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IRRADIATION "FACTOR-DEPENDENCY":

Exploratory Studies

and

Irradiation-Induced Polymerization

of Styrene

By

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FOREWORD

Inasmuch as the Proceedings of the Second International Congress of Radiation Research will not be available for some months, and then in a limited edition only, this preprint has been prepared to make this report on Radiation Research more readily available to those who may desire it at or subsequently to the meeting.

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Irradiation "Factor-Dependency": Exploratory Studies and Irradiation-Induced Polymerization of Styrene

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Early in 1954 the Radiation Chemistry Laboratory was asked to explore the potential applications of ionizing radiation for the improvement of quartermaster materials and items. It was observed from numerous studies that the deterioration of mechanical and physical properties is the most obvious effect of electron bombardment (in air at 2 megarads per exposure) of natural and synthetic fabrics, leathers, plastics, rubbers, and similar materials.[1] When high tenacity nylon was irradiated in an evacuated system and leather was irradiated in the presence of moisture, however, the deterioration was significantly decreased.[1] These studies provided an indication of the importance of experimental variables on irradiation-induced reactions.

A survey of the literature indicates that very little attention was given by radiation scientists to experimental variables such as atmosphere, dose rate, irradiation cycle, purity of the system, temperature, or other factors. In the cumulative index of Nuclear Science Abstracts for 1954, for example, dose rate is not even listed. Attention seemed to be centered instead on the amount of energy delivered to a given system.

This outlook existed, no doubt, as a natural consequence of the then available radiation facilities. The electron accelerator, which made available for the first time wide variations

Table I.[3]

Comparison of 0. 1 and 2 megareps per Exposure on a 20 Minute Cycle at 25°C., to a 2 Mev Accelerator

Monomer (no heat)	Megareps for Solidification at 0. 1 Megarep/pass	at 2 Megareps/pass
Ethyl acrylate	1. 6	4
Methyl acrylate	1. 5	16
Methyl methacrylate	3. 8	40
Isoprene	2. 0	12
Stearyl methacrylate	0. 8	32
Styrene (10% Acrylic acid)	5. 7	118
Triallyl cyanurate	2. 7	14
Vinyl acetate	6. 3	20
Vinyl butyrate	6. 3	24
Vinyl triethoxysilane	8. 6	160

Table II. Styrene: Dose Rate, Temperature (D-568)[4]

Dose Rate, Megarad/Pass	Passes	% Polymerization per 0. 1 Megarad at 45° C.	at 75° C.
0. 025	4	---%	19. 7%
0. 05	4	4. 0	18. 2
0. 1	3	2. 0	5. 8
0. 2	2	1. 2	4. 1
0. 4	2	1. 0	2. 6
0. 8	2	0. 8	1. 8
2. 0	2	0. 4	0. 7

All samples under vacuum at about 1 mm. of mercury.

in both dose rate and the irradiation cycle, was just coming into general use.

It should be indicated that, using a scanning beam with a width of 1/4 of an inch and an 18-inch shuttle, moving at the rate of 93 inches per minute, any portion of the sample being irradiated is under the electron beam on an average of only about 1/70th of the time required for each cycle of the shuttle. The time lapse between successive bombardments with electrons, or the irradiation cycle, accordingly, becomes an important experimental variable.

The results reported here were obtained by control of the dose rate and the irradiation or time cycle, with total dose dependent on the dose rate and the number of irradiation cycles. In any given series, accordingly, the irradiation cycle was held constant, although it may vary from series to series.

Additional importance was placed on the time cycle at a Post-Irradiation Effects Symposium in 1959, where it was shown that in certain systems at least there is a post-irradiation effect.[2]

Having observed that deterioration might be significantly inhibited by appropriate selection of experimental conditions, the studies in this laboratory were directed toward a consideration of the effect of variables on the irradiation-induced polymerization of vinyl monomers.

1. Dose Rate:

In the initial studies on the effect of dose rate on irradiation-induced polymerization of vinyl monomers, the monomers (5 ml.) were packaged in Mylar in such a way as to exclude bubbles of air, and irradiated at 0.1 and 2 megareps per exposure on a 20-minute cycle at 25° C. until solidification occurred (Table I). Obviously the end point is qualitative, but the significance of dose rate is definitely shown by the tabulated results (Table I).[3]

Table III. Styrene-Benzene (1/1): Dose Rate and Temperature Effects (D-567)[4]

Dose Rate, Megarads/Pass	Passes	% Polymerization per 0.1 Megarad at 45° C.	% Polymerization per 0.1 Megarad at 75° C.
0.025	4	7.0%	9.4%
0.05	4	3.6	5.7
0.1	3	1.8	3.7
0.2	4	1.1	1.7
0.4	4	0.7	0.9
0.8	2	0.3	0.8
2.0	4	0.2	0.3

All samples under vacuum at about 1 mm. of mercury.

Table IV. Non-Additivity of Dose (D-576)[4]

Dose Rate, Megarads/Pass	Per cent Polymerization per 0.1 Megarad for 1 Pass	2 Passes	3 Passes
0.025	92.4%*	29.1%	16.1%
0.050	57.7	14.1	11.8
0.1	25.6	8.4	7.5
0.2	12.4	4.4	
0.4	6.3		

* This figure is four times the experimental value obtained so as to place it on the basis of 0.1 megarad of energy. Appropriate factors have been applied elsewhere as required.

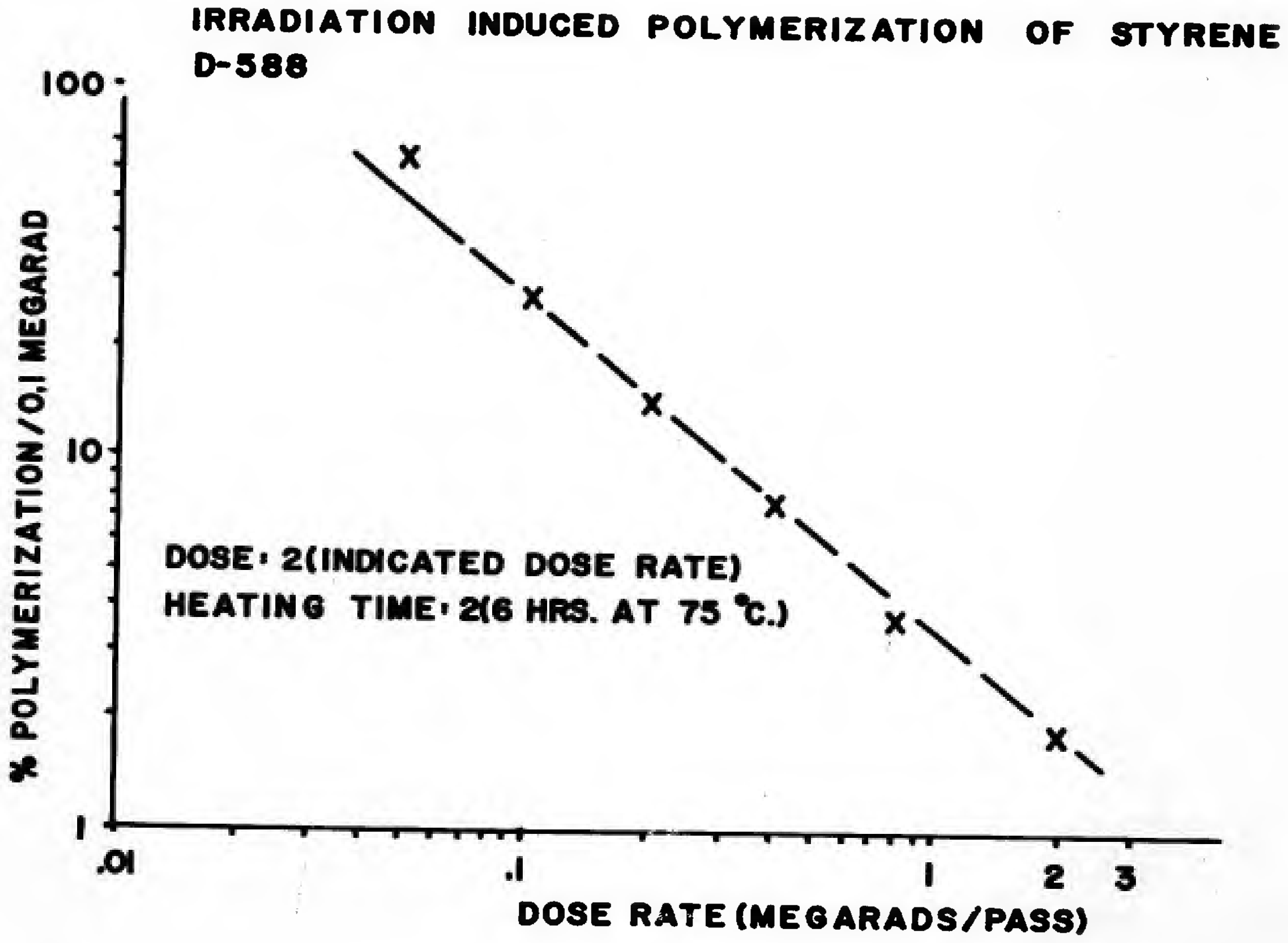

Figure 1. Styrene: Effect of dose rate and dose level on efficiency of irradiation-induced polymerization, on a 6-hour cycle at 75° C. Dose rates, left to right, 0.05, 0.1, 0.2, 0.4, 0.8, and 2 megarads per exposure. Dose, twice indicated rate.

