

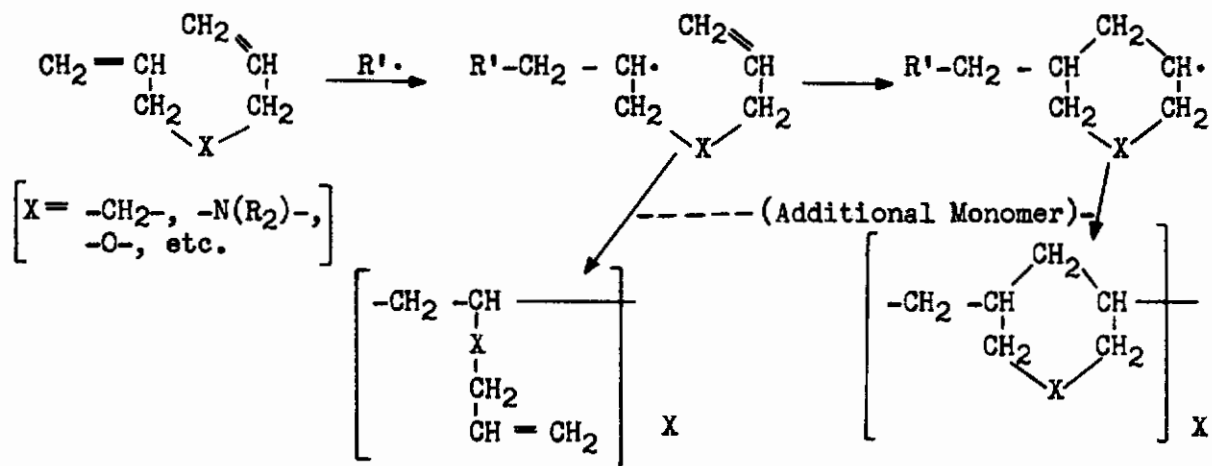
POLYMERIZATION OF NON-CONJUGATED DIOLEFINS

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I. INTRODUCTION

The concept of alternating inter-intramolecular propagation (cyclopolymerization) occurring during the polymerization of certain non-conjugated diolefins, as first discovered by Butler (1) (2), has become a subject of considerable interest (3) (4). During the past one to two years our laboratory has carried on a research program in an effort to achieve two main objectives: (a) to elucidate more fully the nature of the cyclopolymerization mechanism and (b) to extend the boundaries of the known scope of the reaction to obtain additional new and/or unique structures. This paper describes work in both of these areas. In the first section a summary is given of our efforts and those of others, to elucidate, more completely, the reaction mechanism. In the second section some experimental studies are reported on a cyclopolymerization process which occurs in the solid state.

Basically the inter-intramolecular propagation reaction may be illustrated as:



II. CYCLOPOLYMERIZATION IN SOLUTION

The detailed kinetics of cyclopolymerization have not been reported in the literature. The following scheme is set forth to describe free radical initiated reactions which may take place and to evaluate the rate expression obtained when various methods of chain termination are postulated which appear to be applicable.

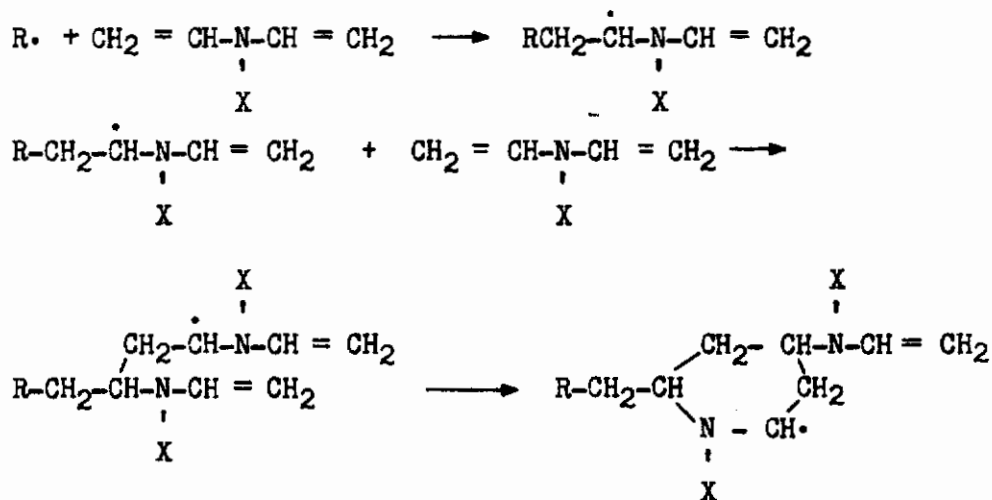
<u>Type</u>	<u>Reaction</u>	<u>Rate Constant</u>	<u>Reaction</u>
Initiator Decomposition:	$\text{A}_2 \rightarrow 2\text{A}\cdot$	k_d	(a)
Chain Initiation:	$\text{A}\cdot + \text{M}_1 \rightarrow \text{M}_1\cdot$	k_I	(b)

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<u>Type</u>	<u>Reaction</u>	<u>Rate Constant</u>	<u>Reaction</u>	
Chain Propagation: (cyclization) (crosslinking) (crosslinking) (crosslinking)	$M_1 \cdot + M_1 \rightarrow M_1 \cdot$	k_{11}	(c)	
	$M_1 \cdot \rightarrow M_2 \cdot$	k_c	(d)	
	$M_2 \cdot + M_1 \rightarrow M_1 \cdot$	k_{21}	(e)	
	$M_1 \cdot + M_3 \rightarrow M_3 \cdot$	k_{13}	(f)	
	$M_2 \cdot + M_3 \rightarrow M_3 \cdot$	k_{23}	(g)	
	$M_3 \cdot + M_3 \rightarrow M_3 \cdot$	k_{33}	(h)	
	$M_3 \cdot + M_1 \rightarrow M_1 \cdot$	k_{31}	(i)	
	Chain Termination:	$2M_1 \cdot \rightarrow$	k_{11}	(j)
		$2M_2 \cdot \rightarrow$	k_{22}	(k)
$M_1 \cdot + M_2 \cdot \rightarrow$		k_{21}	(l)	
$M_3 \cdot + M_1 \cdot \rightarrow$		k_{31}	(m)	
$M_3 \cdot + M_2 \cdot \rightarrow$		k_{32}	(n)	
$2M_3 \cdot \rightarrow$		k_{33}	(o)	

In the above treatment, M_1 is either double-bond of the previously unreacted diolefinic monomer, $M_1 \cdot$ is the unsaturated radical produced directly from M_1 , $M_2 \cdot$ is the cyclized radical, M_3 is a pendant double-bond and $M_3 \cdot$ is the pendant radical from M_3 . It may be noted that the radical $M_1 \cdot$ also contains a double-bond. The formation of M_3 is by reactions (c) and (f) as well as by (j), (l), and (m).

