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SUMMARY

This present study was undertaken to obtain kinetic data on the photolytic decomposition of poly(isobutyl-methacrylate) using a new technique of direct weight measurement during the reaction rather than the indirect pressure measurement systems previously used. The results obtained were used to fit the isobutyl ester into the pattern of information already obtained from the other members of the poly(alkylmethacrylate) series and in particular to determine whether a relationship existed between the Tg and the type of degradation reaction which occurs.

The use of an adapted thermobalance to continuously register weight changes during degradation had a considerable advantage in terms of throughput of data, but, although producing information consistent with that obtained using more traditional methods could not compare in accuracy. The inherent lack of sensitivity of the thermobalance system and the appearance of a previously unreported local pressure phenomenon called the "thrust" effect produced results whose calculated error margin could cast serious doubt upon conclusions drawn from data obtained from all types of thermobalance work.

The kinetic data obtained for poly(isobutylmethacrylate) indicated that the photodegradation reaction is random initiation followed by complete unzipping the overall Activation Energy for a sample of molecular weight 2.71×10^6 being 42 kJ mole^{-1} and for a sample of molecular weight 3.09×10^5 being 39 kJ mole^{-1} . Comparing these results with those obtained by Schoff¹⁰ for poly(ethyl and methy-methacrylate) it is apparent that the reaction is not viscosity controlled because degradation takes place at temperatures well above the Tg and attempts to analyse the data using Schoffs equation proved unsuccessful.

A STUDY OF THE PHOTOCHEMICAL DECOMPOSITION

OF

POLY(ISOBUTYLMETHACRYLATE).

A Thesis

presented for the degree of

MASTER OF SCIENCE

in the Faculty of Science of the

University of St. Andrews

by

Alan Torbet, B.Sc.



July, 1973

United College of St. Salvator
and St. Leonard, St. Andrews

DECLARATION

I declare that this thesis is my own composition, that the work of which it is a record has been carried out by me, and that it has not been submitted in any previous application for a Higher Degree.

This thesis describes results of research carried out at the Department of Chemistry, United College of St. Salvator and St. Leonard, University of St. Andrews, under the supervision of Dr. J.R. MacCallum.

ALAN TORBET

CERTIFICATE

I hereby certify that Alan Torbet has spent four terms of research work under my supervision, has fulfilled the conditions of Ordinance No. 16 (St. Andrews), and is qualified to submit the accompanying thesis in application for the degree of Master of Science.

J. R. MacCallum
Director of Research

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Introduction

Energy put into any molecular system can be dissipated by chemical or physical changes taking place within the system. In the case of polymer molecules, the most common form of chemical change is degradation i.e. the breaking of bonds within the polymer chain to either form smaller fragments which have approximately the same empirical formula as the parent molecule or to cross-link to give larger amorphous structures.

Ever since it was observed that light and heat perish natural rubber,^{1,2,3} much work has been done on the photolytic and thermal degradations of synthetic polymers, with a view to developing susceptibility or resistance to attack depending on the particular commercial application.

This present study was undertaken to obtain kinetic data on the photolytic decomposition of poly(isobutylmethacrylate) using a new technique of direct weight measurement during the reaction rather than the indirect pressure measurement systems previously used. The results obtained will be used to fit the isobutyl ester into the pattern of information already obtained from the other members of the poly(alkylmethacrylate) series, and in particular to determine whether a relationship exists between the T_g and the type of degradation reaction which occurs.

A great deal of work has been done on polymethacrylates, all but a very small amount of it involving temperatures well below the glass transition. Most of the work has been on poly(methylmethacrylate) mainly because of its commercial importance. Investigators seem to agree that the mechanism of the room temperature photo-degradation of this polymer, in solution, or as a solid, is one of random initiation without unzipping. No such agreement exists about results of the reactions above the T_g .