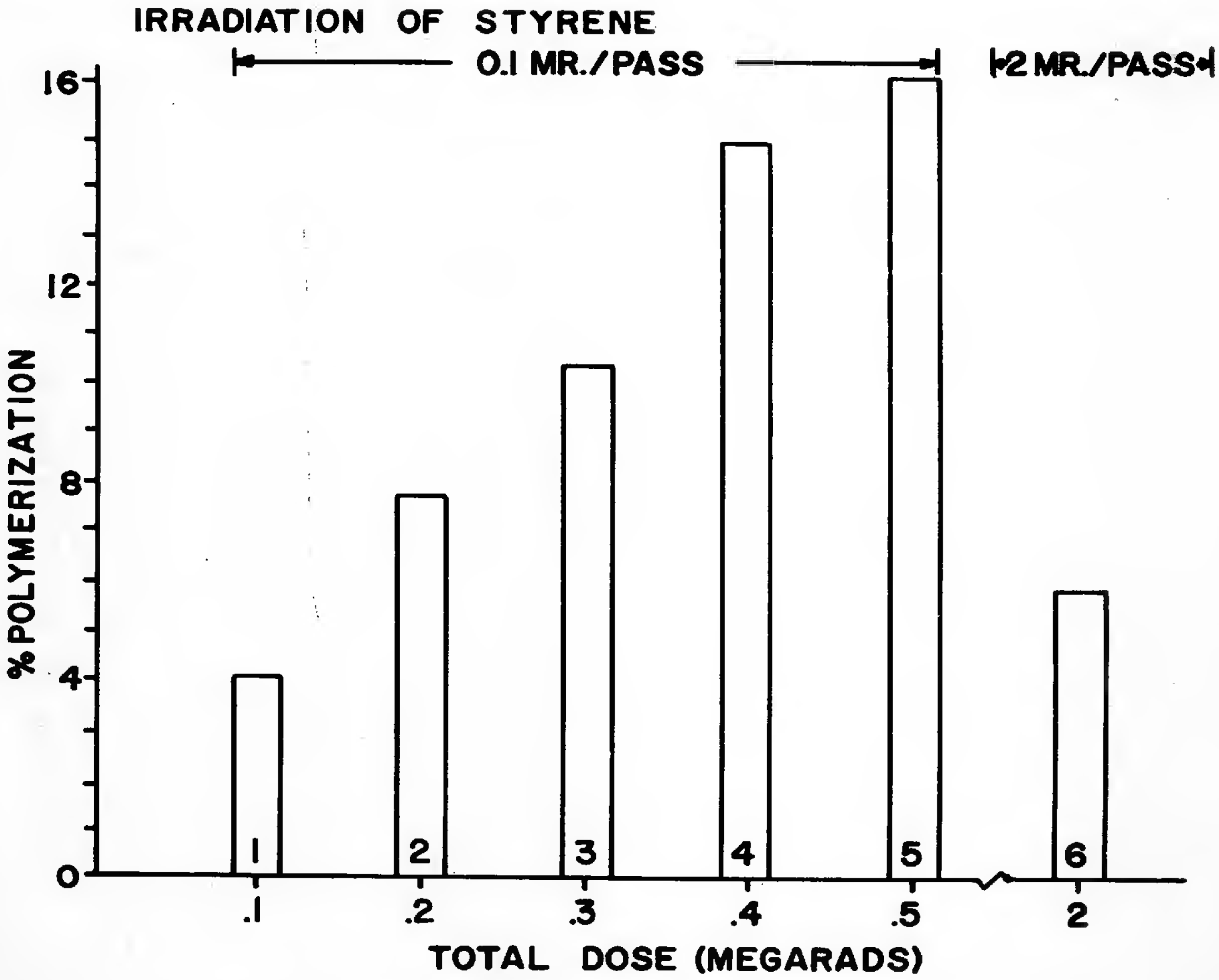

Figure 2. Styrene: Percent polymerization as a function of dose at dose rates of 0. 1 and 2 megarads per exposure.

The combined effect of dose rate and temperature on monomeric styrene is illustrated by the data of Table II,[4] whereas Table III records the combined effect of diluent, dose rate, and temperature.[4] It is observed that the temperature effect decreases significantly at the higher dose rates. The non-additivity of the effects of total dose is shown by Table IV.[4]

On Figure 1 the percent polymerization per 0.1 megarad is plotted as the ordinate against dose rate as the abscissa.[3,5] It is observed that a pronounced decrease in the efficient utilization of radiation energy occurs with an increase in dose rate. On the bar graph of Figure 2, percent polymerization is the ordinate and total dose the abscissa. The bars indicate a marked decrease in efficiency as the dose rate is increased from 0.1 to 2 megarads per exposure.

2. Statistical Evaluation of Atmosphere, Dose Rate, and Temperature Effects on Irradiation-Induced Polymerization of Styrene:

The effect of parameters on the data obtained in the preceding studies indicated the importance of a statistical analysis in order to evaluate more accurately the significance of experimental variables on irradiation-induced polymerization of styrene.[3]

A 4 × 4 Latin square experiment[4] was designed, in which atmosphere and temperature were environmental factors and dose rate was the treatment. A schematic representation of the study is shown in Table V.[4] The numerals in the respective blocks give the percent polymerization obtained for each set of experimental conditions, per unit of radiation energy.

The analysis of variance for the data of Table V is given in Table VI, from which it is observed that atmosphere, dose rate, and temperature are all significant factors for the irradiation-induced polymerization of styrene, and that dose rate is more significant than either atmosphere or temperature under the conditions of this experiment.[4]

Table V. Per cent Conversion of Styrene to Polymer per 0.1 Megarep as a Function of Dose Rate Dose Level, Atmosphere and Temperature[4]

Dose Rate - Megarad/Pass

Temp.	0.025	0.05	0.1	2.0
25°C.	Vac 0.36	He 0.24	N_2 0.52	Air 0.04
45°	Air 2.33	Vac 0.74	He 0.28	N_2 0.05
60°	N_2 3.52	Air 2.23	Vac 0.44	He 0.06
75°	He 2.45	N_2 2.79	Air 1.86	Vac 0.13

Table VI. Analysis of Variance for Data of Table V.[4]

Source of Variance	S. S.	D. F.	Mean Square	"F"
Temperature	4.7841	3	1.5947	13.17
Dose Rate	9.3674	3	3.1225	25.78
Atmosphere	4.1176	3	1.3725	11.33
Residual (chance)	0.7266	6	0.1211	

For significance at 1% level "F" should exceed 9.78.

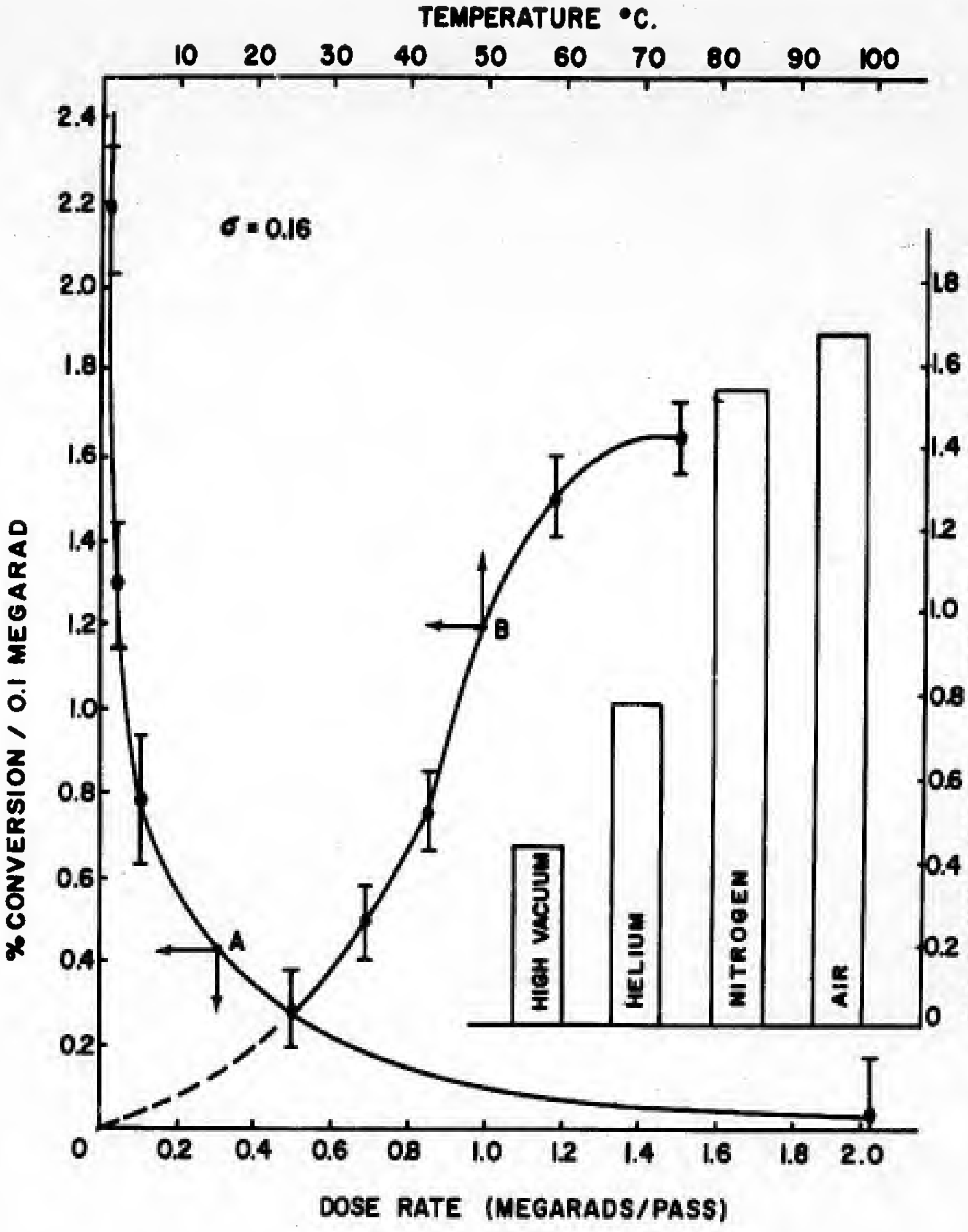

Figure 3. Styrene: Curve A, efficiency or % conversion per 0.1 megarad as a function of dose rate and dose level; curve B, efficiency as a function of temperature; with relative effect of atmosphere indicated by the bar graphs and the right ordinate.

Table VII. Molecular Weights of Styrene Polymers Produced on Irradiation[4]

Dose Rate: Megarads/Pass

Temp.	0.025	0.05	0.1	2.0
25°C.	Vac 121,800	He 85,890	N_2 105,600	Air 39,060
45°C.	Air 62,890	Vac 140,300	He 167,300	N_2 37,460
60°C.	N_2 203,700	Air 96,360	Vac 182,200	He 41,100
75°C.	He 386,600	N_2 283,500	Air 340,900	Vac 38,610

Table VIII. Analysis of Variance for Data of Table VII[4]

Source of Variance	S. S.	D. F.	Mean Square	"F"
Temperature	76,211 x 10^6	3	25,404 x 10^6	4.71
Dose Rate	66,194	3	22,065	4.09
Atmosphere	5,923	3	1,974	
Residual	32,390	6	5,398	

Values of "F" for significance: at 1% level 4.76
at 5% level 3.29

The effect of atmosphere, dose rate, and temperature on the molecular weight of the polystyrene, obtained under the conditions of Table V, is indicated by the molecular weight data in the respective blocks of Table VII. The highest molecular weight (386,000) was obtained in helium at a dose rate of 0.025 megarads per exposure at 75° C., whereas at dose rates of 2 megarads per exposure,[4] all four atmospheres at each of the four temperatures, gave products with molecular weights of only about 40,000.

