



University of
Massachusetts
Amherst

The solid state polymerization of crystalline tosylates.

Item Type	Thesis (Open Access)
Authors	Patel, Ashwinkumar M.
DOI	10.7275/6871452
Download date	2026-06-16 19:11:19
Link to Item	https://hdl.handle.net/20.500.14394/45376

THE SOLID STATE POLYMERIZATION
OF
CRYSTALLINE TOSYLATES

A Thesis Presented

by

ASHWIN M. PATEL

Submitted to the Graduate School of the
University of Massachusetts
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 1969

Polymer Science and Engineering Program
University of Massachusetts
Amherst, Massachusetts

THE SOLID STATE POLYMERIZATION

OF

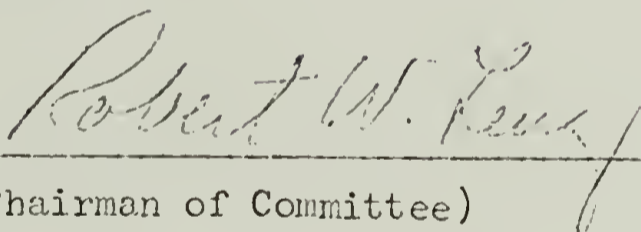
CRYSTALLINE TOSYLATES

A Thesis

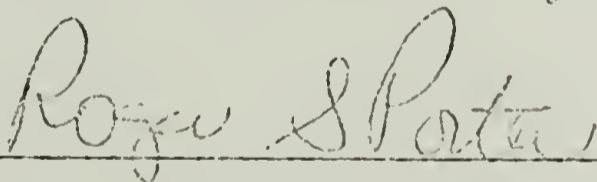
by

ASHWIN M. PATEL

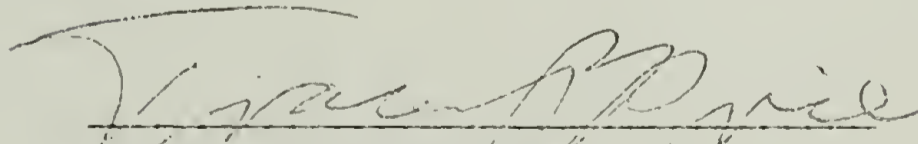
Approved by:



(Chairman of Committee)



(Member of Committee and Head of
Department)



(Member of Committee)

August 1969

ACKNOWLEDGEMENT

The council, advice and guidance of Dr. Robert W. Lenz is gratefully acknowledged. Thanks are due to Dr. F. Price for his help in the microscopic work, to Dr. R. S. Porter for his guidance, and to the Organic Polymer Research Group for their kind help.

The author wishes to acknowledge the financial assistance given by the Xerox Corporation, the General Electric Corporation, the National Science Foundation, and the Department of Defense (Project Themis).

TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORY	3
POLYBENZYL	3
Benzylation Reaction	7
Polymer Structure	8
Linear Polymers	11
Polymerization Mechanism	13
PREPARATION AND REACTIONS OF TOSYLATES	15
SOLID-STATE POLYMERIZATION	18
EXPERIMENTAL	24
Purification of <u>p</u> -toluenesulfonyl chloride	24
Preparation of Tosylates	24
Method 2a	24
Method 2b	25
Method 2c	26
Polymerization Reactions	26
Rate study at 50° C	26
Reaction at 55° C	27
Polymerization of Benzyl Tosylate at Various Temperatures by HBr Vapour	27
Vacuum Polymerization	29
Polymerization of (i) <u>p</u> -methylbenzyl tosylates (ii) <u>o</u> - <u>p</u> -methylbenzyl tosylates and (iii) <u>p</u> -methoxy- benzyl tosylates	29

Termination of Reactions, Precipitation and Purification of the Polymer	30
Some Preliminary Observations on Solution Polymerization	31
Polymer Characterizations	32
Microscopic Study of Benzyl Tosylate Crystals	32
RESULTS AND DISCUSSION	33
Tosylate Monomers	33
Mechanism of the Reaction	34
Rate and Molecular Weight Study	39
Solid-State vs. Melt Polymerization	41
Mechanism of Solid-State Polymerization	42
Structure of the Polymer	43
Molecular Weights and Softening Points	45
Polymerization of Substituted Benzyl Tosylate	46
Polymerization within Single Crystal	47
CONCLUSION	50
REFERENCES	55
TABLES	58
FIGURES	66
PHOTOGRAPHS	81

INTRODUCTION

The field of solid-state reactions, which is being studied extensively in inorganic chemistry, has received little attention in organic chemistry. In recent years, however, work in the latter area has been accelerated. In the case of inorganic solid-state reactions, the mechanism of diffusion through the crystal lattice is fairly well understood, but organic molecules, which are larger and more complex than metal ions, will require very high activation energies for diffusion in the crystalline state.¹

The research described in this thesis will be of wide interest and importance to both polymer and organic chemists as it involves the Friedel-Crafts reactions applied to a condensation polymerization. When this work was started, we believed that it might be possible by crystal lattice restraints (which are known to effect reaction stereochemistry in solid-state organic reactions) to prepare a linear polymer not obtainable in homogeneous media and obtain a higher molecular weight.

The method of preparation of the monomers for this study, benzyl tosylate and its derivatives, have been extensively studied by Kochi and Hammod.² The property which is characteristic of benzyl tosylate and substituted benzyl tosylate is the spontaneous transmutation of the white crystalline solids into colored, amorphous materials. The color of the reaction products varied widely with the nature of the substituent and with time. The change in color was believed by previous workers to be due to the presence of intermediate carbonium

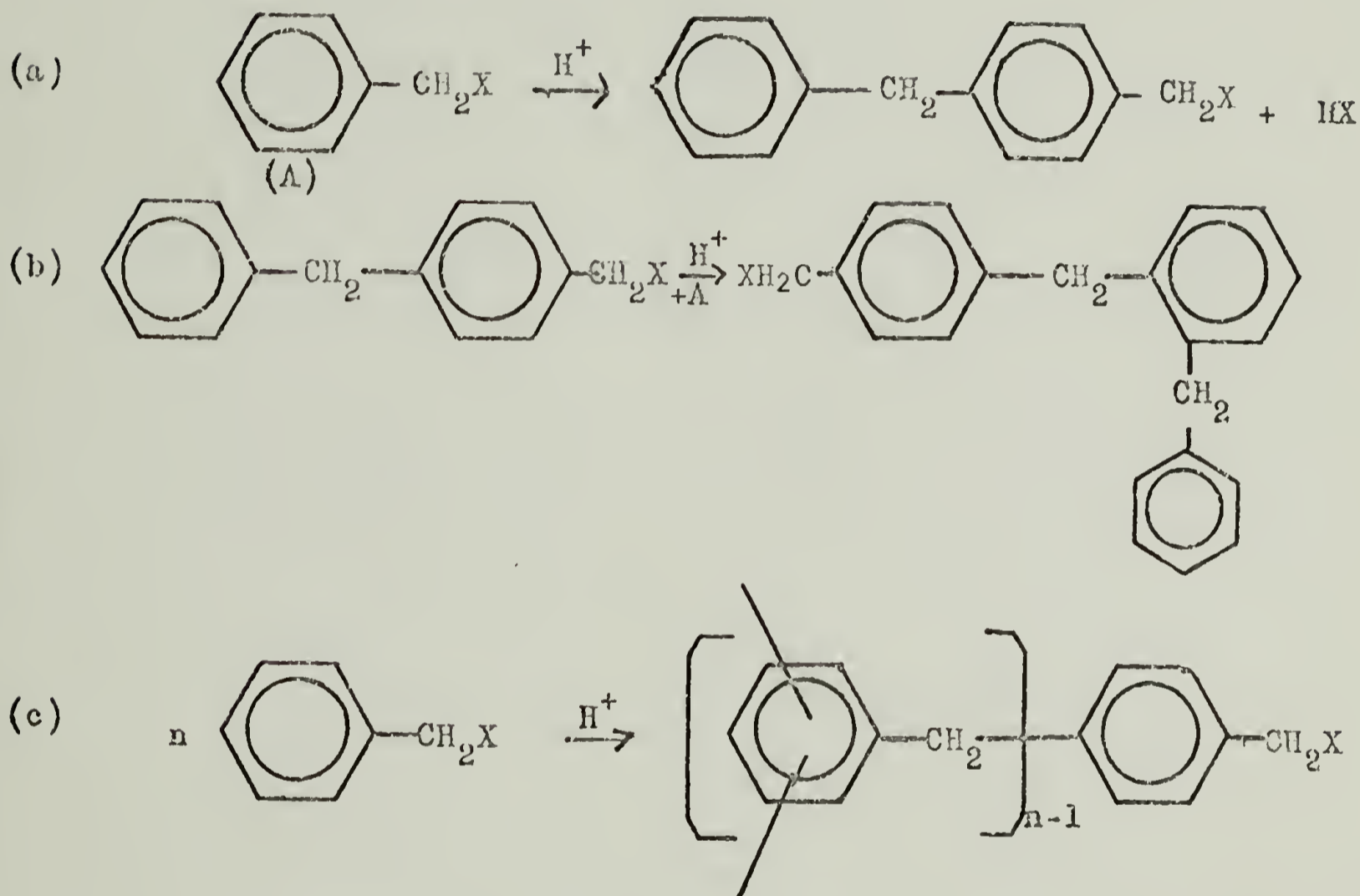
ions.

Stable crystals of benzyl tosylate and substituted benzyl tosylates were prepared. The effect of polymerization temperature on molecular weight and structure was studied. An attempt was made to correlate the exothermic behaviour of the polymerization reaction, by differential scanning calorimetry, to rate studies. The results suggest that the formation of a nucleus of the product is required in the solid state, and photographs of a benzyl tosylate crystal obtained during microscopy studies indicate that the reaction within a crystal may be pictured as radial expansion. At the same temperature, the rate, molecular weight and yield varied with change in reaction environment. The polymers obtained under various conditions were amorphous and of low molecular weight. The infrared results are similar to that of polybenzyl prepared from benzyl halides in solution.

HISTORY

POLYBENZYL

A chain-growth polymerization which produces an unusual polymer of the condensation type is the acid-catalyzed Friedel-Crafts reaction of benzyl halides with itself.

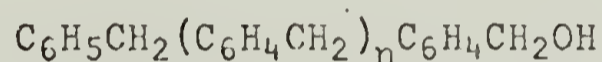


The initiation (a) and propagation steps (b) and (c) differ in rate because the monomer reacts with the polymer chain faster than with itself.

Cannizzaro³ in 1854 reported the formation of an amorphous hydrocarbon analyzing $(C_7H_6)_n$ from the action of either boron trifluoride, boron oxide, sulfuric acid, phosphorous pentoxide or zinc chloride on benzyl alcohol or benzyl ether. Friedel and Crafts⁴ in 1885 reported the same type of product from the reaction of benzyl chloride with

aluminum chloride, and in the same year, a similar material was obtained from benzyl bromide treated with a copper-zinc couple.⁵

Benzyl fluoride when touched with a rod moistened with concentrated sulfuric acid yields a hydrocarbon $(C_7H_6)_x$, which was reported to be an opaque white glass.⁶ The effects of catalysts such as aluminum chloride, ferric chloride and stannic chloride on the polymerization of benzyl chloride has been studied by Jacobson.⁷ Aluminum chloride yielded mainly an insoluble polymer, but stannic chloride yielded an entirely soluble polymer. Shriner and Berger⁸ reported that when benzyl alcohol was added dropwise to a well-stirred cooled solution of concentrated sulfuric acid, salmon-red, stringy solid mass floated on the acid. Analytical data of the purified solid indicated a general composition equivalent to the following structure:



Illari⁹ obtained amorphous powder which decomposed above 210° C, and this product was represented as a mixture of hydrocarbons, $(C_7H_6)_x$. A detailed study of the effect of various anhydrous catalysts on the polymerization of benzyl chloride was carried out by Denmer and Hopper.¹⁰ All polymers obtained in their experiments were thermo-plastic resins varying in color from red through orange to brown and even gray blue.

Yamada et al.¹¹ reported the benzyl chloride polymerized rapidly in n-heptane at room temperature in the presence of an organometallic catalyst, triethylaluminum. When inert solvents such as n-heptane, i-octane or petroleum ether were used, the polymers obtained were

white or pale yellow powders. But in the case of aromatic hydrocarbon or halogenated solvent, a viscous oily polymer was produced.

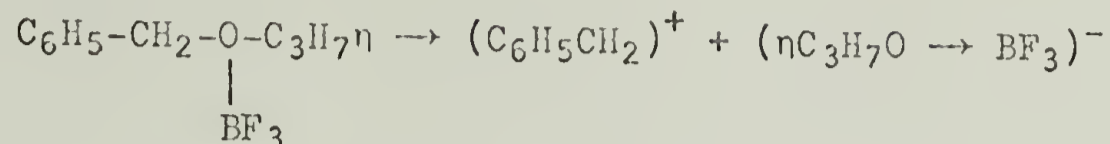
The bulk polymerization of benzyl chloride at 20° C and 65° C in the presence of various Friedel-Crafts catalysts was carried out by Hashimoto and Furukaya.¹² It was reported that the rate of reaction and molecular weight increased with increasing concentration of the catalyst. The kinetics of the polycondensation of benzyl chloride to form polybenzyl was studied by Valentine and Winter.¹³ Analysis of the conversion time plots indicated that the reaction was of the first order in benzyl chloride with the following empirical rate expression:

$$\frac{+d[\text{HCl}]}{dt} = \frac{-d[\text{PhCH}_2\text{Cl}]}{dt} = \frac{K_1[\text{PhCH}_2\text{Cl}][\text{SnCl}_4]}{1 + K_2[\text{SnCl}_4]^2}$$

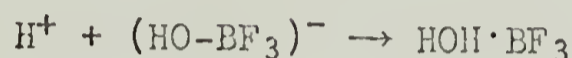
An extensive study of polycondensation of benzyl chloride including effect of catalyst, nature of molecular weight obtained and effect of monomer structure was carried out by Montaudo et al.¹⁴ They observed that when benzyl chloride was polymerized in the presence of SnCl₄ and AlCl₃ in PhNO₂, the reaction was second order with respect to benzyl chloride and first order with respect to the catalyst.

Polymerization of benzyl alkyl ethers, PhCH₂OR where R is Me, Et or *i*-Pr in hexane with AlCl₃, ZnCl₂, FeCl₃ or Et₂O·BF₃, yielded low molecular weight polymers (M.W. 261-1260).¹⁵ Chlorine was found in the polymer when AlCl₃ was used as catalyst. It was proposed that the chlorine present was probably substituted on the benzene ring since it was not washed out by alkali. The mechanism of polymerization of benzyl n-propyl ether has been explained¹⁶ on the assumption that

the reaction is promoted by the formation of ether-boron fluoride complex which gave rise to the positive benzyl fragment and the pro-poxyboron fluoride anion.



The positive benzyl fragment transformed to viscous or solid polymer.



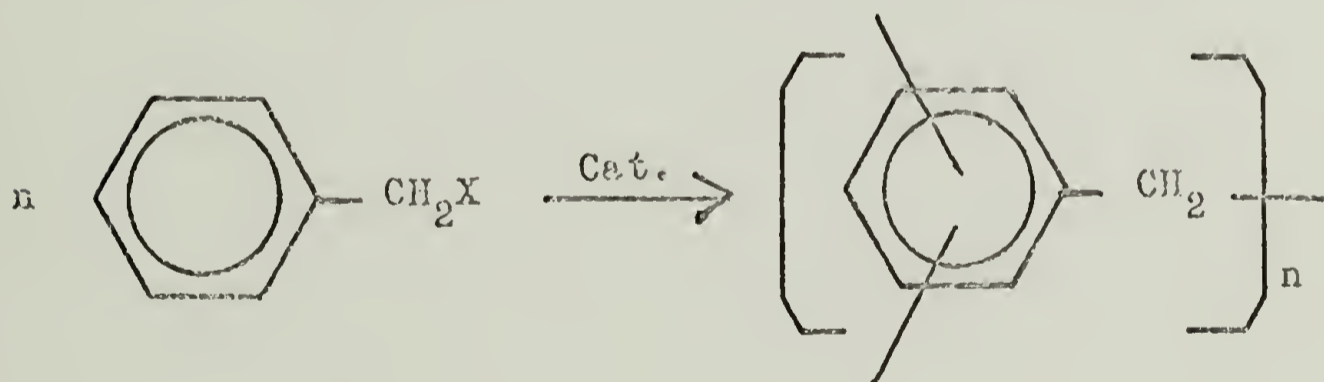
In all the above cases, the polymer products were either amorphous powders or highly viscous liquids of highly branched, low molecular weight. In some cases the structure of the polymer remained ambiguous. It appears that Kennedy and Isacson¹⁷ were the first to prepare crystalline, linear polybenzyls by direct polycondensation of benzyl halides. These crystalline polymers were obtained under extremely mild conditions, at a low temperature ($\approx -135^\circ\text{C}$) with AlCl_3 catalyst in ethyl chloride. Low temperature polymerization was also studied by Finocchiaro, *et al.*,¹⁸ who reported that the number average molecular weight was independent of reaction temperature in the range from -120°C to -149°C .

The formation of polybenzyl other than from benzyl halides, alcohols and ethers is also reported. 1-Benzyl-3,4-cyclotetra-methylene pyrazolin-5-one and related compounds in the presence of polyphosphoric acid produced poly(p-phenylenemethylene) in small yield (Mol. Wt.

890-1490).¹⁹ It is believed that formation of polymer proceeded by an ionic mechanism and the chains were terminated by a PhCH_2 and a heterocyclic groups. When 2-phenyl-1,3-dioxolane was heated at $94^\circ \text{C} \pm 1^\circ \text{C}$ for 46 hrs. in the presence of five moles of BF_3OEt_2 , a polymeric hydrocarbon (max. mol. wt. 3500) having the composition $(\text{C}_7\text{H}_6)_n$ was obtained. Infrared and NMR spectra indicated a benzyl type of structure for this polymer.²⁰ Benzaldehyde, which does not polymerize through the carbonyl function either by γ -radiation or by treatment in solution or in bulk with various catalysts, has been successfully polymerized to a polymer identified as polybenzyl on heating with BF_3OEt_2 at 150° in the absence of a solvent.²¹

Benzylation Reaction

The benzylation reaction of aromatic compounds applied to the preparation of polybenzyl is a typical Friedel-Crafts alkylation

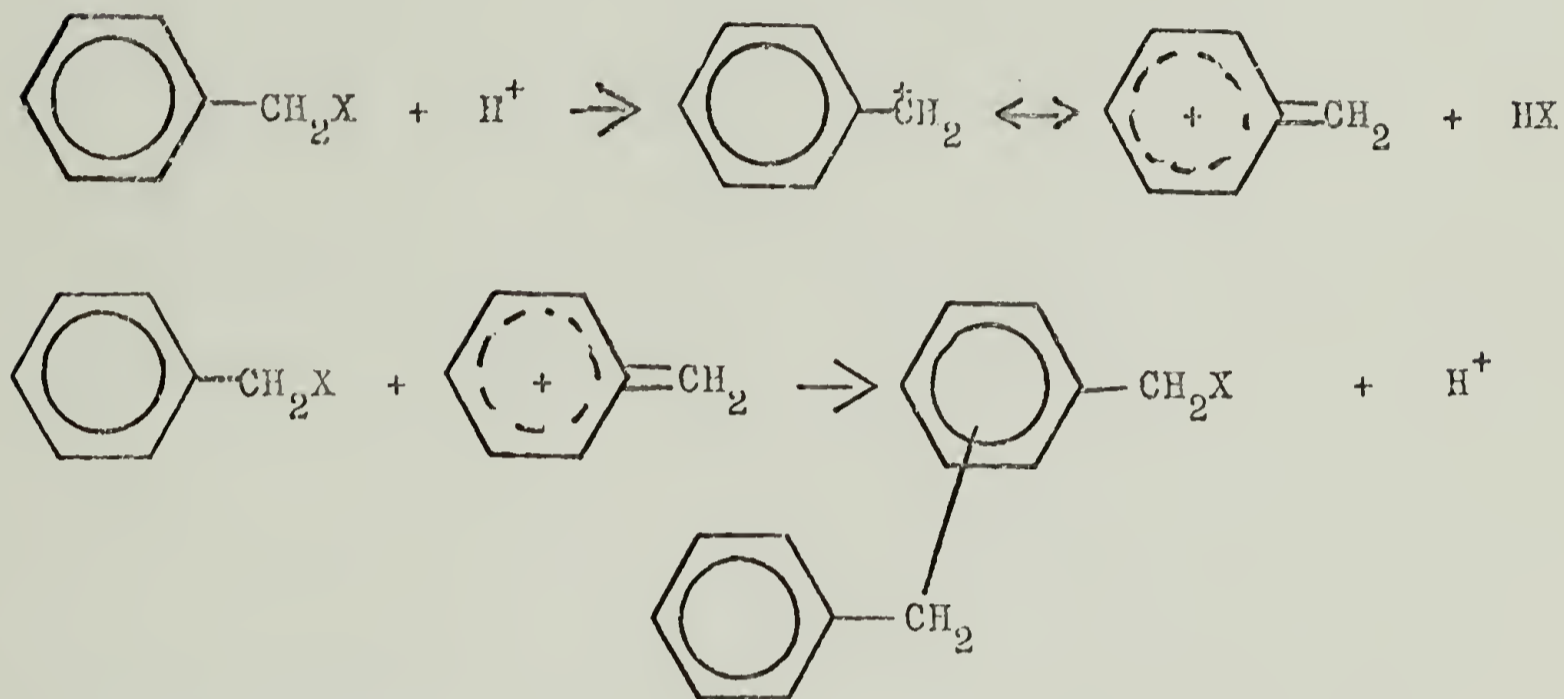


reaction.²² The mechanism of this reaction has two characteristics of importance in view of the probable structures of the polymer formed, namely:

- (a) polysubstitution on an aromatic ring is favored over monosubstitution because benzyl groups substituted on an aromatic ring activate the ring to further substitution; and

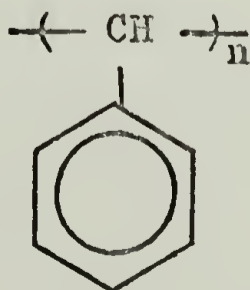
(b) the reaction is highly reversible, so that both intra- and intermolecular rearrangements occur readily.