One series of reactions is not represented in the scheme which may be of considerable consequence when the diolefin is capable of forming only a four or five membered ring. This may be illustrated as:



This resulting cyclic radical may possibly react intramolecularly once again to give a bicyclo radical or it may attach monomer directly, leaving residual unsaturation in the polymer. This series of reactions is not treated in the following discussion.

The disappearance of carbon-carbon double-bonds (DB) in the systems of interest here may be written formally as

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$$-d(DB)/dt = k_{11}(M_1\cdot)(M_1) + k_c(M_1\cdot) + k_{13}(M_1\cdot)(M_3) + k_{33}(M_3\cdot)(M_3) + k_{21}(M_2\cdot)(M_1), \quad (1)$$

following the usual procedures of neglecting the monomer consumed in the initiation reaction (b) for reasonably long kinetic chains. Since crosslinking represents only a minor disappearance of double-bonds, further simplification results from neglecting the double-bonds consumed in crosslinking reactions (f), (g), and (h).

$$-d(DB)/dt = k_{11}(M_1\cdot)(M_1) + k_c(M_1\cdot) + k_{21}(M_2\cdot)(M_1) \quad (2)$$

Furthermore, for a monomer capable of undergoing essentially complete cyclization, reaction (c) is rare, hence:

$$-d(DB)/dt = k_c(M_1\cdot) + k_{21}(M_2\cdot)(M_1) \quad (3)$$

Following conventions established in treatment of copolymerization kinetics, the steady-state relationships may be listed as:

$$d(M_1\cdot)/dt = k_{21}(M_2\cdot)(M_1) - k_c(M_1\cdot) = 0 \quad (4)$$

$$d(M_2\cdot)/dt = k_c(M_1\cdot) - k_{21}(M_2\cdot)(M_1) = 0 \quad (5)$$

Hence: $(M_2\cdot) = k_c(M_1\cdot)/k_{21}(M_1) \quad (6)$

Therefore, equation (3) may be written as:

$$-d(DB)/dt = 2k_c(M_1\cdot) = 2k_{21}(M_1)(M_2\cdot) \quad (7)$$

In this system there are three main methods possible for radical chain termination. These involve (A) termination by interaction of two cyclized radicals ($M_2\cdot$), (B) termination by interaction of two non-cyclized radicals ($M_1\cdot$), and (C) crossed termination.

(A) Termination Involving Only ($M_2\cdot$) Radical Interaction

Following usual procedures of equating the formation and termination of chain radicals:

$$k_I(A\cdot)(M_1) = 2k_{22}(M_2\cdot)^2 \quad (8)$$

Hence: $(M_2\cdot) = ((A\cdot)(M_1)k_I/2k_{22})^{1/2} \quad (8a)$

From the steady state assumption

$$d(A\cdot)/dt = 2fk_d(A_2) - k_I(A\cdot)(M_1) = 0 \quad (9)$$

or $(A\cdot) = 2fk_d(A_2)/k_I(M_1) \quad (9a)$

Thus equation (8a) becomes

$$(M_2\cdot) = (fk_d(A_2)/k_{22})^{1/2} \quad (8b)$$

and substitution of $M_2\cdot$ into equation (7) gives the following rate expression:

$$-d(DB)/dt = 2k_{21}(M_1)(fk_d(A_2)/k^{22})^{\frac{1}{2}} \quad (10)$$

(B) Termination Involving Only ($M_1\cdot$) Radical Interaction

Following a procedure similar to that used in (A) above:

$$k_I(A\cdot)(M_1) = 2k^{11}(M_1\cdot)^2 \quad (11)$$

Hence: $(M_1\cdot) = ((A\cdot)(M_1)k_I/2k^{11})^{\frac{1}{2}} \quad (11a)$

Utilizing the expression for $(A\cdot)$ from equation (9a) above, equation (11a) becomes:

$$(M_1\cdot) = (fk_d(A_2)/k^{11})^{\frac{1}{2}} \quad (11b)$$

Therefore, termination by only $M_1\cdot$ leads to a rate expression independent of monomer concentration:

$$-d(DB)/dt = 2k_c(fk_d(A_2)/k^{11})^{\frac{1}{2}} \quad (12)$$

(C) Termination Involving Only Unlike Radical Interaction

For the case of termination by inaction of $M_1\cdot$ and $M_2\cdot$ as depicted by reaction (1) of the kinetic scheme:

$$k_I(A\cdot)(M_1) = 2k^{21}(M_2\cdot)(M_1\cdot) \quad (13)$$

From equation (6) and (13) it follows that

$$k_I(A\cdot)(M_1) = 2k^{21}k_c(M_1\cdot)^2/k_{21}(M_1)$$

or $(M_1\cdot) = (k_{21}k_I(A\cdot)(M_1)^2/2k^{21}k_c)^{\frac{1}{2}} \quad (14)$

Equation (9a) is again employed to remove $(A\cdot)$. Thus, equation (14) may be expressed as follows:

$$(M_1\cdot) = (k_{21}fk_d(A_2)(M_1)/k^{21}k_c)^{\frac{1}{2}} \quad (15)$$

This expression for $(M_1\cdot)$, when substituted into equation (7) gives the following rate equation for disappearance of double bonds:

$$-d(DB)/dt = 2(k_c k_{21} f k_d(A_2)(M_1)/k^{21})^{\frac{1}{2}} \quad (16)$$

It may be noted that the derived rate expressions, (10), (12) and (16), differ markedly with regard to dependence upon monomer concentration for the various termination mechanisms listed. The bimolecular termination of the cyclized ($M_2\cdot$) radicals leads to an expression with a first-order dependence on monomer concentration (eq. 10); the bimolecular termination of the non-cyclized ($M_1\cdot$) radicals leads to a non-dependence of rate on monomer concentration (eq. 12);

whereas the crossed-termination mechanism yields a square-root dependence of rate upon monomer (eq. 16). All rate expressions show a square-root dependence upon initiator concentration.