The analysis of variance for the data of Table VII, is given in Table VIII, from which it is seen that both dose rate and temperature are approaching significance at the 1% level.[4]

The effect of dose rate on efficiency of polymerization, or percent conversion to polymer per 0.1 megarad of radiation energy, is indicated by the A-curve of Figure 3, the effect of temperature on efficiency by the B-curve, and the relative effect of atmosphere on conversion to polymer by the bar graphs.[4]

The results obtained for the relative efficiency of irradiation-induced polymerization of styrene at 45° and 75° C., as a function of dose rate and dose level, are given by the lower two curves (right ordinate) of Figure 4, whereas the combined effect of dose rate, dose level, and temperature on molecular weight are shown by the upper two curves (left ordinate).[4]

Some effects of atmosphere on the irradiation-induced polymerization of styrene at 75° C. in a one-to-one mixture with benzene is shown by Figure 5, where viscosity is plotted against dose rate. Although the relative effect of atmosphere on viscosity or molecular weight in this series seems to be relatively small, the effect of dose rate and total dose is definitely significant.[4]

The consistency of the pattern for atmospheres of air, carbon dioxide, helium, and nitrogen, suggest that serious changes are occurring with respect to the reaction-mechanism steps of initiation, propagation, and termination, with an increase

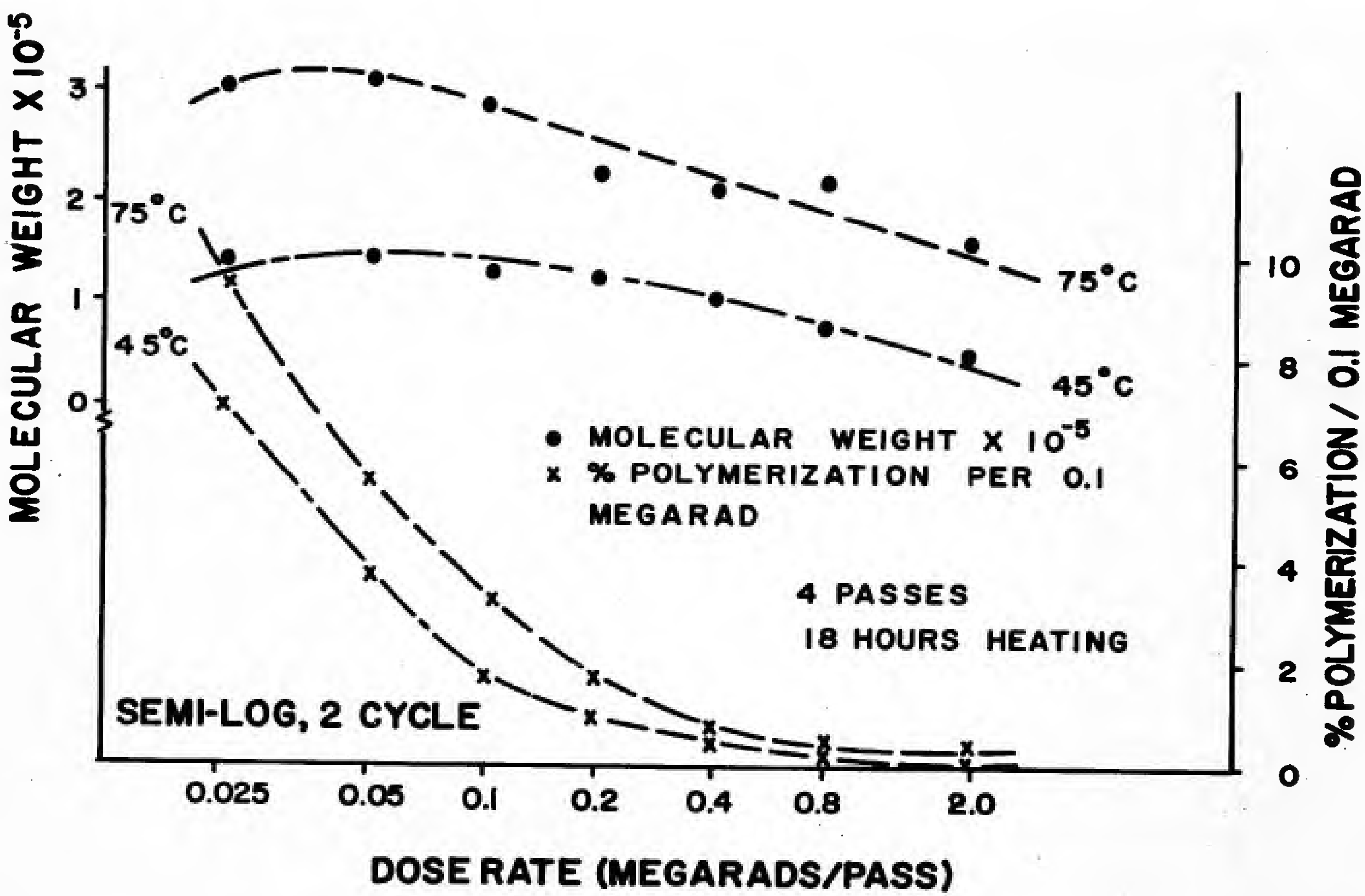

Figure 4. Styrene: Effect of dose rate, dose level, and temperature on molecular weight (left ordinate, upper curves), and effect of dose rate, dose level, and temperature on efficiency or % polymerization per 0. 1 megarad (right ordinate, lower curves)

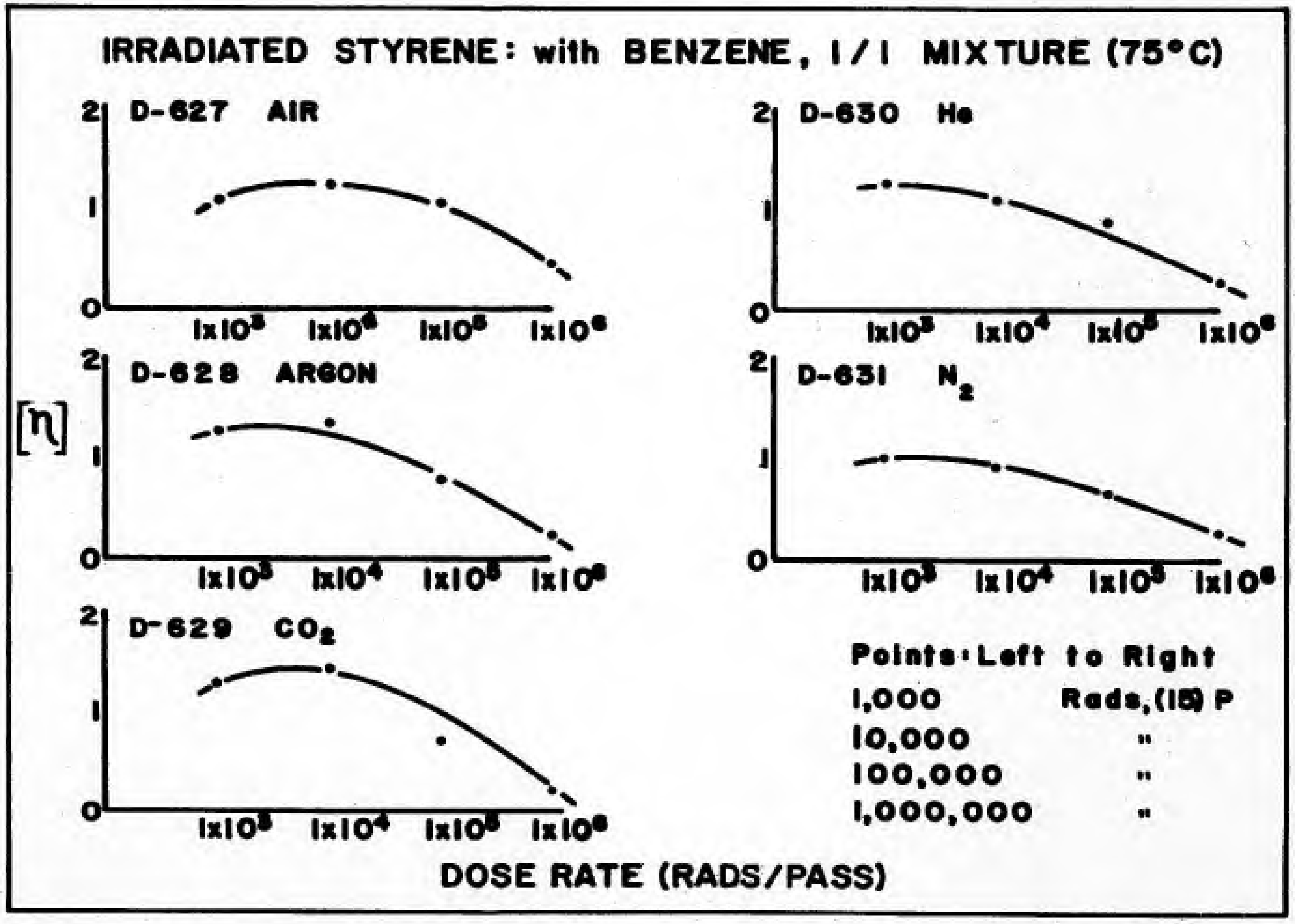

Figure 5. Styrene in benzene (v/v): Effect of atmosphere, dose rate, and dose level on viscosity, with pre- and post-irradiation heating on a 1-hour cycle at 75° C.