Because of these characteristics, significant differences are often found in the product of Friedel-Crafts alkylation reactions for different reaction conditions and different reactant ratios.²³



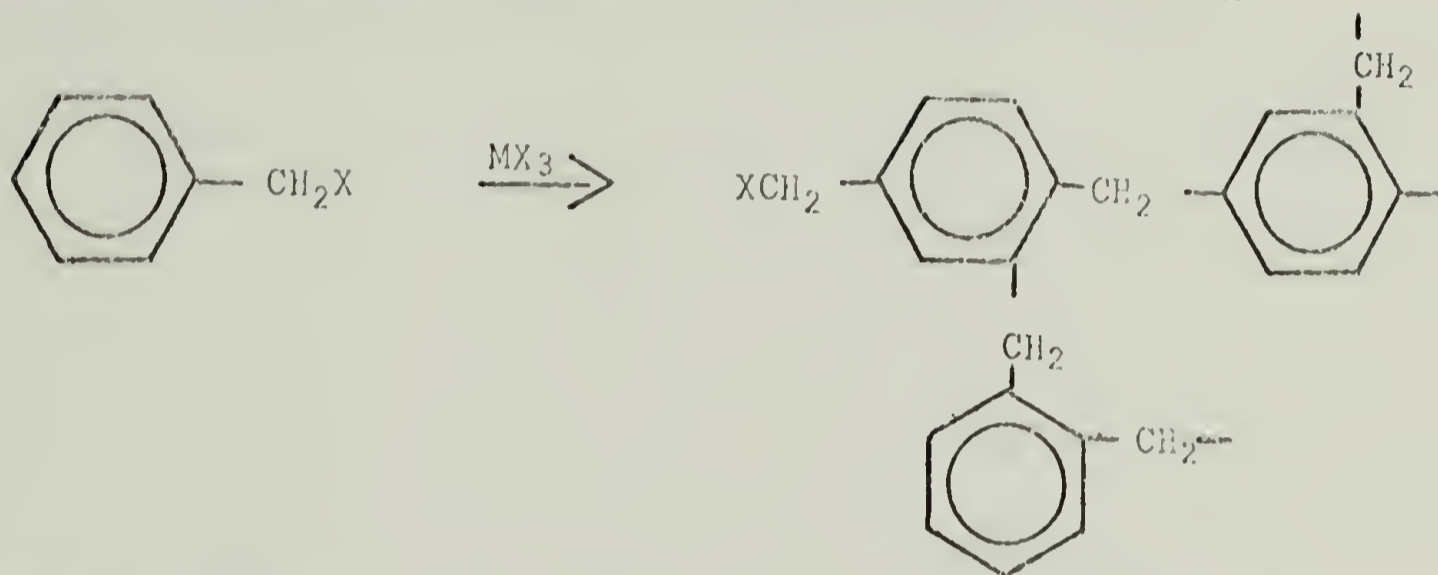
Polymer Structure

Jacobson⁷ assumed that coupling occurred mainly in the position para to the methylene groups, since the para isomer is usually obtained in larger amounts than the ortho or meta isomers when the Friedel-Crafts reaction is applied to toluene, diphenyl and related compounds. On the other hand, Henry²⁴ thought that in benzyl fluoride the loss of hydrofluoric acid occurs between two distinct molecules and results in the formation of ethylenic polymer having the pendant type of structure.



This structure is very doubtful, and ring alkylation is probably the only important reaction.

The oxidation study⁸ of the polymer obtained from benzyl alcohol and sulfuric acid suggested that a ratio of para to ortho linkage in this polymer was approximately 6:1. In contrast, Flory²⁵ assumed that the polymer obtained from the benzyl halides had the following structure with random branching but without net-work formation.

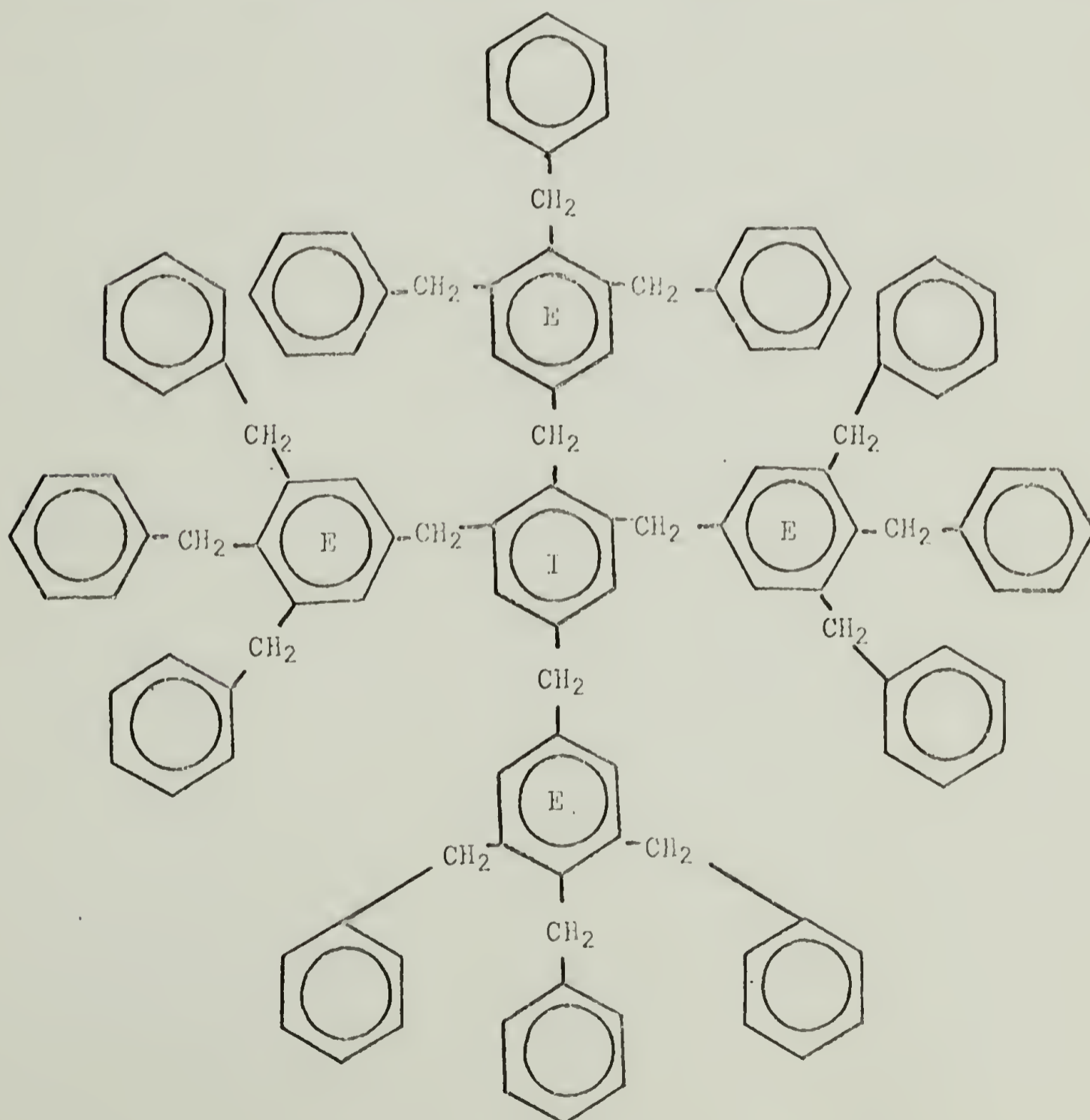


Hass et al.²⁶ were the first to carry out a detailed study on the polybenzyl structure. The infrared, x-ray, chemical and other evidence made them believe that these polymers contain a nucleus of almost completely substituted phenyl rings with a periphery of pendent benzyl groups. The structure is illustrated in Figure 1. Such a structure is also supported by many other workers in this field.

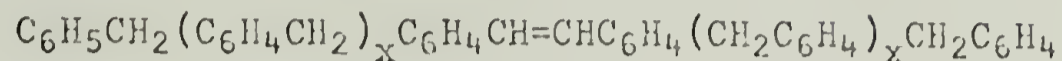
This structure is formed because of the general characteristics of the Friedel-Crafts reaction mentioned above; that is, if two molecules react to form a dimer, the dimer will be more reactive to electrophilic substitution than the monomer. The higher reactivity of the dimer can be explained by the presence of a methylene bridge which is more electronegative than the $-\text{CH}_2\text{X}$ substituent in the monomer. The dimer has also a higher statistical probability of reaction

because it contains seven ortho or para sites compared th three in the monomer. Further growth of the dimer results in the highly reactive polymer which is favored both electronically and statistically. As a result, polymer products are highly substituted and have many short branches.

Assuming that the internal aromatic ring (I) has a maximum number of substituents sterically possible (i.e., four) and if further substitution of the external aromatic ring (E) is limited to three, then the globular structure of the polymer may be represented as follows:²⁷



One question remains on this structure, and that pertains to the status of the last ArCH_2X group because the mechanism of termination of the polybenzyl is uncertain. One possible fate of this group is suggested in the structure:



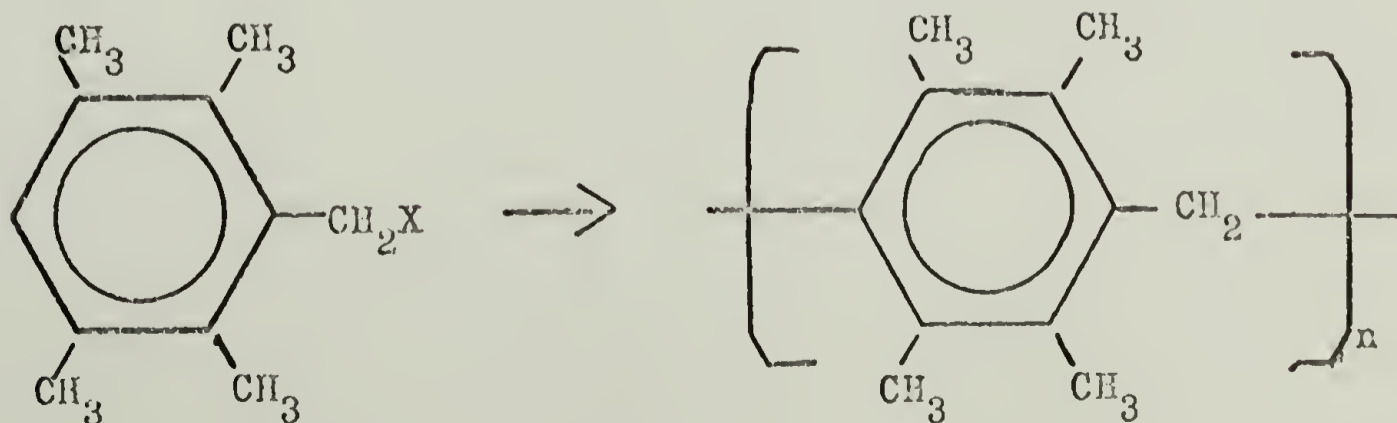
Alternatively, in case of polycondensation by benzyl chloride, it is believed that terminal chloride atoms may react with a side chain benzyl group to form a dihydroanthracene derivative as follows:¹³



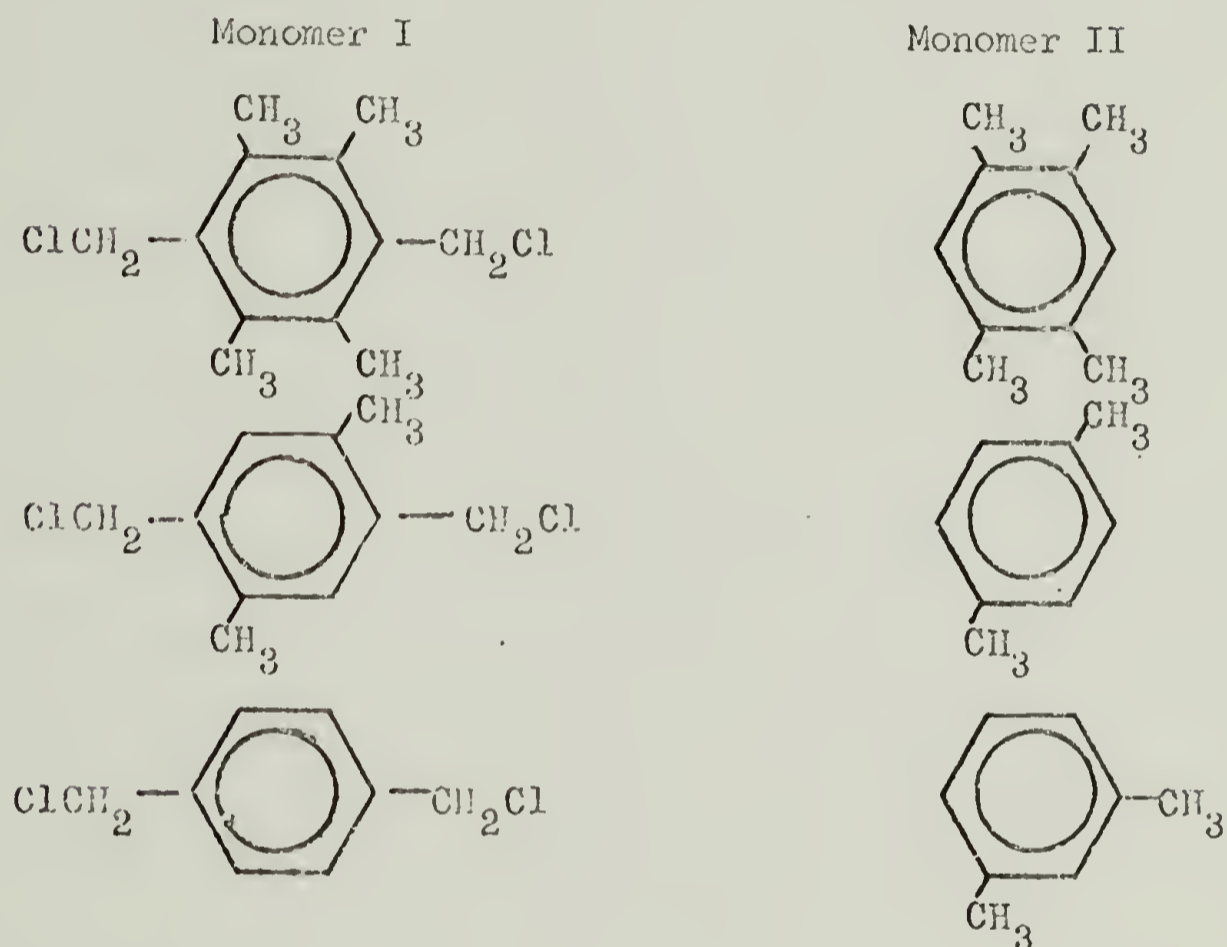
Unfortunately, such terminal groups are not detectable by infrared or chemical means probably because of their similarity to the repeating units.

Linear Polymers

If all except the position of the chloromethyl group and one other are blocked, then a highly crystalline linear polymer can be obtained.²⁴



A systematic study of the effect of this type of monomer structure on the polymer properties has been done by Overhults and Ketley.²⁸ The effect of branching on crystallinity, solubility, and molecular weight was carried out by copolymerizing bis(chloromethyl) aromatic compounds and an aromatic compound, Monomers I and II, respectively:



The results obtained by copolymerization of the above monomers may be summarized as follow:

- (a) When the number of methyl groups on monomer I was kept at a constant value 4, the polymers obtained were crystalline, insoluble in organic solvents and of low molecular weight.
- (b) When both monomers contained only two methyl group in para positions, the resulting product was crystalline insoluble and of low molecular weight.

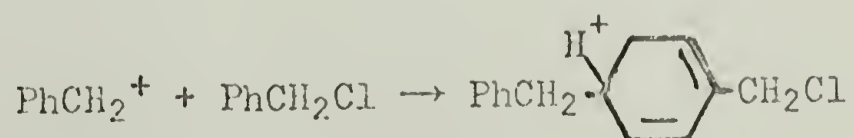
(c) Further reduction in the number of methyl groups on the aromatic ring resulted in amorphous product.

It may be concluded from the above results that crystallinity and linearity of the polymer can be increased by blocking the available site other than the para on the aromatic ring by other groups.

High melting crystalline, linear polybenzyls were obtained¹⁷ by the polymerization of benzyl chloride at low temperature (-75 to -134° C) in the presence of AlCl₃ catalyst. The NMR spectra of these polymers indicated a peak at $\delta = 7.05$ ppm (aromatic protons) and another at $\delta = 3.08$ ppm (methylene proton) in the ratio 2:1. The infrared spectrum had a strong peak at 805 cm⁻¹ which is attributed to 1-4 disubstituted aromatic nuclei. For the same type of reactions, amorphous polymers were isolated at higher temperature. This may be due to the increasing tendency of polysubstitution on aromatic ring with increasing temperature.

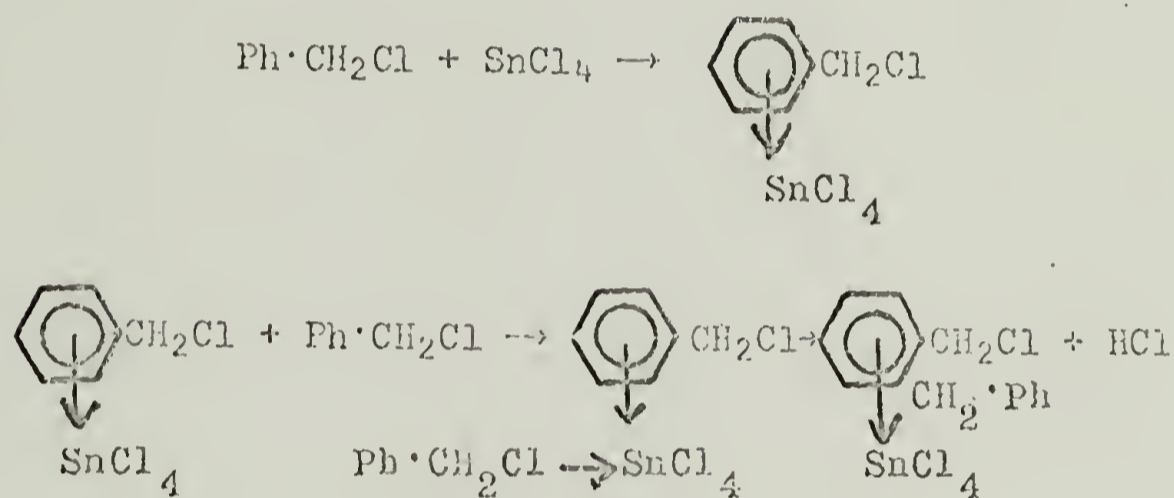
Polymerization Mechanism

The data obtained in the polymerization of benzyl chloride catalysed by stannic chloride¹³ showed unusual behaviour for a step-growth polycondensation, and the following proposed simple mechanism of formation of the benzyl cations remained ambiguous:





It was suggested in this study that the reaction might take place by the way of either benzyl cations or complexes of former with stannic chloride.



The complex between dimer and catalyst could then be further substituted.

After the formation of dimer, the benzylation is much faster.²⁶ The formation of dimer, in terms of the chain reaction, may be regarded as the initiation step.

The kinetic study of the above reaction revealed that the degree of polymerization increased rapidly in the early stages of the reaction and became constant at or above 30% conversion in the reaction. The degree of polymerization was unaffected either by temperature or concentration of catalyst at higher conversions. Therefore, behaviour of this reaction was considered to be different from polycondensation.

Formation of high molecular weight polymer in the early stages of the reaction indicates that the reaction proceeded by a chain-growth mechanism.

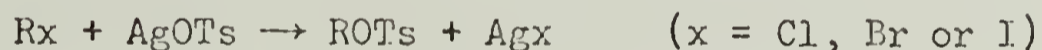
PREPARATION AND REACTIONS OF TOSYLATES

The most common method for the preparation of *p*-toluenesulphonate esters can be represented by the following equation:



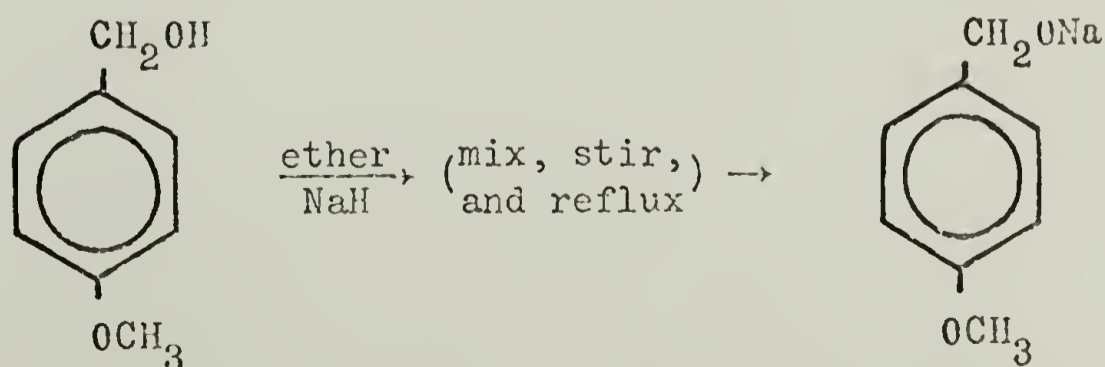
Although it has been applied successfully to a number of primary alcohols,²⁸ it is extremely difficult to prepare unstable esters of *p*-toluenesulfonic acid by this method.

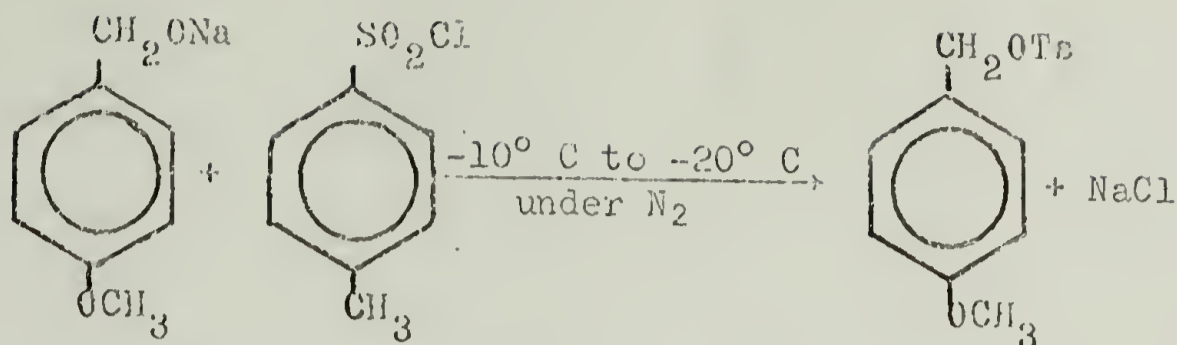
A second method used for preparation of the ester is the reaction of a silver salt of toluene sulfonic acid:



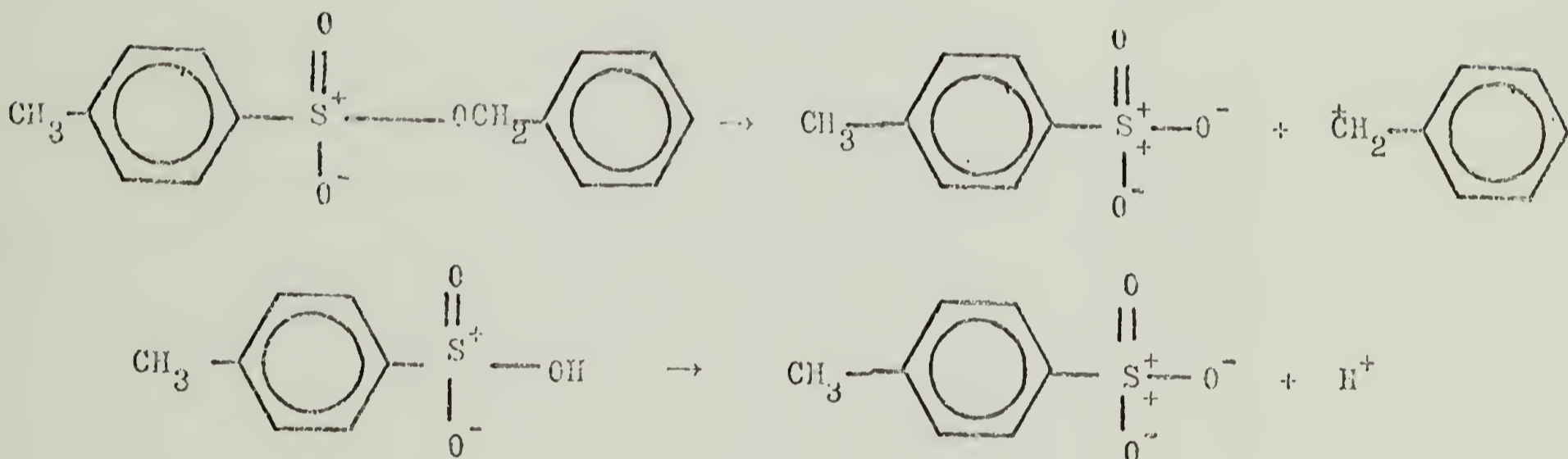
Acetonitrile is the best solvent for these reactions.

