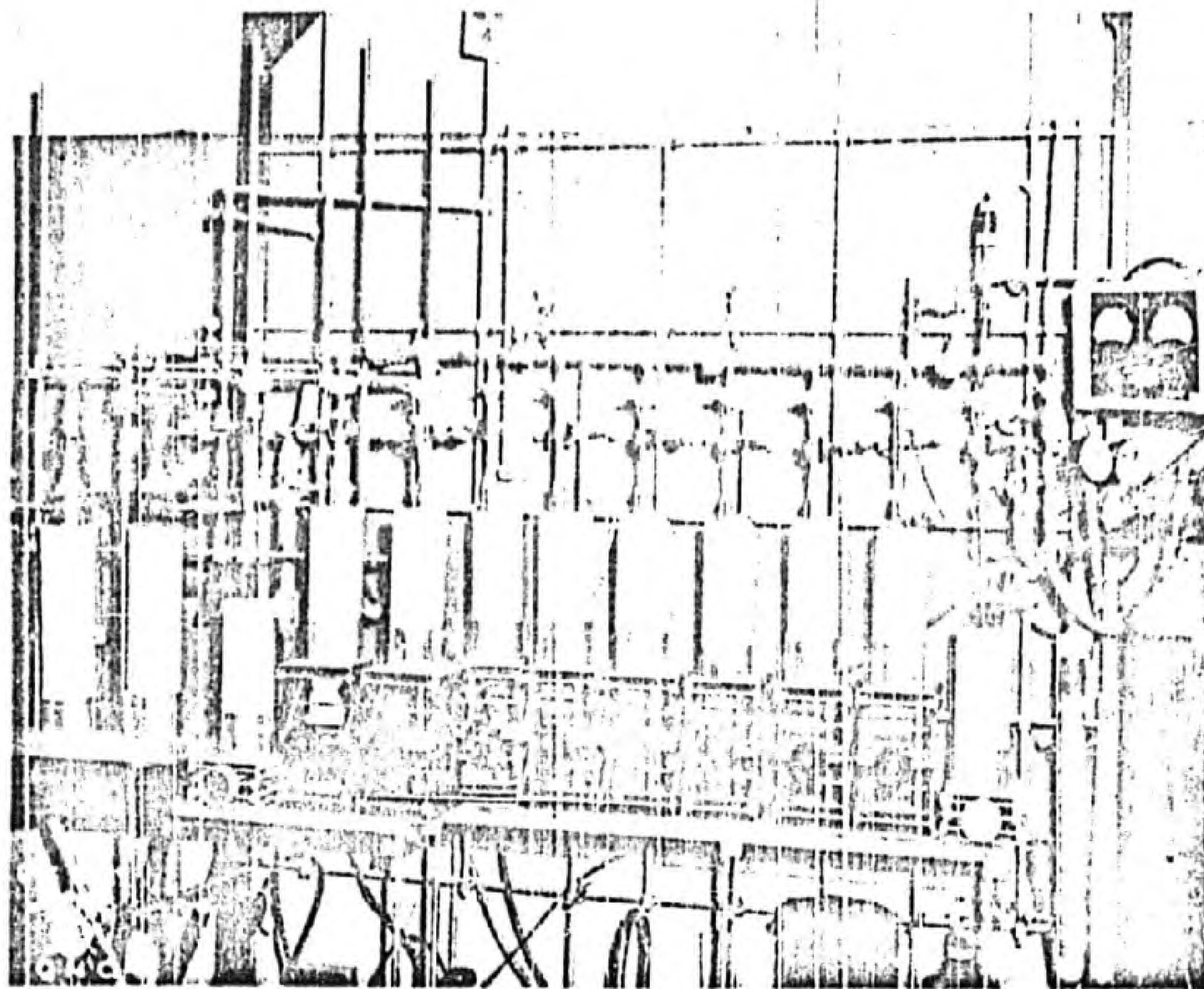


Figure 1. Apparatus used in preparation of samples.

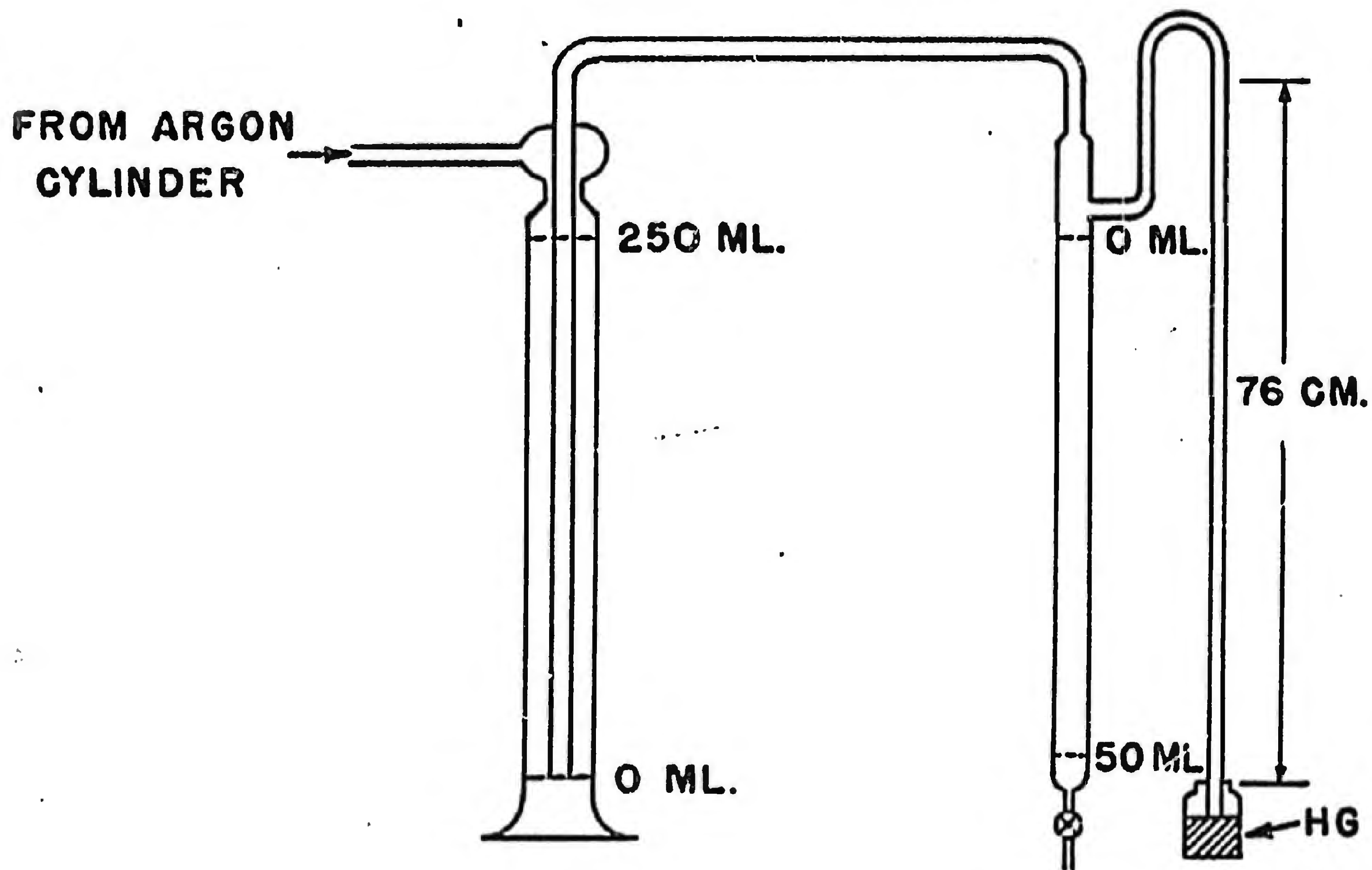


Figure 2. Apparatus for measuring out samples of monomer in the presence of argon with slow flow of argon through the system to exclude both air and moisture.

to an argon-filled automatic burette. The burette is filled in turn by use of slight argon pressure inside of the graduate (Figure 2, page 2).<sup>1</sup>

Ten constricted 1 × 12 inch pyrex test tubes, fitted with ground glass joints, are placed on the vacuum manifold (Figure 1, page 2), flamed out twice at 300 microns and once at 5 microns, and filled with argon. A 20 ml. portion of the monomer is transferred from the burette (through which a slow stream of argon flows) to each of the argon-filled test tubes, which are then replaced in turn on the manifold. Then Dewar flasks filled with liquid nitrogen are slowly raised by means of jacks in order to freeze the monomer. The respective stopcocks are opened one by one to the manifold and the tubes evacuated to about 300 microns by an auxiliary pump, which is connected to the right end of the manifold (Figure 1, page 2).<sup>2</sup> The auxiliary pump is shut off from the manifold, which is opened in turn to the high vacuum system at the left. The system is lowered to a pressure of five microns, the stopcocks closed, the Dewar flasks lowered, and the monomer allowed to melt and degass. The monomer is frozen again by raising the Dewar flasks, the stopcocks opened, and the system again evacuated initially by use of the auxiliary pump and subsequently by the high vacuum system. The pressure is reduced once again to five microns, the stopcocks turned off, the tubes sealed off, and stored at -20°C until all of the samples are ready for packaging. They are then strip-packaged in polyethylene, according to scheduled dose rate, and returned to the cold room until time for irradiation.

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<sup>1</sup> The samples containing the various additives were made up in individual bottles (flushed with argon) with 99 ml. of styrene and 1 ml. of the additive and stored under argon in a refrigerator until used.

<sup>2</sup> The auxiliary pump is used to avoid contamination of the high vacuum system, particularly in the case of a broken tube.

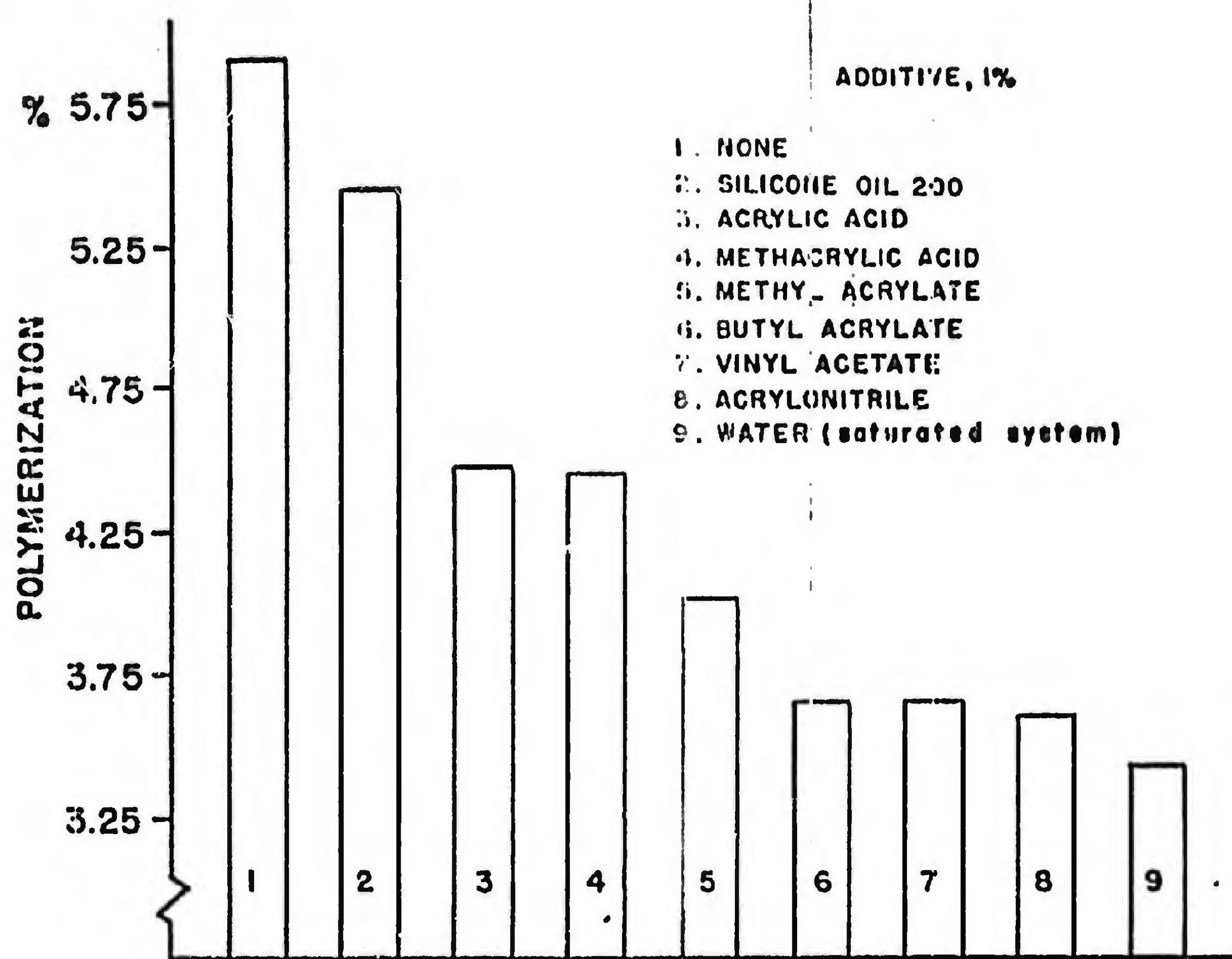


Figure 3. Styrene: Average yields, from 5 exposures at each of 14 dose rates on a 45-minute cycle at 75°C, for the nine additives indicated.