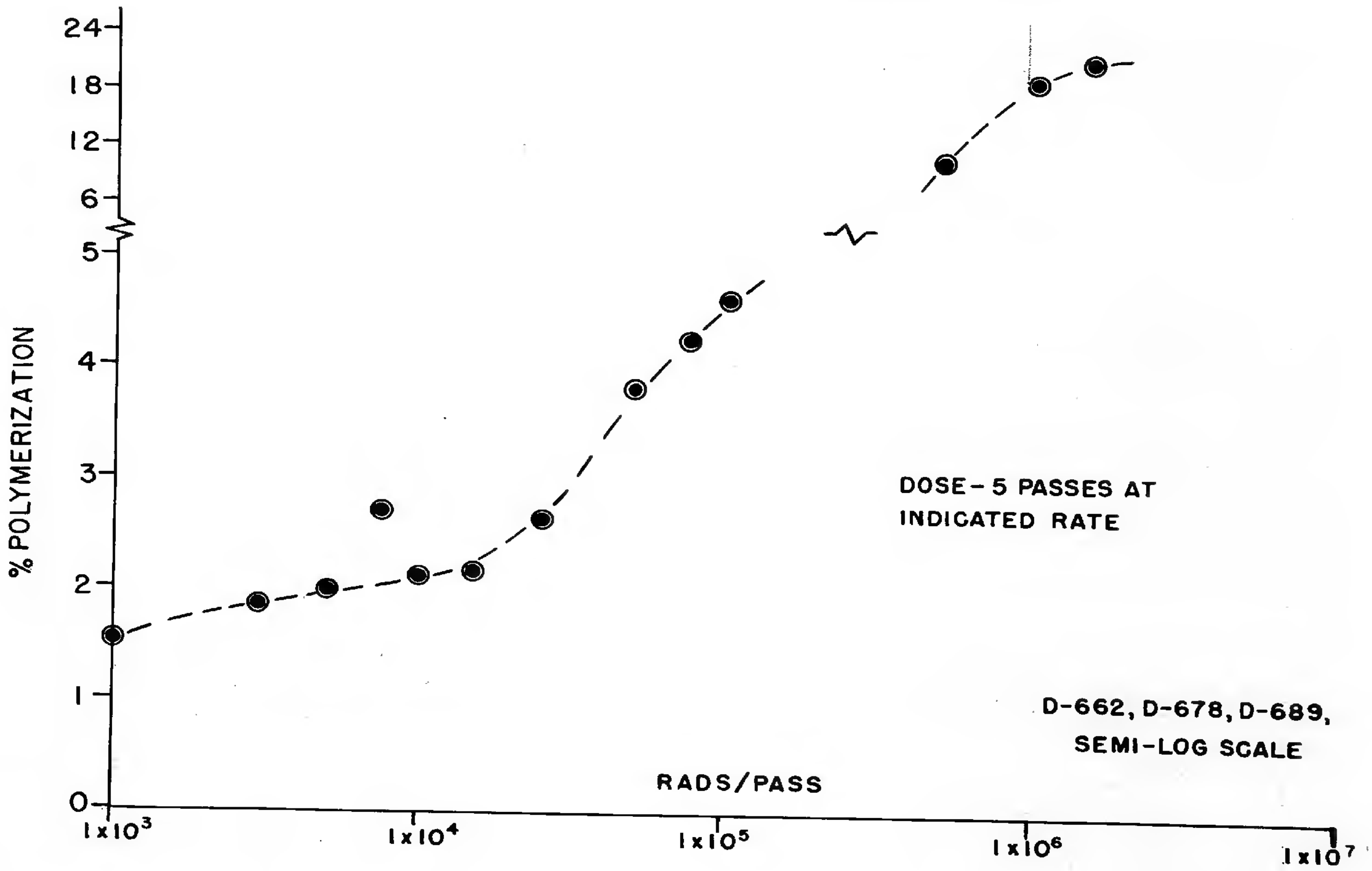

Figure 6. Styrene: Percent polymerization as a function of dose rate and dose level, on a 1-hour cycle at 75° C., when tubes are flamed out at 10 microns, samples degassed at 7 microns, samples sealed off at 5 microns, and irradiated as indicated by legends on above figure.

in dose rate and total dose. At the lower dose rates, initiation and propagation appear to dominate the reaction mechanism, but with an increase in dose rate the termination step becomes more and more predominant and/or there is a significant amount of reversion and/or some other type of molecular deterioration is initiated.

3. Effect of 1% of a Vinyl Monomer as an Additive to Styrene on Irradiation-Induced Polymerization and Molecular Weight as a Function of Dose Rate and Dose Level:[5]

The percent polymerization of styrene, with no additive, as a function of dose rate and dose level is shown by Figure 6, where the abscissa is rads per exposure and the total dose is five times the indicated dose rate.[6] It is observed that about 1.5% of polymer is obtained at a dose rate of 1,000 rads per exposure and a dose level of 5,000 rads, whereas at a dose rate of 2 megarads and a dose level of 10 megarads the conversion is only about 20%, that is, with 2,000 times the dose rate and 2,000 times the dose level, the increase in polymer formation is only about 13-fold.

The effect of dose rate and dose level on the molecular weight of the styrene obtained from the procedure used for the data of Figure 6, is shown by Figure 7. It is observed that there is a gradual but persistent decrease in molecular weight with an increase in dose rate and total dose.[6]

The effect of 1% of acrylic acid on the polymerization of styrene is obtained by comparing Figure 8 with Figure 6, where the initial value obtained with 1% of acrylic acid is about twice that obtained without an additive, whereas at higher dose rates and dose levels the effect is reversed. The effect of the additive on molecular weight is obtained by contrasting the results of Figure 9 with those of Figure 7. The 1% of acrylic acid effects a decrease in molecular weight at the lowest dose rate and dose level by almost 200,000, but the effect of the additive at the highest dose rate and dose level does not appear to be significant.[6]

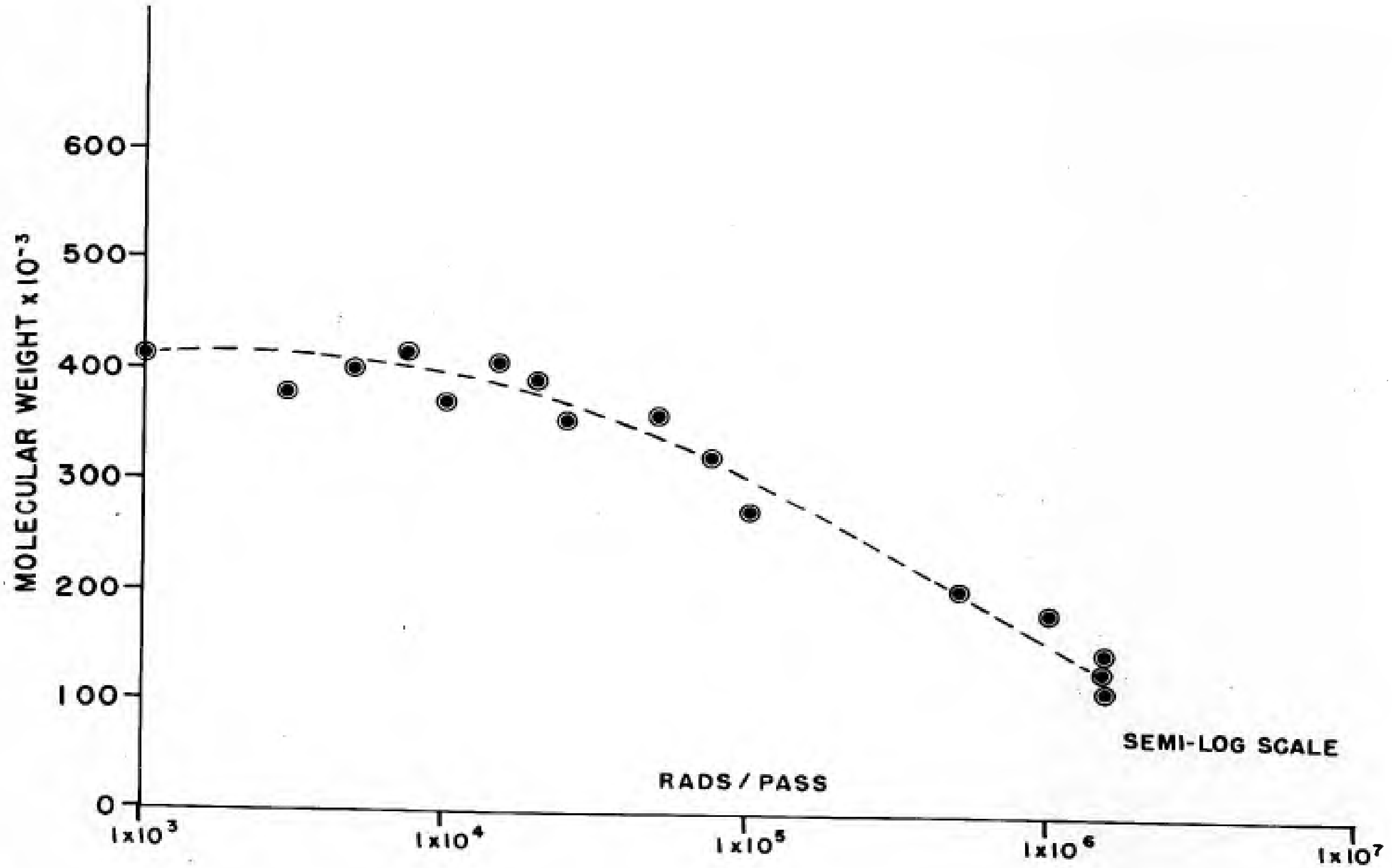

Figure 7. Styrene: Effect of dose rate and dose level on molecular weight, under conditions for Figure 6.