Other interesting relationships may be derived from a further consideration of copolymerization type treatments. For example, when comparing the relative rates of formation of various structures in the polymer:

$$d(M_1)/dt = k_{11}(M_1\cdot)(M_1) + k_{21}(M_2\cdot)(M_1) \quad (17)$$

$$= (M_1\cdot)(M_1)(k_{11} + k_c/(M_1)) \quad (17a)$$

$$d(M_3)/dt = k_{11}(M_1\cdot)(M_1) \quad (18)$$

$$d(M_1)/d(M_3) = 1 + (k_c/k_{11})(1/(M_1)) \quad (19)$$

The conditions under which these expressions are valid are relatively high dilution of monomer and low conversion of monomer to polymer. Under these conditions reactions of (M_3) and $(M_3\cdot)$ may be safely disregarded. In addition, since the conversions are low, the actual polymer composition may be used as the differential ratio:

$$m_1/m_3 = 1 + (k_c/k_{11})(1/(M_1)) \quad (20)$$

Therefore, from the concentration of pendant groups in the polymer and the total weight of polymer, one may evaluate the k_c/k_{11} ratio.

Mercier and Smets⁽⁵⁾ have reported a measurement of k_c/k_p (units unspecified) where k_p is probably the same as k_{11} here for acrylic anhydride in cyclohexanone at 35°C. The k_c/k_p ratio was 0.17. In addition, they report an activation energy for cyclization 2.4 kcal./mole higher than that of propagation.

The experimental work in our laboratory has been concerned with the cyclopolymerization of methacrylic anhydride (MA). Some of the results of this work have been reported⁽⁶⁾. This monomer was known to yield high molecular weight polymer by a cyclopolymerization process⁽⁷⁾. In addition, some information was available on the properties of its hydrolysis product, poly(methacrylic acid).

Figure 1 illustrates a typical reaction rate curve obtained in this work. A linear conversion-time curve was observed from 1-2% conversion up to at least 15-20% conversion, so no ambiguities were involved in calculation of the rate data.

The variation of R_p with initial monomer concentration, observed at six monomer concentrations covering nearly a twenty-fold range, was found to vary as the 3/2 power of the monomer concentration (see Figure 2). At the highest initial monomer concentration used (4.799 moles/liter), which is not shown on this plot, R_p was observed to be higher than would be predicted from this relation.

A 3/2 power dependency has been previously observed to occur when the efficiency of initiation is low⁽⁸⁾ (i.e., the styrene-benzoyl peroxide system in benzene)⁽⁹⁾, although methyl methacrylate, a monomer which one might expect to

more closely resemble MA, does show ideal behavior with AIBN(10). The kinetic scheme presented earlier does not offer any other basis than low efficiency of initiation to account for the 3/2 order in monomer found.

The variation of R_p with initiator concentration was observed to obey the square-root law over a sixteen-fold change in initial initiator concentration. This is illustrated in Figure 3.

A consideration of the kinetic schemes presented earlier also leads to various relationships for the activation energies of the several processes occurring in cyclopolymerization. Assuming that the sole process of chain termination is the bimolecular termination of $M_2\cdot$ radicals the overall activation energy (E_T) is related to the activation energies for: initiator decomposition (E_d); the reaction of $M_2\cdot$ with M_1 (E_{21}); and chain termination E_{22} by:

$$E_T = E_d/2 + (E_{21} - E_{22}/2) \quad (21)$$

This may be compared with the equation obtained for vinyl polymerization(11):

$$E_T = E_d/2 + (E_p - E_t/2) \quad (22)$$

In order to determine the overall activation energy in cyclopolymerization, measurements of the R_p values of MA in DMF were carried out in the temperature range between 35 and 50°C. In addition, a study was also made with methacrylic acid. The logarithm of R_p values of both these systems are plotted versus $1/T$ in Figure 4. The values calculated from the slopes of these curves are given in Table 1, along with values available in the literature for methyl methacrylate, styrene, and butadiene.

TABLE 1

ACTIVATION ENERGIES FOR METHACRYLIC ANHYDRIDE AND METHACRYLIC ACID			
Monomer	E_T (*)	$E_d/2$ (*)	$(E_p - E_t/2)$ (*)
Methacrylic Anhydride	23.0	15	8.0
Methacrylic Acid	24.8	15	9.8
Methyl Methacrylate(17)	--	--	5.0
Styrene (18)	--	--	6.5
Butadiene (19)	--	--	9.8 - $E_t/2$
*Units of kcal/mole			

It is obvious from Table 1 that the E_T terms for MA and methacrylic acid (the latter chosen because it bears a very strong resemblance to one half of a MA monomer) are very close together--almost within experimental error. Significantly, (the $E_p - E_t/2$) values for both MA and methacrylic acid are in the proximity of, however slightly higher than, values for other typical monomers. These data would suggest that there is very little, if any, difference in the energetics for inter-inter- and inter-intramolecular propagation. This is in opposition to previously reached conclusions based upon data obtained with allylsilanes(12).