Unstable, substituted benzyl *p*-toluenesulphonates have been prepared² by carrying out the reaction below -20° C . *p*-Methoxybenzyl ester, which is least stable of all, was prepared by very carefully controlling the temperature of the reaction as summarized below:





The $-\text{SO}_2-$ group in tosylates is a powerful electron-withdrawing group which facilitates separation of proton or alkyl groups. Thus, tosylates are described as effective leaving groups in S_{N}^2 reactions.



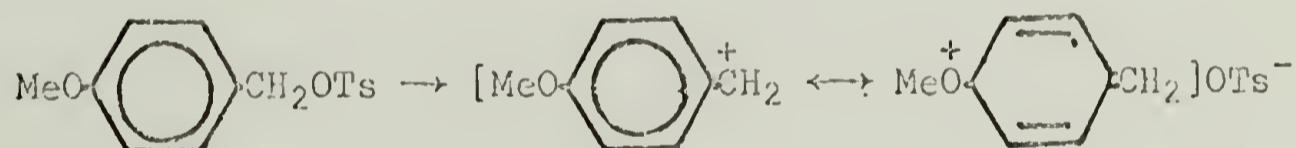
However, the sulfonic acid esters resemble alkyl halides and enter into similar reactions of displacement, elimination and hydrolysis.

Benzyl tosylates and its derivatives illustrate the high reactivity of tosylates by their tendency to undergo spontaneous transmission from crystalline solids into colored amorphous materials. The color depends upon the type of substituent group on the aromatic ring and will fade with time. Benzyl benzenesulfonate decomposes only over several days while benzyl tosylate with little impurities decomposes even at room temperature.

Gilman and Beaber³⁰ observed that when the benzyl tosylate crystals

were allowed to stand in a highly evacuated desiccator for one hour, they changed to a dark tarry mass which was almost completely soluble in water. Hoffman²⁹ reported that 1-phenylethyl *p*-toluenesulphonate turned brick red on decomposition, which was rapidly induced at room temperature. The colors of the amorphous materials derived from *p*- β -styryl-, *p*-methyl- and *p*-methoxybenzyl tosylates were blue, pink and deep red, respectively.² *p*-Methoxybenzyl tosylate decomposed rapidly even at -60° C. The change in color may be due either to the presence of an intermediate benzyl carbonium ion, or to the formation of a charge transfer complex.¹³

The order of stability of these tosylates appeared to be roughly consistent with the expected nucleophilic reactivity of the aromatic ring and also with the stability of derived benzyl carbonium ions

$$\text{ArCH}_2^+$$


In contrast, *m*-methoxybenzyl tosylate was described as relatively well-behaved compound.

The purification of these unstable esters is very difficult because of the spontaneous decomposition of their crystals. Esters with low melting points are hard to crystallize and need to be stored at a temperature well below their melting points. However, esters which are liquid can be purified by distillation under vacuum.

Little attempt has been made in the past to identify the amorphous

materials formed from these compounds on standing. Drahowzal and Kiamanu³¹ related the properties of this material with the polymer obtained from the condensation of benzyl chloride under the influence of catalysts such as powder silver or copper and stannic chloride. The empirical formula of this non-crystallizable material was $(C_7H_6)_x$.

SOLID-STATE POLYMERIZATION

Extensive study in the field of solid-state polymerization started only a few years ago. Unlike polymerization reactions in liquid phase which developed against the background of organic reactions, the polymerization in solid state had to be carried out with very little knowledge of reaction mechanism of molecular crystals.

Stereochemistry in solid-state organic reaction is effected by crystal lattice restraints, and the reaction is often influenced by the crystal structure of the monomer (topochemical reaction). It is unlikely that polymerization takes place in the interior of a perfect monomer crystal. One would assume instead that the reaction takes its start at defects or at the surface. This assumption is supported by the fact that the induction period can be reduced by powdering the monomer crystals.⁴¹ The collision between monomeric molecules is necessary to bring about effective reaction. However, in the crystal-line state the motion of the molecule is restricted, and as a result, there can be a reduction in reactivity.

A survey of compounds that undergo polymerization in the solid state supports the topochemical postulate that such a reaction is

possible only if the monomer crystal structure affords close contact between the reactive centers of neighbouring molecules.³² It was observed that dimerization in several systems occurs when reactive sites were no further apart than 4\AA . In the monomer crystals the reaction between reactive monomer A^X with its neighbouring B results in the formation of dimer AB^X , but at the same time, the covalent linkage between A and B increases the distance between B and its neighbouring C. If the distance between B and C is sufficient for reaction, a trimer is formed ABC^X . If the distance between the developing oligomers and neighbouring monomers are favourable, the reaction results in the formation of a polymer. In several cases, the mobility of the molecules to diffuse is hindered by side reactions or for some other chemical reasons, and as a result, dimer, trimer or oligomer are incapable of further growth. Such a compound is classified as incapable of solid state polymerization or yields only low molecular weight oligomers.

The important factors which determine the structure of a polymer formed as a result of a solid-state polymerization are temperature and nature of polymerization reaction. In the past, it was reported that not only the rate of polymerization changes with temperature, but also the degree of polymer orientation is affected. If polymerization temperatures are not sufficiently far below the melting point of the monomer crystals or polymers, the polymer will undergo a transition which may effect the final structure. The reaction can either take place by monomer diffusion which may form a polymer having a disordered

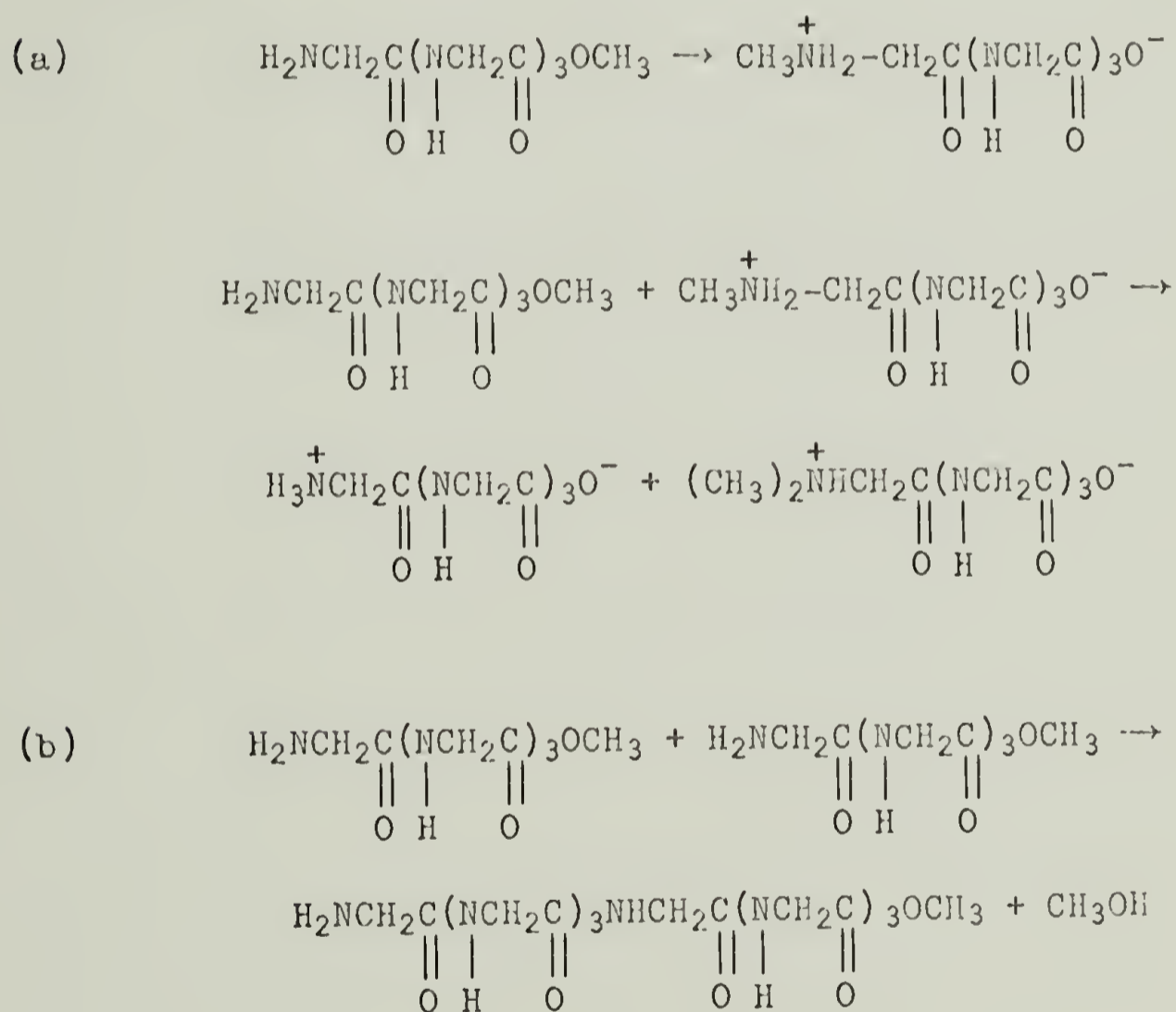
structure or by crystal lattice control which helps in the formation of linear or stereoregular polymers. It is believed that formation of a polymer having a disordered structure at one temperature does not eliminate the possibility of forming a polymer having a regular structure at another temperature.

The mechanism of solid-state polymerization is further complicated by the crystal structure. Some monomers may exhibit more than two crystalline phases which may effect the rate of propagation as well as polymer structure. Also, in the same phase, the ratio of diffusion-controlled polymerization may vary either with temperature or with degree of conversion.

Both radical and ionic solid-state polymerization reactions have been reported in the past. There are several questions still to be answered including: (1) Whether or not ionic end groups acting in the polymerization are the same as those in catalytic ionic polymerization, and (2) Whether polymer crystallites obtained in a solid state polymerization process exhibits the chain folding phenomena so characteristic of polymer crystals prepared in other ways?⁴⁰

Morawetz³³ has reviewed polycondensation reactions starting with the monomer in the solid state. Amidation is almost unique among step-growth polymerization; e.g., preparation of polypeptides from esters of α -amino acids, of nylon 66 from its salt, and of polyamides from ω -amino acids. Another type of step-growth polymerization reaction reported to occur in the solid state is aromatic nucleophilic substitution reaction used in the preparation of poly(phenylene sulfide).

When methyl esters of diglycylglycine and triglycylglycine are heated at a temperature 20° C below the melting point (at 80° C and 185° C respectively), they both yield polymeric products.³⁴ An unusual phenomena was observed when the triglycylglycine methyl ester was heated at 100° C. A slow transformation of the methyl group from the ester function to the nitrogen atom of the amine function took place resulting in a mixture of triglycylglycine, sarcosyl, diglycylglycine and N,N-dimethylglycyldiglycyl glycine. The reaction may be represented symbolically as follows:



In contrast to the above, when the solution of triglycylglycine methyl ester in *m*-cresol was heated at 100° C, polycondensation occurred and not to the products resulting from the migration of

methyl groups. Piperazine-2:5-dione was formed instead.⁴⁶ It is assumed that the unusual migration of the methyl group from the ester function to the amino end of oligopeptide can only take place under the constraint of the crystal lattice, where the geometry of the packing of the reagent molecules is in questions.

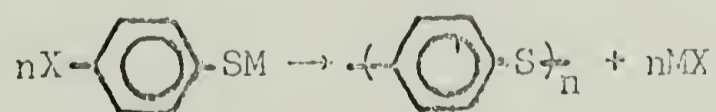
The kinetics of polyamidation in solid state of three aliphatic ω -amino acids,³⁵ namely aminoenantoic, aminopelargonic and aminoundeca-noic acid, have been studied. The reactions proceeded in solid phase 10° C below the melting point of the amino acids.

An interesting investigation was carried out with a series of amino acids of the type:



It was observed that the temperature interval, ΔT , below the melting point of the monomer in which the polycondensation could be observed and the apparent activation energy of the maximum rates in the solid state were both sensitive to n and m .¹

Another nucleophilic substitution reaction which is topochemical and involves a monomer in solid state is polymerization of alkali salts of p -halothiophenols:³⁶



A slow polymerization 10°C to 20°C below the melting point of the polymer resulted in a crystalline, linear, high molecular weight polymer. Whereas, reaction in the melt resulted in a highly branched and crosslinked polymer.

Very highly oriented nylon 6 was obtained by heating ω -aminocaporic acid in vacuum below the melting point of the monomer.³⁷

Some of the possible practical applications of the solid-state polymerization technique were summarized by Morawetz.³⁸ They are as follows:

- (a) Polymerization in the solid state may be feasible where an undesirable side reaction, such as cyclization or chain branching, renders the corresponding process unattractive if carried out in the liquid state.
- (b) If two monomers exist in an ordered state in the crystal structure, a regular alternating co-polymer may be obtained by solid-state polymerization.
- (c) The preparation of highly oriented polymer, without the need of mechanical drawing, is a unique feature of solid-state polymerization.

EXPERIMENTAL

Purification of p-toluenesulfonyl chloride

100 g. of p-toluenesulfonyl chloride (TsCl) was dissolved in 250 ml. of dry CHCl_3 , and the resulting solution was diluted with 1250 ml. of petroleum ether, and filtered by means of suction pump. The clear solution was collected in a 2000 ml. beaker, and the filtrate was concentrated to 500 ml. in a steam bath. Two tablespoons of Norit (carbon decolorizer) was added to the solution, and after stirring for 15 min., the resulting mixture was filtered by suction pump using a celite filter and allowed to stand overnight. The fine needle-like crystals formed by the next morning were transferred to a 500 ml. round-bottom flask and dried in vacuum at room temperature.

Melting point observed: $67^\circ \text{C} - 69^\circ \text{C}$.

Preparation of Tosylates

Method: A. 5 g. of benzyl alcohol (4.75 ml.) was dissolved in 63 ml. of redistilled collidine in a 250 ml. round-bottom flask, and the complete solution was maintained at $-10^\circ \text{C} \pm 1^\circ \text{C}$ by means of an ice-salt bath. 10 g. of recrystallized p-toluenesulfonyl chloride was rapidly added to the solution. The reaction mixture was allowed to stand at $-10 \pm 1^\circ \text{C}$ for 2 hrs. while the formation of white crystals was observed. The complete reaction mixture was dissolved to a clear solution in 125 ml. of precooled methylene chloride. The resulting solution was washed three times with 125 ml. of precooled 10% H_2SO_4

and two times with cold distilled water in a 500 ml. separatory funnel. The lower organic layer was removed and dried overnight over anhydrous sodium sulfate. After standing one hour, the colorless solution became slightly blue and on further standing turned pink, indicating that either polymerization of the tosylate was taking place or benzyl cations were being formed. These reactions could have been caused by impurities such as TsCl or remaining traces of 10% H₂SO₄ and water. The anhydrous sodium sulfate was filtered off and CH₂Cl₂ was evaporated under vacuum. The resulting residue was dissolved and reprecipitated in anhydrous ether yielding a brown mass with a softening point of 57° C - 59° C. This precipitate was completely soluble in benzene and methanol, indicating that only low molecular weight polymer was formed.

Method: B. 10 ml. of benzyl alcohol was dissolved in 100 ml. of anhydrous ether under N₂ in a 250 ml. three-neck flask at room temperature. The resulting solution was cooled in a dry ice-acetone bath and 61 ml. of n-butyllithium in heptane were slowly added to the solution by means of 10 ml. hypodermic syringe. After 30 minutes, TsCl dissolved in anhydrous ether was slowly added to the reaction vessel. The temperature of the reaction was slowly increased, and the dry ice-acetone bath was replaced by an ice-salt bath. After some time, the formation of a suspension of lithium chloride was observed. A paddle-type stirrer was found useful in stirring the reaction mixture, which was maintained at $-15 \pm 2^\circ$ C for 2 hrs. and then at room temperature for about an hour. The suspension was then filtered repeatedly with a minimum exposure to air. It was found helpful to use a medium grade

sintered glass funnel for the filtration. A clear ethereal solution was obtained in the filtering flask which on cooling to about -15° C, yielded a copious precipitate of fine white needles. The crystals were quickly filtered and recrystallized several times from anhydrous ether and dried under vacuum at 0° C.

Method: C. Preparation of (i) p-methylbenzyl tosylates, (ii) o/p-methylbenzyl tosylates, (iii) p-methoxybenzyl tosylates.

Method 2b was used for the preparation of the above monomers, although a few changes in the reaction conditions were made as indicated in Table 1. However, the use of this method for the preparation of p-methoxybenzyl tosylate was unsuccessful even though a number of reactions were run under different conditions and for different periods of time. In all cases the yield of p-methoxybenzyl tosylate was very low, and it was not possible to recrystallize the monomer from the anhydrous ether solution.

Polymerization Reactions

3a. Rate study at 50° C.

Seven glass tubes, each one-foot in length with an internal diameter of 8 mm., were sealed at one end, cleaned and dried in an oven at 200° C for 24 hrs. for use in the rate studies. These tubes were each filled with 1 g. of benzyl tosylate (prepared by Method 2b) by use of a glass rod 6 mm. in diameter. A reasonable packing among the crystals were obtained by applying a gentle pressure through the glass rod. All the tubes were numbered and suspended at the same time

inside the constant temperature bath maintained at $50 \pm 1^\circ \text{C}$ by means of copper wire. Throughout the experiment, precaution was taken that none of the tubes were disturbed or removed from the bath until needed. After 35 hrs., the formation of light brown mass within the packed crystals was observed. As time passed, the color became more and more intense. The rate of the polymerization reaction was followed by measuring the amount of polymer formed after different intervals of time as indicated in Table 2. The polymers were isolated by dissolving the reaction mixture in benzene and reprecipitating in methanol.

3b. Reaction at 55°C

A similar reaction to the one described above was carried out at $55^\circ \pm 1^\circ \text{C}$, which was just below the observed melting point of the sample of benzyl tosylate. After 2.5 hrs. the crystals inside the tube started melting to a colorless liquid, and after approximately another 30 min., the liquid was changed to brown mass with the final results shown in Table 3 for a reaction time of 13 hours.

Polymerization of Benzyl Tosylate at Various Temperatures by HBr Vapour

4a. The apparatus was connected as shown in Figure 2. A clean, dried U-tube was used as a reaction vessel. One neck of the U-tube was connected to a T-tube, which was connected to a nitrogen tank on one side and an HBr cylinder on the other (B.P. of HBr -56°C). Nitrogen was dried by passing through concentrated H_2SO_4 (96%).

Air from the apparatus was removed by allowing a constant flow of nitrogen for 30 minutes after which 1 g. of benzyl tosylate was introduced inside the U-tube while the flow of nitrogen through the apparatus was increased to prevent any air from entering. The system was then closed except at the outlet, and the nitrogen flow was reduced to the original rate. After 15 min., HBr gas was introduced into the U-tube by opening clip A, and at the same time, the nitrogen flow was closed by clip B (the rate of flow of gas through the U-tube was measured by counting the number of gas bubbles coming out per minute in the bubbler C).

Variations in reaction conditions were simply achieved by changing the temperature of the bath in which the U-tube was immersed throughout the experiment. The temperature of the bath was checked periodically and necessary adjustments were made and an estimate of the rate of HBr flowing out of the apparatus was obtained by holding a drop of NH_4OH on a glass rod in front of the outlet. As soon as white fumes were observed, the flow of HBr gas was reduced to one bubble per minute. This rate was kept constant.

The results of these experiments are collected in Table 4a.

The reactions were terminated by stopping the HBr flow, and the excess HBr gas in the apparatus was swept out with a flow of nitrogen gas. The complete removal of HBr gas from the reaction vessel was again determined by holding NH_4OH drop in front of outlet.

4b. The above apparatus was modified by replacing the U-tube with a three-neck 250 ml. flask. The side necks were used as inlet

and outlet for gases. An overhead paddle stirrer was inserted through the center neck, and 1 g. of monomer was suspended in 75 ml. of hexane at $-73^{\circ}\text{C} \pm 3^{\circ}\text{C}$. The procedure described in the above experiment, 4a, was repeated, although the reaction mixture was vigorously stirred during the experiment. The results of this experiment are listed in Table 4b,

Vacuum Polymerization

A 50 ml. round-bottom flask, previously cleaned and dried, was used as the reaction vessel. 1 g. of benzyl tosylate was placed in the flask, which was connected to a high vacuum line. The conditions for the reactions were varied by immersing the flask in a constant temperature bath. When the reaction was run at 50°C , the contents of the flask were converted into a brown mass, but when the same reaction was run at room temperature, there was only a slight change in the physical appearance of the crystals, which first exhibited a faint pink color that gradually disappeared within time. The reactions were terminated by the usual method, and the results are collected in Table 5.

Polymerization of (i) *p*-methylbenzyl tosylates (ii) *o/p*-methylbenzyl tosylates and (iii) *p*-methoxybenzyl tosylates

6a. Para and ortho-para mixtures of methylbenzyl tosylate readily polymerized in vacuum within 2 to 3 hrs. forming a pink and pink-brown mass, respectively. The product was worked up as usual, and the polymers thus obtained were characterized with the results in Table 6.

6b. When crude *p*-methoxybenzyl tosylate was exposed to sunlight for 36 hrs., it turned pink. The pink mass was then dissolved in benzene and reprecipitated in methanol. The infrared spectrum of the methanol insoluble mass was different from that of polybenzyl.

Termination of Reactions, Precipitation and Purification of the Polymer

All the reactions were terminated by introducing a few drops of methanol into the reaction vessel.

The total reaction mixture was first dissolved in a minimum amount of benzene (10 to 15 ml.) and stirred for 30 minutes until all of the brown mass was dissolved. The benzene solution was then added dropwise to 50 to 60 ml. of methanol in a 200 ml. beaker and vigorously stirred by means of a magnetic stirrer. After complete addition of benzene solution to methanol, the contents of the beaker were further stirred for 30 minutes. In most of the cases, the polymer precipitated out in methanol as a solid, but in some cases, it was found to be a heavy oil. In the former case the polymer was separated by simple filtration, while in the latter case separatory funnel was used.

In all the cases the polymer was purified by redissolving in benzene and reprecipitating in methanol as described above. The last traces of solvents from the polymer were removed by drying the polymer under high vacuum at room temperature for 24 hrs. In all cases the final state of the polymer obtained was solid unless stated otherwise.

Some Preliminary Observations on Solution Polymerization

8a. 4 ml. of concentrated H_2SO_4 (96%) in a small conical flask were cooled down to -10°C in an ice-salt bath and slowly, crystal by crystal, benzyl tosylate was added to the cold acid. As soon as the crystals came in contact with the acid surface, they at once turned pink but remained insoluble. After introducing about 0.25 g. of crystals, the reaction mixture was allowed to stand for half an hour, and the contents of the flask were then slowly poured onto ice-cubes in a 100 ml. beaker. After a few hours of reaction, a white powder accumulated at the bottom of the beaker, and the contents of the beaker were washed several times with cold distilled water, filtered and dried. The white amorphous powder thus obtained was dissolved in benzene and reprecipitated in methanol.