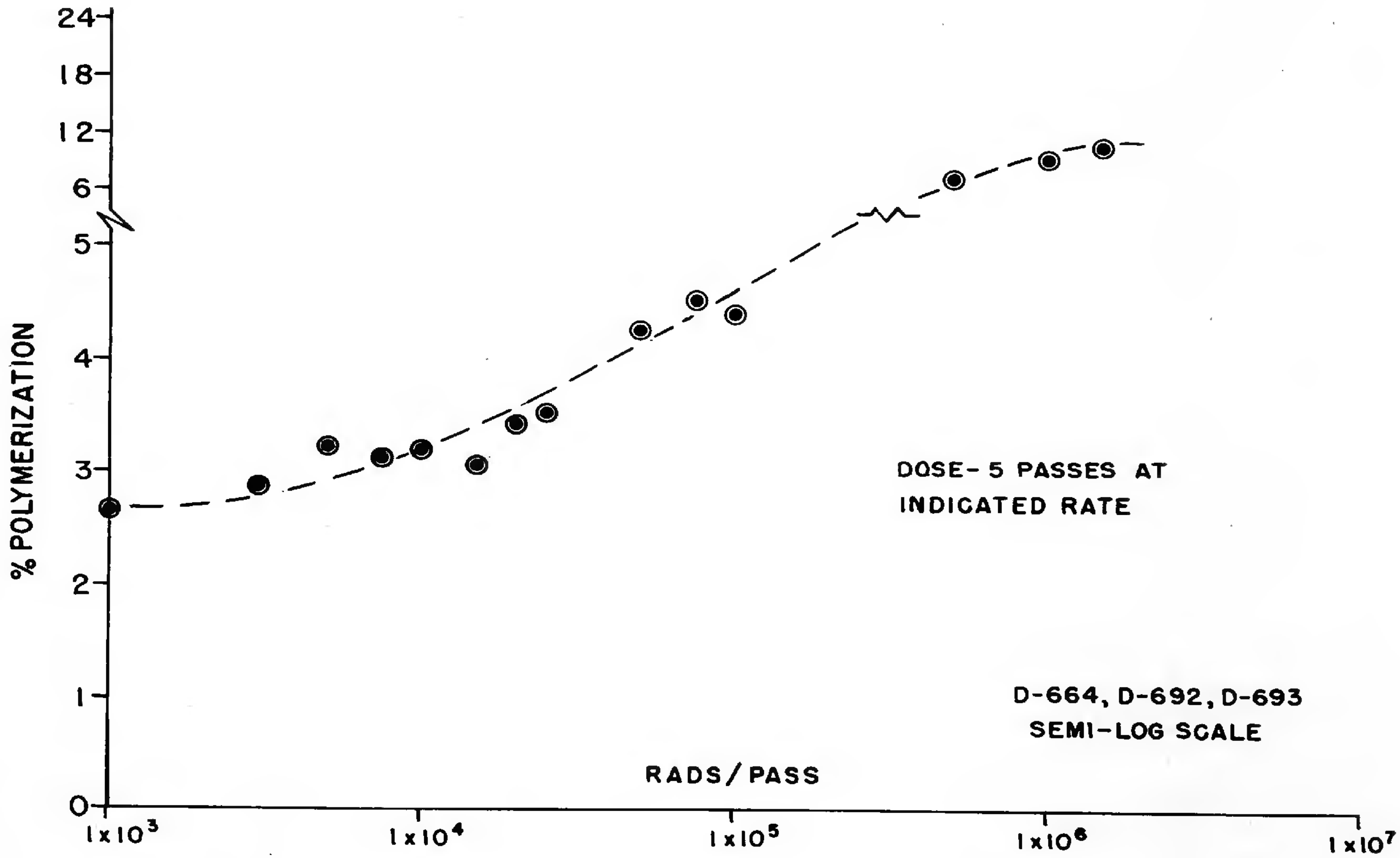

Figure 8. Styrene: Effect of 1% acrylic acid, dose rate, and dose level on irradiation-induced polymerization of styrene (cf. Fig. 6).

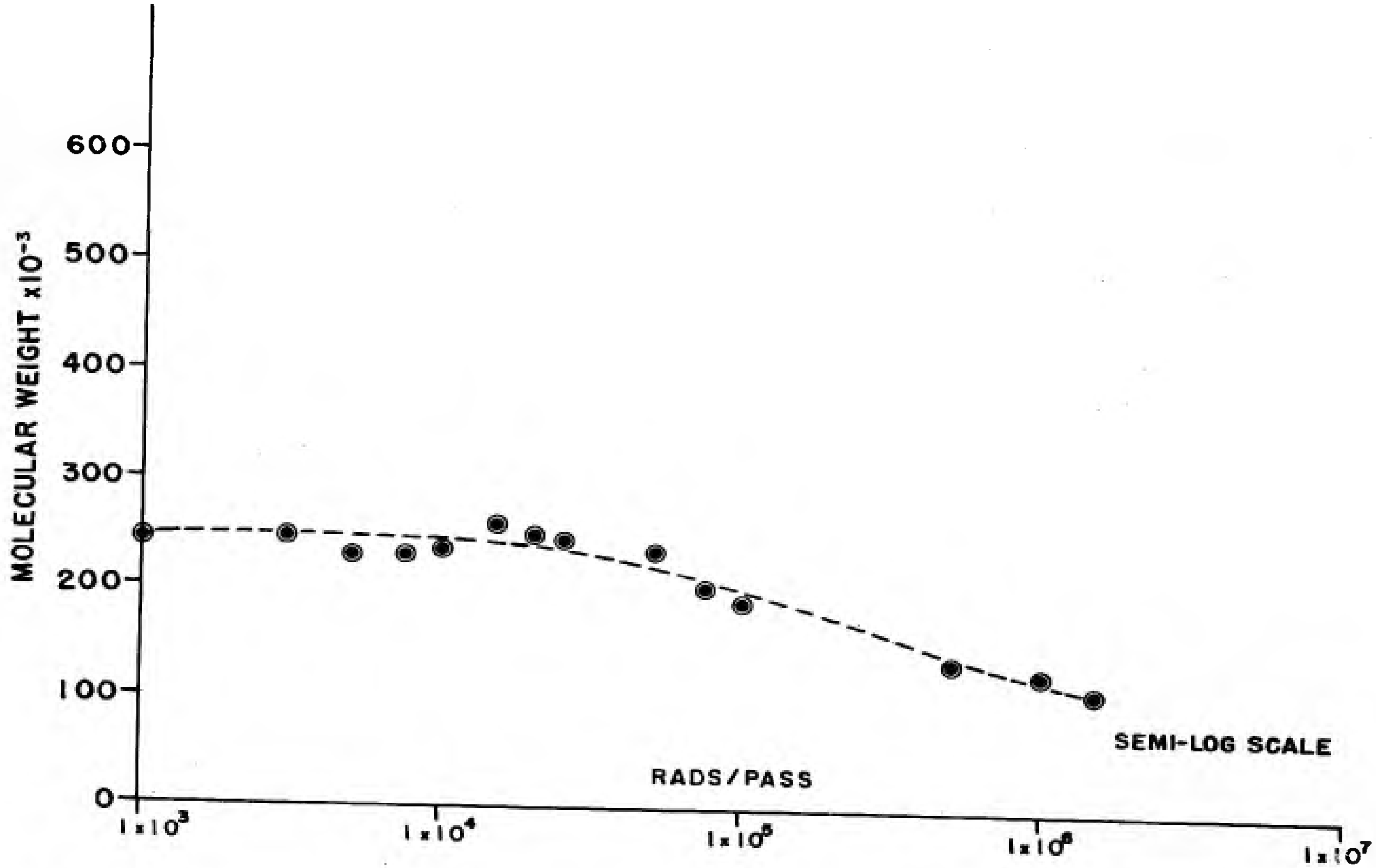

Figure 9. Styrene: Effect of 1% acrylic acid, dose rate, and dose level on molecular weight of polymer obtained (cf. Fig. 7).

With 1% of vinyl acetate as the additive, the amount of polymer formation is slightly more than with no additive, at the lower dose rates and dose levels, but only about half as much at the higher dose rates and dose levels as indicated by a comparison of Figures 10 and 6. The effect on molecular weight is obvious from a comparison of Figures 11 and 7. The results obtained with 1% of methyl acrylate as an additive are quite similar to those obtained with 1% of vinyl acetate.[6]

4. Effect of Irradiation or Time Cycle on the Irradiation-Induced Polymerization of Styrene:[7]

The polymerization of styrene as a function of dose rate, dose level, and the irradiation or time cycle is illustrated by Figure 12. The A-curve is for results obtained on a 45-minute cycle at 75° C., the B-curve for those from a 1- to 3-minute cycle at 25° C., and the C-curve for those from continuous irradiation at 25° C. Whereas the B- and C-curves may be compared directly (comparable conditions used except for the irradiation or time cycle), the results for the A-curve cannot be compared with those for the B-curve without consideration of the temperature differential.

At a dose rate of 100,000 rads per exposure to a total dose of 500,000 rads on a 45-minute cycle, a polymerization value of 1.4% was obtained at 25° C. and over 6% at 75° C. The corresponding values for the 1- to 3-minute cycle (B-curve) and the continuous irradiation (C-curve) are, respectively, 1.1% and 0.5%. It is apparent, therefore, that something longer than a 1- to 3-minute cycle is the most efficient for the irradiation-induced polymerization of styrene, and that the combination of a longer irradiation or time cycle and an elevation of temperature, contribute most significantly to polymer formation under the conditions of these experiments. Studies are in progress in this laboratory to determine the effect of the irradiation cycle on molecular weight.

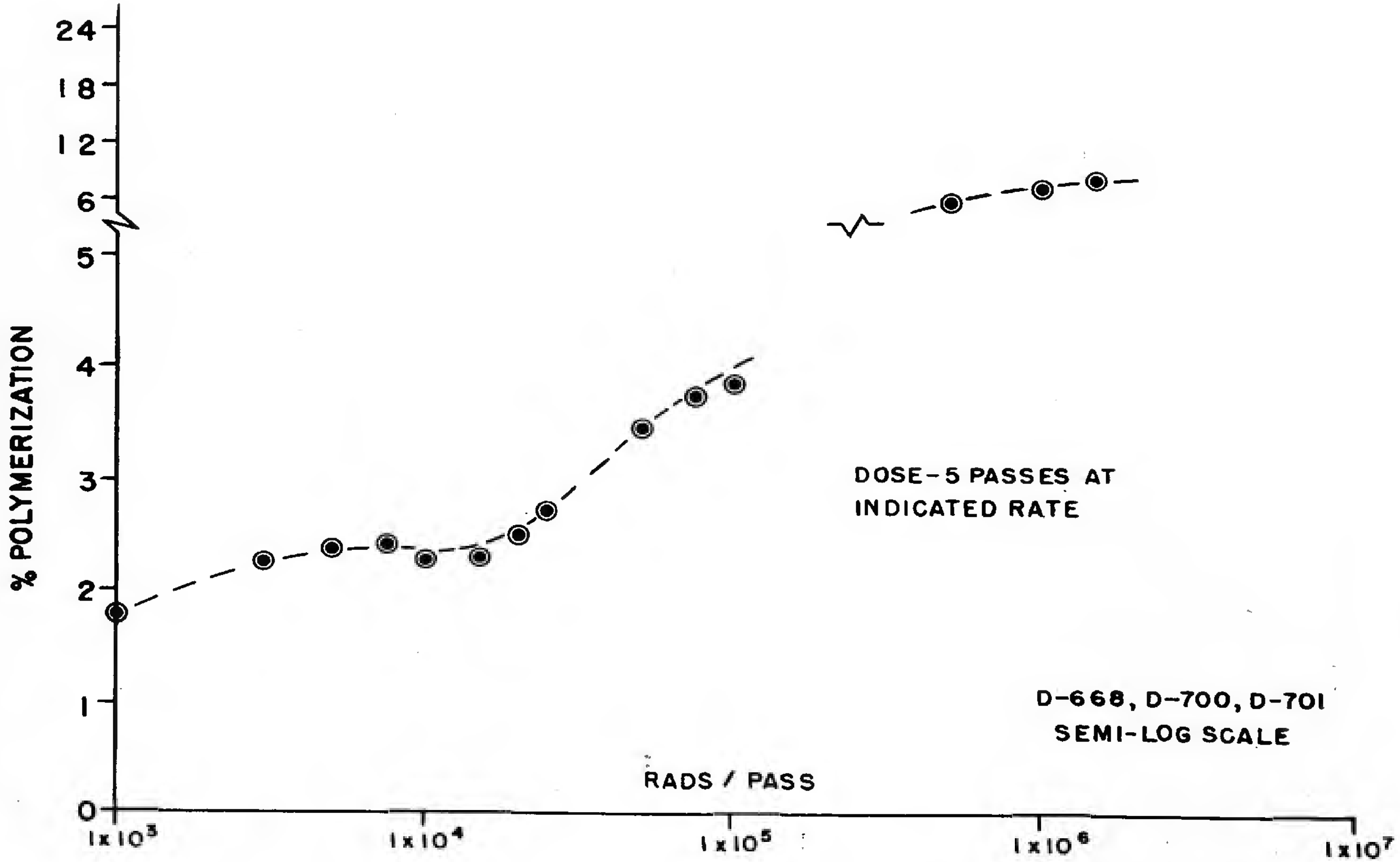

Figure 10. Styrene: Effect of 1% vinyl acetate, dose rate, and dose level on irradiation-induced polymerization of styrene (cf. Fig. 6).