The first detailed photodegradation studies were made by Cowley and Melville⁴ on poly(methylmethacrylate). They concluded that the primary process was photo-initiation at the chain ends, while Charlesby and Thomas⁵ later suggested that random initiation in fact occurred. Grassie and MacCallum⁶ working on the thermal degradation of the poly(n-butyl) and poly(t-butyl) members found that photochemically they behaved like poly(methylmethacrylate) in that they produced quantitative amounts of monomer but that intramolecular anhydride structures produced by thermal treatment prevented the depolymerisation reaction. MacCallum⁷ pointed to both random and end initiation. Since then MacCallum⁸ has shown by theoretical analysis that random initiation with complete unzipping can give the same sort of molecular weight - conversion to monomer relationship as had been predicted for end initiation.⁹

The results of the photo-degradation of poly(n-butylmethacrylate) at 170°C indicate random initiation,⁷ while similar work on poly(ethylmethacrylate)¹⁰ which has a lower Tg, and would be less apt to be complicated by diffusion effects, gave the same result.

Theoretical Considerations

Photolytic degradation is caused by the absorption of energy into the polymer molecules in the form of photons. If the energy of excitation that the molecules then possess is greater than, or equal to the bond dissociation energy of the weakest link within a molecule, then cleavage reactions are likely to occur. This most often leads to free radical reactions which ultimately lead to main chain scission, cross-linking, unsaturation and the formation of small molecular fragments.

When a polymer molecule absorbs a photon, the molecule can

- a). revert to the singlet ground state most common in organic

molecules by emission of a photon (fluorescence),

b). revert to the ground state by radiationless transitions with the generation of heat,

c). change state by intersystem crossing to an excited triplet level of lower energy. This triplet state can further degrade by reversion to the ground state by photon emission (phosphorescence) or heat emission. All these possible transitions are shown in Fig. 1. If the molecule has sufficient energy in the triplet or excited singlet states dissociation or rearrangement may take place. Photo-lytic changes can be separated into primary and secondary processes. A primary process involves the immediate effect of the photon on the absorbing molecule: deactivation through fluorescence, heat emission, energy transfer etc., or destruction by transformation of the starting material into new compounds. Secondary processes are the reactions of the molecules, atoms or radicals produced by the primary process. Some examples of these occurrences are as follows:-