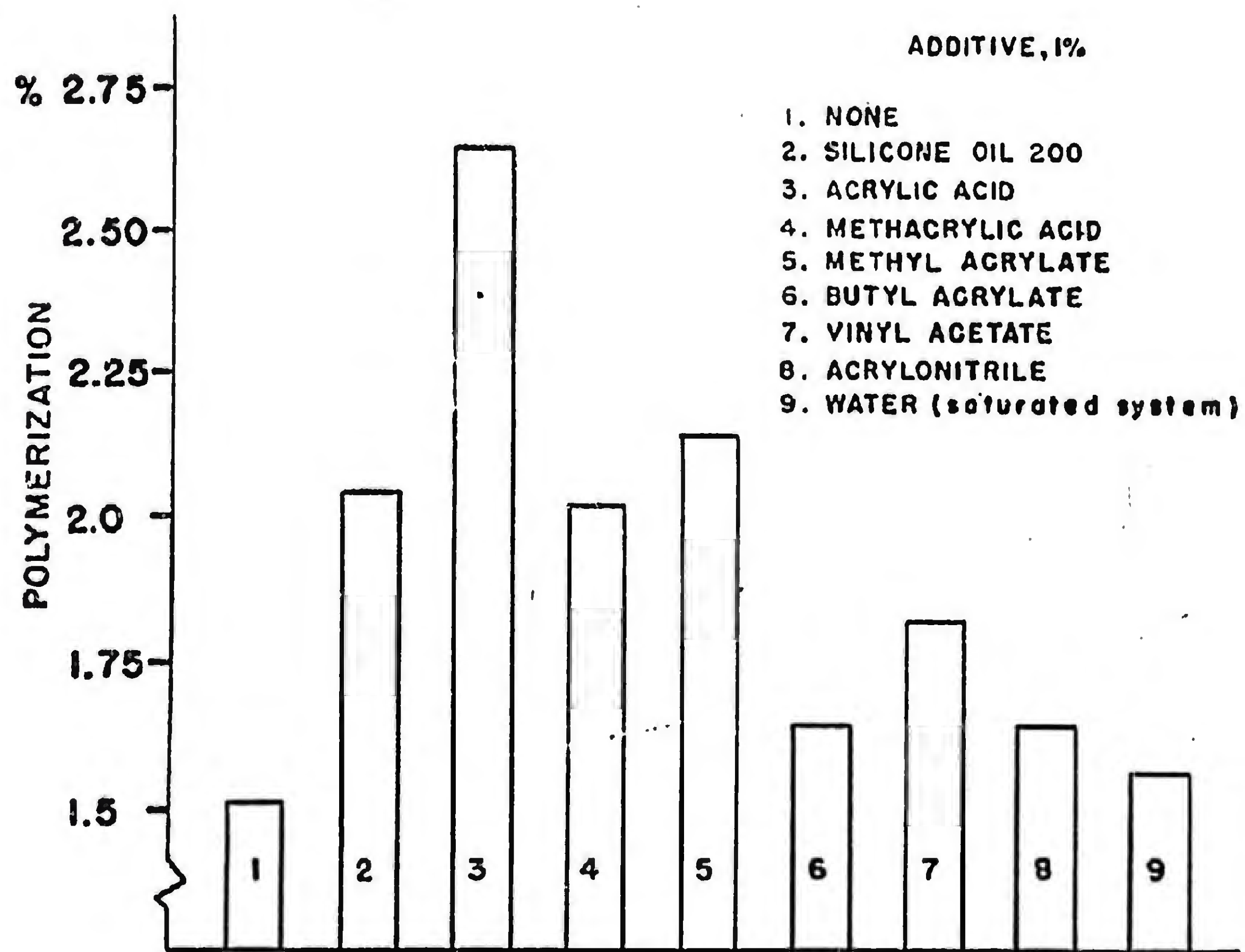


Figure 4. Styrene: Relative yields, from 5 exposures at 1,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

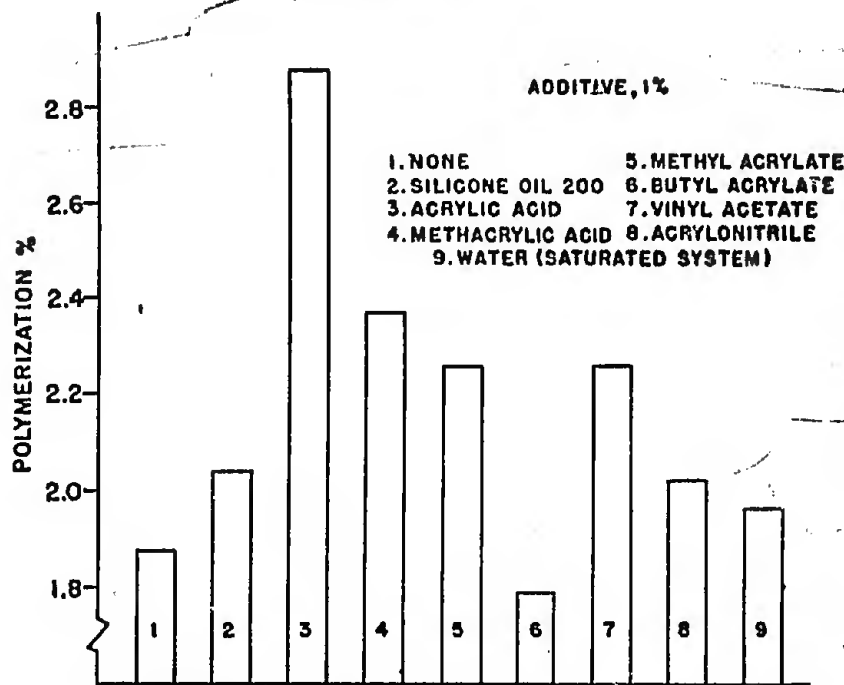


Figure 5. Styrene: Relative yields, from 5 exposures at 3,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

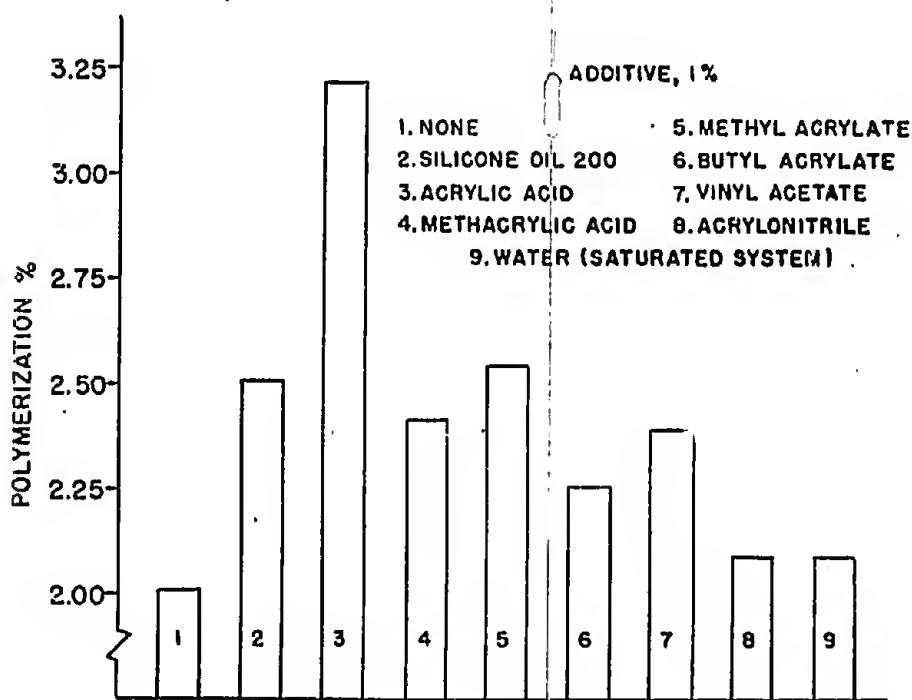


Figure 6. Styrene: Relative yields, from 5 exposures at 5,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

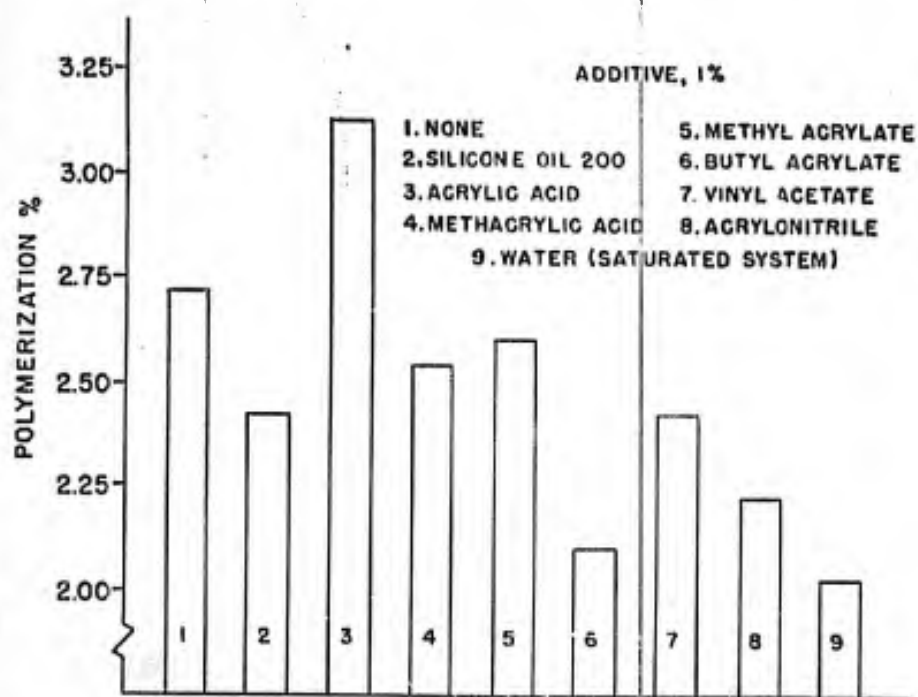


Figure 7. Styrene: Relative yields, from 5 exposures at 7,500 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

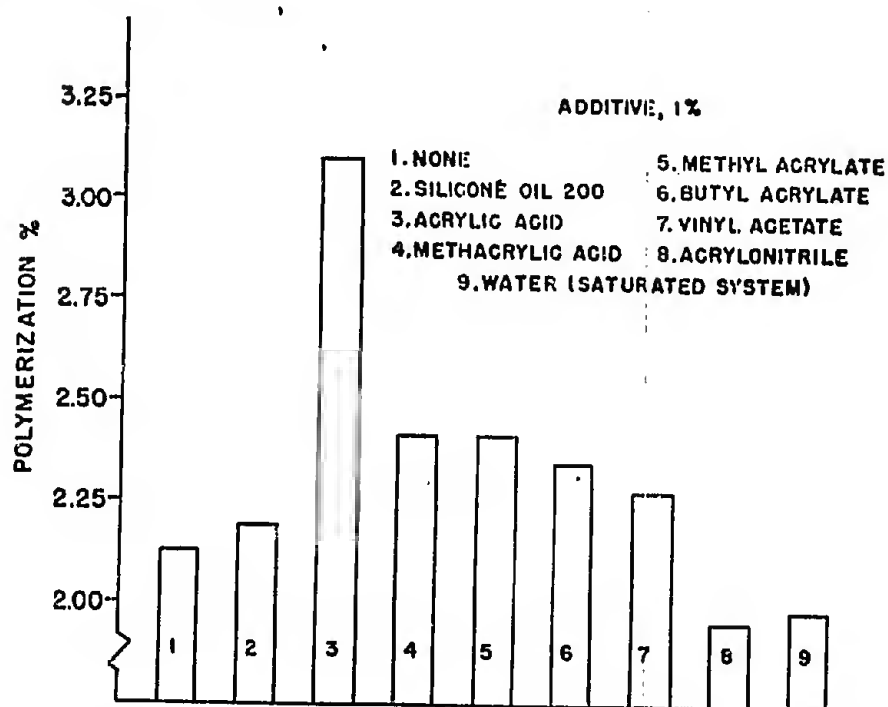


Figure 8. Styrene: Relative yields, from 5 exposures at 10,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

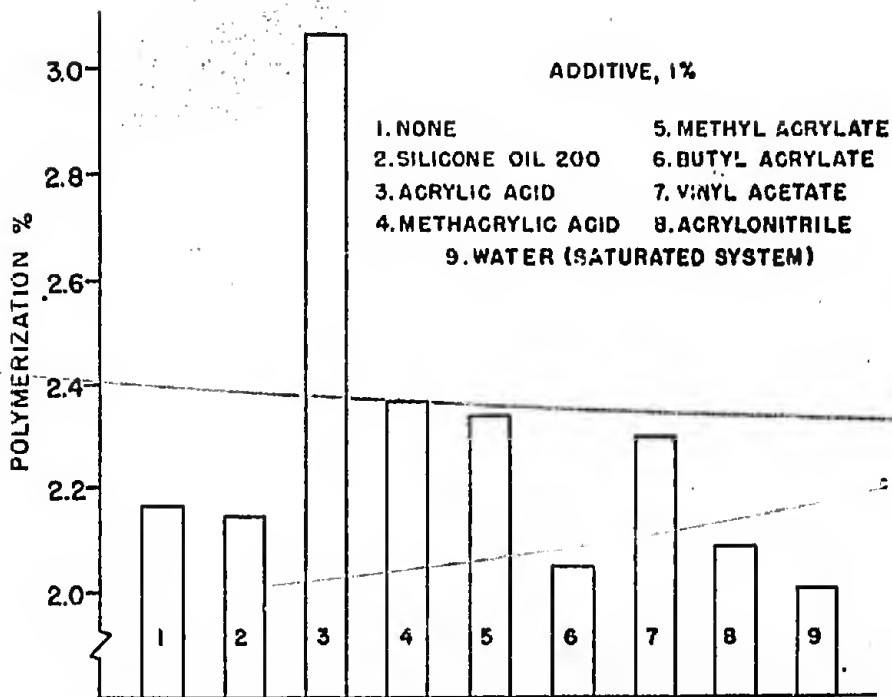


Figure 9. Styrene: Relative yields, from 5 exposures at 15,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

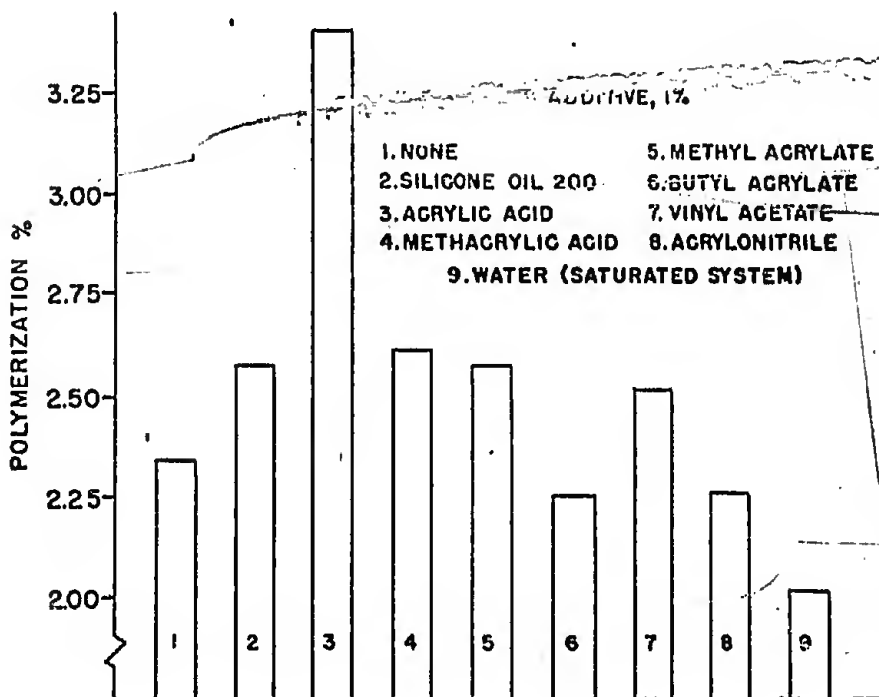


Figure 10. Styrene: Relative yields, from 5 exposures at 20,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