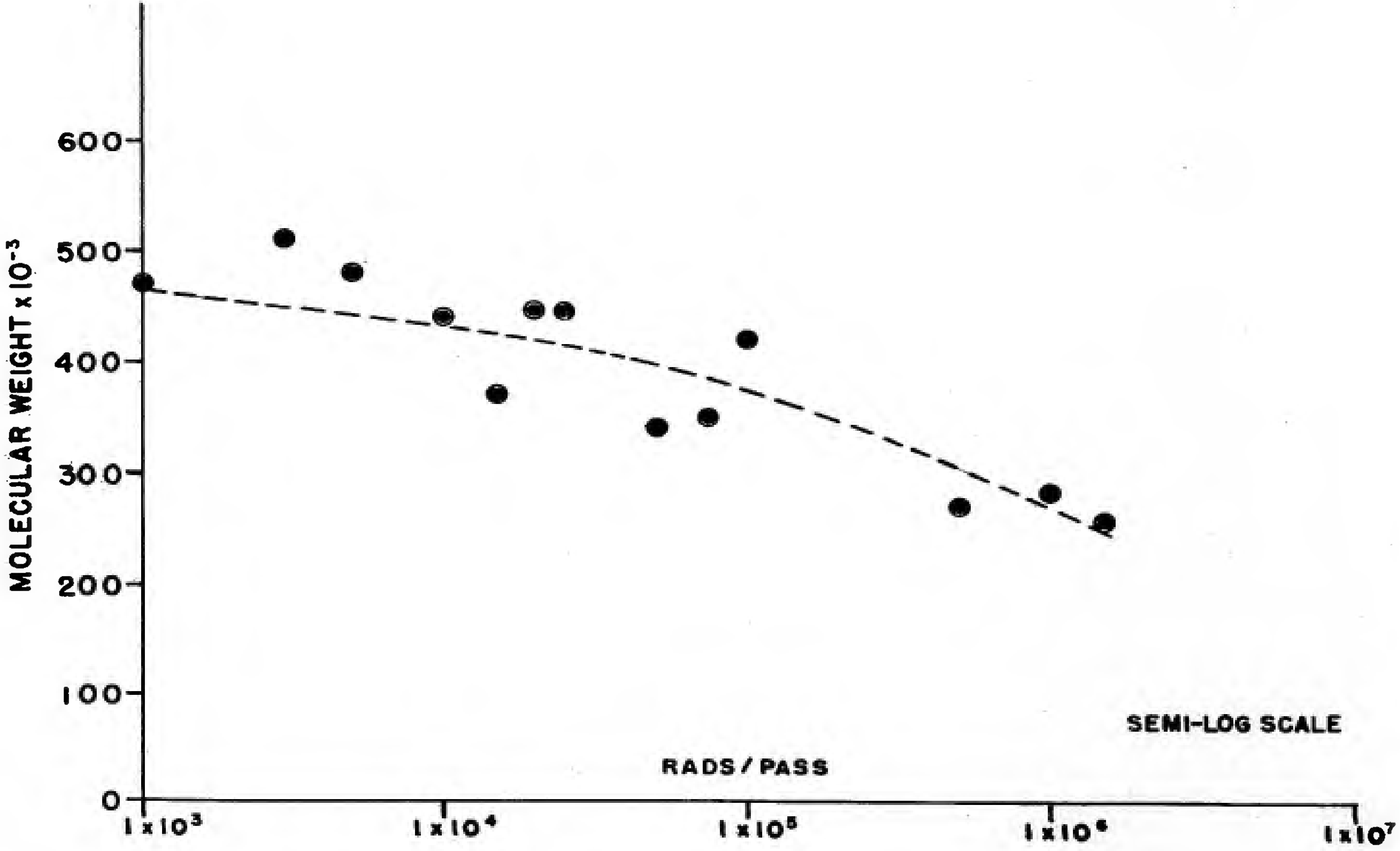

Figure 11. Styrene: Effect of 1% vinyl acetate, dose rate, and dose level on molecular weight of polymer obtained (cf. Fig. 7).

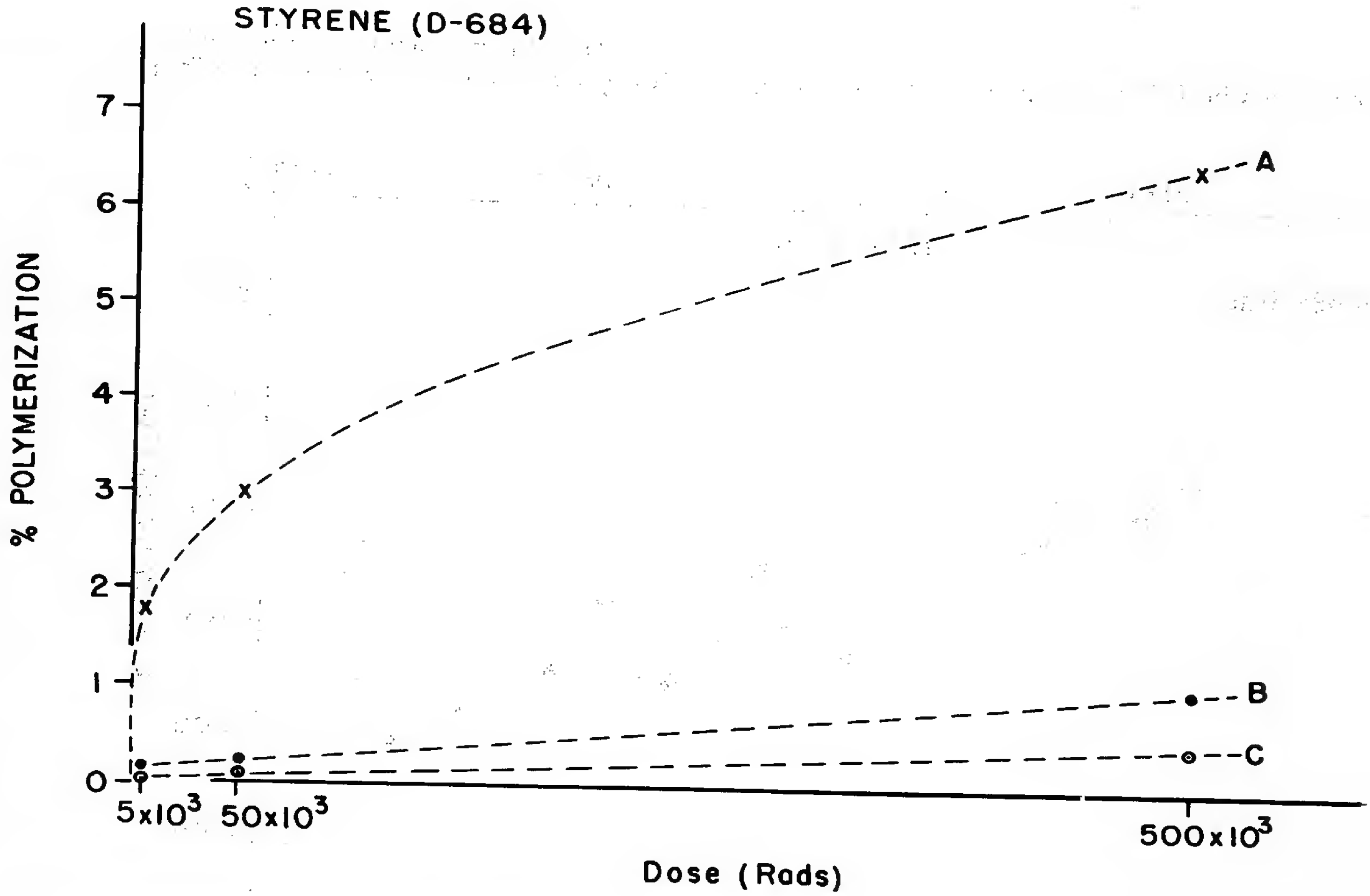

Figure 12. Styrene: Effect of dose rate, dose level, and irradiation or time cycle, where the A-curve is for values obtained on a 45-minute cycle at 75°C., the B-curve for the average of a 1- to 3-minute cycle at 25°C., and the C-curve for continuous irradiation at 25°C.

5. Effect of Small Amounts of Oxygen and Moisture on the Irradiation-Induced Polymerization of Styrene:[8]

Styrene was subjected to 5 exposures at 100,000 rads, on a 45-minute cycle at 75° C. (bars 1 to 7 of Figure 13) and 25° C. (bar 8, Figure 13). Under the conditions of this experiment, the least polymer was obtained when the tubes were subjected to 3 flame-outs at 5 microns, the styrene given 3 degassings at 5 microns, and then irradiated at 25° C. The variation in the conditions used to obtain the data for bars 2 to 7 had no apparent significant effect on polymer formation.[8] Further work in this area is indicated, and additional studies are in progress.

In another series, styrene was given 10 exposures at a dose rate of 3.6 megarads per second, on a 45-minute cycle at 75° C., with five variations in atmosphere, as reported by the bar graphs of Figure 14. The two bars at the left are for values for heat controls. The effect of irradiation may be seen by a comparison of bars 1 and 3. The variations of bars 3, 4, and 5 may not be significant, although these values represent (as usual) the average of triplicate determinations. It should be noted that, under the conditions employed, there is a significant increase in polymerization when the sample is degassed as is evident from a comparison of bars 4 and 6. There is a distinct increase in polymerization also when the tubes are flamed out, as observed by comparing bars 6 and 7.

The effect of oxygen and moisture on the limiting viscosity number of the polystyrene is clearly indicated by the bar graphs of Figure 15, where the ordinate is the limiting viscosity number and the abscissa indicates the experimental variables. The mean value from triplicate samples, as well as the deviation from the mean, is shown. Each tenth of a unit on the ordinate represents a change of about 40,000 in molecular weight. The dose rate was 100,000 rads per exposure on a 45-minute cycle at 75° C. (except for results for bar 8, at 25° C.) to a dose level of 500,000 rads.