Mikulasova and Hrivik⁽¹²⁾ compared the bulk polymerization of monoallyltrimethylsilane and diallyldimethylsilane by t-butyl peroxide and reported apparent overall activation energies (E_T) of 35 and 50 kcal/mole, respectively. These authors did not acknowledge the possibility of cyclopolymerization occurring with the diallyl monomer, although this is known to be the case when Ziegler type catalysts are used⁽¹³⁾⁽¹⁴⁾. Making the likely assumption that cyclization does occur with the diallyl silane monomer and that effective termination in both cases is first order in radical concentration, Mikulasova and Hrivik⁽¹²⁾ report that the R_p values for both monomers were functions of the first power of the initiator concentration, the simplest expression for the activation energies would be:

$$E_T = E_d + E_p - E_t \quad (23)$$

where the subscripts have the same meaning as before. For the diallyl silane monomer, however, E_p is E_{21} as in the case of MA (reaction (e) in kinetic scheme). Based on the variation in R_p or degree of polymerization with temperature for these allylic systems, it is possible to calculate various activation energies. These values are given in Table 2. The values of $(E_p - E_t)$ from the variation in

TABLE 2

POLYMERIZATION OF MONO- AND DI-ALLYLMETHYLSILANES				
Activation Energies of Silanes	Observed(a)	Calculated(b)		Calculated(c)
	E_T	E_d^*	$E_p - E_t$	$E_p - E_t$
Monoallyltrimethyl-	35	38	-3	3.7
Diallyldimethyl-	50	38	12	12.6

(a) Mikulasava and Hrivik⁽¹²⁾.

(b) Assuming that $E_T = E_d + E_p - E_t$ (Eq. 23) applies.

(c) From the $\bar{P}_n (= k_p/k_t)$ vs. T data of Mikulasova and Hrivik⁽¹²⁾.

* From the data of Lossing and Tickner (gas phase)⁽¹⁵⁾.

molecular weight are believed more reliable for the monoallyl silane monomer than those based on the rate measurements. This is due to the fact that the degree of polymerization gives directly the ratio k_p/k_t whereas rate measurements are more complicated in these cases.

It may be noted that the $E_p - E_t$ terms are considerably different for the two silane monomers. The $E_p - E_t$ term for the cyclopolymerizing monomer is about 3.5 times greater than for the monoallyl silane monomer.

In our work with the methacrylic acid and anhydride pair this large difference is not obtained. Some preliminary data obtained in our laboratory on the dimethyl - 2,2' - dimethylenepimelate system (which also undergoes cyclopolymerization) indicates an overall activation energy comparable to methyl methacrylate.

To our way of thinking it is not too surprising that no large differences in activation energies are found between mono vinyl polymerization and

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the cyclopolymerization systems we have examined. The difference between the alternating inter-intra and the usual inter-inter types of polymerization is the occurrence of intramolecular cyclization in the former. The ring formation reaction step involves a very specific orientation for the radical and double-bond. As with most reactions which involve such a rigid transition state, the reaction should take place with a significant decrease in entropy. This should result, therefore, in a markedly different frequency term for the intramolecular step as compared with the intermolecular step.

Occasionally IR spectra of poly(MA) revealed relatively small amounts of residual unsaturation, although attempts to accurately determine these amounts were not satisfactory for quantitative conclusions.

To obtain more information on the contribution of the inter-inter reaction in the polymerization of MA, the intrinsic viscosities of polymers formed at varying stages in the polymerization were examined. At high enough concentration, unsaturated pendant groups in the polymer, would be expected to participate in crosslinking to a detectable degree. Since the intrinsic viscosity is more sensitive to the higher molecular weight species present, and the higher molecular weight species are more subject to crosslinking (on a molecule to molecule basis), a convenient and sensitive measure of the occurrence of crosslinking was afforded by intrinsic viscosity-conversion measurements. Such measurements were carried out at 40.0°C at three initial monomer/solvent ratios: 17.0/83.0, 34.9/65.1 and 50.0/50.0, by weight. The data obtained are given in Table 3.

TABLE 3

INTRINSIC VISCOSITY - CONVERSION DATA FOR METHACRYLIC ANHYDRIDE		
Monomer Concentration (%)	Conversion (%)	$[\eta]$ (dl/g)
17.0	6.2	1.04
	12.2	1.04
	17.9	1.03
	20.7	0.99
34.9	6.2	1.4
	17.4	0.8
	24.1	2.2
	27.3	1.1
	37.1	3.0
50.0	7.0	0.36
	11.6	0.56
	12.7	0.52
	16.6	0.50

At the lowest initial monomer level, the intrinsic viscosity data is essentially constant, at least as far as the highest conversion point recorded (20.7 percent). The polymer was completely soluble in DMF. At 34.9 percent monomer gel was detected in all samples taken. These data show a wide variation between 0.8 and 3.0 dl./g.. At 50.0 percent monomer concentration the intrinsic

viscosities are all lower than those at 17.0 or 34.9 percent, but appear to have a much smaller overall variation than at 34.9 percent. Gel was present in these samples as well.

The data suggest, as might be expected, that the concentration of monomer markedly affects the course of the reaction. This would be expected on two accounts. Firstly, at low monomer concentrations, the intramolecular reaction is given a greater time interval in which to occur. Secondly, at low monomer concentrations there is the possibility of forming highly branched structures which are still soluble via the crosslinking reaction⁽¹⁶⁾. The data obtained at 17 percent monomer, however, indicate that the molecular weight of the polymer formed is essentially constant. Hence, the branching is probably negligible at the dilution.

III. CYCLOPOLYMERIZATION IN THE SOLID STATE

Inter-intramolecular polymerization in the solid state was also investigated in our laboratory⁽¹⁷⁾. The non-conjugated diolefin used in this study was N,N-diallylmelamine (DAM), m.p., 140-10C.

Although several studies of solid state polymerizations had appeared in the literature, evidence that cyclopolymerization could occur in the solid state had not been reported. Comprehensive studies of vinyl polymerizations of acrylamide have appeared⁽¹⁸⁾⁽¹⁹⁾.

Solid state polymerizations of DAM were carried out in our laboratory by irradiating evacuated ampules containing monomer in a Co⁶⁰ source and subsequently thermostating the unopened samples at various constant temperatures for various time intervals. Polymers were then isolated by gravimetric precipitation techniques.