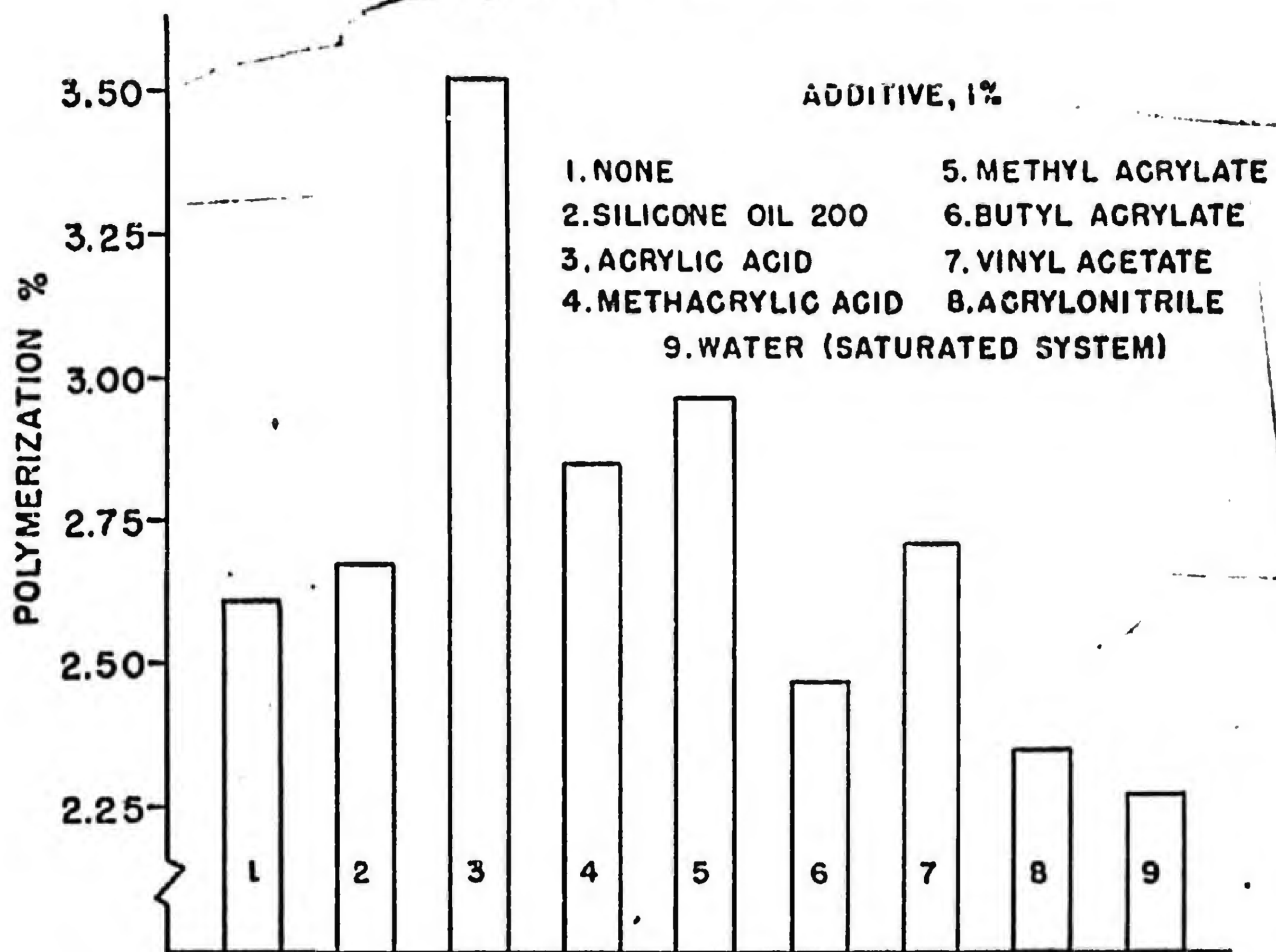


Figure 11. Styrene: Relative yields, from 5 exposures at 25,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

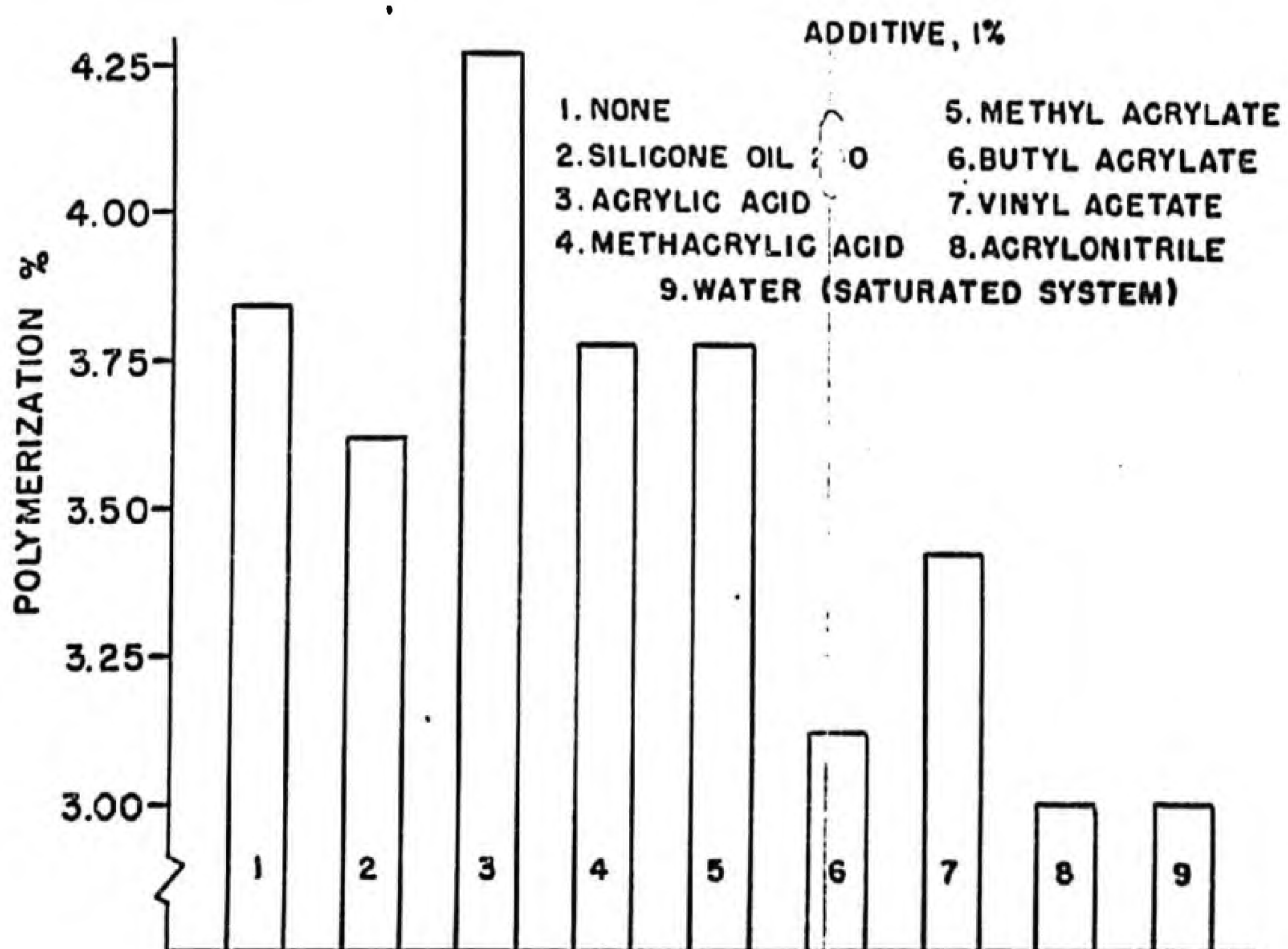


Figure 12. Styrene: Relative yields, from 5 exposures at 50,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

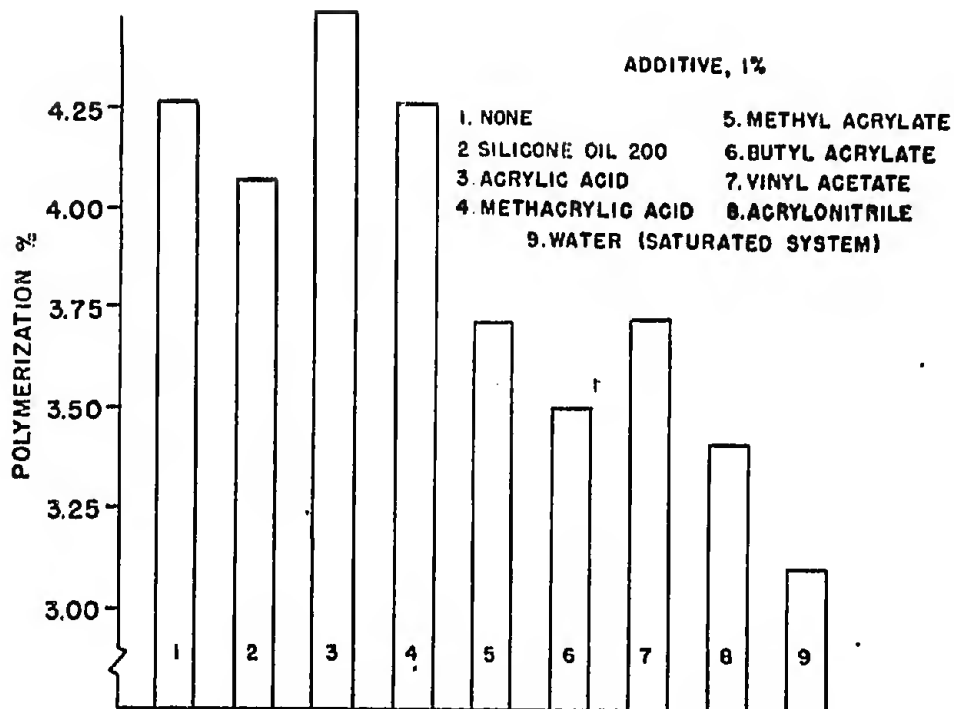


Figure 13. Styrene: Relative yields, from 5 exposures at 75,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

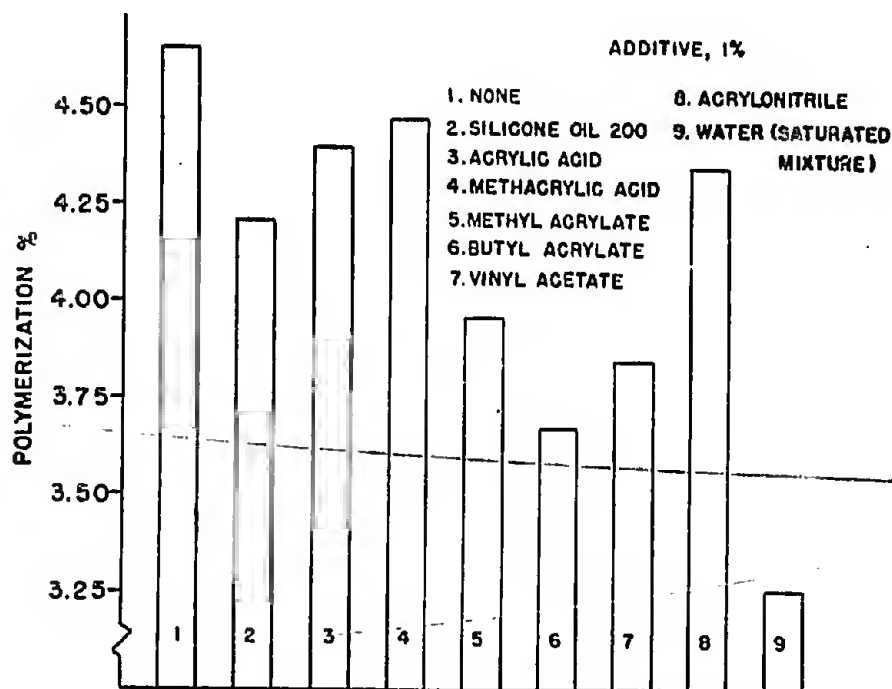


Figure 14. Styrene: Relative yields, from 5 exposures at 100,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

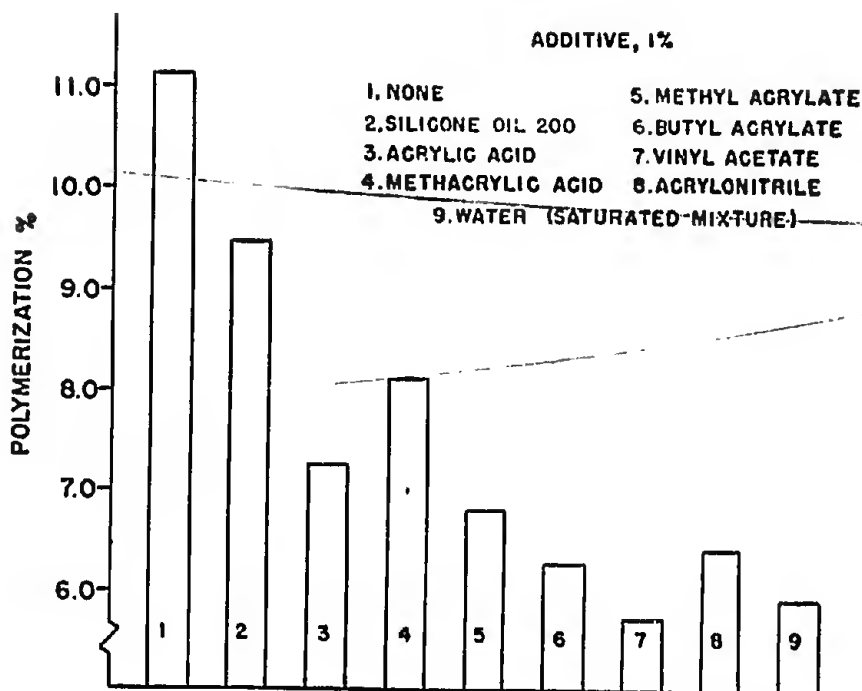


Figure 15. Styrene: Relative yields, from 5 exposures at 500,000 rads each on a 45-minute cycle at 15°C, for the nine additives indicated.