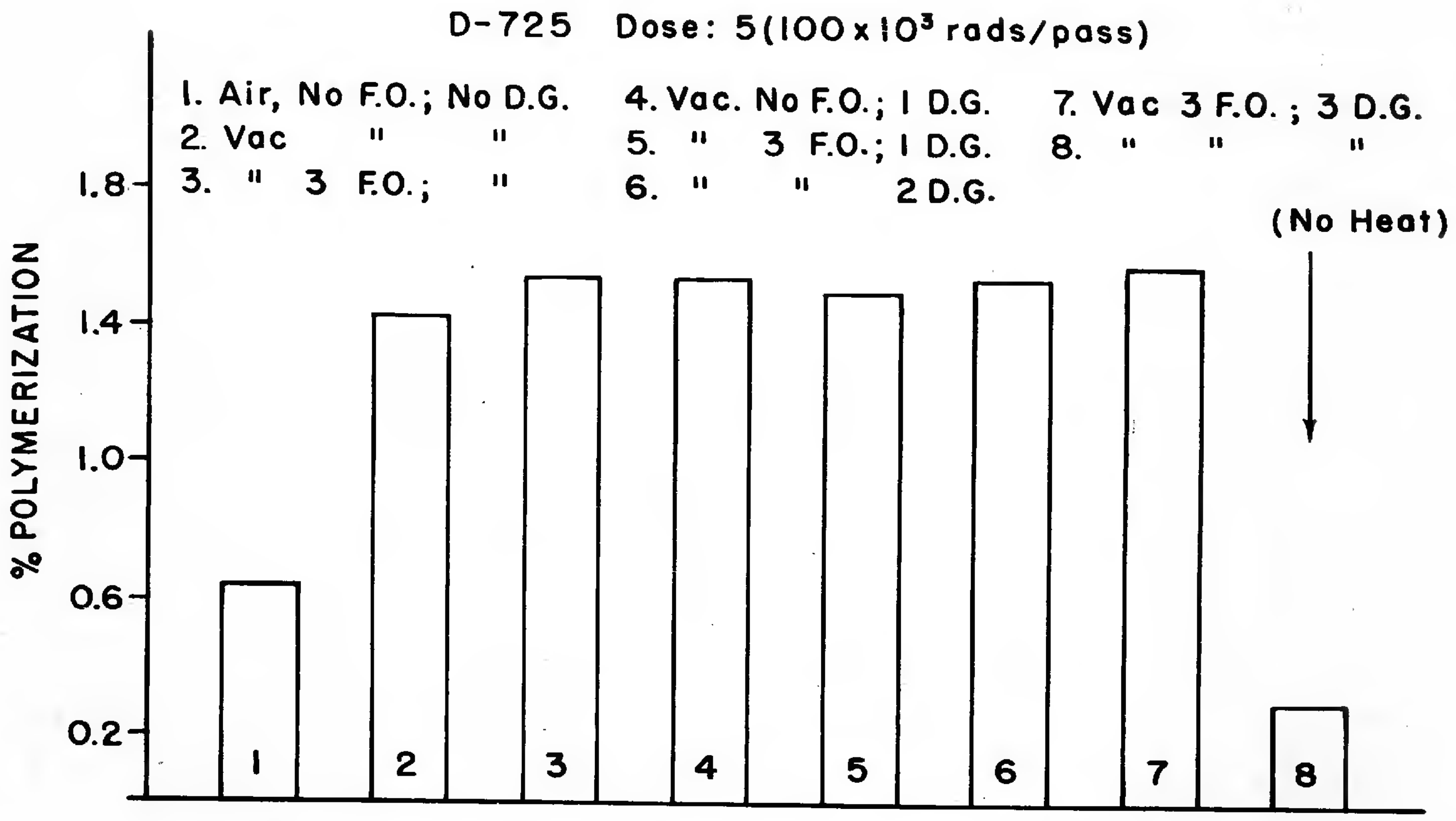

Figure 13. Styrene: Effect of variations in atmosphere and temperature on irradiation-induced polymerization of styrene on a 45-minute cycle at 75°C., where F. O. is for flame-out of tubes and D. G. is for degassing of the monomer prior to irradiation.

Under these specific sets of conditions, the highest limiting viscosity number was obtained with 3 flame-outs and 3 degassings at 25° C., and the next highest value was obtained in air with no flame-out of the tubes and no degassing of the styrene. The lowest value, moreover, was obtained in an evacuated system, but with no flame-out of the tubes and with no degassing of the monomer.

The effects of experimental variables on the irradiation-induced polymerization of styrene, sections 1 to 5, have been observed in general for other vinyl monomer systems, such as acrylonitrile, butyl acrylate, vinyl acetate, 1, 1, 3-trihydroperfluoropropyl acrylate, 1, 1, 7-trihydroperfluoroheptyl acrylate, and one-to-one mixtures of acrylonitrile-styrene, butyl acrylate-styrene, and vinyl acetate-styrene.

6. Effect of Oxygen on the Molecular Structure of Polystyrene Obtained by Irradiation-Induced Polymerization:

From tentative infrared evaluations of polymers obtained by irradiation-induced polymerization of styrene in the presence of different gases, as given by Figure 16, it appears that the molecular structure of the polymer is dependent to some extent at least on the atmosphere in the system.

The A-tracing for the 5 to 6 micron region is for polystyrene obtained by conventional means in the presence of air,[9] whereas the other five tracings are for polymers obtained in this laboratory by use of irradiation-induced polymerization under different atmospheric conditions. All samples received the same treatment otherwise. The B-tracing is for samples of polystyrene obtained in air with no vacuum flame-out of the reaction tube and with no degassing of the monomer prior to irradiation, whereas the C-tracing is for samples obtained in nitrogen with 3 flame-outs and 3 degassings, those of the D-tracing in nitrogen with no flame-out and no degassing, those for the E-tracing in vacuum with 3 flame-outs and 3 degassings, and those for the F-tracing in vacuum with no flame-out and no degassing.

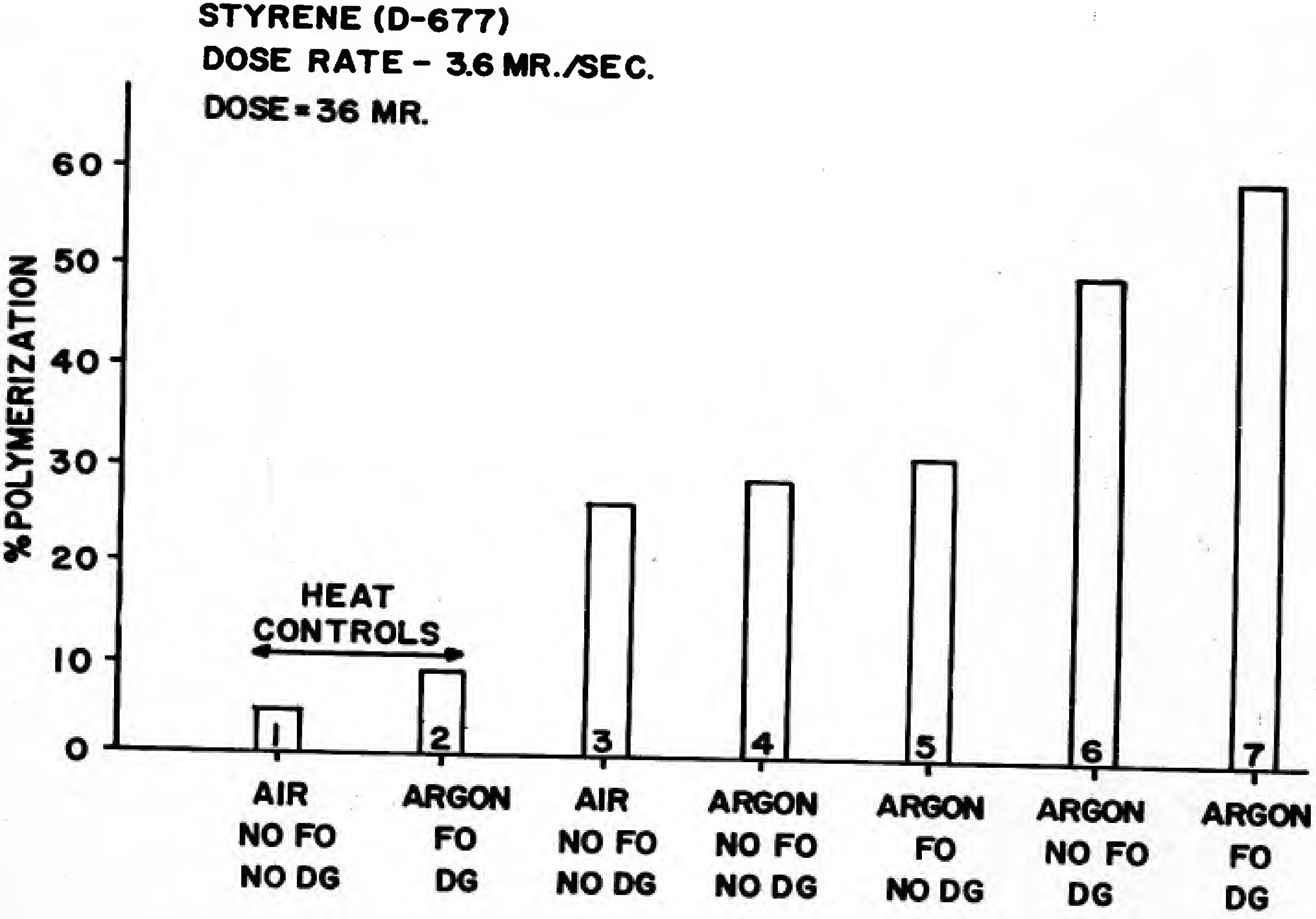

Figure 14. Styrene: Effect of high dose rates, dose levels, and variations in atmosphere on irradiation-induced polymerization of styrene on a 30-minute cycle at 75°C.

The films, from which the spectra of the polystyrene produced by irradiation-induced polymerization were obtained, were cast from a 20% solution of the polymer in toluene onto potassium bromide pellets in a desiccator and the toluene removed by prolonged evacuation at about 60° C.

The data in columns A and B of Table IX give the relative changes in the absorbance ratios of the 5.18 μ to the 5.83 μ bands and of the 5.18 μ to the 6.00 μ bands. These exploratory data indicate that the polystyrene obtained in this laboratory by irradiation-induced polymerization is structurally different from the polystyrene produced by conventional means, which was used by Plyler for obtaining the standard infrared spectra as shown by A of Figure 16. An atmosphere effect is indicated also by contrasting the tracings of B, C, D, E, and F.