8b. About 0.5 gm. of benzyl tosylate was dissolved in 10 ml. of CH_2Cl_2 in a small round-bottom flask, and the resulting solution was cooled down to $-15 \pm 2^\circ \text{C}$ in an ice-salt bath. 1 ml. of concentrated H_2SO_4 , which was previously cooled to -10°C , was added dropwise to the solution; at the same time, the contents of the flask were stirred with a glass rod. On addition of H_2SO_4 , the solution first turned orange in color, and after a few minutes, it became pink. The contents of the flask were then poured onto ice-cubes in a beaker. The white powder was separated and treated as described in experiment 8a.

The results of experiments 8a and 8b are collected in Table 7.

In both the above cases, the infrared spectra obtained for the methanol-insoluble part was almost identical to that obtained from

previous experiments.

Polymer Characterizations

All melting points of tosylate monomers and softening points of polymers were measured on a Fisher-Johns melting point apparatus.

A double beam Perkin Elmer 257 infrared spectrophotometer was used to obtain IR spectra of the polymers prepared by various methods. Most of the infrared spectra were obtained on KBr pellets, but where appropriate an NaCl cell was used. Number average molecular weights were obtained with a vapour phase osmometer on the Hitachi Perkin-Elmer Model 115 molecular weight apparatus using 0.09 to 0.10 g. of the polymer sample dissolved in 25 ml. of benzene at 30° C.

Perkin-Elmer Model DSC-1B Differential Scanning Calorimeter was used for measuring the melting point of benzyl tosylate crystals and for determining the induction period of the polymerization at various temperatures. The results are collected in Table 8 and Figure 3.

Microscopic Study of Benzyl Tosylate Crystals

Large crystals were grown from the dilute solution of benzyl tosylate in anhydrous ether by cooling the solution slowly to -10° C. These crystals were dried under vacuum at 0° C. A single large crystal was mounted on the stage of the polarizing microscope, and a 35 mm. camera loaded with film was adjusted within the focus of the crystal image as viewed from the eyepiece. A number of photographs relating the morphological change in the crystal were taken at a magnification of 200X at room temperature at intervals as shown in Table 9.

RESULTS AND DISCUSSION

Tosylate Monomers

It was found that the preparation of pure benzyl or substituted benzyl tosylate monomers by method A was very difficult, and no stable products were obtained. Attempts to prepare p-methylbenzyl tosylate by both methods A and B were unsuccessful. The colored products obtained in these cases were soluble in methanol, which indicates that only low molecular weight oligomers were formed. In contrast, the stable crystals of benzyl tosylate prepared by method B readily polymerized in the presence of protonic acids such as hydrogen bromide and sulphuric acid. It appears that traces of impurities such as water and sulphuric acid in the final product obtained by method A catalyzed the decomposition of the tosylates into colored products.

The brown mass obtained in the case of benzyl tosylate (Method A) was soluble in methanol even after it was heated at 50° C for several hours. The formation of the polymer took place at 55° C when the same was heated for six hours. This observation suggests the impurities shorten the induction period for polymerization but cause a decrease in the molecular weight of the polymers obtained.

The instability of substituted benzyl tosylate monomers varies with the nature of group substituted on the ring. Benzyl tosylate was found to be more stable than the methylbenzyl tosylates, which readily polymerized even at room temperature. m-Methylbenzyl tosylate was more stable than either the para or ortho isomers. p-Methoxybenzyl tosylate

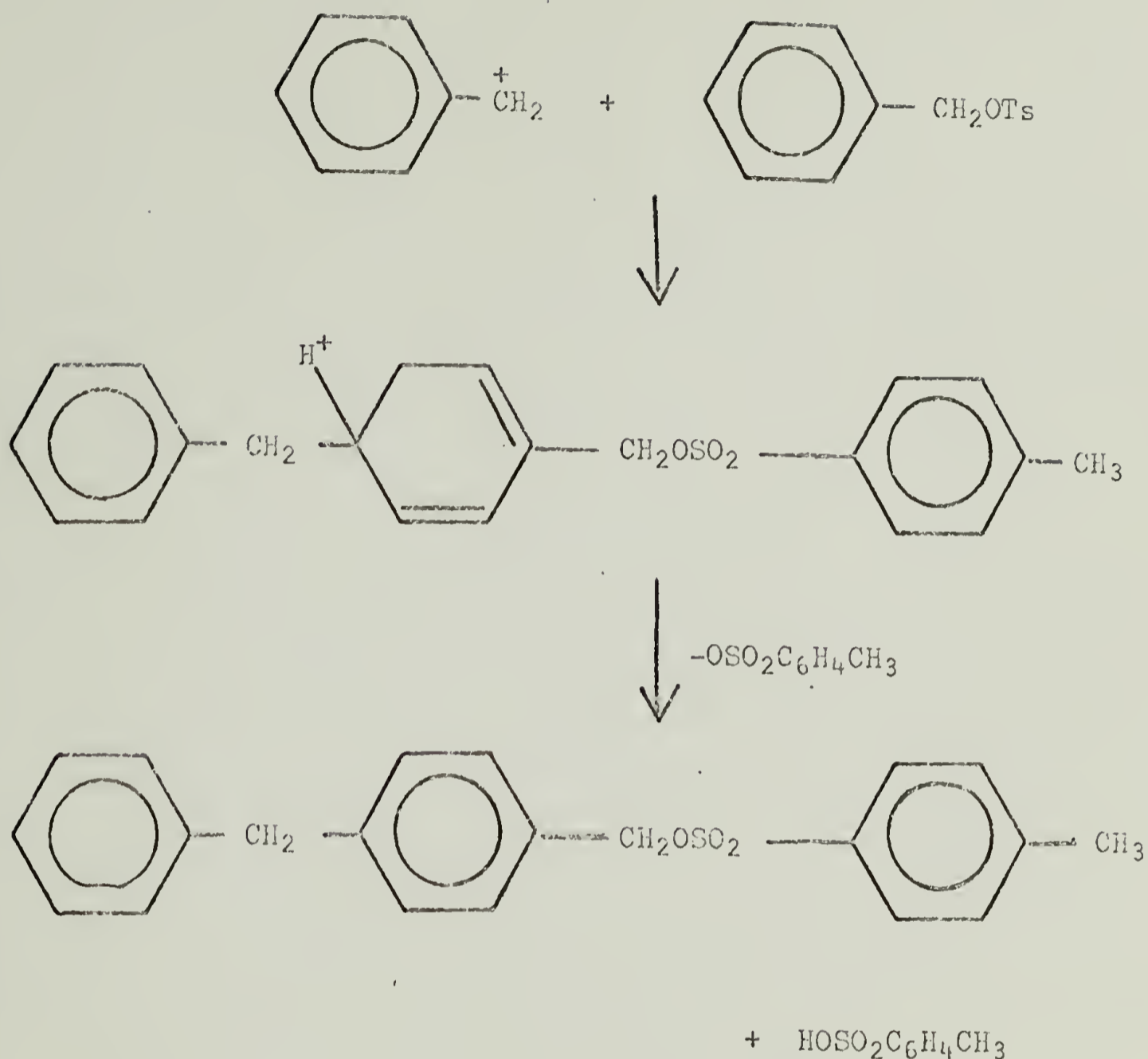
was unstable even at -70°C . The preparation of mesylates was extremely difficult as they were found to be unstable even at very low temperature.

The various colors observed during the polymerization reactions of the different monomers are summarized in Table 10. It was found that, for the same monomer, the color varied with reaction conditions (Table 11). When a solution of benzyl tosylate in dichloromethane was allowed to stand at room temperature, it remained unchanged for several hours. On addition of a water drop, it turned orange after a few hours and deep red on further standing. The same phenomenon was observed when concentrated sulphuric acid was added dropwise into the solution at -10°C .

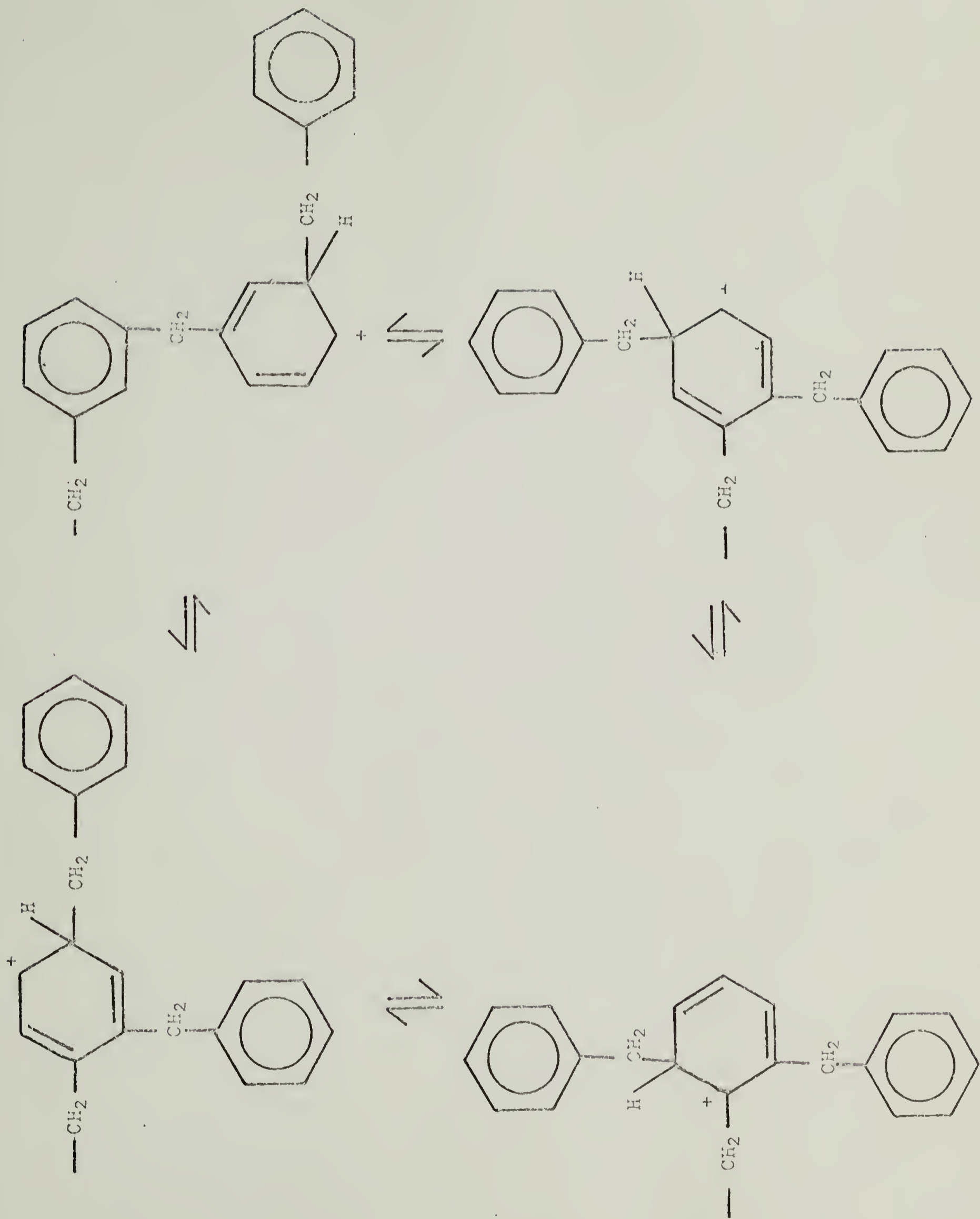
Benzyl tosylate crystals, on addition of acid at -15°C , turned reddish in color. During the solid-state polymerization of benzyl tosylate at 50°C , the crystals turned light pink in the initial stage of the reaction; and as time passed, the color became more intense and finally dark brown. These changes in the color may be due to the formation of charge transfer complexes between the polymer and the toluenesulfonic acid by-product.

Mechanism of the Reaction

The results obtained from the molecular weight-reaction time studies and from DSC suggest that the mechanism is not of the normal polycondensation type. A theoretical curve for a polycondensation mechanism was calculated in accordance with the equation $\bar{DP} = \frac{1}{1 - \alpha(f - 1)}$,

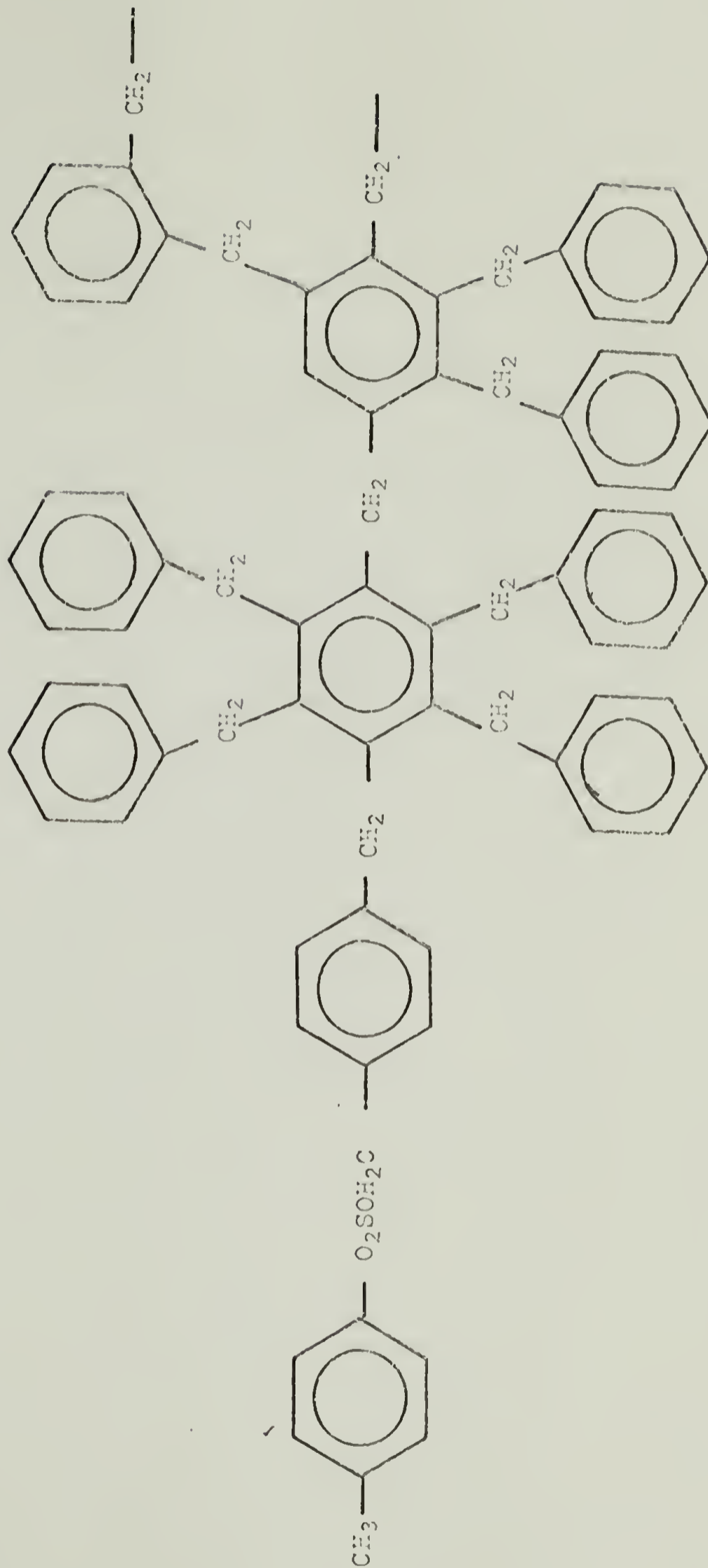
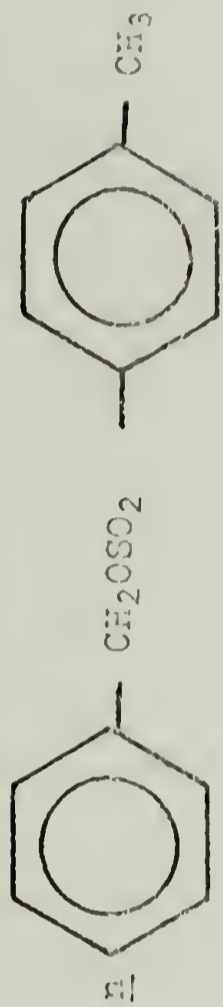


As discussed before, the dimer is expected to be more reactive than the monomer, so the polymer is probably formed by polysubstitution on the dimer, trimer, etc. The by-product p-toluenesulfonic acid forms crystals and separates from the polymer or undergoes sublimation. The high reactivity of the oligomers and the tendency of the reaction to undergo intra- and intermolecular rearrangements causes further complications in predicting the final structure of the polymer.



It is difficult to explain the chain-growth mechanism of the polycondensation reaction by the above scheme. Hass et al. have suggested that once a dimer is formed subsequent benzylation is very rapid. In terms of chain reaction, the time required for formation of the dimer may be regarded as the initial step, and rapid benzylation of the dimer, trimer, etc. corresponds to the propagation step.

The termination step is not known or it may not exist. The amorphous nature of the polymer and IR results suggest that the polymer is highly branched as follows:



Rate and Molecular Weight Study

The variation in the molecular weight with reaction time was studied. The polymerization reaction was carried out at 6° C below the melting point of benzyl tosylate, and the molecular weight and yield of the polymer obtained was plotted against the reaction time as shown in Figure 5.

In the early stages of the reaction (i.e., after approximately two hours), methanol-insoluble polymer was not formed, but within a short time yield and molecular weight both increased rapidly. This period was followed by a long period during which a negligible increase in the yield was found, but an unusual decrease in molecular weight took place. In the final stages of the reaction, there was a gradual increase in the yield during which molecular weight was built up.

Thus, the reaction-molecular weight pattern can be characterized into four distinct stages. The induction period, followed by a short period when yield and molecular weight both increase rapidly, a long period during which yield remains constant but molecular weight decreases, and finally the yield and molecular weight increase gradually.

In the initial stage, the polymer phase in the solid state apparently has to be nucleated. Formation of such a nucleus was observed with a polarizing microscope [Photograph No. 2]. On the basis of data in Table 8, it was observed that the rate of nucleation was temperature dependent, and the higher the temperature, the shorter was the induction period. The DSC experiments revealed that induction

period at 50° C was shorter than indicated by the rate studies, possibly because of better heat transfer in the former.

In the past, it has been reported that if monomer crystals used in a solid-state polymerization were powdered, there was a decrease in induction period due to the increase in the surface area. The rate of nucleation has also been found to be highly sensitive to the crystal size. It was observed here that a large crystal grown from the dilute solution by slow cooling at -10° C polymerized rapidly at room temperature, with a time for nucleation, as observed under polarizing microscope of ≈ 7 minutes. In contrast, small crystals grown from the solution by rapid cooling to -70° C took 20 to 30 hours to polymerize under the same conditions. It is probable that defects in the crystal play an important part in this reaction, and the larger crystals may have a larger number of defects which can provide a greater number of nucleation sites compared to that of smaller crystals.

Once the polymer phase was nucleated, the growth of polymer chain appeared to proceed rapidly up to a certain degree of polymerization. This region apparently corresponded to the primary period of the polymerization reaction, as indicated in Fig. 5, during which a true solid state polymerization may have taken place, and lattice control of the reaction may have played an important part. This reaction may lead to the formation of a unique polymer which may have a different structure compared to the structure obtained finally.

The secondary period of the polymerization reaction may be associated with rearrangement of the polymer structure. The reaction was

carried out only 10° C below the melting point of the crystals, and the exothermic heat generated during the primary period may have been sufficient to convert the reaction mixture to a melt. As a result, this reaction may generate some of the equilibrium polymer structure. The DSC results of Figure 3 also may indicate the existence of such an equilibrium in the melt during which neither exothermic nor endothermic behaviour is observed. Alternately, a stage may be reached when most of the crystal lattice was destroyed; thus, lattice control over the reaction was lost. As a result, a reversible reaction may have occurred causing rearrangement of the polymer structure to form the final highly branched structure. Further polymerization, then, could have taken place by random diffusion of monomer to growing polymer chain.

In the final period the reaction proceeded toward completion during which molecular weight gradually increased, and a quantitative yield of methanol-insoluble polymer was obtained.

Solid-State vs. Melt Polymerization

A polymerization reaction was carried out at 55° C. It was observed that after one hour, the crystals melted, and finally, after two hours formation of a brown product had taken place. Therefore, it appears that most of the reaction took place in the melt rather than in the solid state. Formation of the solid mass resulted from the fact that the softening point of the polymer was found to be 65° C to 70° C. The nature of the yield and molecular weight obtained when

plotted against the reaction time both indicate that, in the secondary period, the molecular weight obtained in the solid-state polymerization is essentially the same as that for a melt polymerization after sufficiently long reaction time. For shorter times, the DSC investigations indicate that at 60° C, which is slightly above the melting point of the monomer, no reaction took place, indicating that a true solid-state reaction occurred in this system.

Mechanism of Solid-State Polymerization

In all polymerization reactions, the final polymers isolated were amorphous and infrared spectroscopy results indicated that all polymers formed were highly branched. Therefore, random diffusion of the monomer within the crystal may have taken place during the solid state polymerization. One of the possibilities, which has been discussed above for rate-molecular weight study at 50° C, is that the reaction may have actually taken place in the melt because the formation of an intermediate mixture of polymer and unreacted monomer crystals could depress the actual melting point of the monomer.

On the other hand, polymerization reactions were satisfactorily carried out at room temperature under vacuum and below room temperature in the presence of hydrogen bromide gas, and the possibility of a melt reaction occurring may be ruled out under these conditions. Infrared spectroscopy suggested that the polymer formed at the lower temperatures may have had a somewhat different structure. This difference may have been due to the difference in activation energies for

ortho, meta and para substitution on the aromatic ring. However, the formation of branched structures even at very low temperature again suggests that the monomers may be transported to the reactive site within the crystal through the vapour phase (Fig. 6).

Structure of the Polymer

The infrared spectra of polymers isolated at various temperatures were reproducible. The spectra were similar to those of the polybenzyl polymers obtained in homogeneous reactions by other workers, who have suggested highly branched structures for these products (Figure 1).

Infrared spectra were obtained for polymers isolated at various times during the rate-molecular weight study at 50° C. For all polymers, the spectra were very similar to those of the monomer used and showed essentially the same features; that is, two strong bands at 697 and 730 cm^{-1} . Variations in the intensities were observed for different polymers, but the frequencies of the band never altered.

The polymers prepared by the action of concentrated sulphuric acid either on crystals or on the solution of benzyl tosylate in dichloromethane at -10° C, and the polymers prepared under vacuum at various temperatures, had the same spectra, which again suggests branch structures for all of these products.

An attempt was made to obtain a series of spectra relating temperature as well as environment effects to the structure of the polymers. Infrared spectra were obtained on polymers which were prepared from

benzyl tosylate monomer crystals exposed to hydrogen bromide gas as a catalyst at various temperatures. The spectrum obtained for the polymer at 50° C had most features comparable to those obtained from rate study. The spectra of the polymers obtained at lower temperature were slightly different from above. The variation in the frequencies of the bands are summarized in Table 12. The bands other than at 735 and 700 cm^{-1} in the region of 700 to 820 cm^{-1} indicate the presence of a different type of aromatic substitution and presumably the different structure for these polymers. From the infrared spectra, it appears that the band in the region of 810 to 845 cm^{-1} , attributable to para disubstitution, became stronger as the temperature decreased.

The infrared spectroscopy results for all other polymers prepared by various methods (other than low temperature reactions) are similar to those for polymers prepared in solution from other benzyl derivatives by Friedel-Crafts catalysts. The strong bands observed at 697 and 730 cm^{-1} match those obtained by Valentine and Winter (except for inflection at 743 cm^{-1}). Beside these bands, Hass et al. has reported a third band at 675 cm^{-1} which can be attributed to a rocking vibration of the methylene group. The reason for the absence of this band in various spectra is not clear.