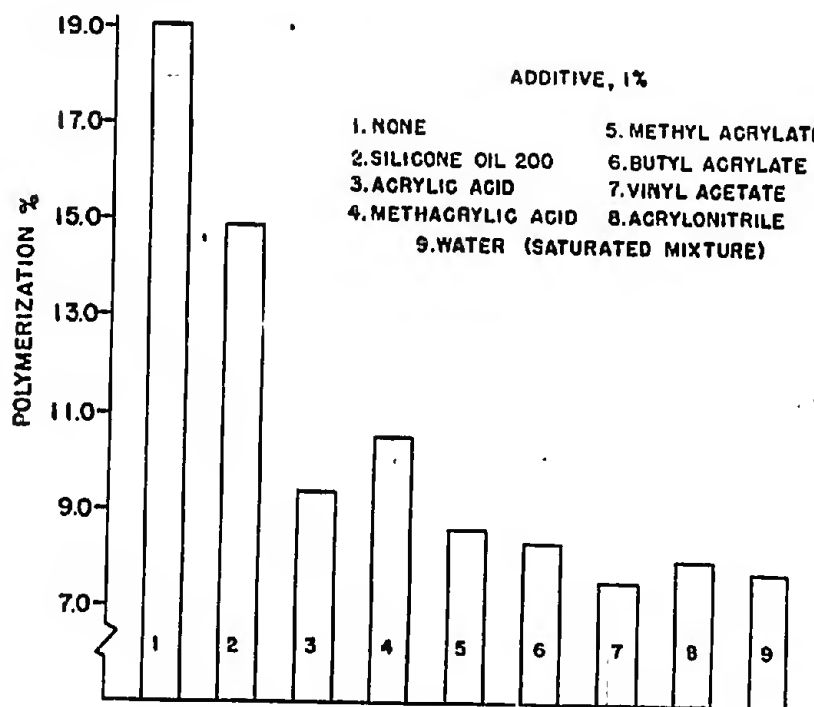


Figure 16. Styrene: Relative yields, from 5 exposures at 1,000,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

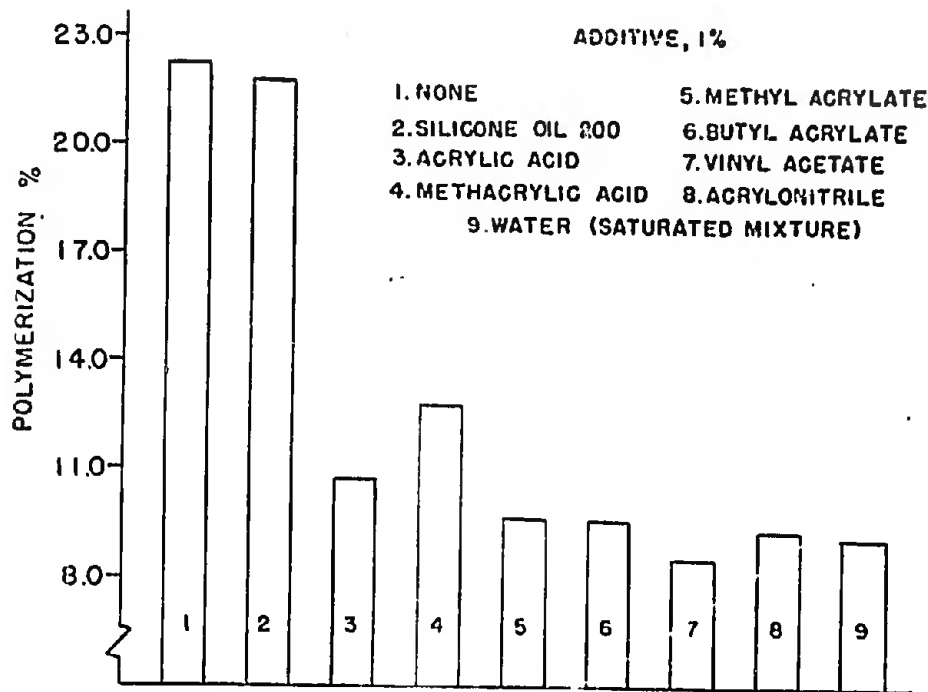


Figure 17. Styrene: Relative yields, from 5 exposures at 1,500,000 rads each on a 45-minute cycle at 75°C, for the nine additives indicated.

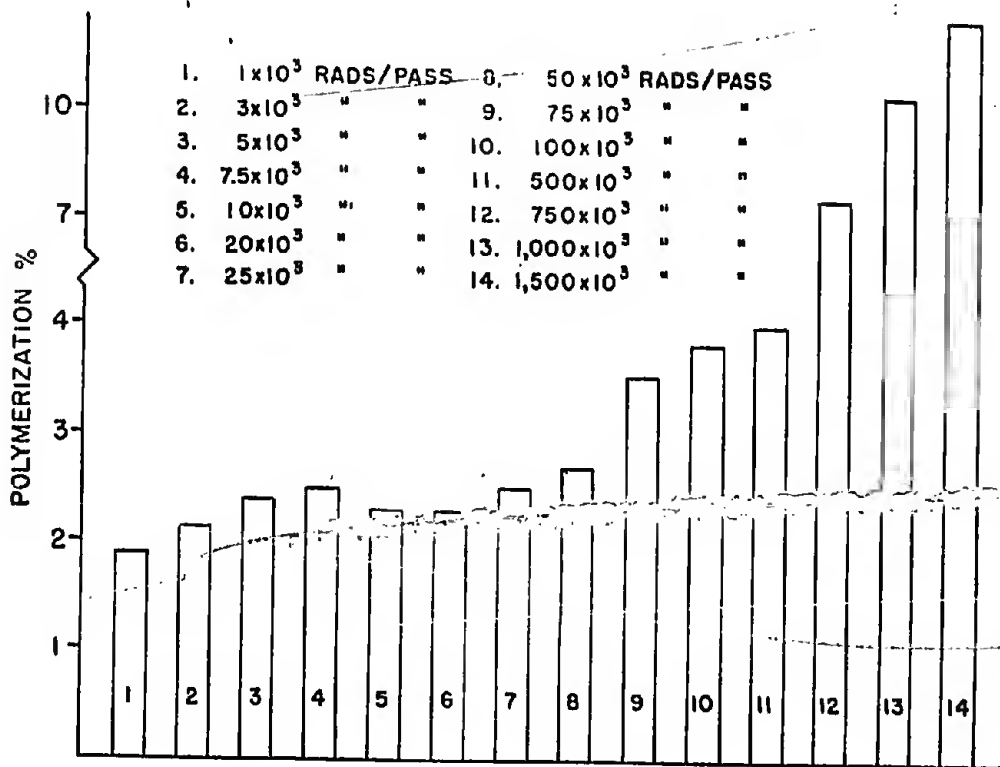


Figure 18. Styrene: Average yields, from 5 exposures at 14 dose rates on a 45-minute cycle at 75°C, for the nine additives indicated.

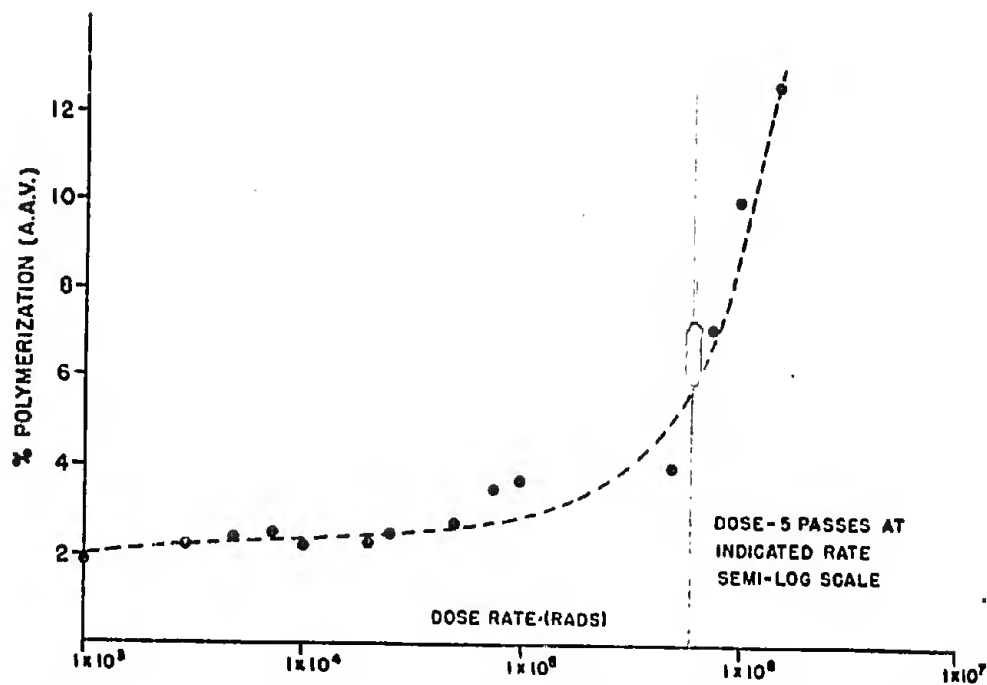


Figure 19. Styrene: Average yields from nine additives by dose rate for fourteen dose levels (D-662 to D-670).

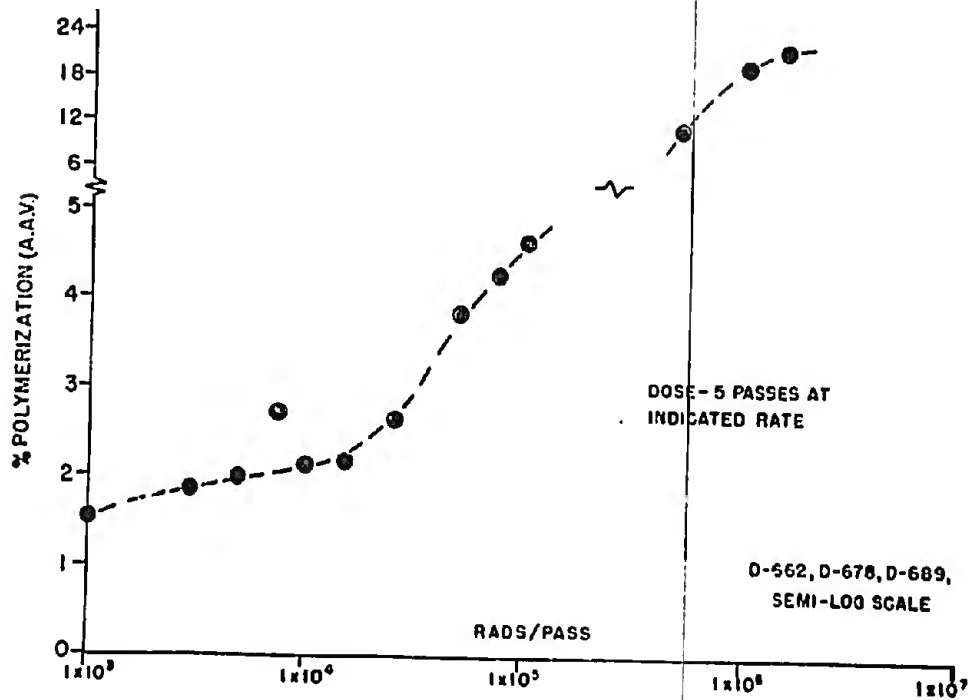


Figure 20. Styrene: Average yields from no additive by dose rate for fourteen dose levels.

### C. Irradiation of Samples

Irradiation is effected with a 1 1/2 Mev Van de Graaff electron accelerator, operating at 2 Mev. The beam current is monitored by use of an ultra-sensitive microammeter.

The samples are placed according to scheduled dose rate in 1 x 1.5 foot aluminum trays, pre-heated in a precision oven at 75°C for 1/2 hour, irradiated at the desired dose rate, and returned to the oven for 45 minutes, and then given another pass under the beam. The aluminum trays are insulated from the conveyer belt by one inch of polystyrene foam. Five such cycles of 45 minutes each were used throughout this study.

After irradiation, the samples are returned to storage at -20°C until the tubes are opened for processing.

### D. Processing of Samples

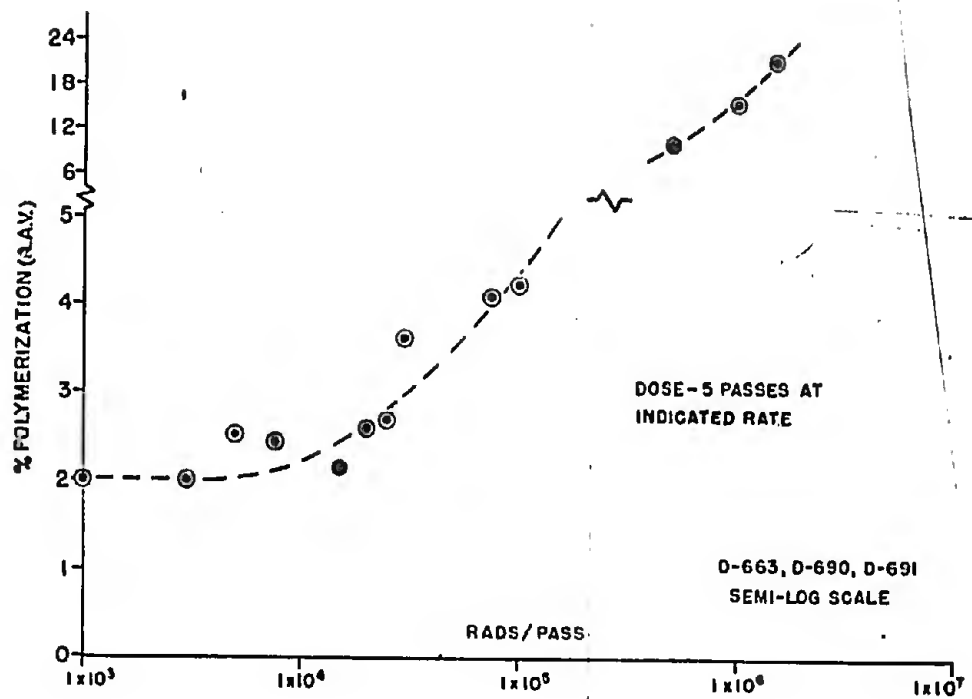
The tubes are scored on an emery wheel, cracked open with a hot glass rod, the contents transferred to a tared aluminum dish on a glass heating plate at about 60°C, the tubes rinsed well three times with methyl ethyl ketone, and the rinsings added to the respective aluminum dishes. The contents of the dishes are evaporated to a residual film. The aluminum dishes are then placed in a vacuum oven at 85°C for approximately four hours in order to remove residual solvent and monomer.

The aluminum dishes are conditioned in the balance room and weighed on a single pan analytical balance. The percent of polymerization is calculated, from the available data.