From these tracings, one may conclude tentatively that the molecular structure of the polymer obtained by irradiation-induced polymerization is a function of atmosphere. Confirmation of this is in process and the effect of these structural changes on the mechanical and physical properties of the polymer is to be evaluated.

There is an indication by these tracings that the molecular structure of a polymer obtained by irradiation-induced polymerization may be varied appreciably by variations in experimental procedure.

7. Summary:

These studies have shown to date that additive, atmosphere, dose rate, dose level, irradiation or time cycle, traces of oxygen or moisture, and temperature are significantly important variables for the irradiation-induced polymerization of styrene, under the conditions employed in these studies.

These observations have been confirmed, in general, for other vinyl monomer systems, but the extent of the effect varies with the monomers.

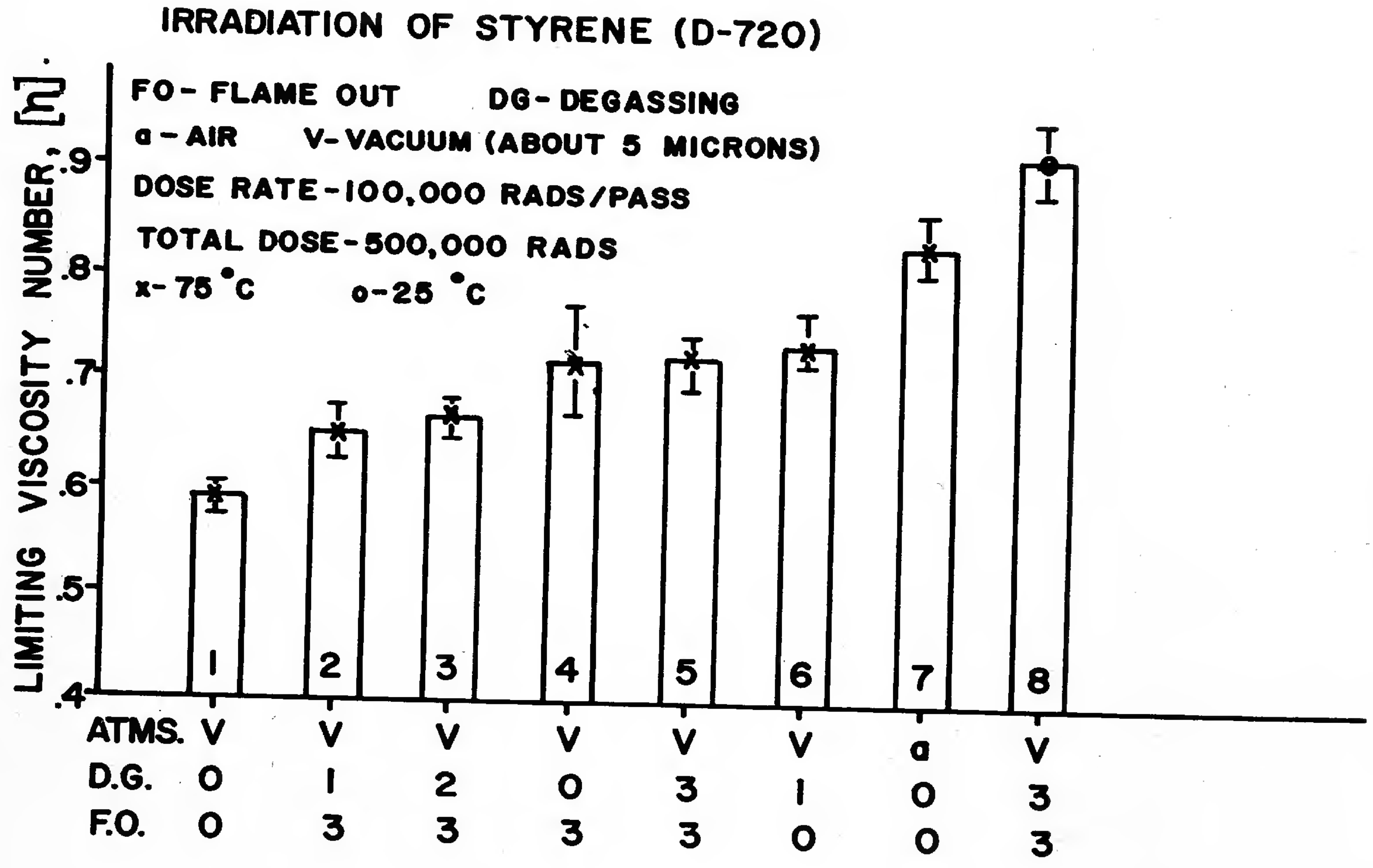

Figure 15. Styrene: Effect of atmosphere and temperature on the limiting viscosity of the polymer, where each 0.1 unit represents a change in molecular weight of about 40,000.

Infrared evaluations of the polymers obtained under different experimental conditions indicate structural variations. Experimental conditions might be used, accordingly, to synthesize modified polymers.

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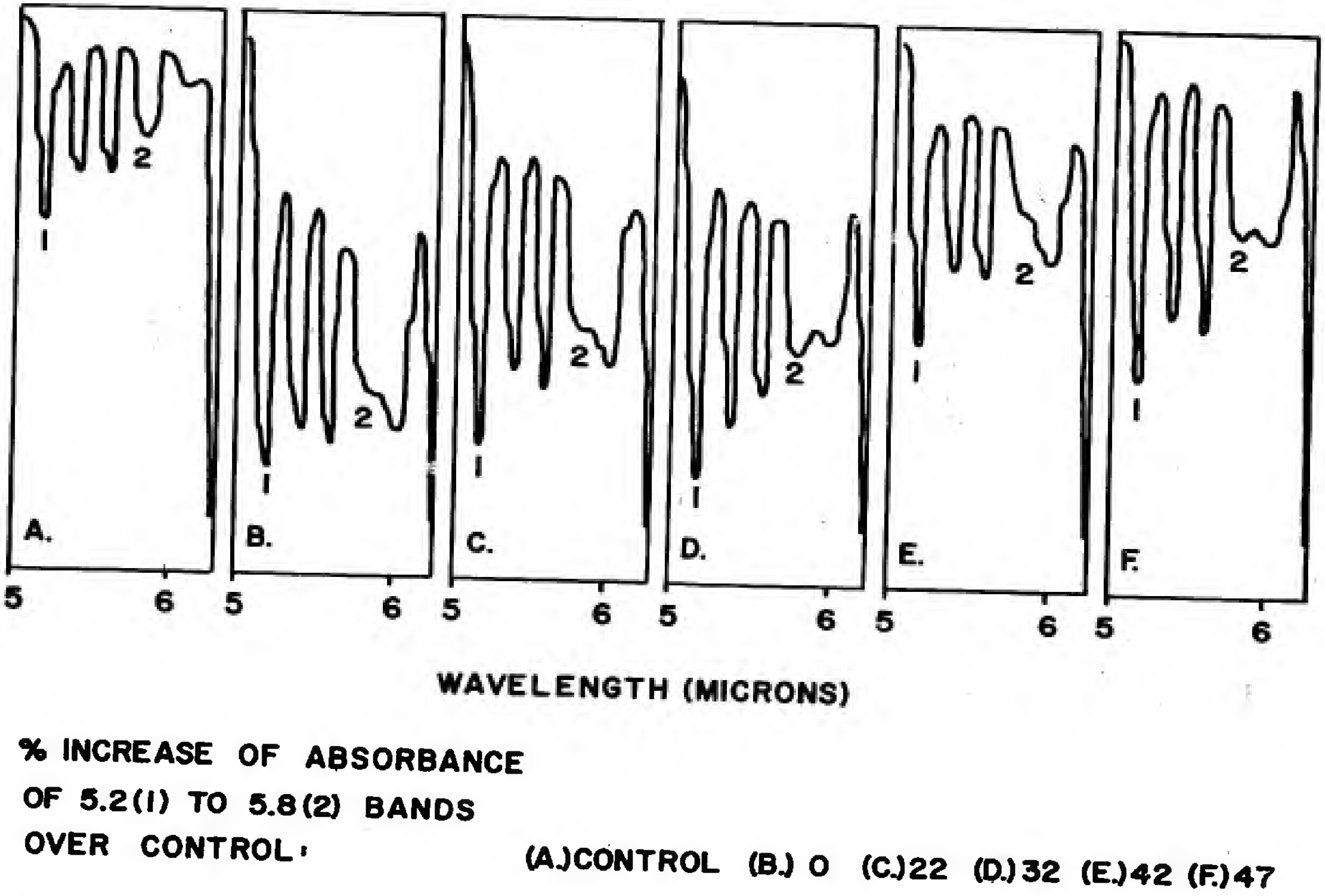

Figure 16. Styrene: Percent increase in absorbence of the 5.2 to the 5.8 bands over the control (A, by Plyler, 1957), where the B-results were obtained under comparable conditions, C-results in N_2 with 3 flame-outs and 3 degassings, D-results in N_2 with no flame-out and no degassing, E-results in an evacuated system with 3 flame-outs and 3 degassings, and F-results in an evacuated system with no flame-out and no degassing, all on a 45-minute cycle at 75°C. Conveyor speed, 93 inches per minute; dose rate, 100,000 rads per exposure; dose, 500,000 rads, with a 2 Mev electron accelerator.

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9. According to calibration for "polystyrene film vs. air" (lambda values after Plyler 1957).

9. <u>Acknowledgements:</u>

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Table IX. Relative Change in Absorbance Ratios of the:

(A) 5.18μ to 5.83μ Bands, and (B) 5.18μ to 6.00μ Bands

Sample No.	Experimental Conditions for Polymerization	A 5.18 to 5.83μ	B 5.18 to 6.00μ
0	Conventional, Plyler	2.26	30.2
1	Irradiated in Air, No FO, No DG	2.37	1.71
10	Irradiated in N_2, 3FO, 3 DG	2.86	2.19
9	Irradiated in Vac., 3 FO, 3 DG	3.78	2.28
2	Irradiated in N_2, No FO, No DG	3.21	2.54
3	Irradiated in Vac., No FO, No DG	2.72	3.49

Note: FO is for 3 flame outs of the reaction tubes at 5μ and DG is for outgassing of the monomer prior to irradiation. In the preparation of these samples, the styrene was irradiated on a 1 hr. cycle at 75°C., at a dose rate of 100,000 rads per pass, on a conveyer with a speed of 93 inches per minute, and to a dose level of 500,000 rads, with a 2 Mev electron accelerator.