The general effects of varying conditions upon percent conversion to polymer can be observed in Table 4 for room temperature irradiations. In-source

TABLE 4

SOLID STATE POLYMERIZATION OF DAM				
Run No.	Rads (x 10 ⁻⁵)	Post-Irradiation Treatment		Total Conversion(%)
		Time(Hrs)	Temp.(°C)	
1	7	24	50	1
2	7	120	50	2
3	7	120	60	3
4	290	120	50	54
5	560	96	60	92
6	360	0	—	48
7	"	24	65	66
8	"	24	85	71
9	"	48	65	76
10	"	48	85	82

polymerization occurs as evidenced by Run No. 6. By irradiating at liquid nitrogen temperature, in-source polymerization could be eliminated to permit the measurement solely of the post-irradiation reaction. The effect of varying thermostat temperatures for such reactions can be noted in Figure 5. The polymers were soluble in acids.

Soluble polymers were also obtained in DMSO solution using AIBN as initiator. Infrared spectra of these polymers indicated that they were identical with those produced in the solid state, but in order to dissolve the solid state polymers in DMSO the addition of dimethylsulfone was required. All polymers were insoluble in other common organic solvents, and they were essentially amorphous, as evidenced by X-ray diffraction examination. The intrinsic viscosities of several poly(DAM) samples were all found to be of a low order as is generally found for allylic polymerization products. Some effect of percent conversion upon the intrinsic viscosity values obtained for solid state polymers was observed.

Since the polymerization of DAM, solely by an inter-intramolecular propagation mechanism would involve the complete loss of unsaturation without producing crosslinks, studies to determine residual unsaturation in polymers were undertaken. IR studies were found to be the more useful in determining poly(DAM) structure than either microcatalytic hydrogenation or NMR analysis. Spectra of monomer, polymer and reduced monomer (N,N-di-n-propylmelamine) were compared. The most commonly used absorption regions for detecting carbon-carbon unsaturation⁽²⁰⁾ were complicated by characteristic absorptions of melamine. Our studies were therefore confined mainly to the 10-11 μ region where two vinyl absorption peaks resulting from out-of-plane deformation vibrations are described near 10.1 and 11.0 μ . Figure 6 illustrates the comparison of spectra where the loss of monomer unsaturation in the reduced monomer and the polymer spectra is observed. We have tentatively interpreted the splitting of the two vinyl bands of monomer in this region to be the result of non-equivalent positioning of allyl groups -- a steric influence.

The low level of residual unsaturation (5 mole percent or less), in conjunction with the solubility properties, would indicate that non-crosslinked, essentially linear polymers resulted from both solid state and solution reactions.

Light-scattering measurements were made on a polymer prepared in solution and a molecular weight of approximately 7,500 was obtained for the weight average molecular weight polymer. By assuming this to be the primary weight average molecular weight and by utilizing the relationships of Stockmeyer⁽²¹⁾ (the presence of one crosslink per weight average molecule is sufficient to produce gelation or insolubility) one can expect the ratio of propagation to crosslinking to be at least 30, and perhaps significantly higher. This also lends support for concluding that if the crosslinking reaction occurs, its magnitude is of a relatively low order.

A comparison of the energetics of propagation between the cyclopolymerization mechanism of DAM and that of the vinyl polymerization of acrylamide⁽¹⁸⁾⁽¹⁹⁾ was of interest. Fadner and Morawetz⁽¹⁸⁾ proposed a kinetic scheme for post-irradiation polymerization based upon the bimolecular termination of active chain end radicals (R):

$$-d(R)/dt = k_t(R)^2 \quad (24)$$

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where $(R) = (R_0)/(1 + k_t(R_0)t)$. (25)

Substituting this expression of (R) into the rate expression, $d(M)/dt = k_p(M)(R)$, the following rate equation was obtained:

$$-\ln(1-Y) = (k_p/k_t)\ln(1 + k_t(R_0)t) \quad (26)$$

where Y equals the weight fraction of polymer at time t; $-\ln(1-Y) = -\ln(M/M_0)$. These workers irradiated at low temperature to eliminate in-source polymerization. They found their experimental curves to be of the form suggested by equation (26), but nevertheless, they point out the inconsistency of such a simplified scheme in light of the fact that the radical concentration was found to decay more slowly than the rate of polymerization.

Fadner and Morawetz found the activation energy for post-irradiation polymerization of acrylamide to be 25 kcal/mole at 25-65°C. Our data on DAM, obtained by similar methods, gave a value of 15.5 ± 1.5 kcal/mole for the activation energy at 50-70°C. A plot of the data is shown in Figure 7.

Baysal, Adler, and coworkers(19) found the following expressions to adequately express their results for post-irradiation polymerizations of acrylamide, where irradiation was carried out at temperatures permitting in-source reaction:

$$-d(M)/dt = k_p(M)(R_0)$$

where $(R_0) = (R) = \text{constant}$. Thus,

$$\ln((M_0)/(M)) = k_p(R_0)t$$

These workers(19) described in-source polymerization by:

$$-d(M)/dt = k_p k_i f I t (M)$$

Here, (R) is related to radiation intensity (I), an initiation rate constant (k_i), and an efficiency factor (f). Activation energies of 3 kcal/mole (in-source) and 10 kcal/mole (post-irradiation) were determined.

Although the complexities of solid state polymerization are not fully elucidated at this time, it does appear that cyclopolymerization is as energetically feasible as vinyl polymerization in the solid state.