The existence of a band between 850 to 810 cm^{-1} for the polymers prepared at low temperature indicates that these polymers may have had somewhat different structures than the normal product. On the basis of spectra obtained for polystyrene and poly-p-xylene, Hass et al. has suggested the monosubstituted benzene derivative generally

shows two strong bands in the region of 675 and 775 cm^{-1} , whereas para disubstituted derivatives show one strong band in the range of 810 to 860 cm^{-1} . Therefore, the absorption in the region of 810 to 845 cm^{-1} is characteristic of para-disubstitution which may suggest that polymers have some degree of linear structure which increased with decreasing temperature.

Molecular Weights and Softening Points

The polymerization reactions were sensitive to environments. To study different effects, reactions were carried out in vacuum, under atmospheric conditions, and in the presence of hydrogen bromide gas. Benzyl tosylates are very stable at 0° C and can be polymerized only in the presence of a catalyst. The low temperature polymerizations were carried out in the presence of acid vapors (HBr). The polymers isolated at higher temperatures had the same molecular structure but were formed in different yields and had different molecular weights and softening points. The molecular weight obtained was temperature dependent.

Table 13 summarizes the effect of various environments on polymer prepared at 50° C. The reaction was very fast in the presence of HBr gas. Slightly higher yields were obtained at atmospheric pressure than under vacuum although molecular weights of the polymers obtained in the vacuum and to some extent in the presence of HBr gas were higher compared to the atmospheric system but softening points were lower.

Little variation is observed in physical properties of the polymers isolated at 50° C and 55° C. The results in Tables 3 and

5 suggest that the yield and molecular weight were higher for the polymers prepared at room temperature under vacuum than at 50° C.

Table 4 indicates the dependency of yield and of molecular weight on the reaction temperature. Both parameters decreased with decreasing temperature. Softening points for the polymer prepared in the presence of HBr were very low.

Polymerization of Substituted Benzyl Tosylate

Crystals of p-methylbenzyl tosylate were successfully prepared. These crystals were very stable at 0° C, but decomposed at room temperature after a few hours. The polymerization reaction of this monomer under vacuum was very rapid.

An attempt was made to copolymerize an ortho/para crystalline mixture of methylbenzyl tosylate. The monomers were prepared as described in the Experimental section. When the polymerization reaction was carried out at room temperature in vacuum, pink and brown spots developed in the crystal and a solid amorphous product rapidly formed. The isolated polymer had two softening points at 55° C - 60° C and at 95° C - 100° C which indicates that the products were probably mixtures of two homopolymers.

The infrared spectra of polymers obtained from the above monomers again suggests a highly branched structure. The nature of the molecular weight and yield obtained are summarized in Table 6.

Polymerization within Single Crystal

Photographs which record formation of amorphous region within the crystal during polymerization were taken at different time periods (Table 9). At room temperature and under atmospheric conditions, the formation of a brown spot was observed between five and seven minutes. The dimensions of the spot increased with time. The Photographs number 1 to 6 indicate growth phenomena of this amorphous region as viewed under a polarizing microscope.

As the amorphous zone advanced, changes in the birefringence of the monomer zone are also seen in the color slides of these photographs. These changes in birefringence may be due to the change in stresses in the crystal. After 2.5 hours the crystal had turned completely brown indicating that all of the monomer within the crystal had polymerized. The brown color subsequently faded with time and ultimately the mass transmitted some light presumably due to the formation of para-toluenesulfonic acid as a crystalline side product.

Tracings (Figure 7a) of the circumference of the actual amorphous region at various time periods indicates that growth is more preferential in one direction within the crystal. For analysis of the rate of polymerization, only two dimensional growth was considered, and the most probable point from which the growth originated was selected as the origin (0.0 coordinate). This point is very clearly defined in photograph No. 2. The surface area of the crystal was then divided into quarters. In Figure 7 it can be seen that there is a reasonably close resemblance between the symmetric drawing of both the upper two

quarters in the early stages, and the lower two quarters throughout the sequence of photographs of an ellipse for the actual growth of the amorphous polymer region within the crystal. Thus, the lower two quarters indicate that the growth of the amorphous region may be described as elliptical when not restricted by crystal edges. Therefore, the bottom two quarters were selected for analysis based upon homogeneous elliptical growth (Figure 7b).

The length of the semi-minor and semi-major axes were measured for various time periods which are tabulated in Table 9 as Y and X respectively. With these data areas of the ellipses were then calculated. A plot (Figure 8) of area vs time indicates that the growth rate is exponential which can be represented by the equation below:

$$A = Ct^n \quad (1)$$

A = Modified area of amorphous region (sq. mm.)

t = Modified time in minutes, where $t = T - \tau$; $\tau = 5$ minutes

C = Intercept on Y axis = 0.327

n = Slope of line = 1.73

If it is assumed that the rate of polymerization, R_p , is proportional to the change in area of amorphous region with respect to time:

$$R_p \propto dA/dt \quad (2)$$

then from Equation (1):

$$dA/dt = Cnt^{n-1} \quad (3)$$

Finally, the following assumptions were made for the determination of the percent conversion of the monomer:

1. Pure crystal = 100% Monomer or 0% Polymer
2. Polymerized crystal = 0% Monomer or 100% Polymer
3. Decrease in % crystallinity = % conversion

The region of the pure crystal, in which unrestricted polymer growth was considered to occur from a single nucleus was taken as an ellipse of area 70.25 mm.^2 ($X = 5.8 \text{ mm.}$ and $Y = 4 \text{ mm.}$). The total time required for this area to polymerize after nucleation was 72 minutes. A calibration curve of area vs % crystallinity was thus generated. The plot (Figure 9) was then used for the determination of % crystallinity and, hence, % conversion at various intervals. Theoretical values of degree of polymerization were calculated from this data for two, step-growth relationships ($DP = \frac{1}{1-p}$ and $DP = \frac{1}{1-3p}$) and plotted against conversion (Figure 10). Finally, % conversion was plotted against time (Figure 11). The data for the preparation of these plots are represented in Table 9.

The theoretical curves of Figures 10 and 11 are characteristic of step-growth mechanisms for linear and two-dimensional growth and should be compared with the observed results obtained from the rate-molecular weight study. It can be seen that the calculated curves differ markedly from the observed growth indicating that the actual polymerization mechanism was not step-growth of either type but may have been a type of chain-growth.

CONCLUSION

The method for the preparation of benzyl and substituted benzyl tosylate was modified. Tosylates prepared by Method 2b were found to be reasonably stable at room temperature except *p*-methoxybenzyl tosylate, which was unstable even at -78° C. The stability of various tosylates may be summarized in the following order:

m-Methylbenzyl \geq Benzyl $>$ *p*- or *o*-Methylbenzyl \gg *p*-Methoxybenzyl

Even the most stable benzyl tosylate crystals, however, readily undergo a solid-state polymerization reaction at 50° C under high vacuum and in the presence of acidic vapour at very low temperatures into amorphous, colored products. The stability of this monomer was found to vary considerably with crystal size, and perfection of crystal structure probably plays an important part in the determination of both the induction period and the rate of polymerization.

Even at low temperature, unlike benzyl tosylate, the preparation of benzyl mesylate was extremely difficult at -10° C. The final product, on standing for two days, decomposed into two separate layers. The upper pink layer was identified as polybenzyl and the lower dark brown layer as methanesulfonic acid, the expected by-product.

The colors of the crystals in each of the polymerization reactions were different for the different monomers and also varied for the same monomer under different reaction conditions. These colors may have been due to the formation of charge transfer complexes between the

polymer and the by-product rather than formation of the intermediate benzyl cations.

The polymers obtained from various monomers were amorphous, low molecular weight and highly branched as shown in Figure 1. That is, the solid-state polymerization of benzyl tosylate resulted in the formation of the same type of polybenzyl as is normally formed in solution, and the highly branched structure of the final product indicated that it was not possible to prevent polysubstitution on the aromatic ring by crystal lattice restraints. Therefore, the mechanism of the solid-state polymerization reaction may involve random diffusion process in which monomers are transported to the reactive site through the vapour phase. Nevertheless, DSC studies revealed that the polymerization reaction was much more favoured in solid state than in the melt, and no polymerization at all occurred in solution at equivalent temperature. The molecular weights of these polymers were somewhat higher, but the softening points were lower than those reported in the literature for polymers prepared by acid-catalyzed Friedel-Crafts reactions of benzyl halides in solution.

The mechanism of the solid-state polymerization reaction appears to be further complicated by unusual inter- and intra-molecular rearrangements. The decrease in molecular weight of the benzyl tosylate polymer obtained during secondary period is attributed to these rearrangement reactions.

The rate-molecular weight results indicate the occurrence of four distinct stages in the solid-state polymerization reaction; namely,

the induction period, the primary period, the secondary period and the final period. The exothermic behaviour of the polymerization reaction observed in the DSC studies is in agreement with conclusions of rate-molecular weight studies. The secondary period obtained in the DSC studies indicates the presence of an equilibrium stage during the polymerization reaction which may be attributed to the rearrangement reactions in the polymer.

The plot of reaction time vs molecular weight of the polymer obtained at various stages is comparable to the plot obtained by Valentine and Winter for the solution polymerization of benzyl chloride. The molecular weight of the polymer obtained from benzyl tosylate in the solid state in the initial stages of the reaction is higher than that obtained from polycondensation of benzyl halides in solution. The formation of high molecular weight polymer in the early stages of the solid-state polymerization reaction indicates that this reaction may have more of a chain-growth mechanism than does the solution reaction.

The rate of the solid-state polymerization appears to be much faster in the case of DSC experiments compared to experiments carried out in a constant temperature bath and within single crystals. This may be due to the packing effects which may increase or decrease heat transfer within the sample. The crystals were packed tightly in the DSC experiments, and lightly in the constant temperature studies, while in the case of the single crystal, the reaction took place within the crystal only. For the last case, crystal size or imperfections may have been more important than heat transfer.

The infrared spectroscopy results of the polymers indicate that the band in the region of 810 and 845 cm^{-1} , attributable to para disubstitution, became stronger as the reaction temperatures were decreased. This may be due to the difference in activation energy for meta, ortho and para substitution.

An attempt to copolymerize an ortho/para crystalline mixture of methylbenzyl tosylate was unsuccessful. Instead a mixture of homopolymers was obtained, apparently because of the formation of mixed crystals instead of a eutectic mixture of the monomer isomers.

Finally, the microscopic study of a single large crystal of benzyl tosylate is of great importance. The photographs obtained for the polymerization reaction within the single crystal indicated that the direction of growth of the amorphous polymer region occurred preferentially within the crystal. The plot of area vs time revealed that this growth was exponential. Therefore, an Arrhenius-type of approach and treatment of data may help in further rate studies of this polymerization reaction in the solid state.

At this stage, it appears that more detailed study on this last topic may contribute more knowledge to the field of solid-state reaction. Further investigations in the following areas may help in understanding the nature of solid-state reaction mechanisms.

- (1) Rate molecular-weight studies at low temperatures to prevent polymerization occurring in the melt state - this study may lead to true solid-state polymerization reaction and may prevent intra- and inter-molecular rearrangement.

- (2) Low temperature solid-state polymerization - this study may lead to formation of linear, crystalline and high molecular weight polybenzyl.
- (3) Solid-state polymerizations under high pressure - this field of solid-state polymerization reaction, which has received very little attention, may contribute some knowledge towards the solid-state reaction mechanisms.
- (4) Effect of crystal morphology on solid state polymerization reaction - this study may attribute more knowledge to understand reaction mechanisms within a single crystal.

REFERENCES

1. D. Fox, M. M. Labes and A. Weissberger, Physics and Chemistry of the Organic Solid State. Volume I., Interscience Publishers, 1967.
2. J. K. Kochi and G. S. Hammond, Benzyl Tosylates. I. Preparation and Properties, *J. Am. Chem. Soc.*, 75, 3443 (1953).
3. S. Cannizzaro, *Ann. Chem. Pharm.*, 90, 252 (1854), 92, 113 (1854).
4. C. Friedel and J. M. Crafts, *Bull. Soc. Chim.*, 43, 53 (1885).
5. J. H. Gladstone and A. Tribe, Researches on the Action of the Copper-zinc Couple on Organic Bodies. Part X. On Bromide of Benzyl, *J. Chem. Soc.*, 47, 448 (1885).
6. C. K. Ingold and E. H. Ingold, The Preparation and Some Properties of Benzyl Fluoride, *J. Chem. Soc.*, 1928, 2249.
7. R. A. Jacobson, Polymers from Benzyl Chloride and Related Compounds, *J. Am. Chem. Soc.*, 54, 1513 (1932).
8. R. L. Shriner and L. Bergli, Condensation Products from Benzyl Alcohol: Polybenzyls, *J. Org. Chem.*, 6, 305 (1941).
9. G. Illari, the Condensation of Benzyl Alcohol by Means of Anhydrous Aluminum Chloride, *Ann. Chem.*, 40, 483 (1950); *C.A.*, 46, 3978 (1952).
10. O. C. Dermer and E. Hopper, Catalysts for the Polymerization of Benzyl Chloride, *J. Am. Chem. Soc.*, 63, 3525 (1941).
11. A. Yamada, M. Yanagita, Y. Yamamuro, and E. Kobayashi, Poly(benzyl chloride). I. Polymerization of Benzyl Chloride by Use of Triethylaluminum as Catalyst, *Rika Gaku Kenkyusho Hokoku*, 37, 445 (1961); *C.A.*, 57, 15338c (1962).
12. S. Hashimoto and I. Furukawa, Synthesis of Polybenzyl, *Doshisha Daigaku Rikogaku Kenkyu Hekoku* 5, 55-66 (1964) (Japan); *C.A.*, 62, 10524h (1965).
13. L. Valentine and R. W. Winter, The polycondensation of Benzyl Chloride Catalysed by Stannic Chloride, *J. Chem. Soc.*, 1956, 4768.
14. G. Montaudo, R. Passerini, F. Bottino, and P. Finocchiaro, Polybenzyls, *Ann. Chem.*, 57, 905 (1967).

15. S. Nishizaki and V. Kurusu, The Synthesis of Polybenzyl from Benzyl Alkyl Ethers, *Nippon Kagaku Zasshi* 85, 504-506 (1964) (Japan); *C.A.*, 62, 13251e (1965).
16. W. J. Mongrelli and G. F. Hennion, Cleavage Reactions of Benzyl *n*-Propyl Ether with Boron Fluoride, *J. Am. Chem. Soc.*, 63, 1722 (1941).
17. J. P. Kennedy and R. B. Isaccson, Synthesis and Characterization of Crystalline Polybenzyl and Polybenzyl Derivatives, *J. Macromol. Chem.*, 1(3), 541 (1966).
18. P. Finocchiaro and R. Passerini, Low-temperature Polymerization of Benzyl Chloride, *Ann. Chim. (Rome)* 1968, 58, 418-28 (Ital.); *C.A.*, 69, 10823j (1968).
19. Yu-Shan Sun and Hua-Chi Lai, Polybenzyls from Degradation, *Sci. Sinica (Peking)*, 14(1), 145 (1965) (Russ.).
20. I. Maruyama, M. Nakaniwa, T. Saegusa, and J. Furukawa, Polymerization of 2-Phenyl-1,3-dioxolane and Benzaldehyde, *C.A.*, 63, 11712b (1965).
21. R. Raff, J. L. Cook and B. V. Ettlign, Benzaldehyde Polymerization and Copolymerization Studies, *J. Polymer Sci.*, 4(Part A), 3511 (1965).
22. F. A. Drahowzal in Friedel-Crafts and Related Reaction. Vol. II Part I, Interscience Publishers, George A. Olah, Ed., (1964), p. 417.
23. R. W. Lenz, Organic Chemistry of Synthetic High Polymer, Interscience Publishers, (1967), p. 228.
24. A. L. Henne and H. M. Leicester, Fluorinated Derivatives of Methane Bering Phenyl Groups, *J. Am. Chem. Soc.*, 60, 864 (1938).
25. P. J. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, (1967), p. 362.
26. H. C. Hass, D. I. Livingston and M. Saunders, Polybenzyl Type Polymers, *J. Poly. Sci.*, 15, 503 (1955).
27. J. H. Lady, I. Kesse and R. E. Adams, A Study of Thermal Degradation and Oxidation of Polymers by Infrared Spectroscopy. Part II. Polybenzyl, *J. Applied Polymer Sci.*, 3, 71 (1960).
28. W. C. Overhuts and A. D. Ketley, Polybenzyl Polymers. 1. The Effect of Monomer Structure on Polymer Properties, *Makromol. Chem.*, 95, 143 (1966).

29. H. Gilman and N. J. Beaber, The Preparation of Hydrocarbons by the Reaction between Alkyl Sulfonates and Organomagnesium Halides, *J. Am. Chem. Soc.*, 47, 518 (1925).
30. H. Hoffman, The Preparation of Unstable Toluene-p-sulphonates, *J. Chem. Soc.*, 1965, 6748.
31. F. Drahowzal and D. Klamann, Zur Kenntnis der Sulfosäureester, *Monatsh.*, 82, 461 (1951).
32. F. L. Hirshfeld and G. M. J. Schmidt, Topochemical Control of Solid-State Polymerization, *J. Poly. Sci.*, 2(Part A), 2181 (1964).
33. H. Morawetz, Thermal Reactions of Organic Solid V. Polycondensation - Physics and Chemistry of the Organic Solid State - Volume I, Interscience Publishers, D. Fox, M. Labes and A. Weissberger, (1963), p. 287-328.
34. C. Sella and R. Bensasson, Sur la Polymérisation á l'Etat Solide de l'Acrylamide, *J. Poly. Sci.*, 56, 51 (1962).
35. L. A. Ac. Sluyterman, Reactions of Polypeptide Esters in the Solid State, *Trav. Chim.*, 71, 137, 277 (1952).
36. R. W. Lenz, C. E. Handlovits, and H. A. Smith, Phenylene Sulfide Polymers. III. The Synthesis of Linear Polyphenylene Sulfide, *J. Poly. Sci.*, 58, 351 (1962).
37. H. Morawetz, Oriented Chain Growth by Polymerization in the Crystalline State and by Related Processes, *Pure and Applied Chem.*, 12, 201 (1966).
38. H. Morawetz, Polymerization in the Solid State, *J. Polymer Sci.*, 12 (Part C), 79 (1966).

Table I
Preparation of Benzyl Tosylate Monomers

Alcohol	Reaction time; Time of addition; vol 15% n-BuLi in Hexane		minutes	grams	T° C	Reaction of TsCl with ArCH ₂ OLi		Yield	M.P.		
	minutes	ml.				minutes	grams			T° C	hours
benzyl	10 cc	30	61	15	19.5	-15	3	30° C	1	high	55-56
p-methylbenzyl	2 g	30	12	15	3.5	-20	2	30° C	.5	high	58-59
o/p-methylbenzyl	4 cc	30	21	15	6.35	-20	2	30° C	.5	high	-
p-methoxybenzyl	2.25 cc	30	12	15	3.4	-20	.5	0° C	.5	--	-

Table 2

Rate and Product Investigations for a Benzyl Tosylate

Solid-State Polymerization at 50° C

Reaction number	1	2	3	4	5	6	7	8
Time of rxs., hrs.	1	2	4.5	8	16	19	20.5	32
Wt. of monomer, g.	1	1	1	1	1	1	1	1
Wt. of polymer, g.	-	-	0.252	0.254	0.269	0.262	0.351	0.359
Yield, %	-	-	73	74	78	75.5	98	99
Softening Point, ° C	-	-	60-65	60-65	60-65	60-65	60-65	65-70
\bar{M}_n	-	-	2500	2800	2200	2200	2400	3200

Table 3

Melt Polymerization of Benzyl Tosylate at 55° C

Time of reaction, hrs.	13
Wt. of monomer, g.	1
Wt. of polymer, g.	0.242
Yield, %	70
Softening point, ° C	60-65
\bar{M}_n	2600

Table 4a

Polymerization of Benzyl Tosylate by HBr Vapour

Reaction number	1	2	3	4
Temperature of rxs.	50° C	Room temperature	0° C	-70° C
Time of rxs., hrs.	4	8	24	24
Wt. of monomer, g.	1	1	1	1
Wt. of polymer, g.	0.238	0.215	small	small
Yield, %	68.8%	62.1%	small	small
Softening Point, ° C	35-40	26-30	semi-solid	viscous liquid
\bar{M}_n	2700	2400	semi-solid	low

Table 4b

Polymerization of Benzyl Tosylate at -75° C in Hexane

Temperature of reaction, ° C	-75
Time of reaction, hrs.	48
Wt. of monomer, g.	1
Wt. of polymer, g.	small
Yield, %	small
Softening Point, ° C	viscous liquid
\bar{M}_n	low

Table 5

Vacuum Polymerization of Benzyl Tosylate

Reaction number	1	2	3
Temperature of reaction	50° C	Room temp.	0° C
Time of reaction, hrs.	16	16	16
Wt. of monomer, g.	1	1	1
Wt. of polymer, g.	0.255	0.264	-
Yield, %	73.3	76.3	-
Softening point, ° C	45-50	50-55	-
\bar{M}_n	3500	3900	-

Table 6

Polymerization of Substituted Benzyl Tosylates

Monomer	<u>p</u> -MeBzOT's	<u>o/p</u> -MeBzOT's	<u>p</u> -MeOBzOT's
Reaction temperature	Room temperature under vacuum		
Time of reaction, hrs.	3	6	6
Wt. of monomer, g.	1	1	0.5
Wt. of polymer, g.	0.246	0.34	-
Yield, %	60	83	-
Softening Point, ° C	50-55	55-60, 95-100	-
\bar{M}_n	2000	2500	-

Table 7

Solution Studies at approximately -10°C

<u>Reactions</u>	<u>Time, hrs.</u>	<u>Softening Point, $^{\circ}\text{C}$</u>	<u>\bar{M}_n</u>
Benzyl tosylate + conc. H_2SO_4	2	60-65	2100
Benzyl tosylate in CH_2Cl_2 + conc. H_2SO_4	2	60-65	2400

Table 8

Induction Periods at Various Temperatures
(measured on DSC)

<u>Isothermal Polymerization temperature, $^{\circ}\text{C}$</u>	<u>Induction period in minutes</u>
36.5	81-87
40	29-33
50	14-15
60 (melt)	no polymerization in 60 minutes

Table 9

Data for Microscopic Studies

X, mm	Y, mm	Area = πXY mm ²	time t = (T - τ) minutes	Monomer, % Crystalline	% Conversion = 1 - % Crystalline	Calculated \bar{DP}	
						I $\bar{DP} = \frac{1}{1 - P}$	II $\bar{DP} = \frac{1}{1 - 3P}$
0.70	0.40	0.830	6	98.75	1.250	1.010	1.03
1.00	0.60	1.820	9	97.25	2.750	1.039	1.08
1.50	1.00	4.540	14	93.50	6.500	1.070	1.10
2.15	1.50	9.770	24	83.50	16.500	1.200	1.90
3.00	2.33	21.170	34	70.00	30.000	1.430	10
3.90	2.85	33.660	44	52.00	48.000	1.940	α
4.40	3.20	42.640	56	38.50	61.500	2.600	
4.93	3.60	53.740	62	23.50	76.500	4.250	
5.80	4.00	70.250	72	0	100	α	

T = Time recorded during experiment.

t = Modified time.

τ = Most probable time when nucleation took place.