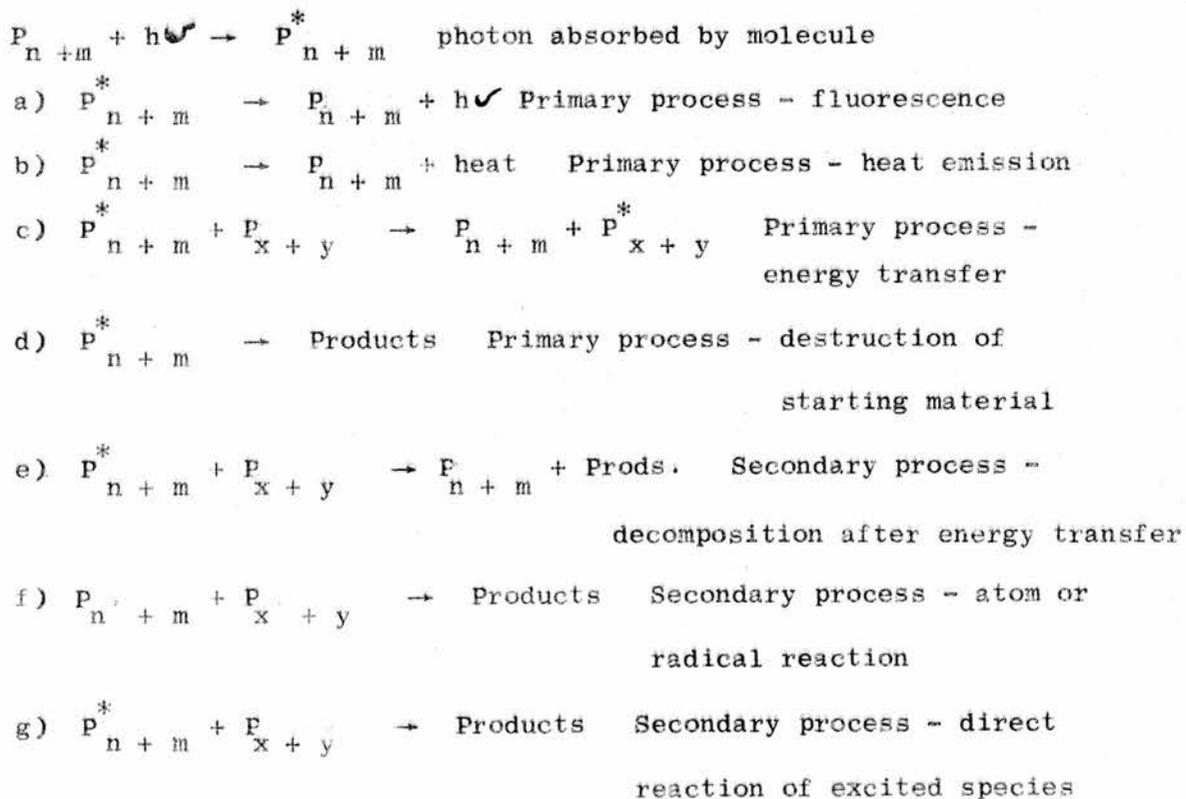
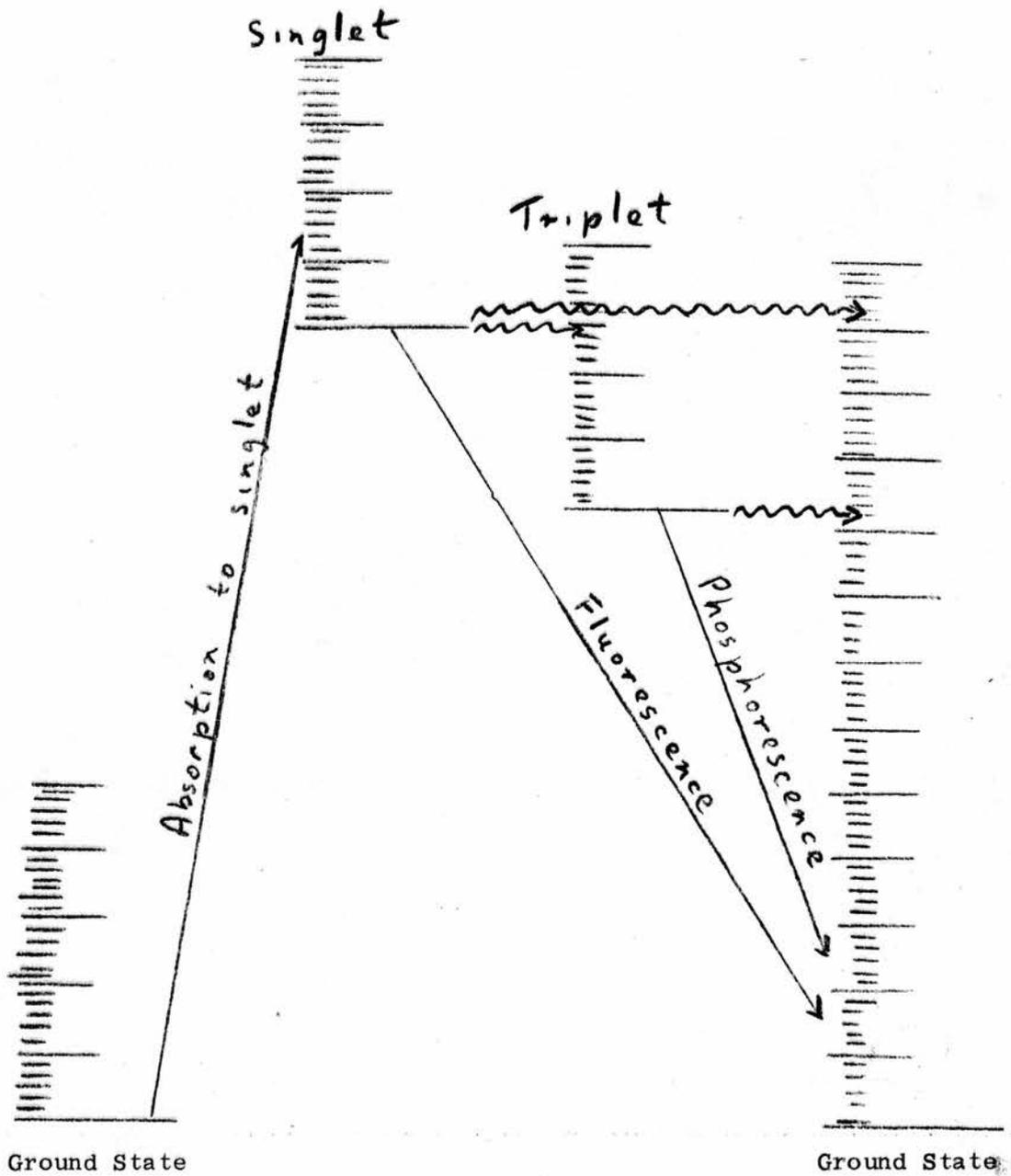