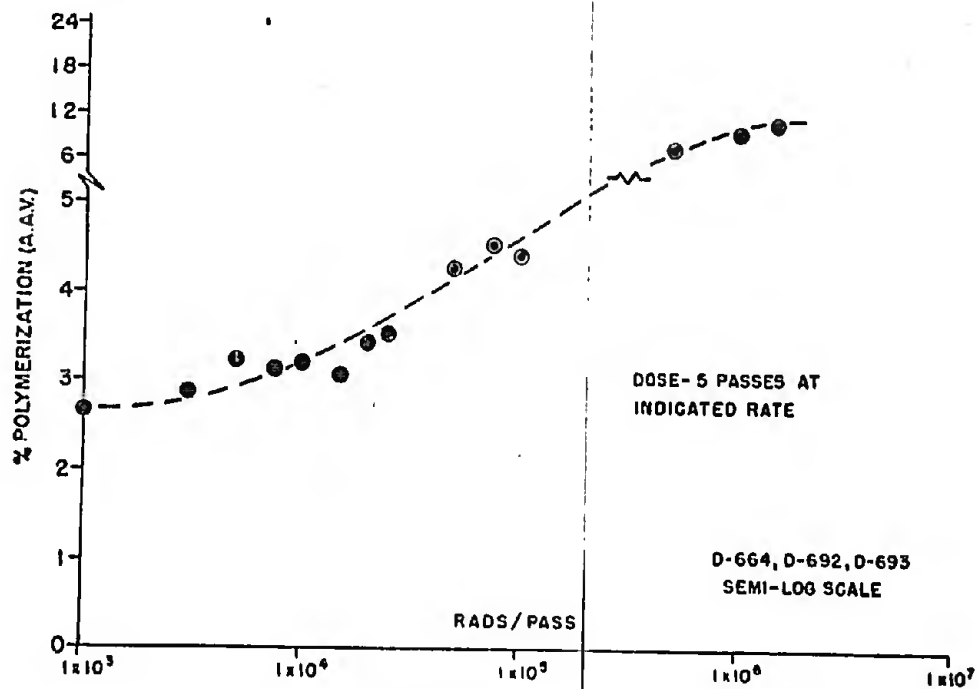
To correct for the variation in wall thickness, the tubes are cut up and 20 micrometer readings taken on each tube in order to obtain an average wall thickness. The wall thickness is then multiplied by the density of the glass (2.23) to give a value from which the percent of ionization may be read directly from a graph.<sup>3</sup> The calculated percent of polymerization is

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<sup>3</sup> Trump, et al., J. App. Phys., 21, 346 (1950).



**Figure 21.** Styrene: Average yield from 1% silicone oil as additive by dose rate for fourteenth dose levels.



**Figure 22.** Styrene: Average yields from 1% acrylic acid as additive by dose rate for fourteenth dose levels.

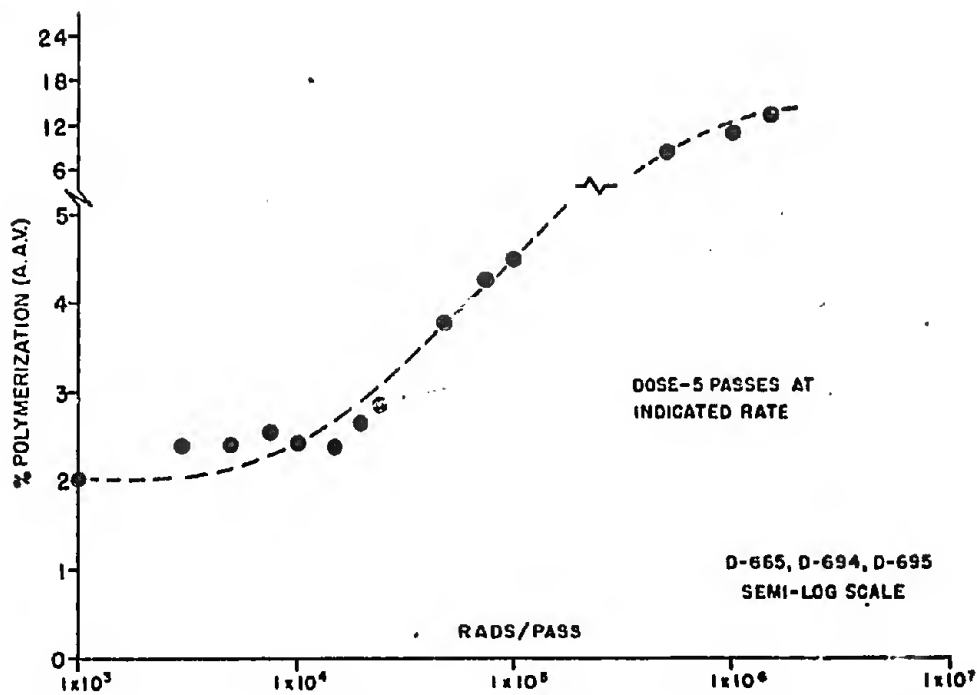


Figure 23. Styrene: Average yields from 1% methacrylic acid as additive by dose rate for fourteen dose levels.

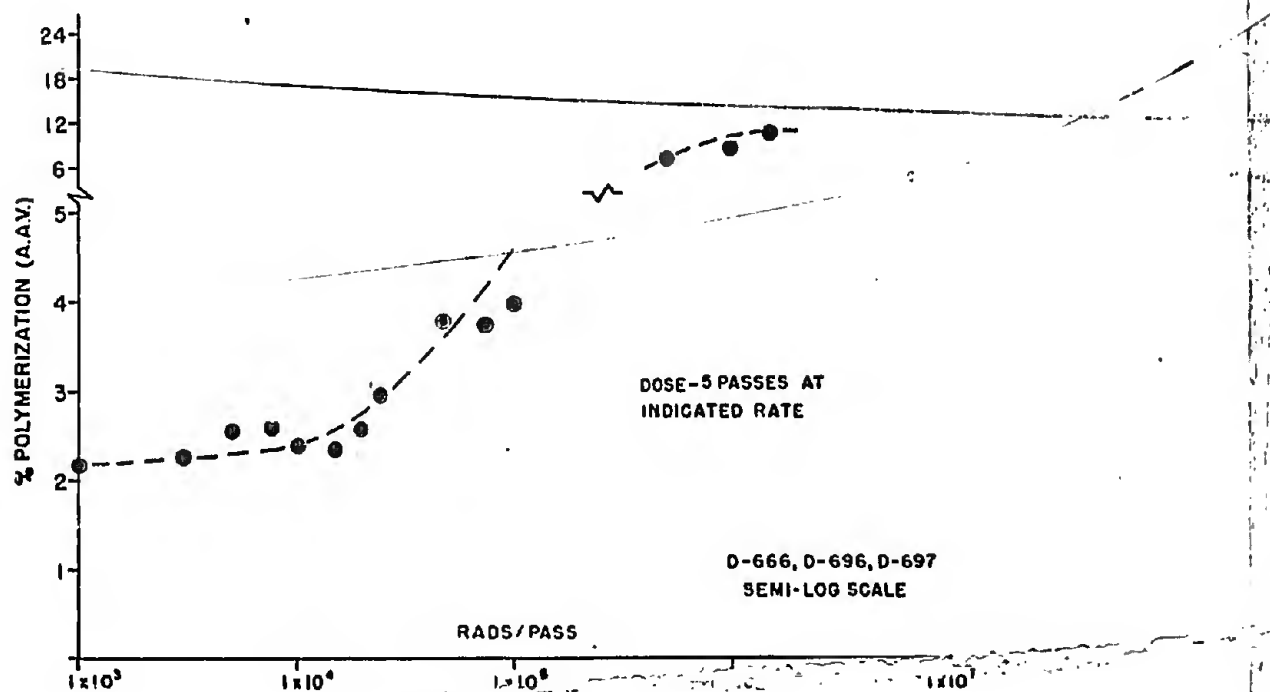


Figure 24. Styrene: Average yields from 1% methyl acrylate as additive by dose rate for fourteen dose levels.

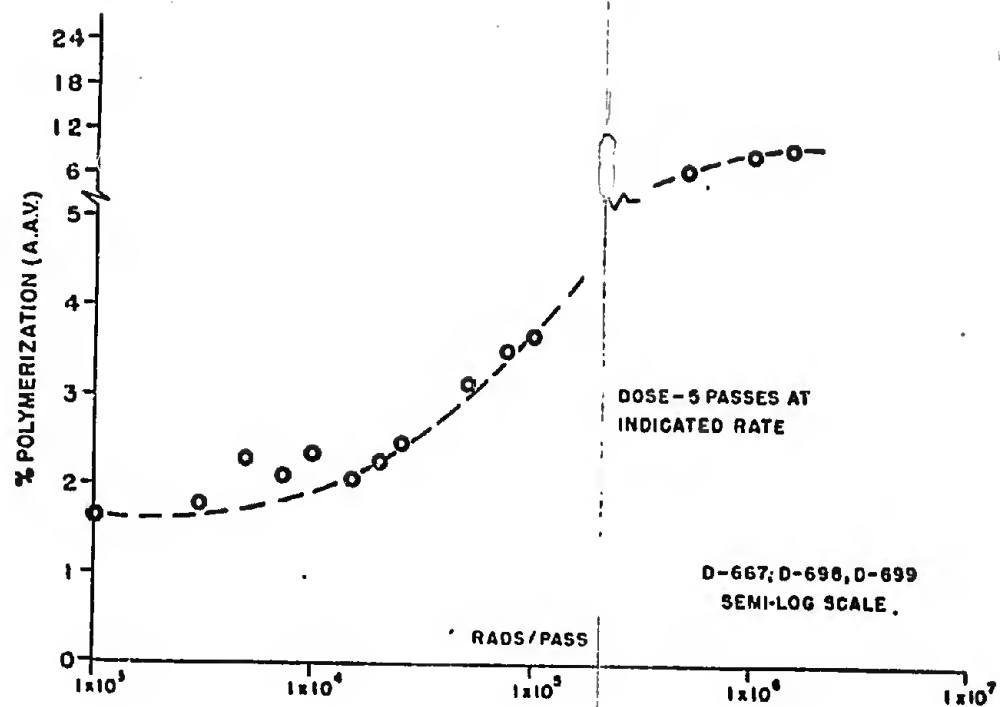


Figure 25. Styrene: Average yields from 1% butyl acrylate as additive by dose rate for fourteen dose levels.

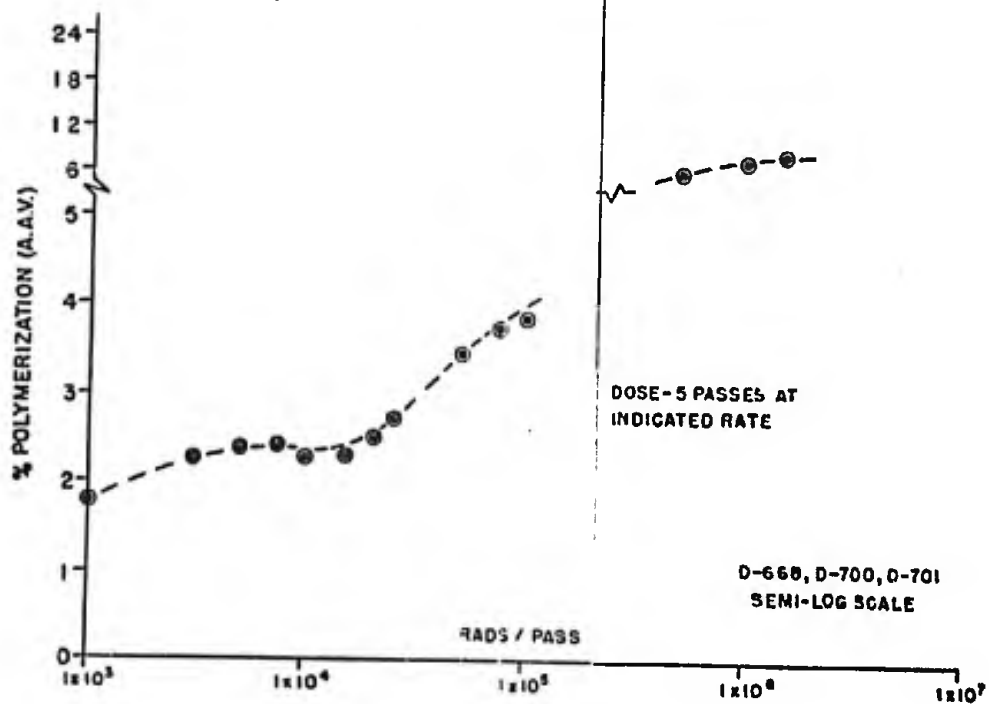


Figure 26. Styrene: Average yield from 1% vinyl acetate as additive by dose rate for fourteen dose levels.

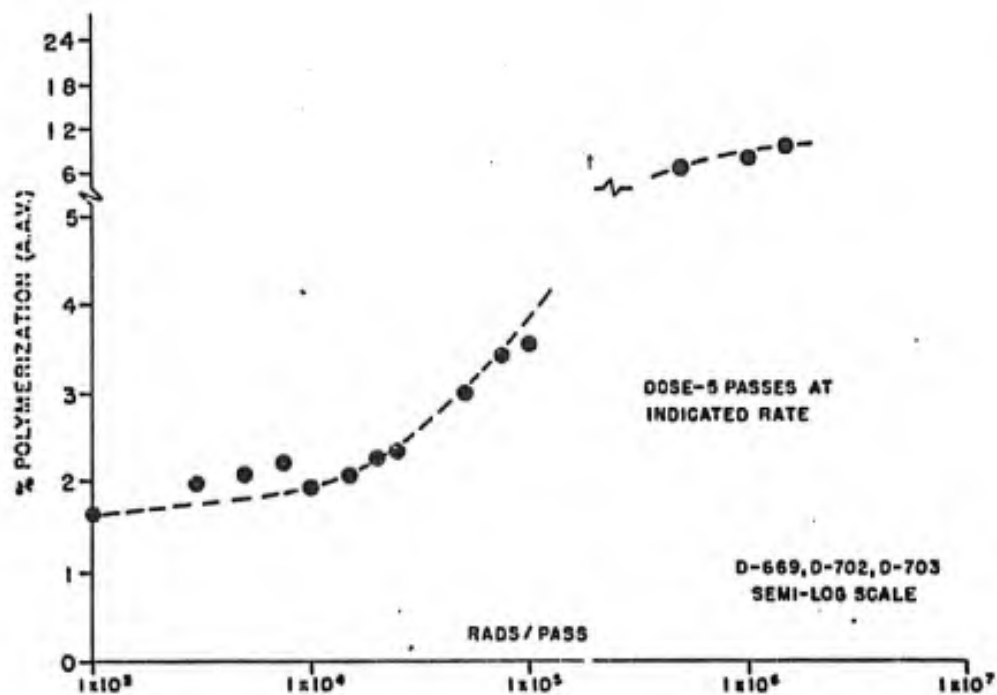


Figure 27. Styrene: Average yield from 1% acrylonitrile as additive by dose rate for fourteen dose levels.