Table 10

Polymerization Color for Benzyl and Substituted
Benzyl Tosylates

<u>Monomers</u>	<u>Polymerization Color</u>
Benzyl tosylate	brown
<u>p</u> -Methylbenzyl tosylate	pink
<u>p</u> -Methoxybenzyl tosylate	deep red
<u>o/p</u> -Methylbenzyl tosylate	brownish-pink
Benzyl mesylate	pink + brown

Table 11

Polymerization Color for Benzyl Tosylate under
Different Environments

<u>Reaction condition</u>	<u>Color</u>
at 50° C	brown
at room temperature under vacuum	light pink
at room temperature in closed tube	black
at 50° C in presence of HBr vapor	green
at room temperature in presence of HBr	brown
at -70° C in presence of HBr liquid	yellow

Table 12

IR Results of Low-Temperature Polymerization

<u>Reaction temperature</u>	<u>Inflection at cm^{-1}</u>	<u>Weak band at cm^{-1}</u>	<u>Strong band at cm^{-1}</u>
50° C	785, 840	810 (v)	702, 735
room temperature	840	805	700, 735
0° C	765, 820	845	700, 735
-70° C	765	820	700, 730
-70° C in hexane	770	-	810, 702, 735

Table 13

Effect of Different Environments on Molecular Weight,
Yield and on Softening Points at 50° C

<u>Reaction Temperature (°C)</u>	<u>Time, hrs.</u>	<u>Yield, %</u>	<u>\bar{M}_n</u>	<u>Softening Points, °C</u>
55° (melt atm.)	13	70	2600	60-65
50° (melt HBr)	4	69	2700	35-40
50° (atm.)	16	78	2200	60-65
50° (vac.)	16	73	3500	45-50

Figure 1. Branch Structure of Polybenzyl

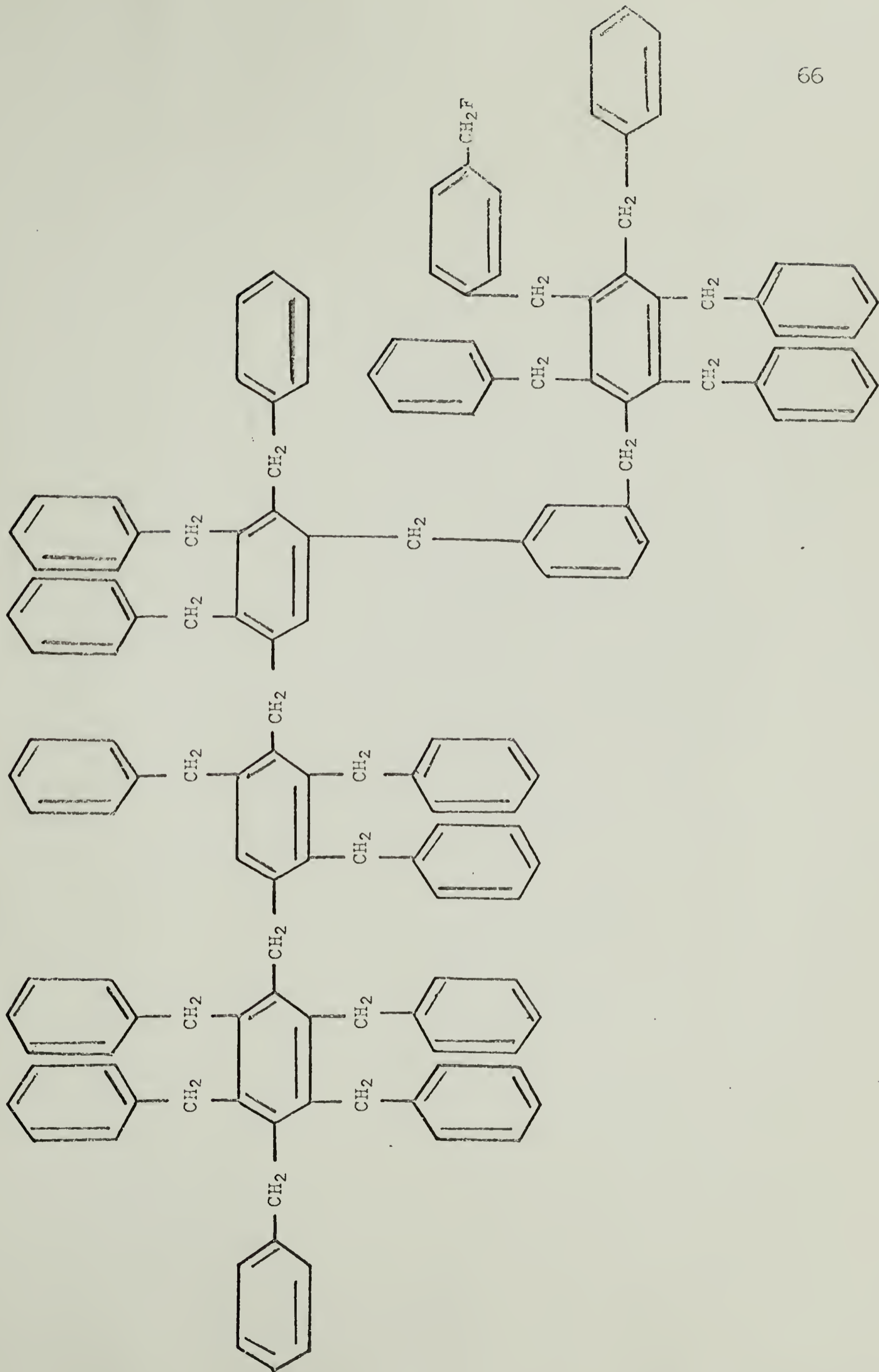


Figure 2. Experimental Set-up for HBr Reactions

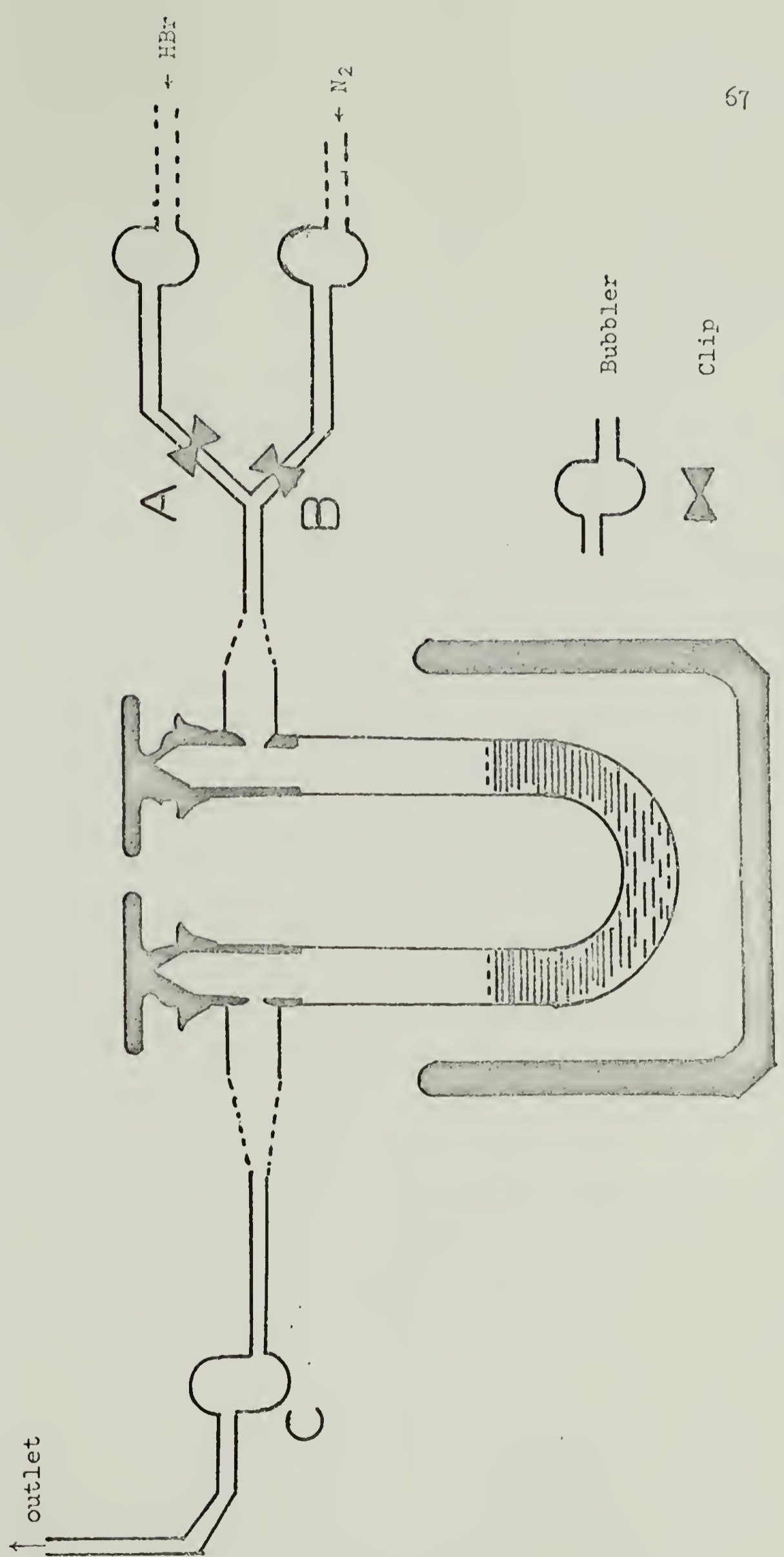


Figure 3e. Solid-State Polymerization
Nature of Exothermic Reaction (DSC) and Induction Periods

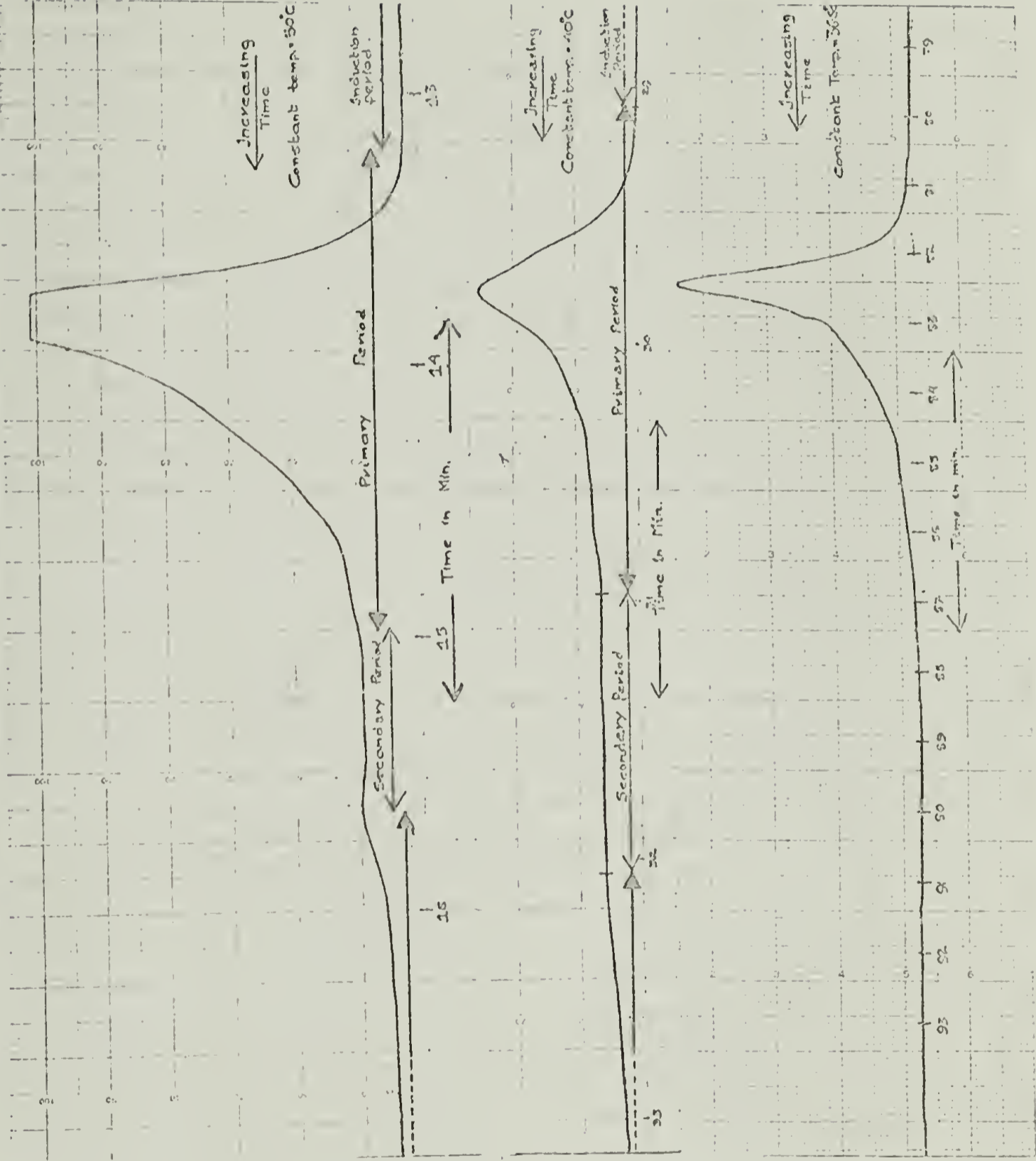


Figure 3b. Melt Polymerization
Nature of Exothermic Reaction (DSC)

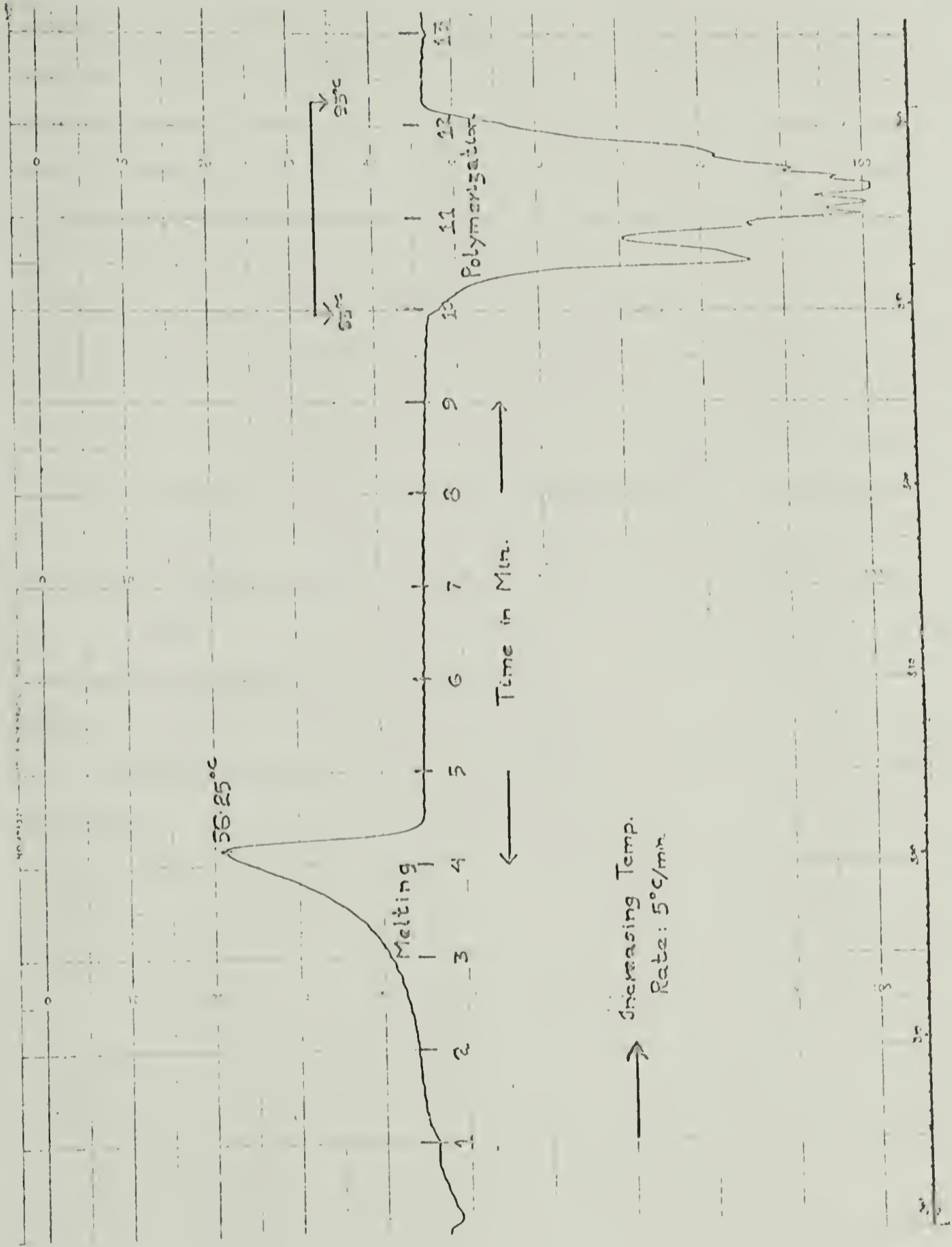
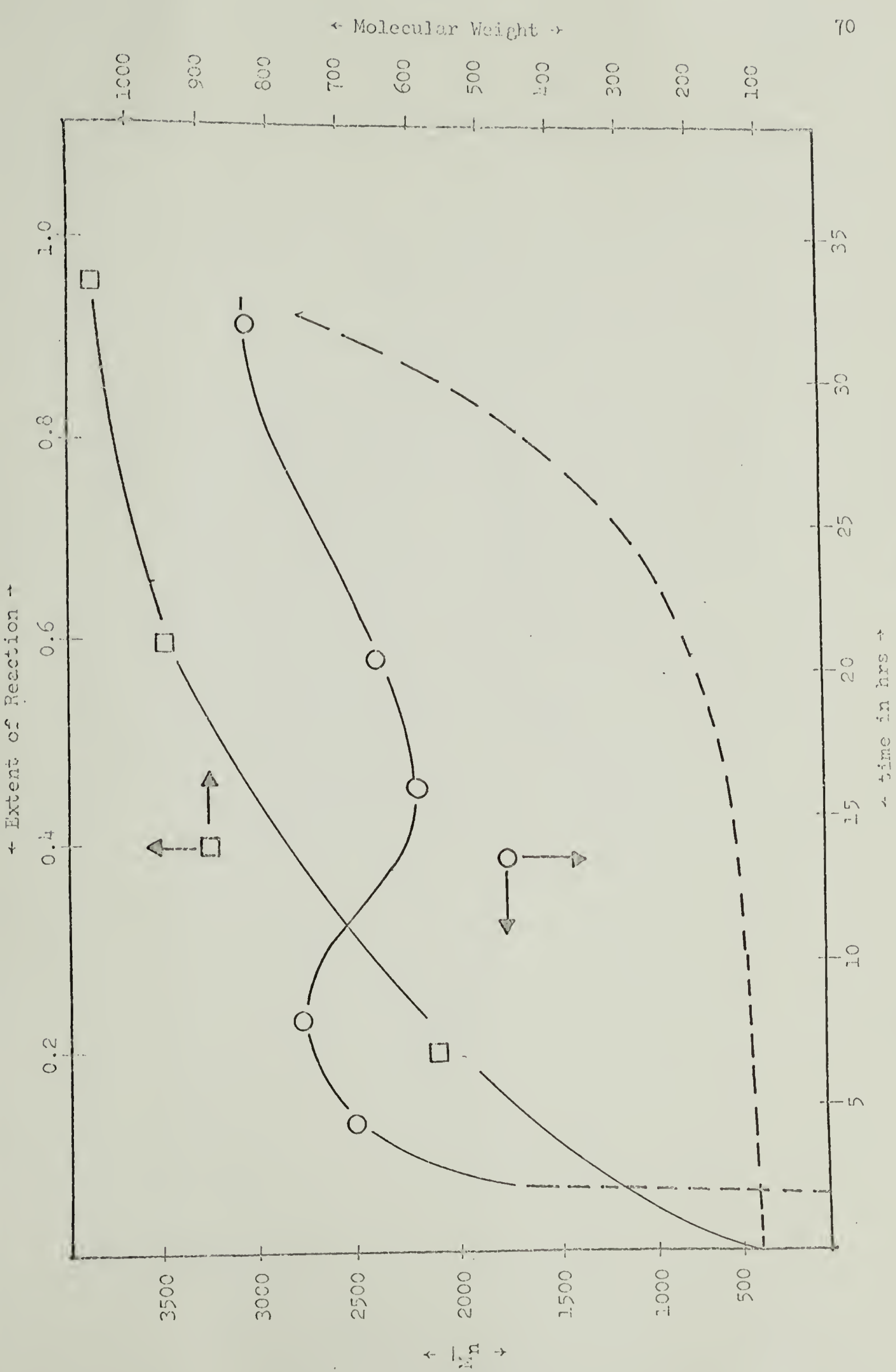


Figure 4. Comparison Theoretical Curve for a Polycondensation Mechanism and Increase in Molecular Weight with Reaction Time



○ Increase in the \bar{M}_n in solid state polymerization
 □ Increase in molecular weight in solution polymerization
 --- Theoretical curve for polycondensation mechanism