FIGURE 1

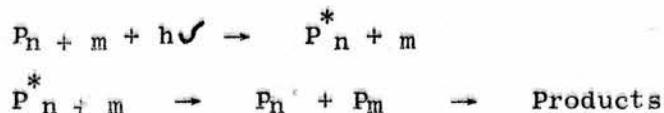
EXCITED STATES AND PHOTOPHYSICAL TRANSITIONS
BETWEEN THESE STATES



Solid lines = Radiative Transitions

Wavy lines = Radiationless Transitions

The reactions occurring in a polymeric system undergoing photolysis may be further classified as direct or indirect. Direct reactions come about from the absorption of a photon by the polymer followed by bond homolysis and the formation of breakdown products. For example if a c-c bond is broken



In the indirect reactions, "foreign" molecules - polymeric or small-molecule impurities - or even other functional groups in the same polymer become involved. They similarly can be excited and undergo reactions to form free radicals. These excited molecules or fragments may eventually interact with the polymer to give products similar to those arising from the direct reaction. The reverse reactions may also occur: excited polymer molecules or radicals may interact with the "foreign" molecules. These indirect processes can lead to degradation and they may involve energy transfer or free radical process e.g.



The four basic polymer reactions are

a) Side chain decomposition.

This type of reaction is usually restricted to thermal degradations and is normally of the ester decomposition variety.

b) Side chain rearrangement.

This type of reaction is associated with the development of colour

in nitrile - containing polymers and the thermal degradation of poly-methacrylonitrile.^{11,12}

In the photochemical field, a review of Smets³⁰ gives several examples of the above reactions in the area of photochromic behaviour in polymers.

c) Main chain scission

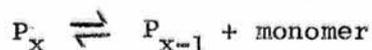
This type of reaction is by far the most important and is divided into distinct stages: initiation and depolymerisation.

1) There are two possible mechanisms for initiation. The first is random initiation in which chain scission occurs at random points along the chain leaving radicals which are large compared to the monomer unit. An example of this is the room temperature degradation of poly(methylmethacrylate).¹³ Grassie⁹ postulated specifically susceptible weak links to explain this type of behaviour although their existence has since been questioned.¹⁴

In the second mechanism, end-initiation, the bonds joining the end units to the rest of the chain are particularly vulnerable because the end units in each chain are chemically different from the rest of the chain repeat units by virtue of having for example a double bond or extra hydrogen or other group attached. The result is the formation of a long chain polymer radical along with a small end-group radical. Reactions in which end initiation is thought to take place include the high temperature photo-degradation of poly(methylmethacrylate)⁴ and the thermal degradation of the same polymer (200-400°C)¹⁵

2) Following initiation the depolymerisation reaction can take place. This is the depropagation reaction in which poly-radicals peel off monomer molecules. Whether the decomposition of a particular

material will result in a high monomer yield depends in the first place on the production of the necessary radicals in the initiation process. The thermodynamic and kinetic aspects of polymerisation and depolymerisation reactions were studied by Dainton and Ivin.¹⁶ Considering the equilibrium between polymer and monomer,



we see that the right to left reaction is normal propagation in addition polymerisation while the left to right reaction is depropagation. At room temperature the right to left reaction occurs but the left to right reaction cannot occur because it would prevent any polymerisation ever taking place. At higher temperatures the left to right depropagation occurs without any polymerisation. There must therefore be a ceiling temperature above which only depropagation will occur no matter how much monomer is added to the system to force the equilibrium to the left. Similarly below the ceiling temperature the reaction is solely polymerisation even though monomer is pumped away from the system. Thus in any room temperature poly(methacrylate) photolysis the U.V. initially forms radicals, but the chains will not depropagate even though the monomer formed from the chain ends is removed under vacuum.