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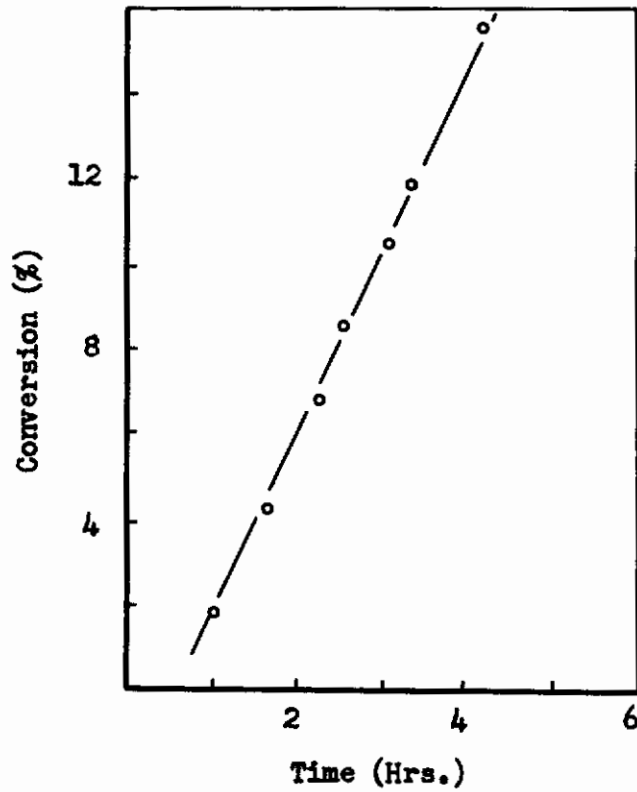


Figure 1. Methacrylic Anhydride Polymerization.

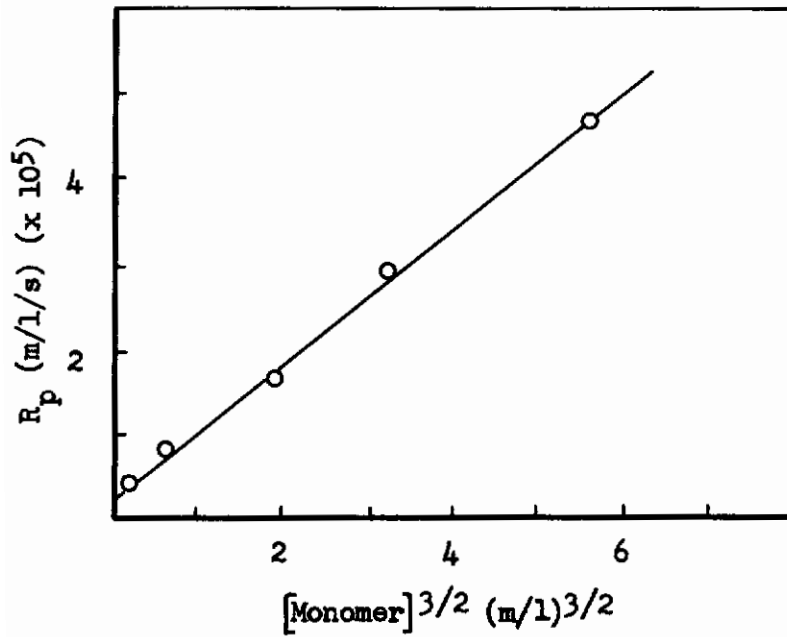


Figure 2. Variation of R_p with Methacrylic Anhydride Concentration.

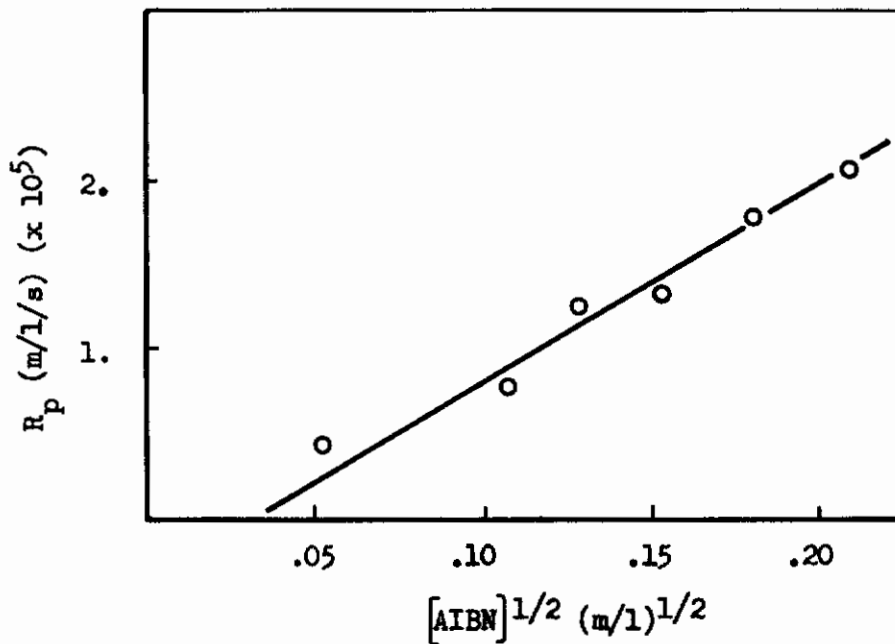


Figure 3. Variation of R_p with Initiator Concentration (AIBN).

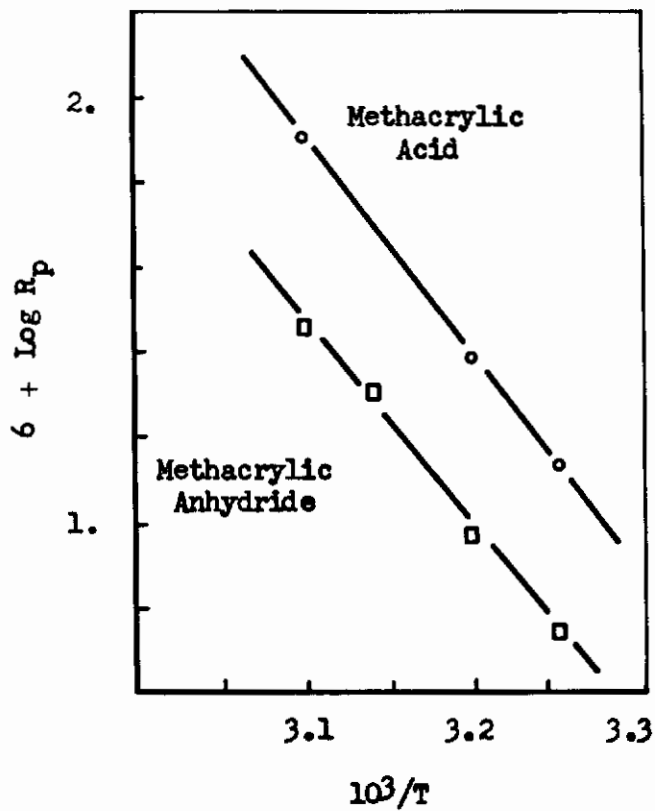


Figure 4. Arrhenius Plot for Methacrylic Acid and Methacrylic Anhydride.