Figure 5. Rate-Molecular Weight Study

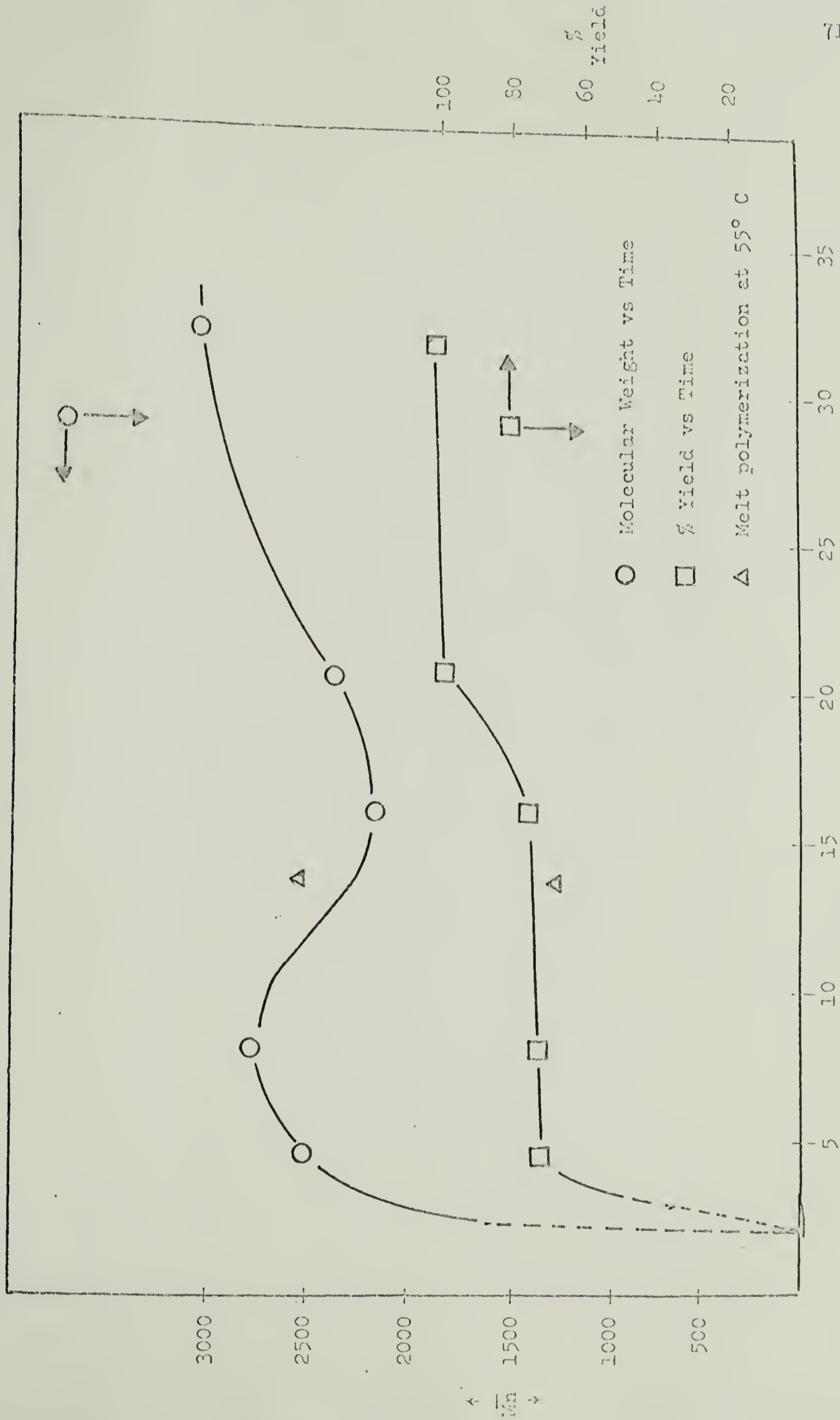
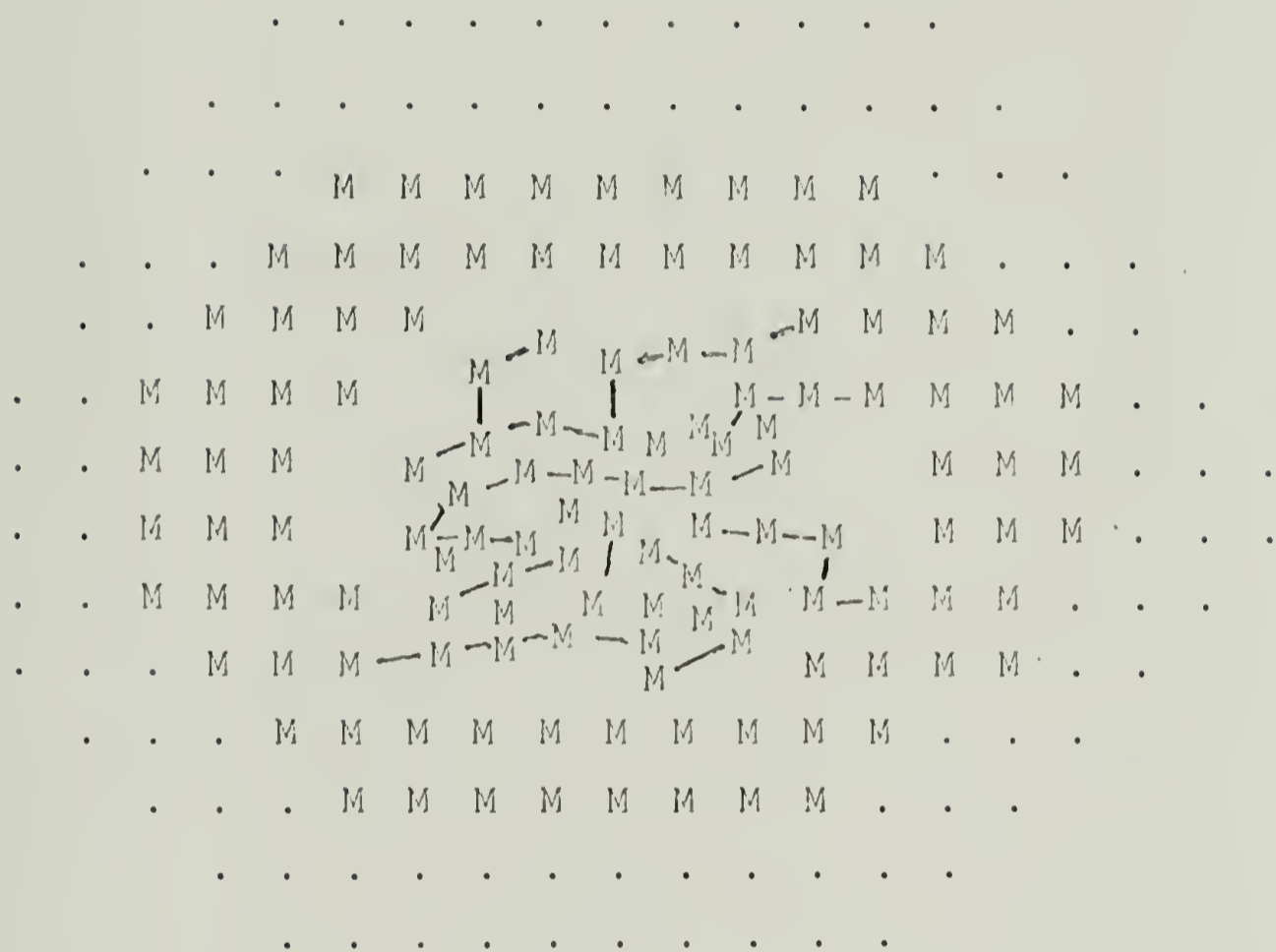


Figure 6. Mechanism of Solid State Polymerization

(M--monomer molecules)



~~Amorphous region~~ Crystal edges

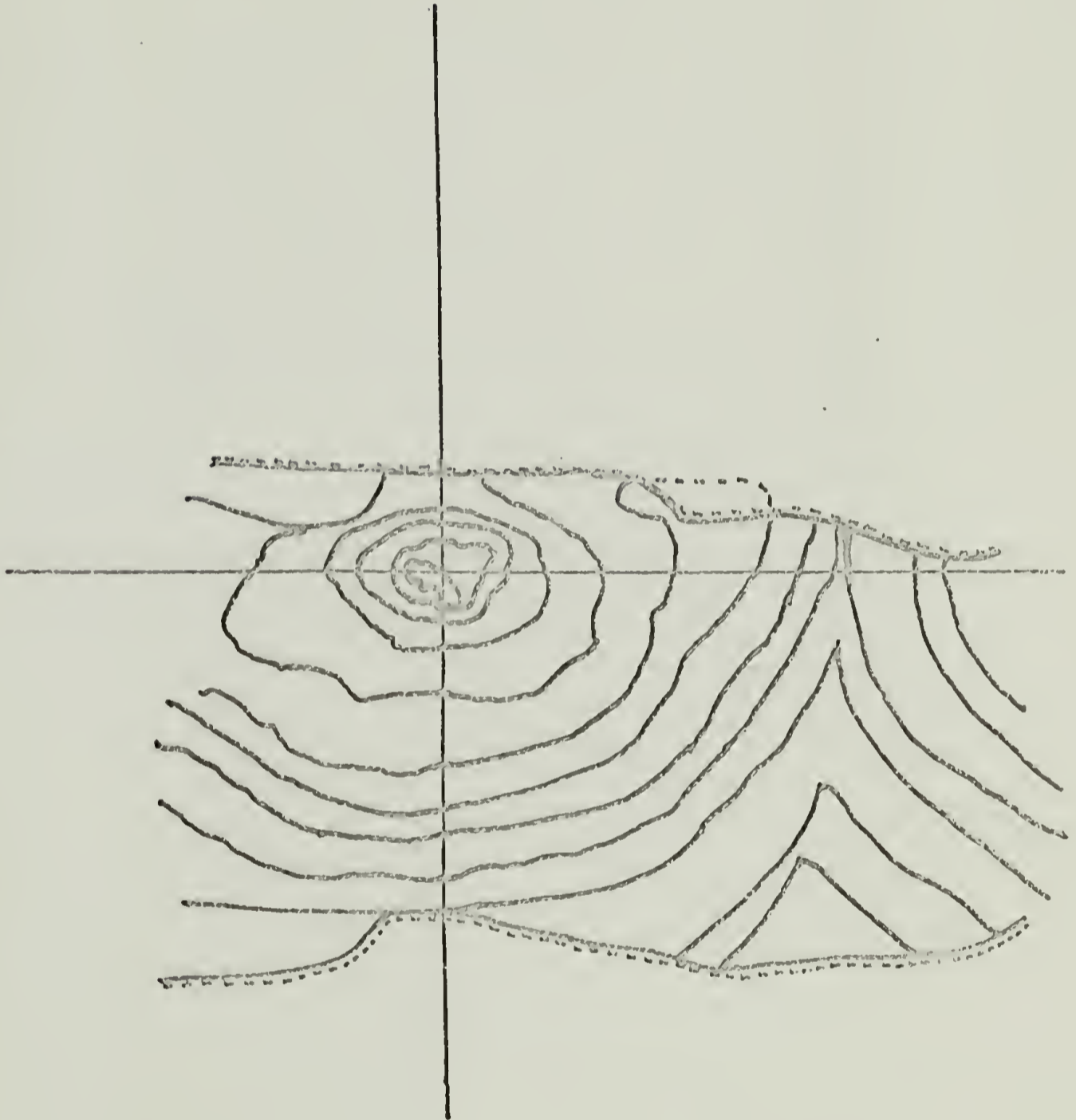


Figure 7a. Tracings of the Circumference of the Actual Amorphous Region at Various Time Periods