Several possibilities exist after initiation. There could be a rapid decrease in molecular weight without any monomer being given off. Thus there is no unzipping as other reactions such as transfer are predominating. As explained, most room temperature photolytic degradations are of this type. A second possibility is partial unzipping in which small amounts of monomer are formed. The final possibility is complete unzipping in which large quantities of monomer are evolved as the chain completely depolymerises. An example

of this type of degradation is the thermal degradation of poly (methacrylate) at temperatures well above 220°C.

d) Main chain crosslinking

Under some circumstances ultra-violet radiation can cause crosslinking, the formation of intermolecular covalent links which lead to a three dimensional network. Crosslinking is more commonly brought about by using high energy radiation. This is the usual method for producing crosslinked polyethylene.¹⁷ Crosslinking can also be caused by heat (thermosetting resins) and by incorporating impurities into the polymer structure to give chemical crosslinking.

Review of Work on the Photochemistry of the Polymethacrylates

Poly(methylmethacrylate)

Perhaps more attention has been paid to the quantitative aspects of the photolytic and thermal degradations of poly(methylmethacrylate) than of any other polymer. This polymer is of interest to the experimentalist, not only because of its manifold practical applications, but because its properties are well characterised and the degradation reactions which it undergoes are relatively simple. To the photochemist the low absorption coefficient of poly(methylmethacrylate) at 253.7 nm means that this useful radiation can penetrate to all parts of a thin film with only slight attenuation whereas with highly absorbing polymers, a "skin effect" will become important. Finally poly(methylmethacrylate) is unusual in that the mechanism for photodegradation at room temperature and for straight thermal degradation are entirely different.

The first work on the photodegradation of poly(methylmethacrylate) at high temperatures was carried out by Cowley and Melville⁴ who irradiated films of thickness 1.8×10^{-3} cm to 8.5×10^{-3} cm with light of wavelength 253.7 nm and intensity 3.1×10^{14} quanta. They studied the formation of monomer during the irradiation of the thin films in vacuum by means of a molecular still, the monomer evolution being followed with a calibrated Pirani gauge. The degradations were carried out at temperatures ranging from 130°C to 200°C, the polymer being a highly viscous liquid at these temperatures. They concluded that the primary process was photo-initiation at the chain ends. Rate constants for the depropagation and termination were obtained by rotating sector technique. The rate constant, k_d ,

for depropagation at 167°C was $5.8 \times 10^2 \text{ sec}^{-1}$. The rate constant for termination was $k_t = 4 \times 10^4 \text{ l mol}^{-1} \text{ sec}^{-1}$ at the same temperature. The energy of activation for the termination reaction was calculated to be 90 kJ mol^{-1} which indicated that termination is diffusion controlled. Simha¹⁸ pointed out that this would mean that there was a viscosity contribution in k_t and that studies over a sufficiently wide range of molecular weights might permit the separation of this contribution. Cowley and Melville determined that the overall activation energy was of the order of 33.5 kJ mol^{-1} . This was determined over the range 170°C to 200°C since there was a break in the activation energy plot at 165°C. Below this temperature the energy of activation appeared to be approximately 125 kJ mol^{-1} . This would appear to confirm the authors' conclusions that the change in activation energy is due to the slower diffusion of the monomer in the more viscous medium.

More recently Schoff¹⁰ studied the photolytic decomposition of poly(methylmethacrylate) thin films under 253.7 nm light at 140 - 180°C, showing that the initial mechanism in the reaction was random scission followed by complete rapid depolymerisation. The only volatile product detected was monomer. The data obtained did not agree with that of Cowley and Melville. Schoff pointed out that their conclusion was based on molecular weight data which could also be interpreted as implying random initiation⁵⁰ and the fact that the decrease in rate with degradation appeared to be far greater than the change in the weight of the polymer would account for. However, their relative rate/percentage degradation data has been shown to be consistent with an order of about two which points to random initiation.