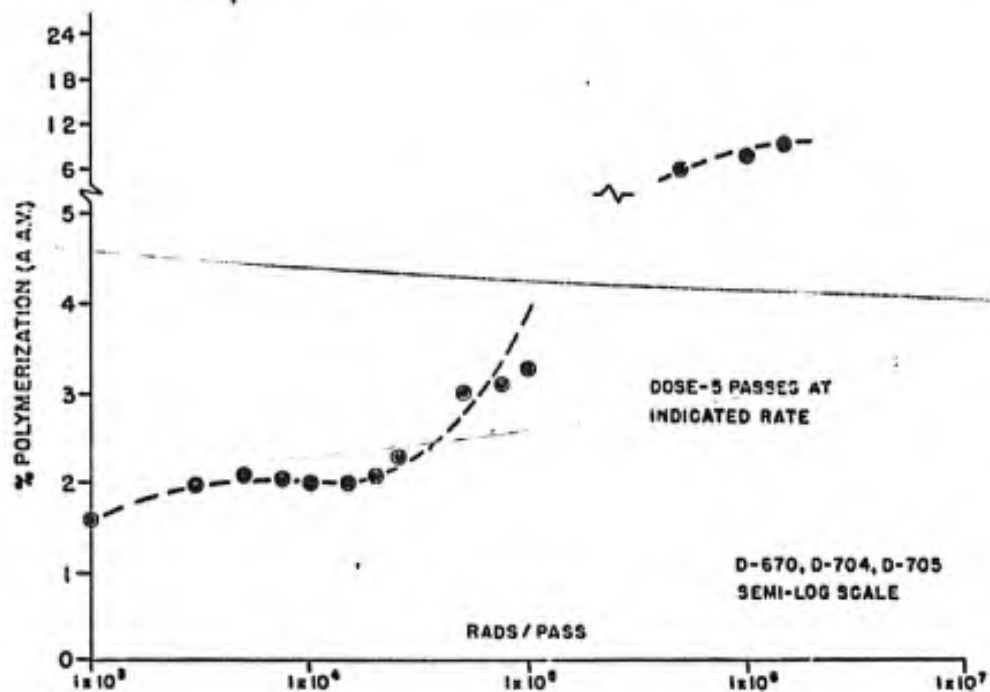
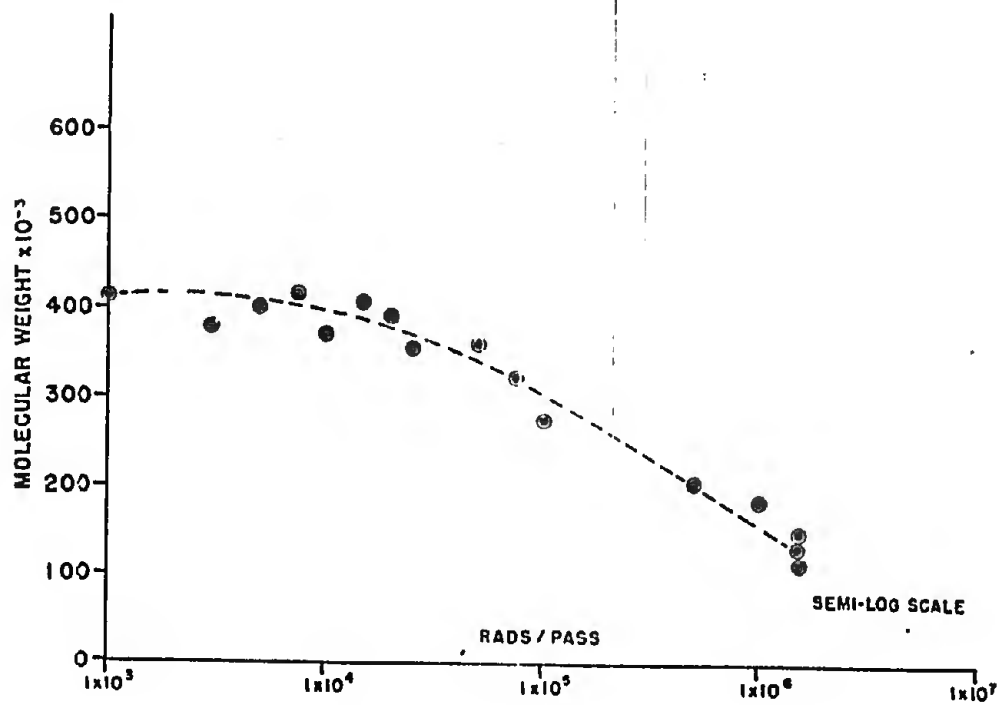
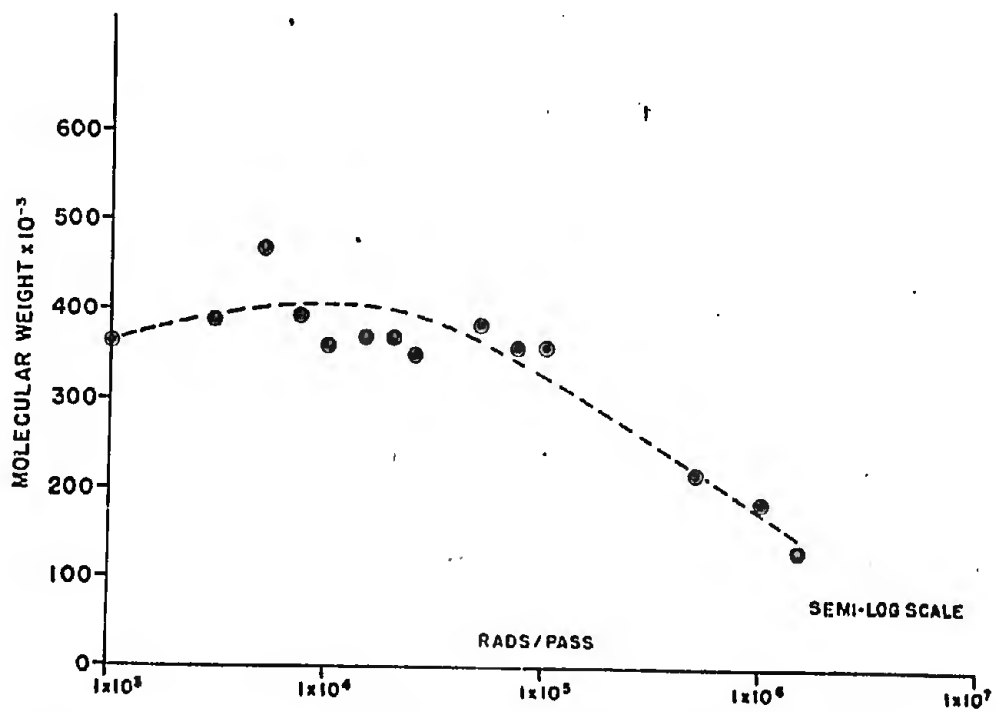


Figure 28. Styrene: Average yield from monomer saturated with water by dose rate for fourteen dose levels.



**Figure 29.** Styrene: Average molecular weight by dose rate with no additive.



**Figure 30.** Styrene: Average molecular weight by dose rate with 1% silicon oil 200 as additive.

corrected to an "adjusted value" for 100% ionization by multiplying by 100 and dividing by the percent ionization indicated by the graph. Adjusted values are used throughout this report inasmuch as they represent better relative results. (cf. Figure 41, page 28).

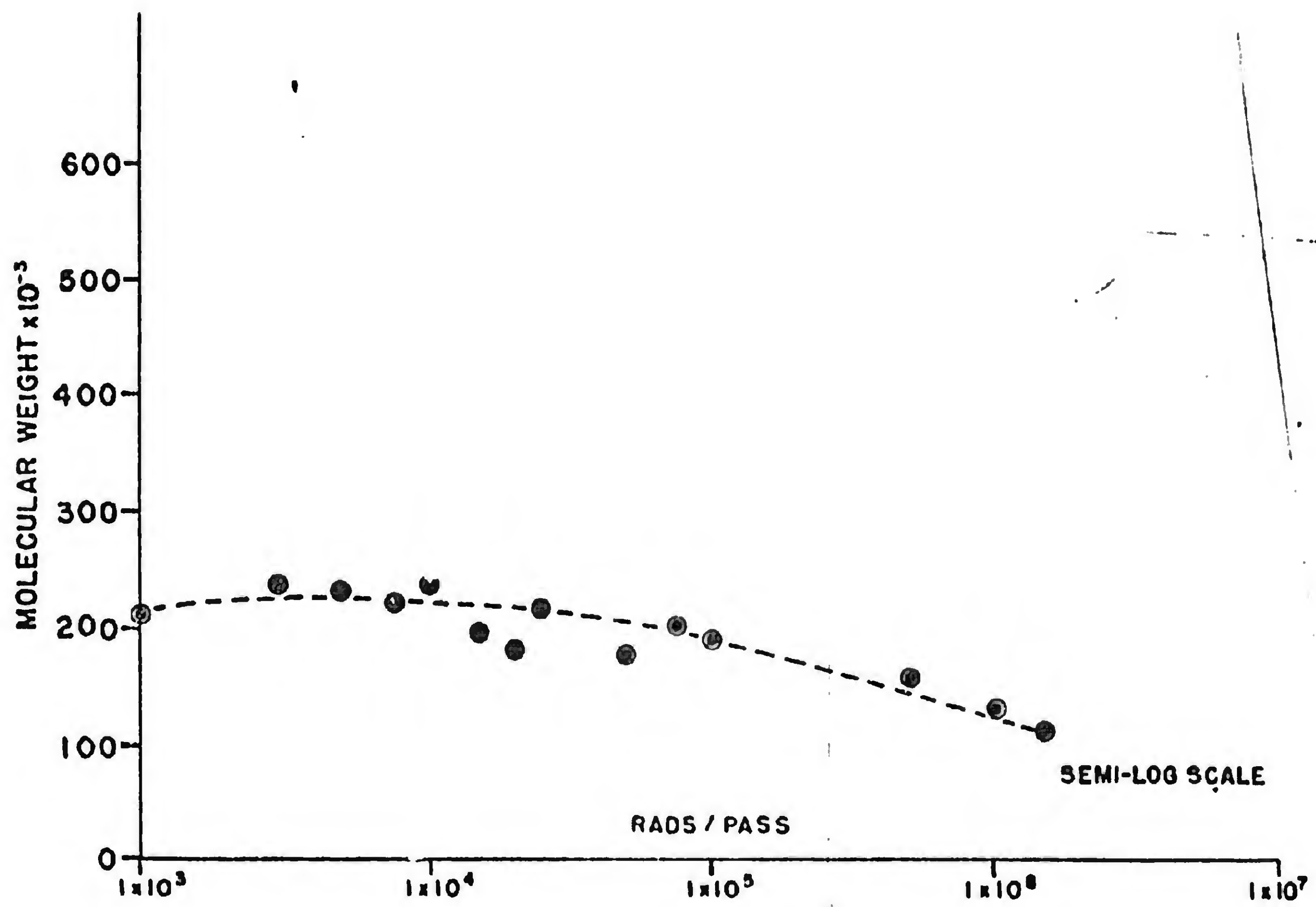
#### E. Discussion of Experimental Results

Bar graphs of the average yields of polymer obtained from five exposures at each of 14 dose rates (Figures 4 to 17) on a 45-minute cycle at 75°C, for the various additives are given in Figure 3 (page 4). The relative effect of the various additives as a function of dose rate and total dose are shown by the bar graphs of Figures 4 to 17 (pages 4 to 11).

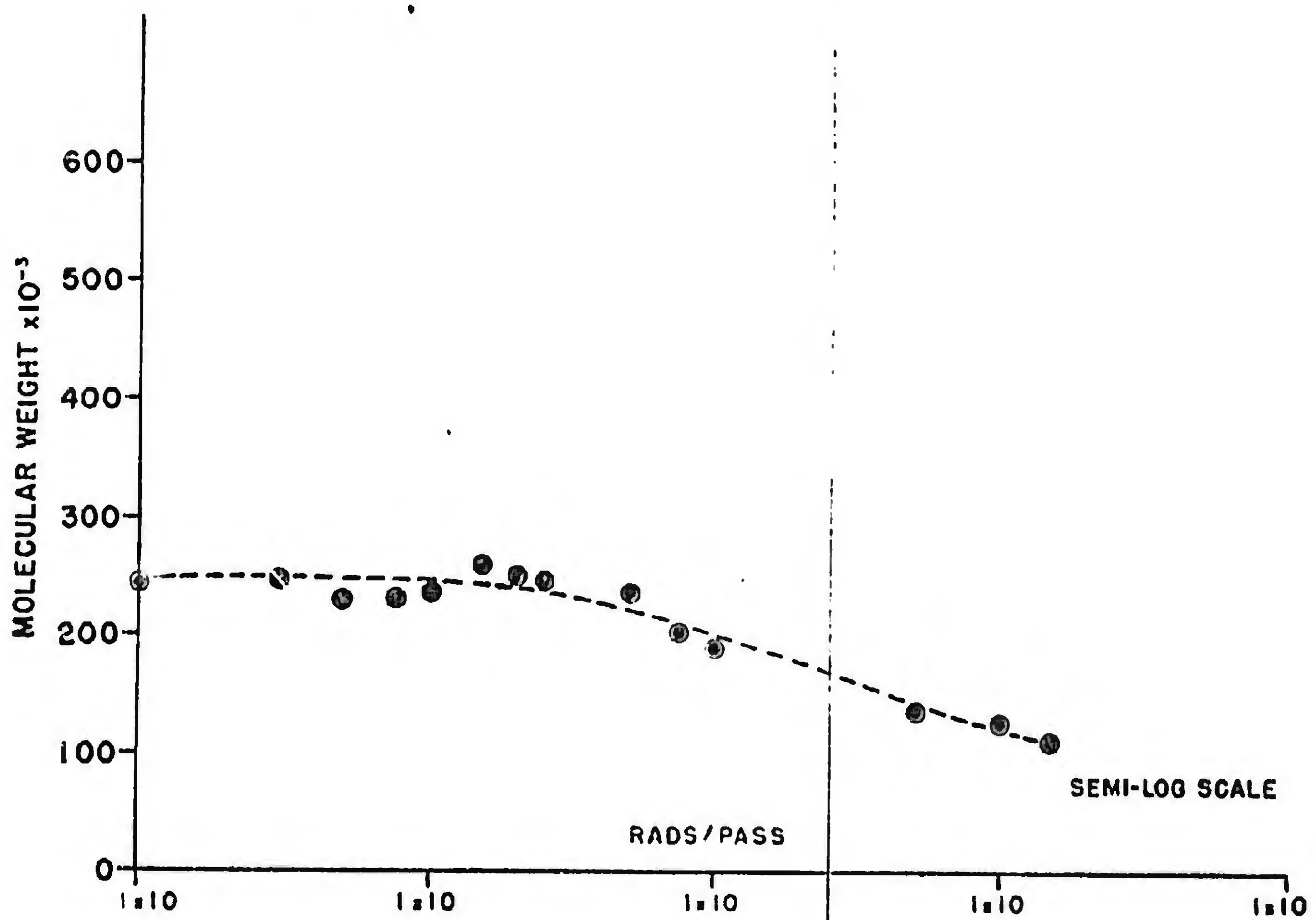
A consistency of pattern is noted with respect to bars 1, 2, 3, and 4 of Figures 4; 5, 6, 8, 9, 10, and 11. In Figure 7 (page 6) this pattern is obscured, which may be attributed to either a critical dose rate or experimental error. The variation appears to be too large, however, to be accounted for as experimental error.