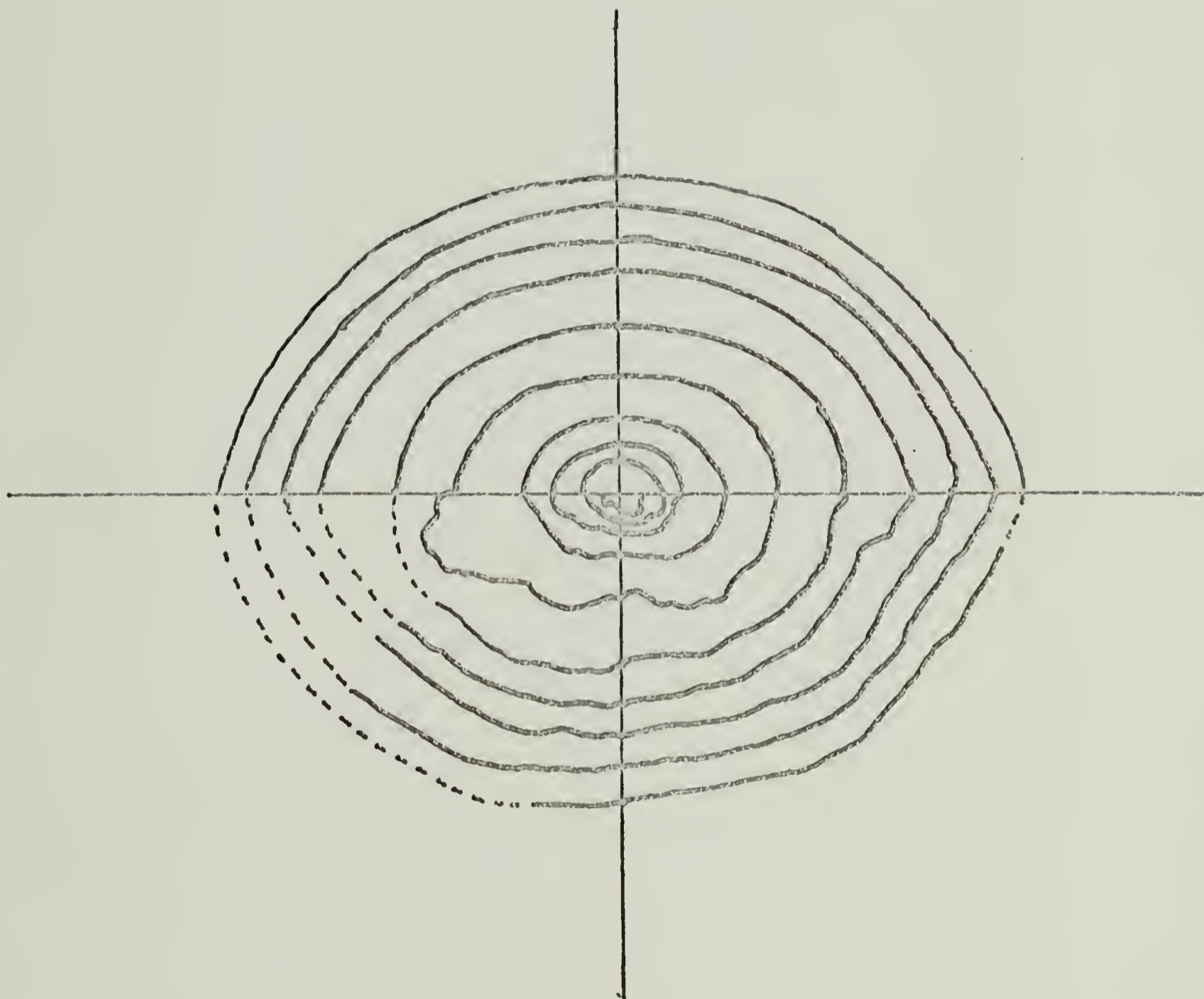


Figure 7b. Symmetric Drawing vs. the Growth of Amorphous Region

Figure 8. Area of Ellipses vs Time in Minute

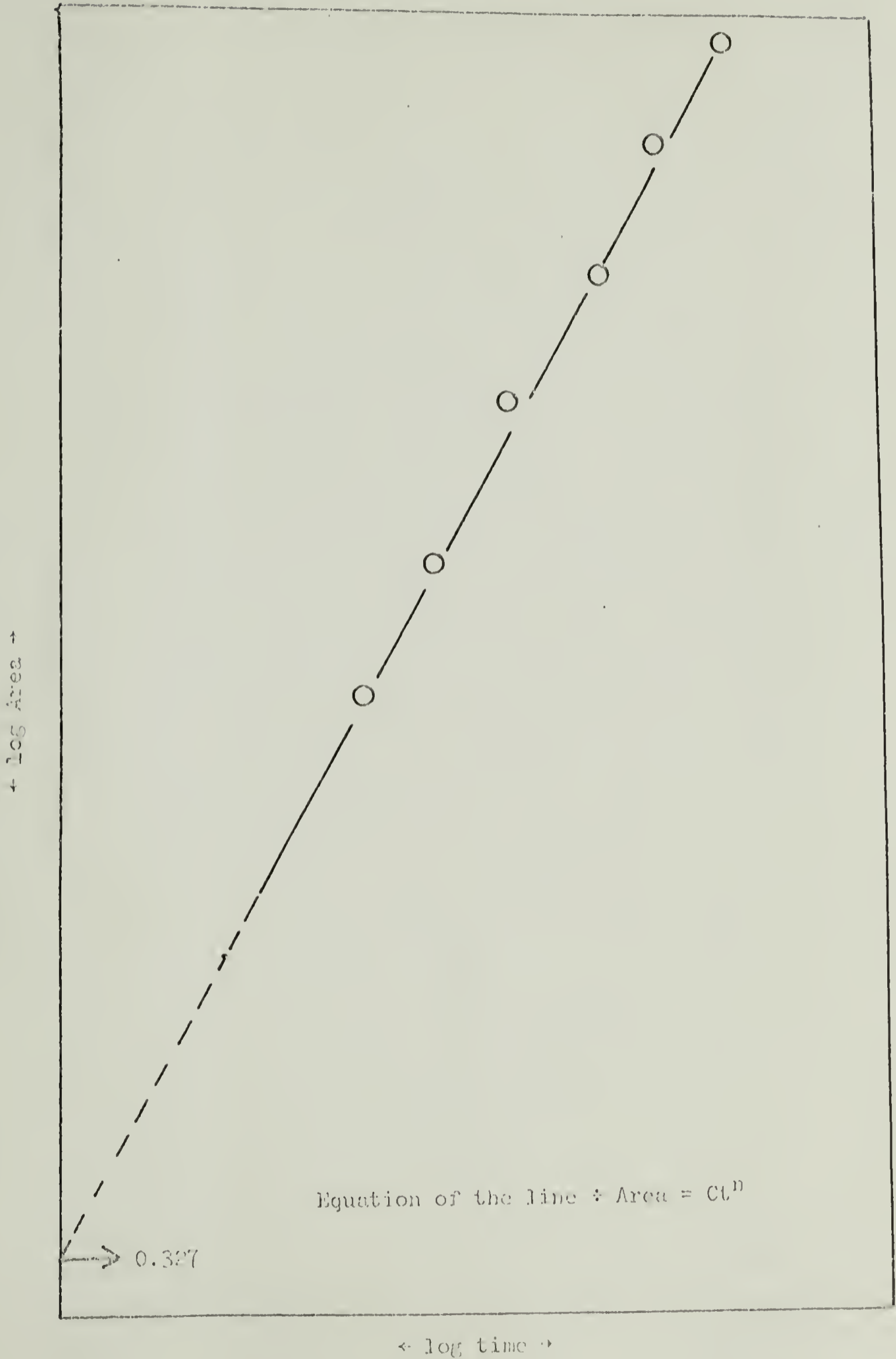


Figure 9. Callibration Curve

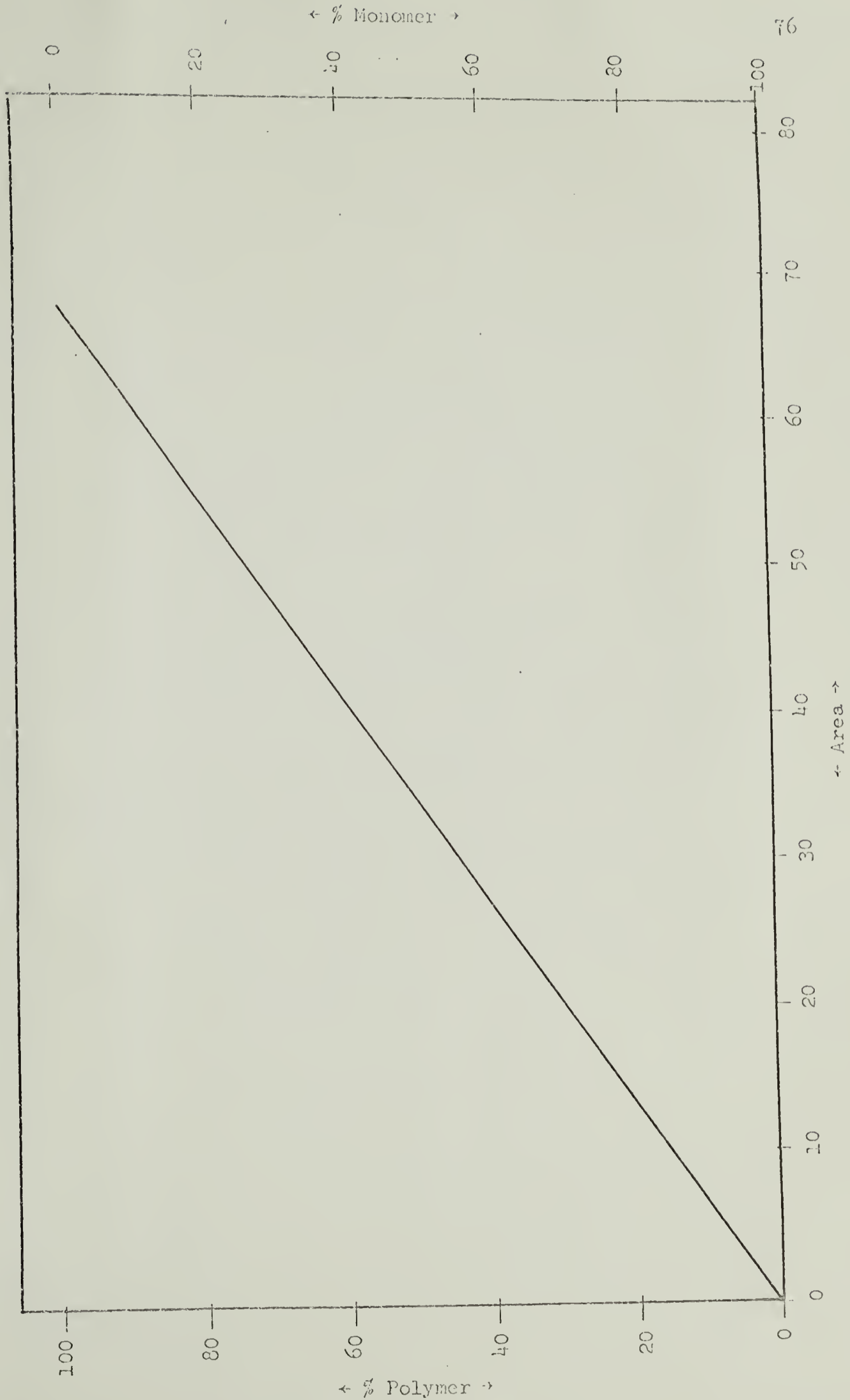


Figure 10. Calculated \bar{DP} vs Time in Minutes

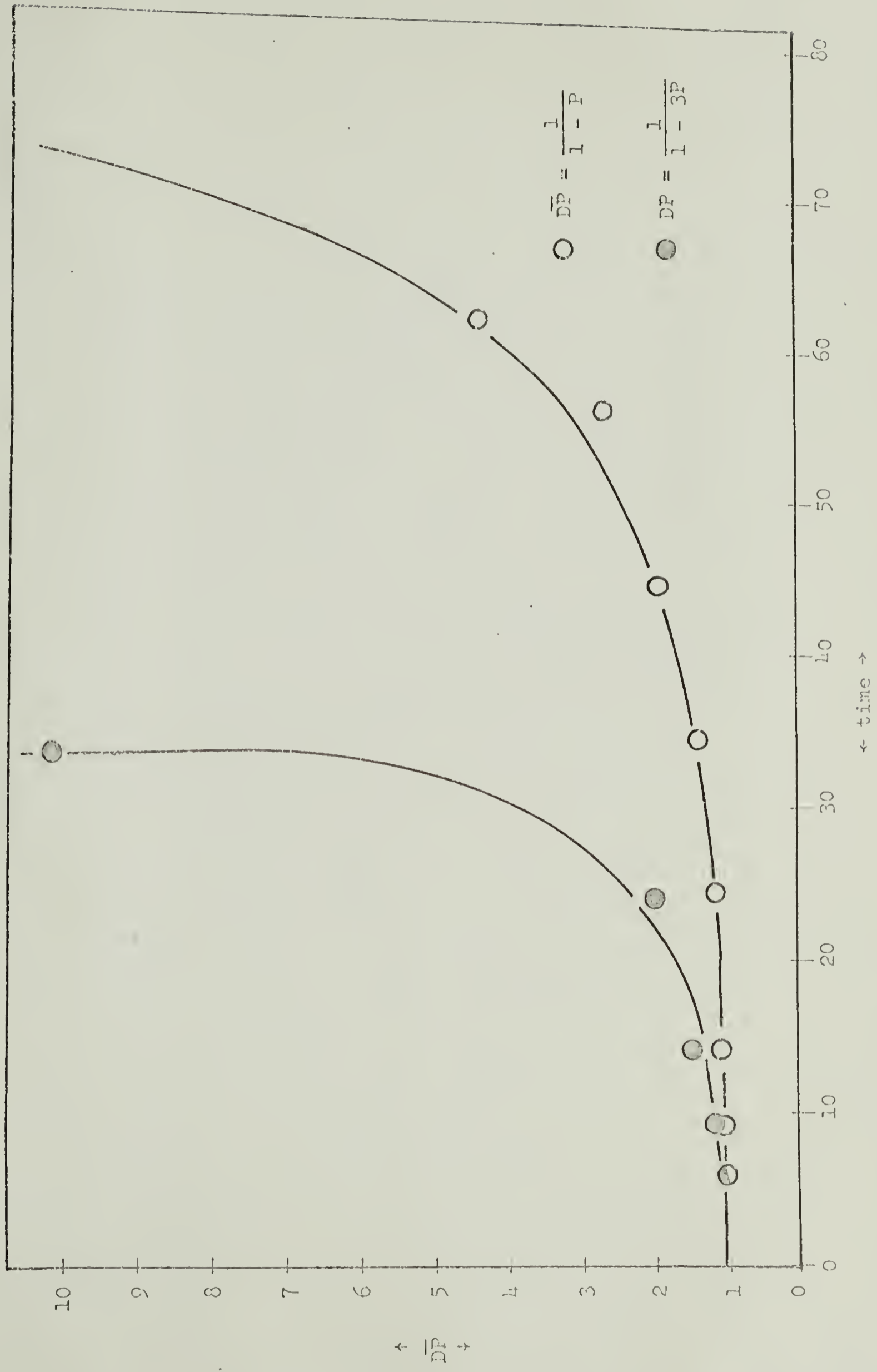


Figure 11. Calculated % Conversion vs Time in Minutes

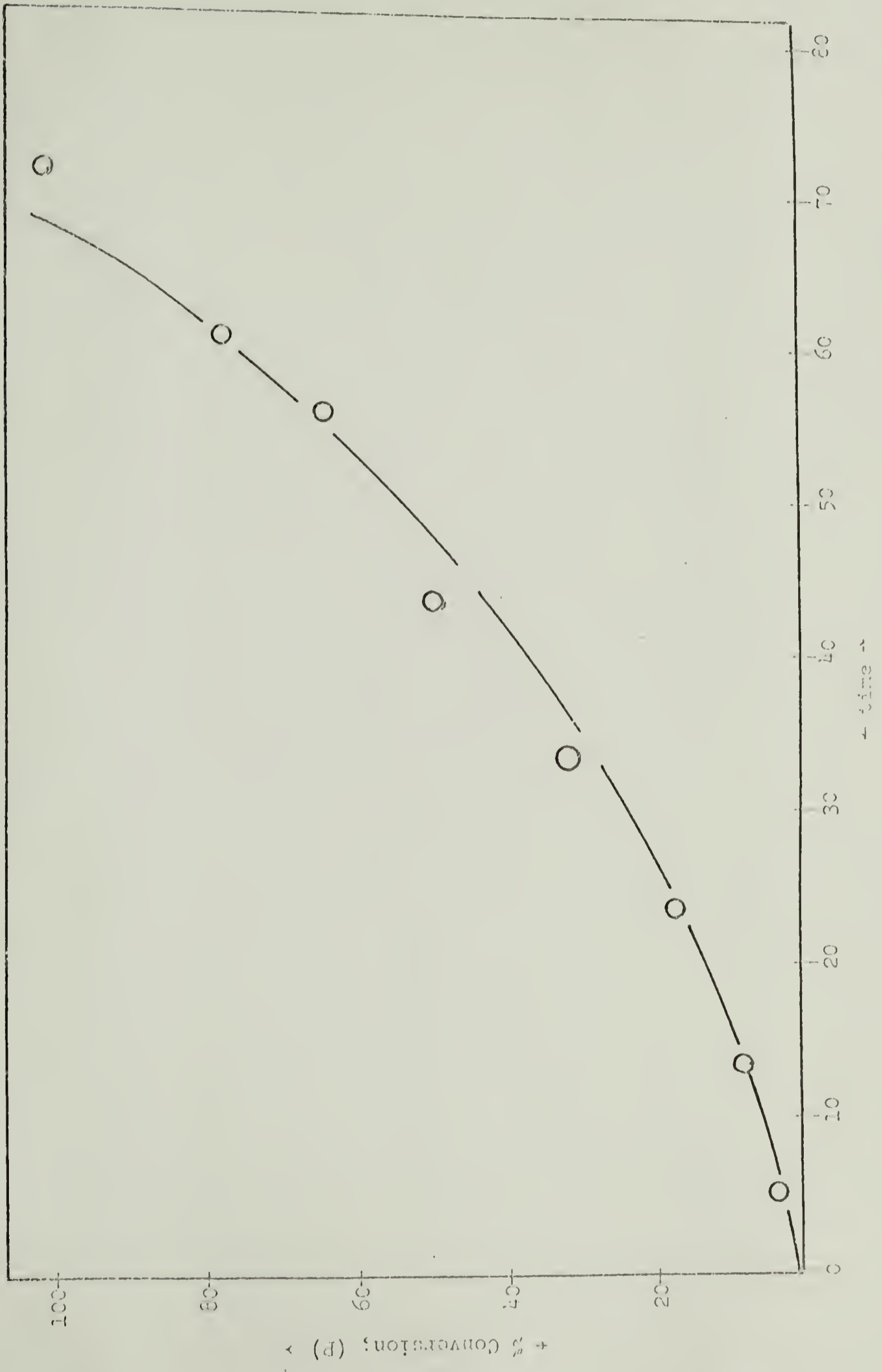




Figure 12. Infrared Spectrum of Benzyl Tosylate

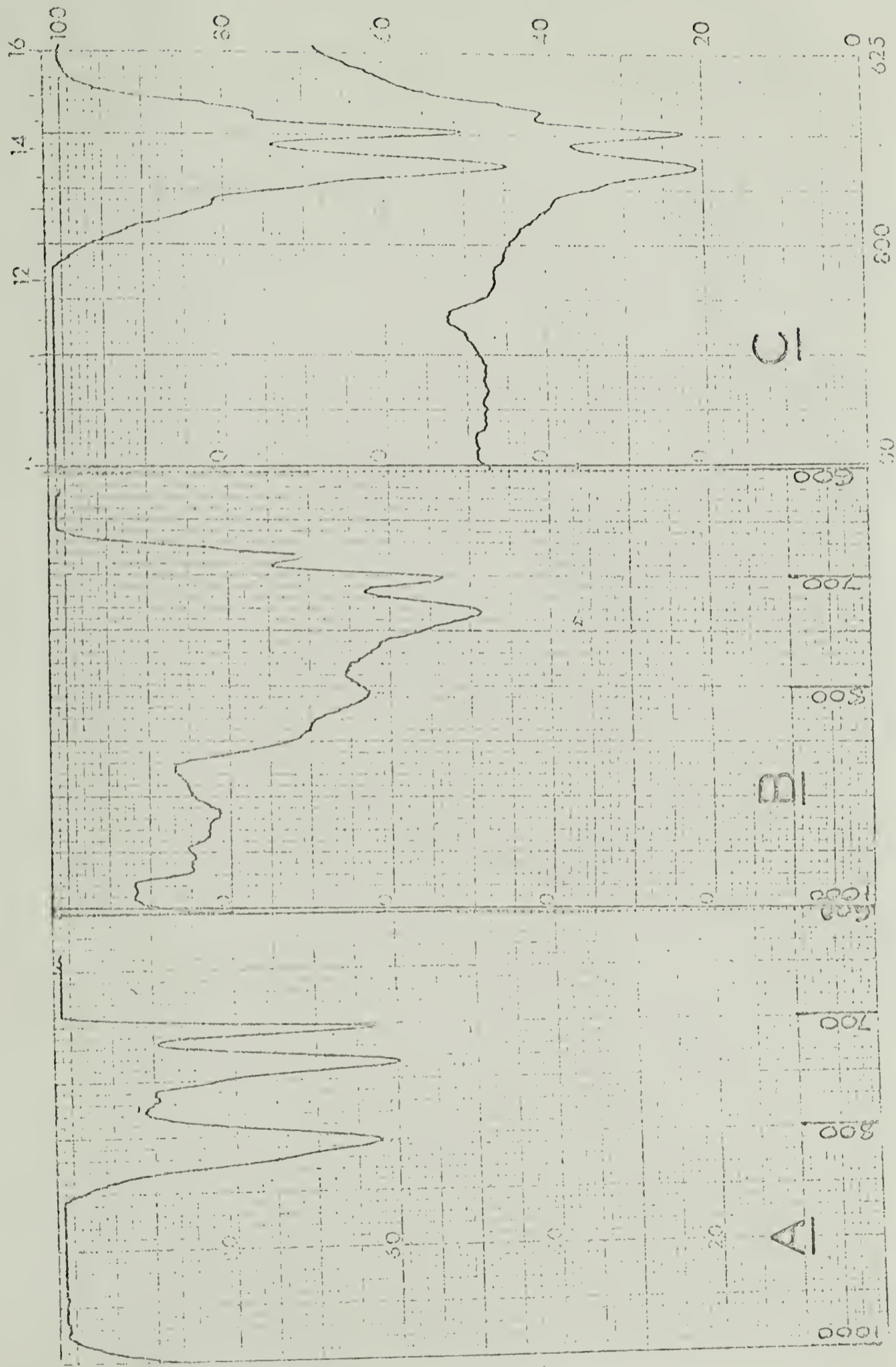
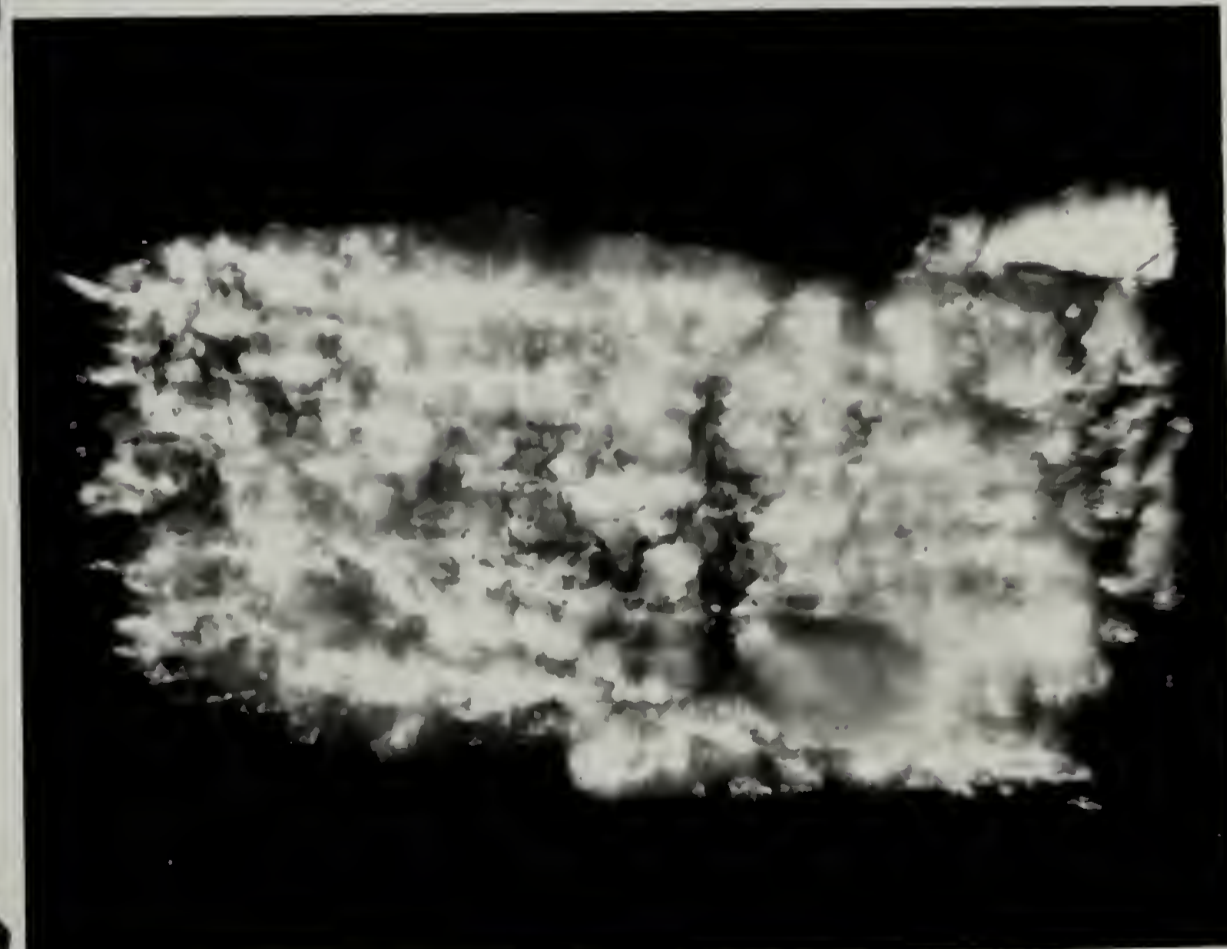
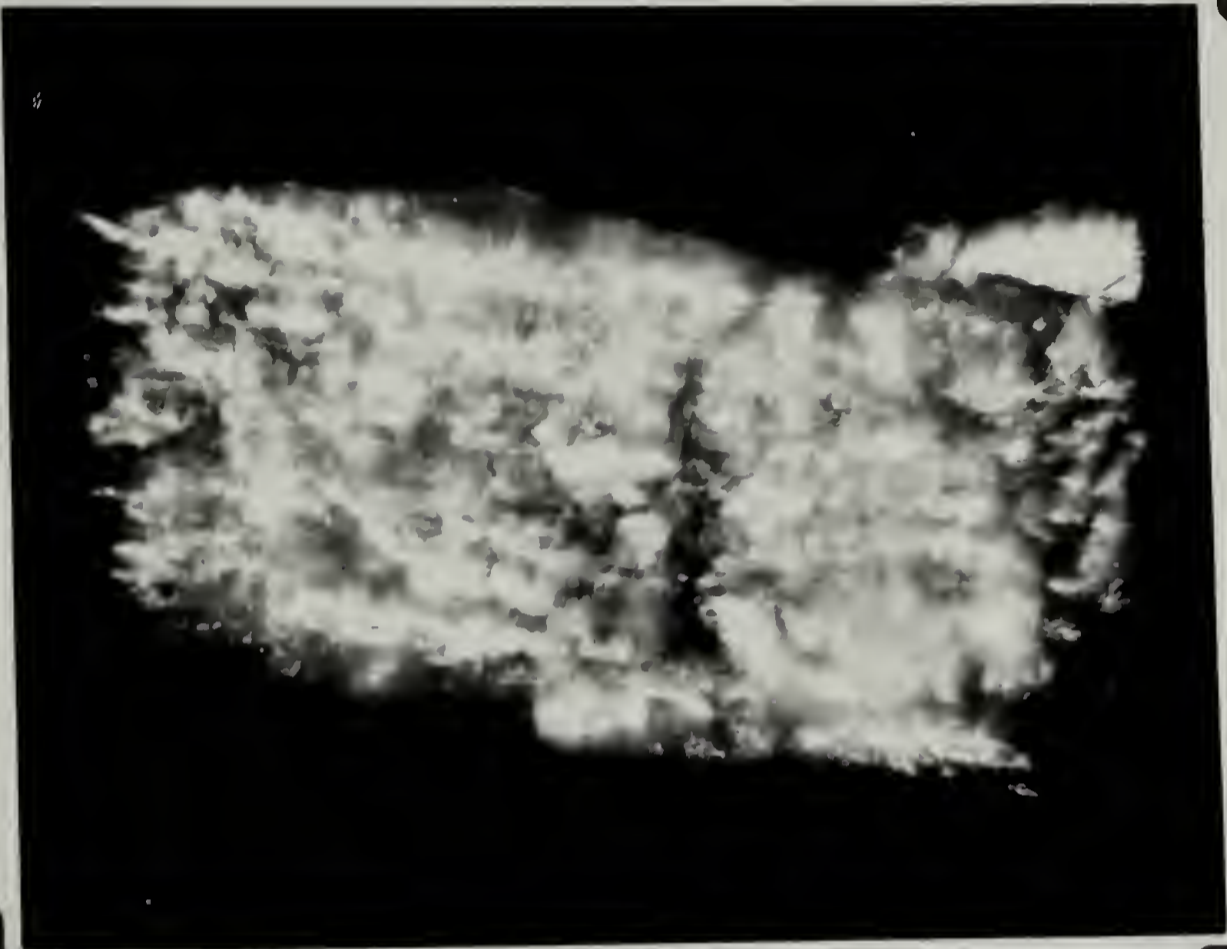
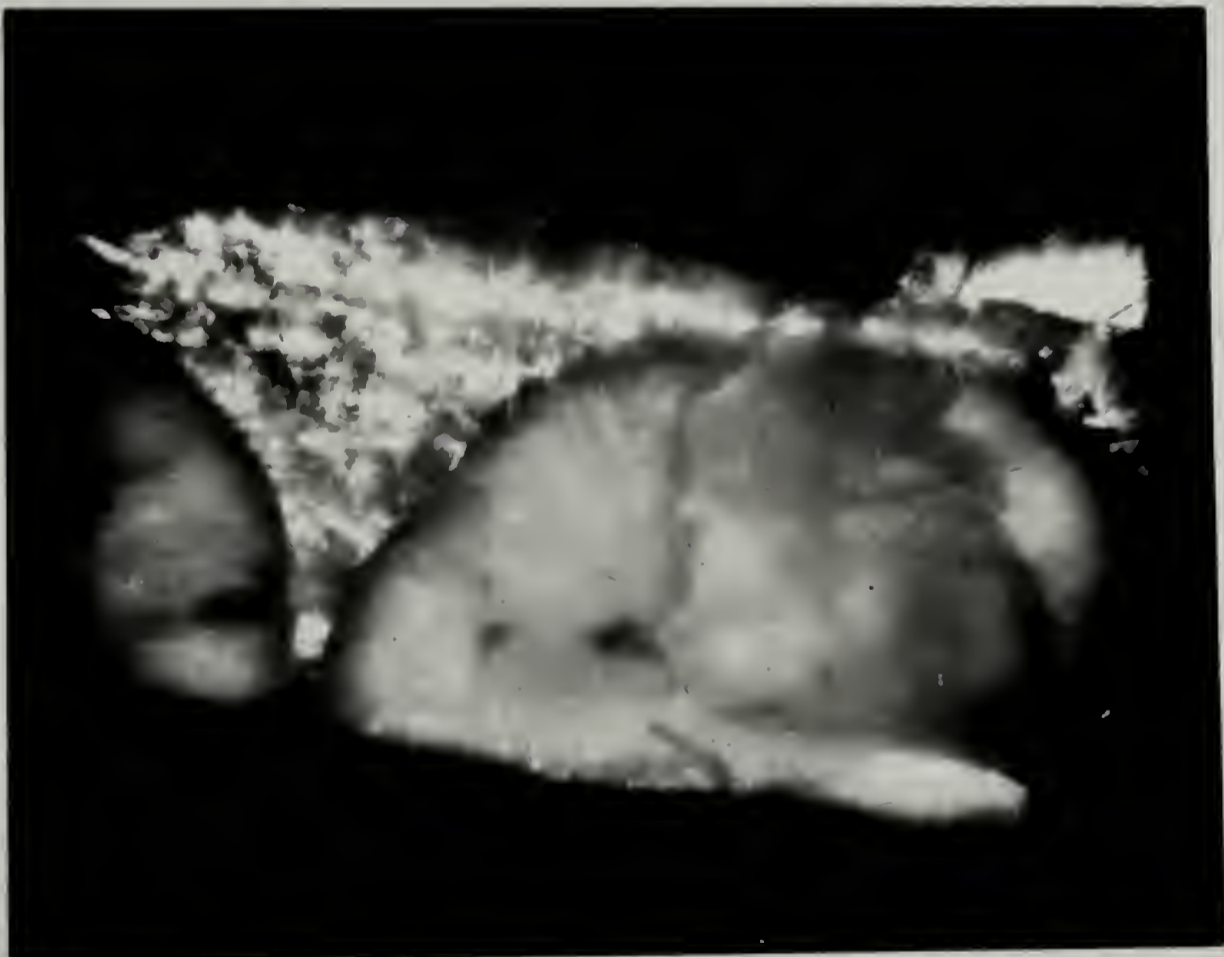
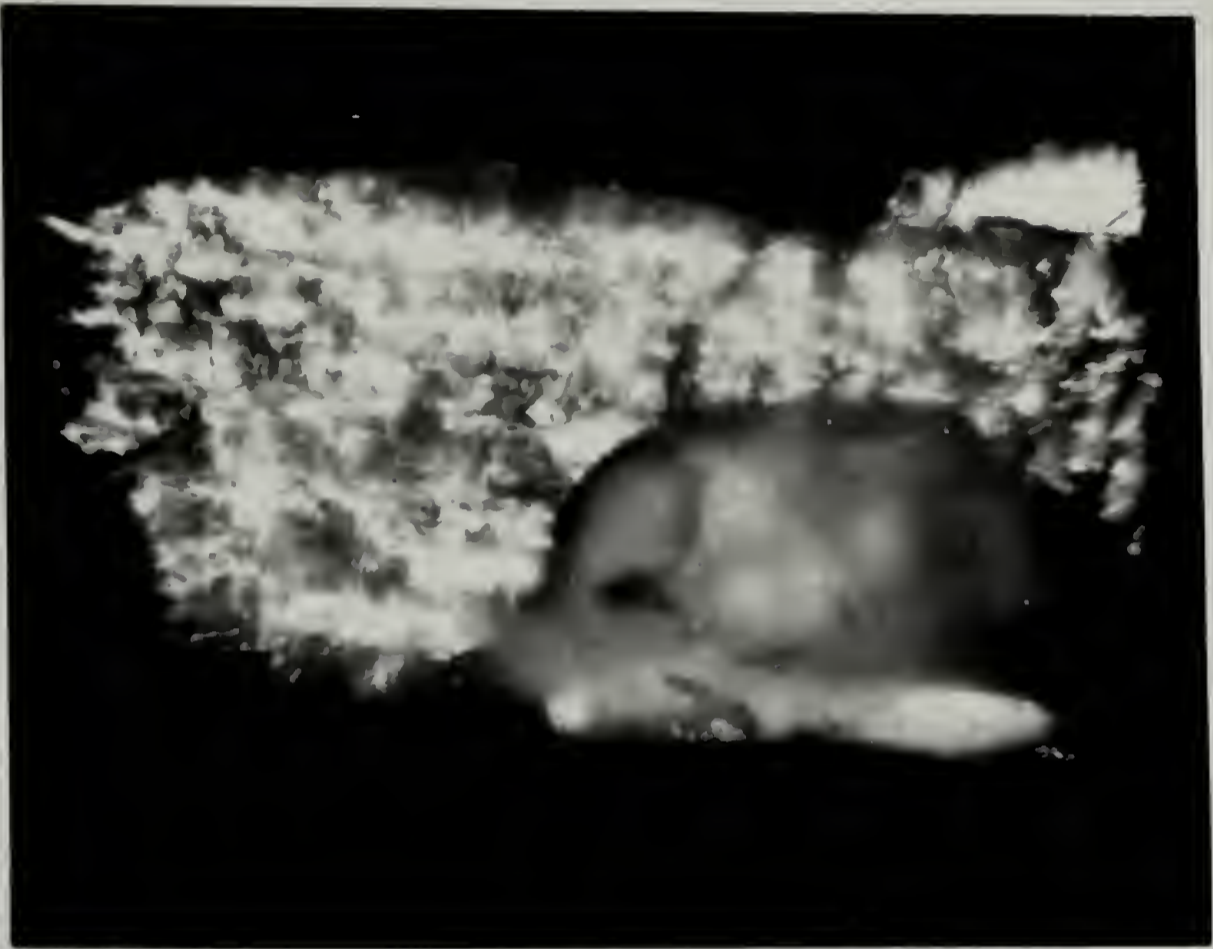


Figure 13. Infrared Spectra of Polymers (between 625-1000 cm^{-1} region) prepared by Various Methods:
 (A) -73°C ; Experiment No. 4 Method (b); (B) Room temperature; Experiment No. 5;
 (C) 50°C ; Experiment No. 3 Method (a).

Photographs



Photographs



Photographs