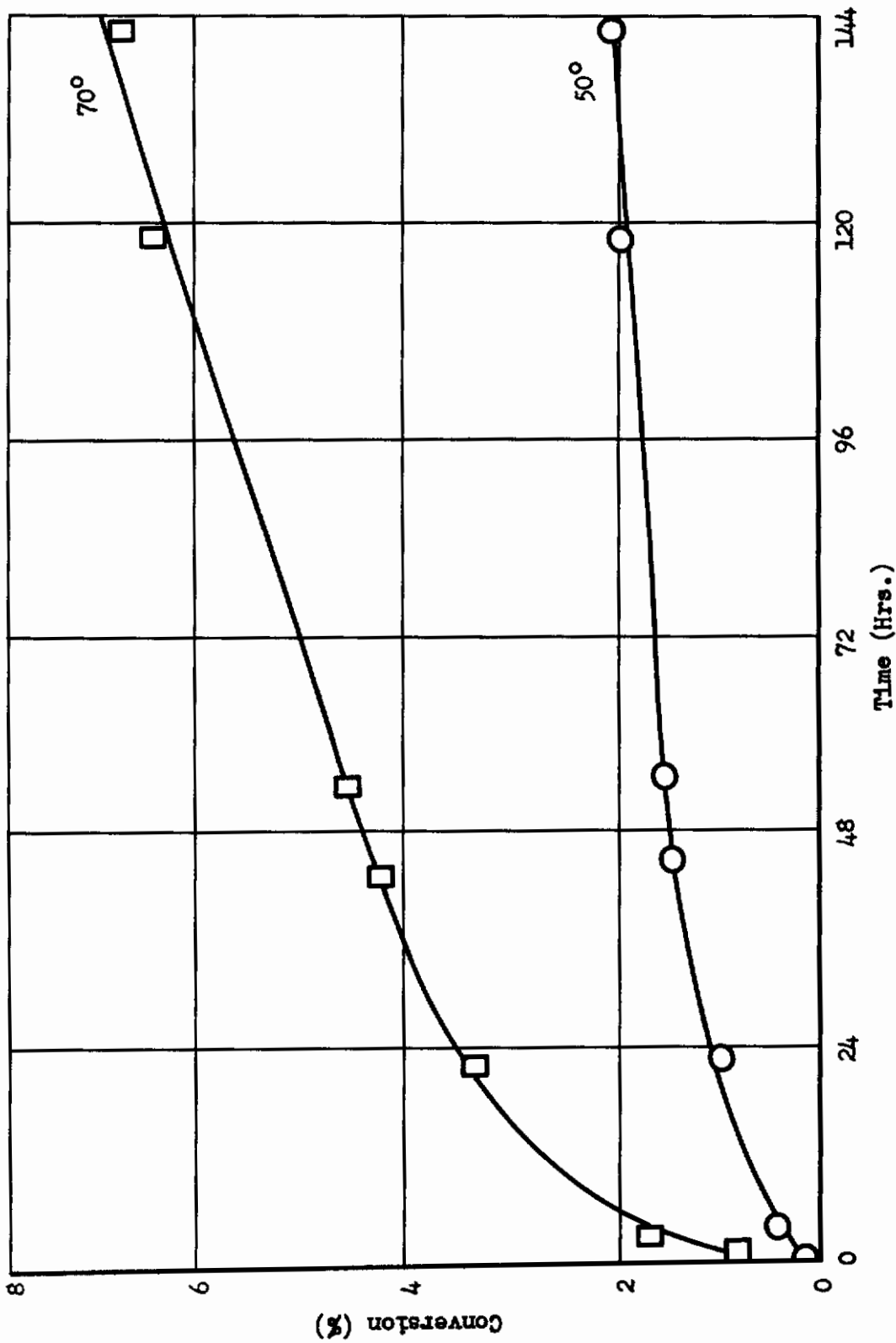


Figure 5. Effect of Time and Temperature upon Post-irradiation Conversion of DAM.