Bars 5, 6, 7, 8, and 9, similarly, show a comparable pattern for Figures 4, 6, 7, 9, and 10. The deviation of these bars from comparable bars of Figures 5, 8, and 12 appear to be in the range of experimental error, but the deviations from this pattern for these bars in Figures 11, 13, 14, 15, 16, and 17 appear to be significant.

Within the range of experimental error, the smallest average amount of polymerization was obtained from water as additive (Figure 3, page 4). Acrylic acid as additive, however, accounts for the highest yields in Figures 4 to 13, but its relative effect decreases somewhat consistently from Figure 14 through 17. The amount of polymer obtained, furthermore, is the least in bar 1 of Figure 4 and the most in bar 1 of Figure 17, both of which represent the absence of any additive. It becomes apparent, therefore, that the effect of an additive in this series at least is a function of dose rate and/or total dose.



**Figure 31.** Styrene: Average molecular weight by dose rate with 1% acrylic acid as additive.



**Figure 32.** Styrene: Average molecular weight by dose rate with 1% methacrylic acid as additive.

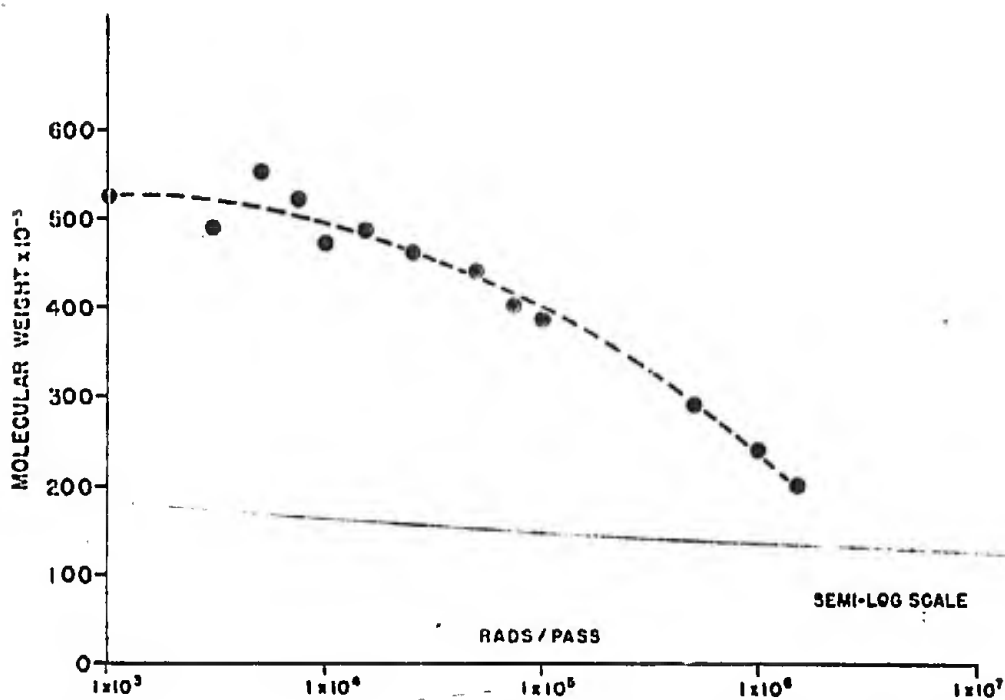


Figure 33. Styrene: Average molecular weight by dose rate with 1% methyl acrylate as additive.

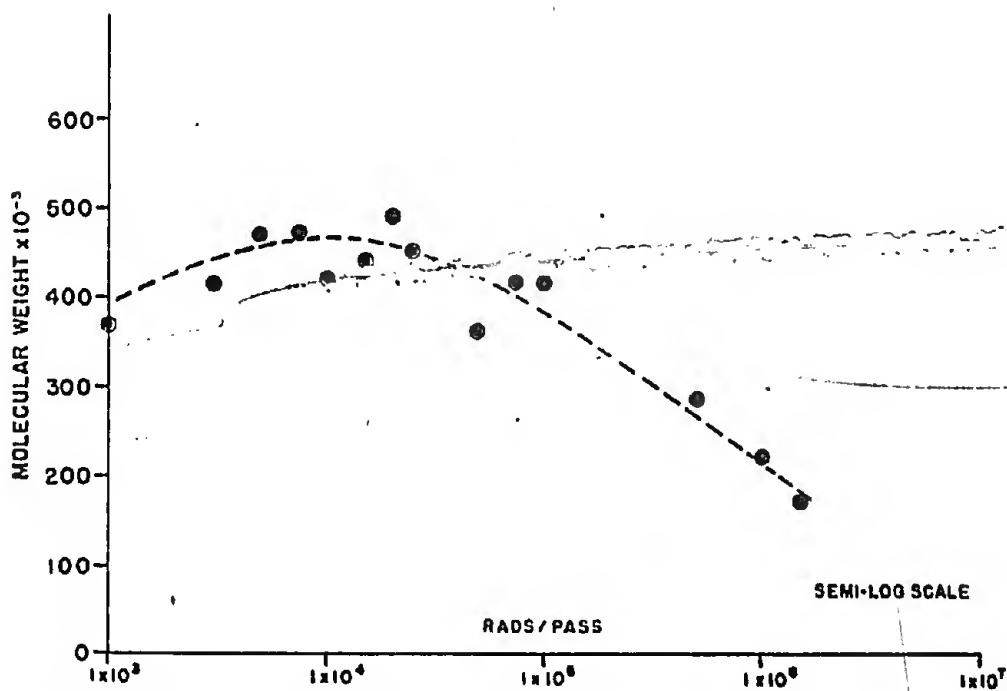


Figure 34. Styrene: Average molecular weight by dose rate with 1% butyl acrylate as additive.

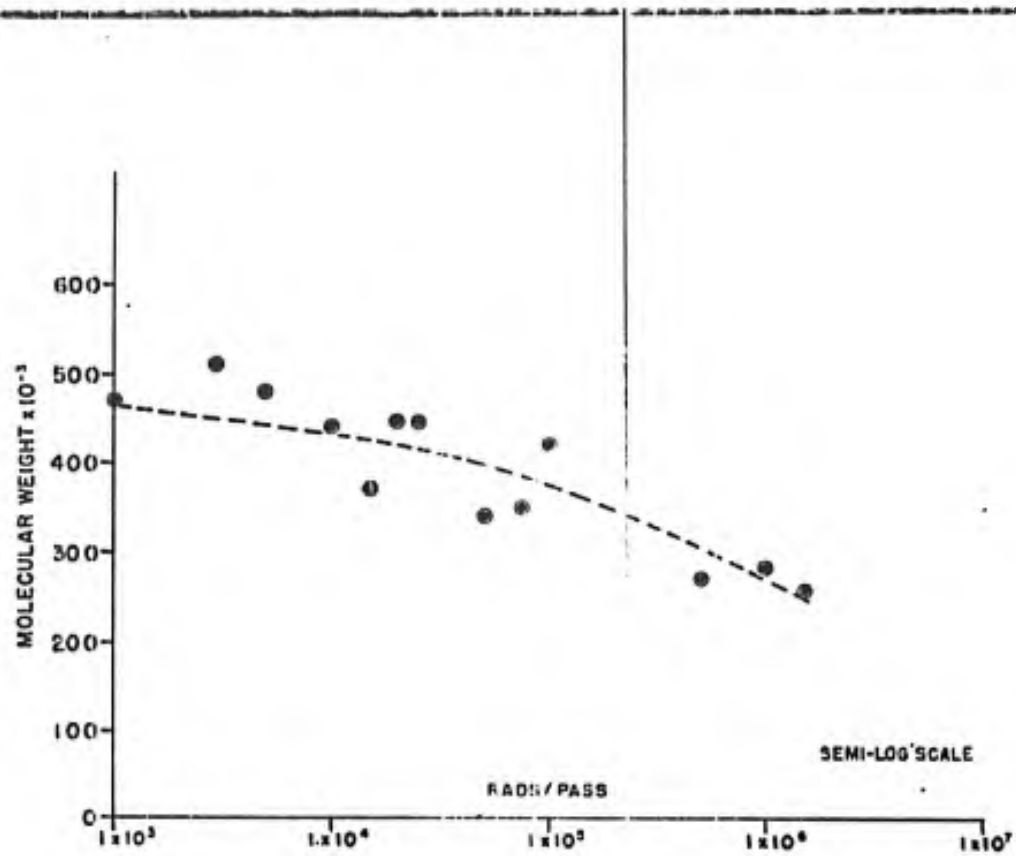


Figure 35. Styrene: Average molecular weight by dose rate with 1% vinyl acetate as additive.

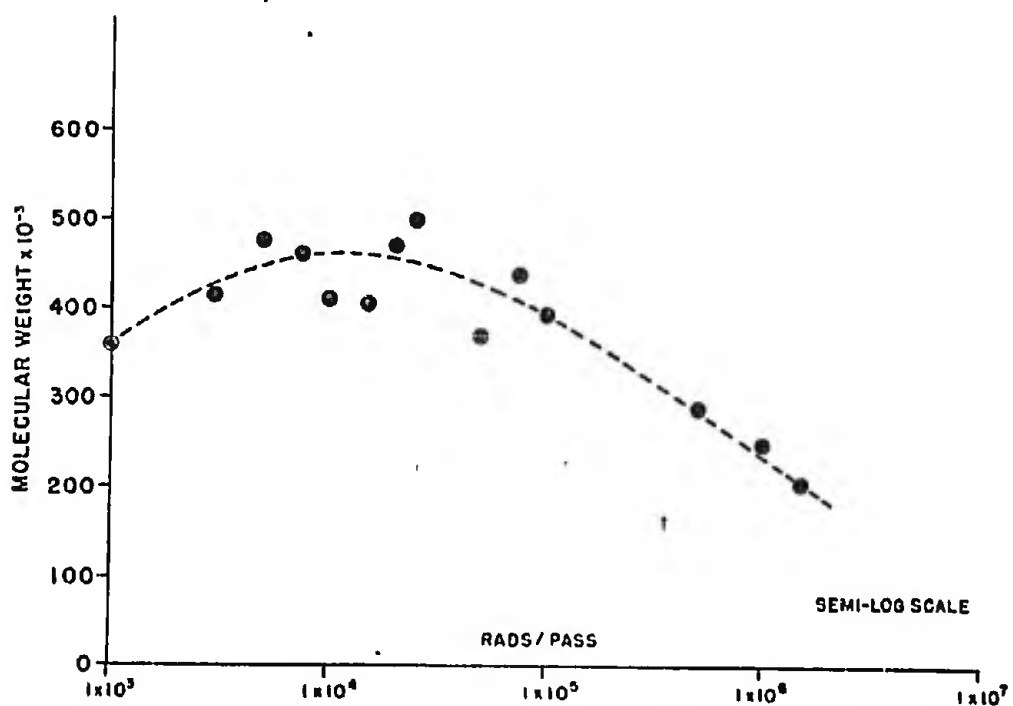


Figure 36. Styrene: Average molecular weight by dose rate with 1% acrylonitrile as additive.

The bar graphs of Figure 18 (page 11) give comparable average yields, irrespective of additive, for the fourteen dose rates and the fourteen dose levels. From this it is observed that for a total dose of 5,000 rads, at a dose rate of 1,000 rads per exposure irrespective of additive, the average yield is about 1.9%, whereas for a total dose of 7,500,000 rads at a dose rate of 1,500,000 rads per exposure the average yield is only 12.6%. Hence 1,500 times the amount of total radiation energy at the high dose rate yields only 6.6 times the quantity of polymer obtained at the low dose rate and the low total dose. Comparing these results in terms of efficiency or the percent of polymer obtained per unit of radiation energy, the lowest dose rate used under the conditions of these experiments is about 225 times as economical or efficient as is the highest dose rate. Stated otherwise, under the conditions of these experiments the amount of energy used at the higher dose rate is 225 times as much as that at the lower dose rate for an equivalent amount of polymer. Possible explanations, based on different mechanisms at different dose rates, have been considered in the two previous reports.

Graphic representations of these results, in which percent polymerization as "adjusted values" is plotted against rads per exposure, are presented in Figures 19 to 29 (pages 12 to 18). Figure 19 is a plot of the average yield obtained from the use of the nine additives for each of the fourteen dose rates and dose levels. The point at the right of each graph, however, represents 1,500 times as much radiation energy as the point at the left. Expressed otherwise, a dose rate of 1,000 rads per exposure is about 225 times as efficient on the average as is a dose rate of 1,500,000 rads per exposure in the production of polymer under the conditions of these experiments.

The results obtained with no additive are given in Figure 20 (page 12), those with 1% silicone oil as additive in Figure 21 (page 14), those with 1% acrylic acid in Figure 22 (page 14), those with 1% methacrylic acid in Figure 23 (page 15), those with 1% methyl acrylate in Figure 24 (page 15), those with 1% butyl acrylate in Figure 25 (page 16), those with 1% vinyl acetate in Figure 26 (page 16), those with 1% acrylonitrile in Figure 27 (page 17), and those with water in Figure 28 (page 17).

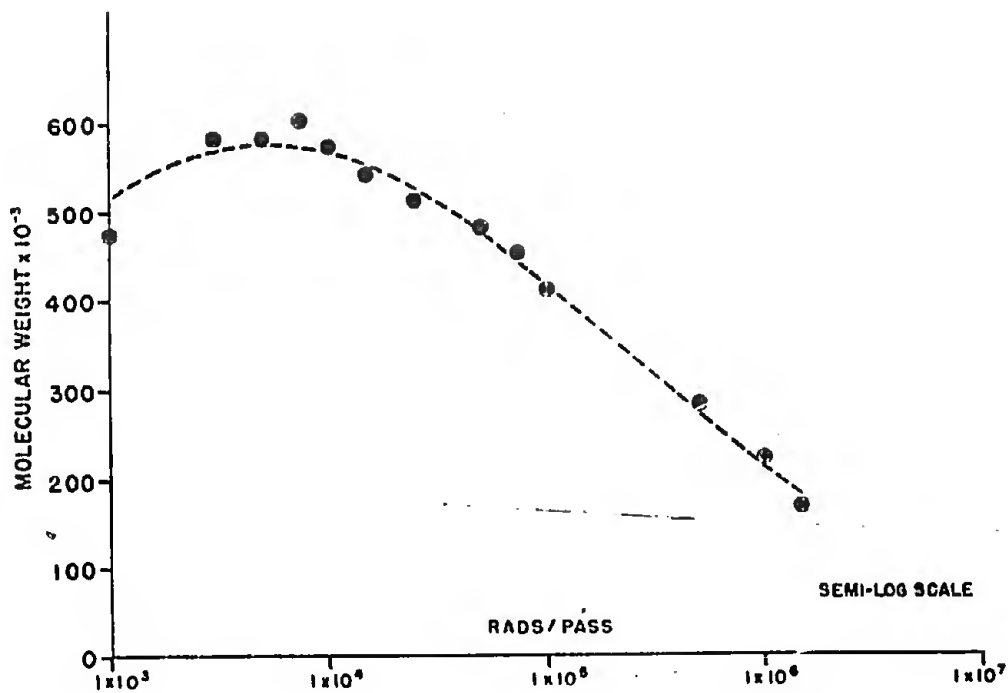


Figure 37. Styrene: Average molecular weight by dose rate with moisture (saturated solution) as additive.

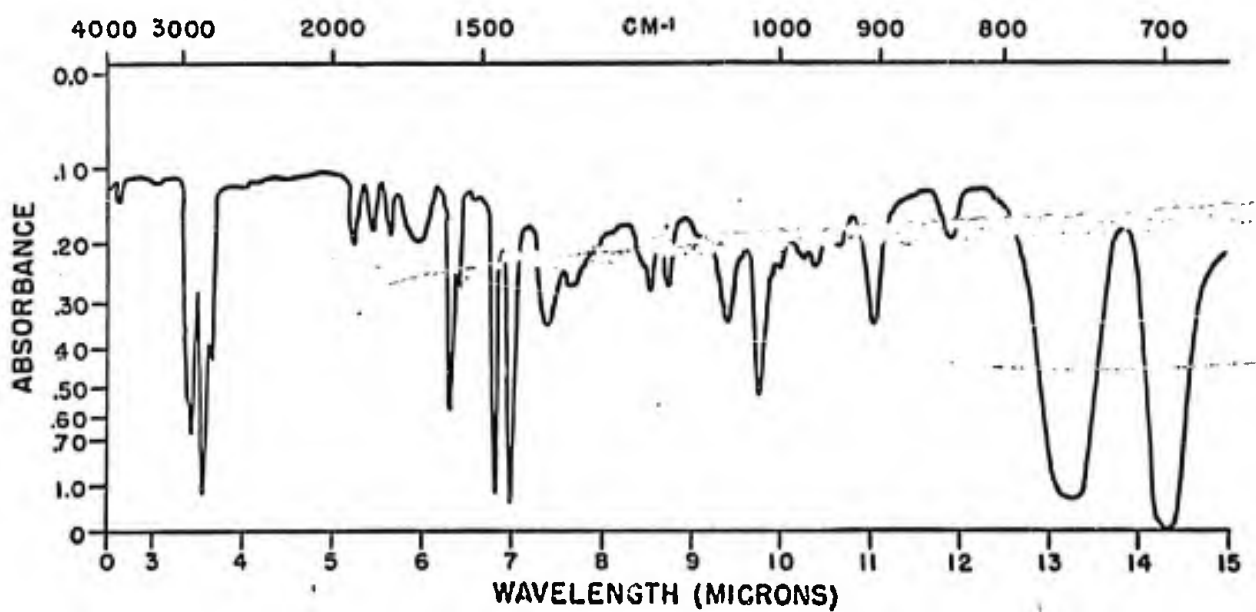


Figure 38. Absorbance curve for polystyrene obtained from monomer with no additive.

It will be noted that the initial point on these graphs varies from 1.5 to 2.7%, and that the final point ranges from approximately 8 to 23%, whereas the dose level for the final point is 1,500 times that for the initial point. Variations in yields in this series range from about twofold at the lower dose rate to threefold at the higher dose rate.

The effect of the additives on the molecular weight of the polymer is indicated in the graphs of Figures 29 to 37 (pages 18 to 24), in which molecular weight is plotted against dose rate for each of the different additives. It may be seen that the molecular weight varies for the low dose rate, as a function of additive, from 210,000 for the use of acrylic acid to 525,000 where 1% methyl acrylate is the additive. By comparing Figures 29 to 37 with Figures 4 to 13, it is observed that there is an inverse trend for yield and molecular weight.

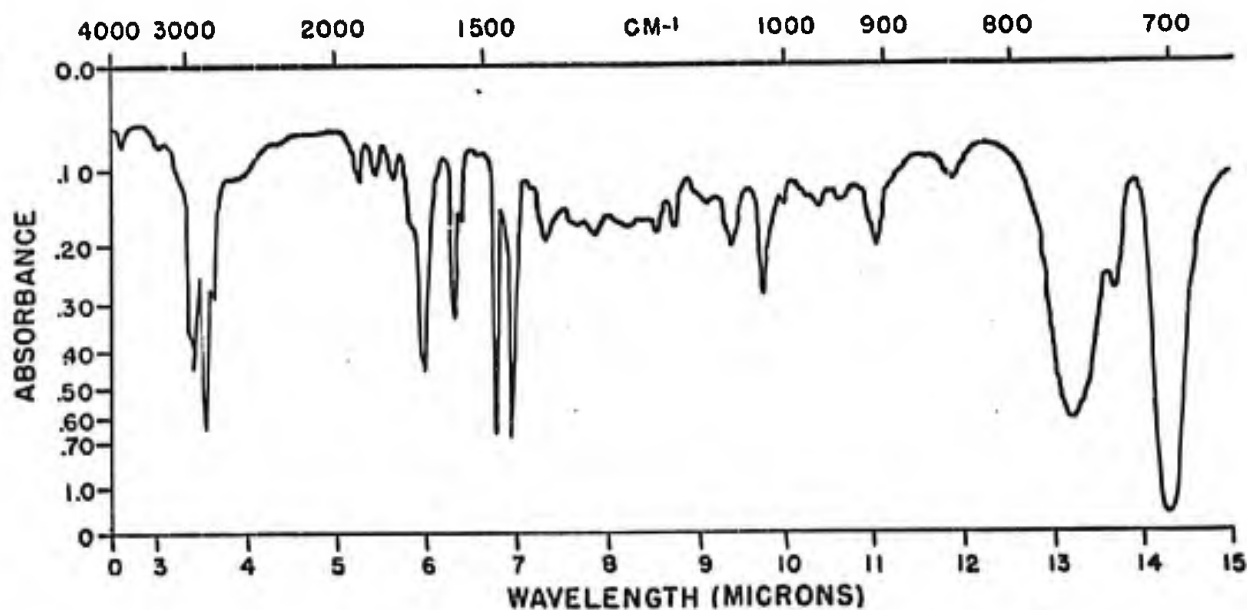
At the higher dose rate the molecular weight, as a function of the additive, varies from about 110,000 for both acrylic acid and methacrylic acid to 250,000 for vinyl acetate, but from Figure 3 it is observed that acrylic acid and methacrylic acid as additives occupy positions 3 and 4 with respect to the average yields by additive from all dose rates.

The infrared absorbance curve of Figure 38 (page 24) is for polystyrene obtained by the irradiation-induced polymerization of styrene with no additive, whereas Figure 39 (page 26) is a comparable curve obtained with 1% methacrylic acid in the monomer system when polymerized by irradiation. The band at 6 microns in the latter is attributed to the presence of carboxyl groups in the polymer.

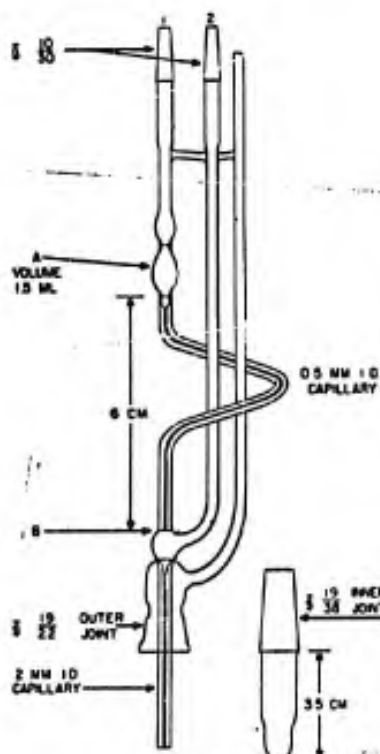
The type of viscometer used in these studies for the determination of intrinsic viscosities is illustrated in Figure 40 (page 26).<sup>4</sup> By the procedure described in the referenced article, the experimental error is of the order of 5% of the molecular weight.

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<sup>4</sup> Viscometer for the Rapid Determination of Viscosities at a Single Concentration, N. Schneider, J. Polymer Science, **32**, 253 (1958).



**Figure 39.** Absorbance curve for polystyrene obtained from monomer with 1% methacrylic acid as additive.



**Figure 40.** Type of viscometer used in determining intrinsic viscosities (N. Schneider, *J. Polymer Science*, **32**, 253, 1958).

## F. Summary

From the experimental results presented in this report, which are based on the specific procedures outlined above, one may postulate that: (1) the effect of an additive is a function of dose rate with respect to both relative yield and the molecular weight of the polymer, (2) the molecular weight decreases in general with an increase in dose rate, irrespective of the additive, (3) an additive which significantly increases the yield tends in general to produce somewhat lower molecular weight polymers than do other additives which give lower yields, (4) an additive, as a function of dose rate, may either increase or decrease the yield of polymer obtained by the irradiation-induced polymerization of some vinyl monomers, and (5) the efficiency of the polymerization (or the amount of polymer per unit of radiation energy), decreases markedly for the higher dose rates used in this study.

## G. Acknowledgments

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PENETRATION PROFILE - 1 MEV and 2 MEV

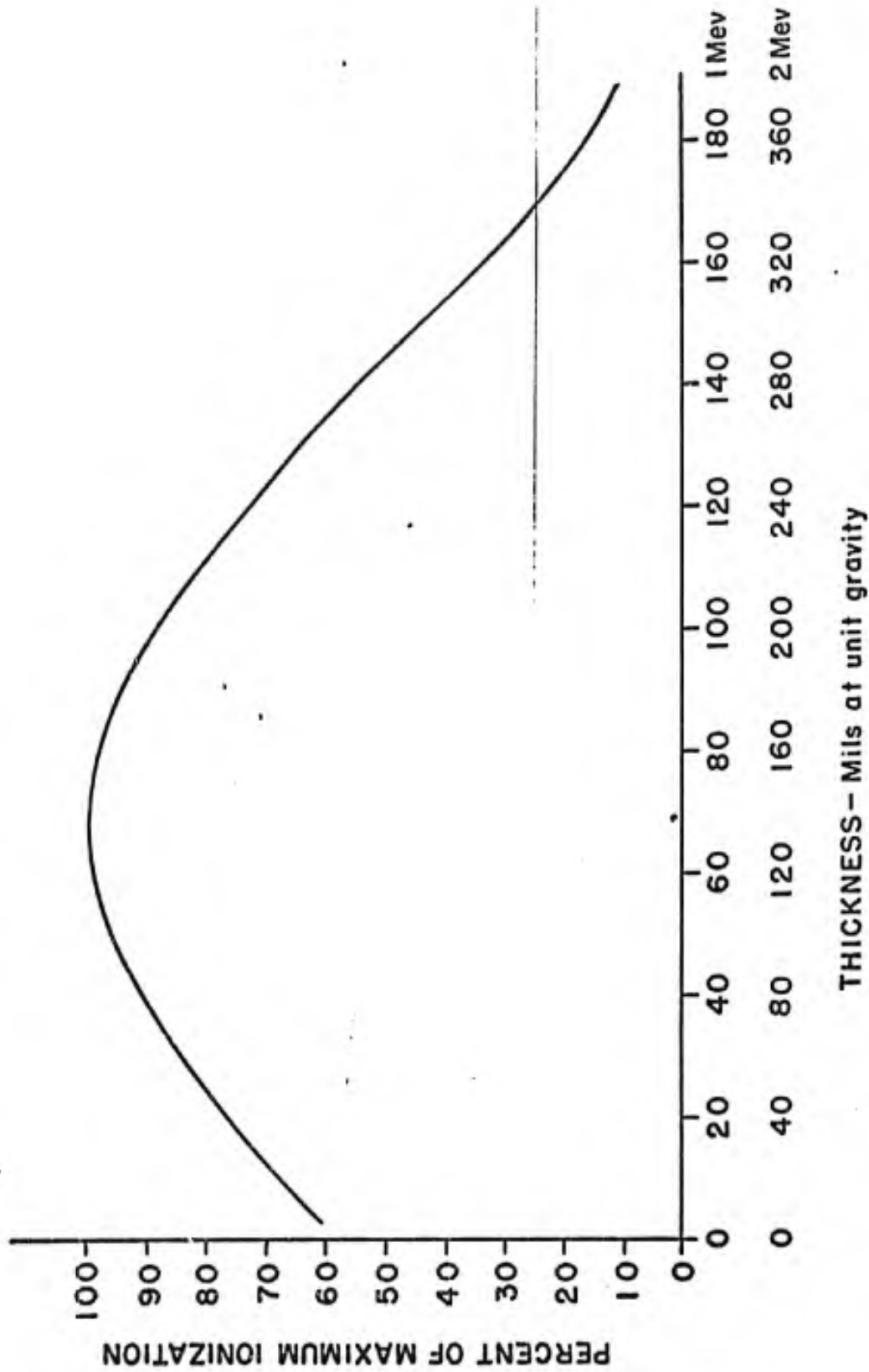


Figure 41. Percent of Maximum Ionization Curve, adapted from Trump, et al., *J. App. Phys.*, 21, 346 (1950).