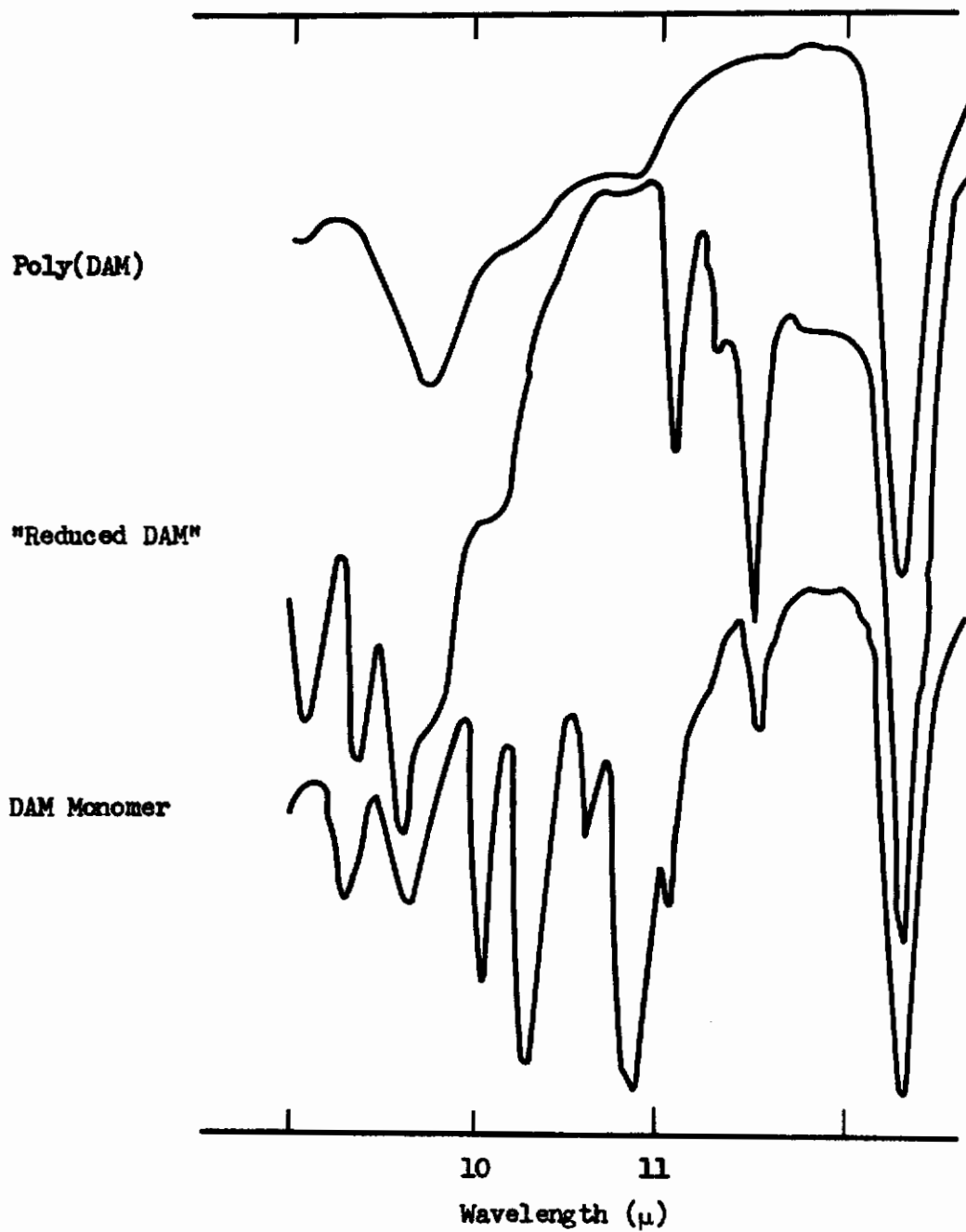


Figure 6. Comparison of IR Absorption Characteristics in 10-11 Micron Region.

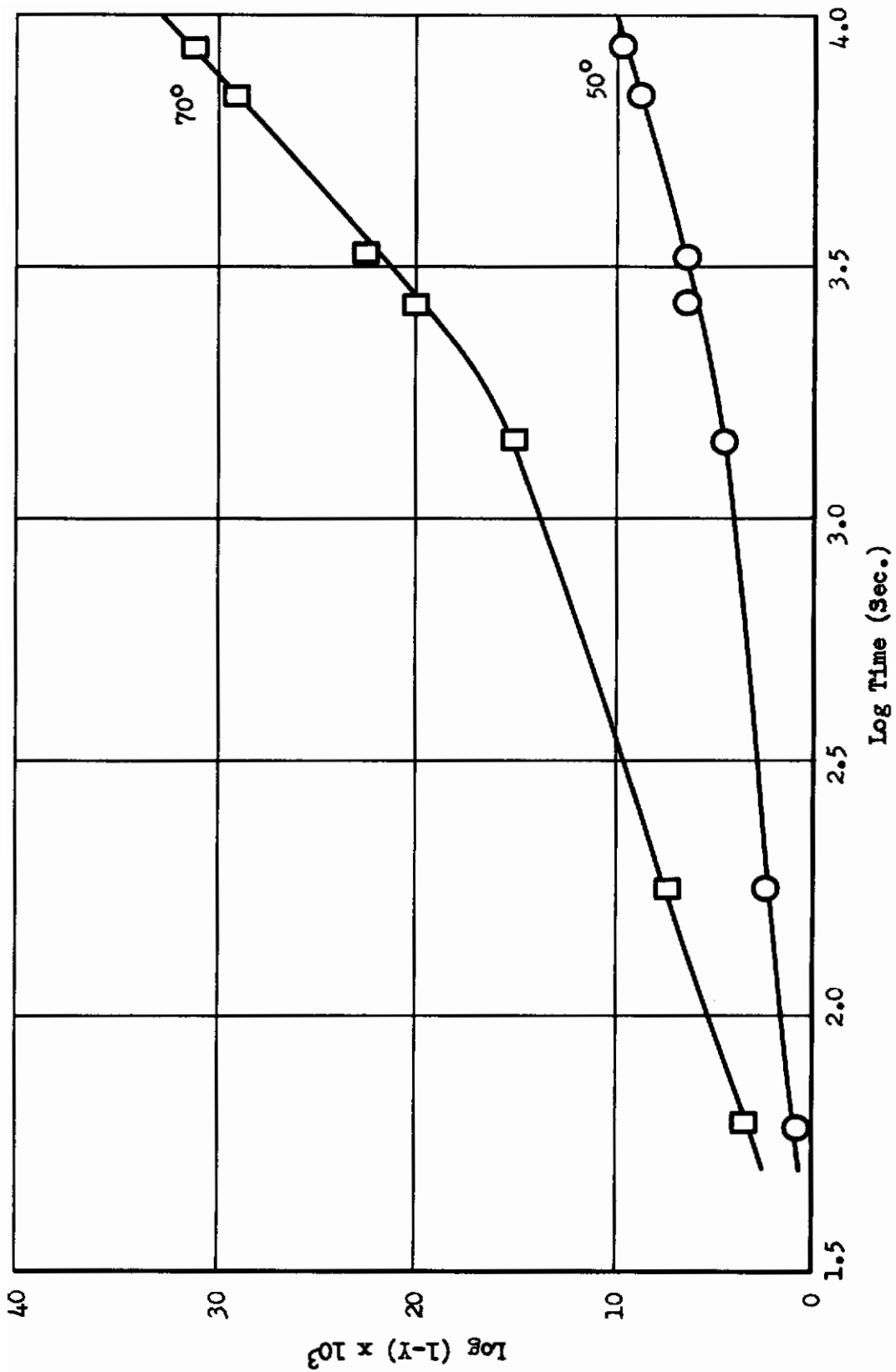


Figure 7. Post-irradiation Data Plotted According to Fadner and Morawetz (18).