Although straight thermal degradation, solution degradation and room temperature ultra violet works are not strictly relevant to this study, a survey of these aspects gives more very useful information regarding the behaviour of poly(methylmethacrylate).

The first serious attempts at the elucidation of the mechanism of the thermal depolymerisation of poly(methylmethacrylate) was made by Votinov, Kobeko and Morei.¹⁹ Their error in deducing, on the basis of rate measurements, that the reaction involves the random scission of interunit bonds, would have been revealed had molecular weights been measured at intervals during the course of the reaction. Grassie and Melville¹⁵ made a consideration of the various possible modes of molecular weight change the starting point in their study of the reaction and concluded from experimental results that the rate of degradation of poly(methylmethacrylate) polymer samples of the same general structure is constant for molecular weights between 36,000 and 200,000, giving direct evidence that degradation is end-initiated with complete unzipping of the macromolecules. Above 200,000 the higher molecular weight molecules are prematurely terminated.

In the field of room temperature irradiation of poly(methylmethacrylate), Frolova and Riabov²⁰ exposed powder and films of thickness $8-9 \times 10^{-3}$ cm to ultra violet light in a high vacuum at 25°C. By shorter U.V. wavelength irradiation of samples tagged with C^{14} , it was shown that the ester groups were the primary source of the gas evolved, and that methyl formate was the major product.²¹ Schulz²² irradiated films of the same polymer of thickness 0.021 to 0.462 cm with 253.7 nm light of intensity 7.41×10^{14} quanta/sec at 26°C in air.

The result was almost solely chain scission, with essentially no crosslinking. This was later confirmed in an investigation by Fox, Isaacs, Stokes and Kagarise²³, which included a study of sedimentation patterns. It is possible to cross-link poly (methylmethacrylate) by ultra-violet irradiation but only in the presence of sensitizers,²⁴ while Fox, Isaacs and Nestler²⁵ irradiated thin films having phenyl or 1-cyano-1-methyl end groups with 253.7 nm light at room temperature in a vacuum observing rapid chain scission with the formation of extremely small amounts of monomer.

Charlesby and Thomas²⁶ irradiated poly(methylmethacrylate) films in air and nitrogen with low and medium pressure mercury lamps and found that degradation was linear with dose. Bands near 240 nm and 250 nm were noted in the absorption spectra of both U.V. and γ irradiated films. These bands decayed with time and decayed more rapidly with heat. Electron spin resonance of U.V. and γ irradiated polymer were identical, indicating that the same free radicals were present. It was concluded that there was random initiation, but that this was not followed by a significant amount of depolymerisation, conclusions which differed considerably from high temperature results such as those of Cowley and Melville. A later study by Charlesby and Moore²⁷ at temperatures up to 180°C amplified the comparisons made at room temperature.

In the field of solution degradations Fox and Price²⁸ irradiated 5gm/l solutions of poly(methylmethacrylate) in methylene chloride and other solvents at room temperature. Since quantum yields for random scission were found to be independent of polymer concentration but markedly dependent on the solvent used, correction was made for optical filtering by the solvent leading to a conclusion that solvent

radical attacks may be of less importance than other means of transferring energy to and from the polymer. Similar work by Charlesby and Thomas²⁶ with benzene solutions gave similar results: in spite of the high energy absorption in the benzene solvent, there is no transfer to the polymer. Jellinek and Wang²⁹ made a kinetic study of the 253.7 nm photolysis of poly(methylmethacrylate) in 2-chloroethanol solution under nitrogen at 25°C to 159°C. The extent to which oxygen was present in these solutions was not known. The experimental rate constants were dependent on polymer concentration which indicated participation of the solvent in the photolysis. Usually, thermal degradation appeared to be negligible at 159°C. An absorption peak at 224 nm increased with time of irradiation at 54°C to 159°C, the increase corresponding to the amount of monomer found. The intensity exponent was approximately 0.6 and the energy of activation for monomer formation was 37.2 kJ mol⁻¹, both of these results being similar to the high temperature bulk degradation results of Cowley and Melville. The kinetic picture differed from that of Cowley and Melville in that even at elevated temperatures random initiation was indicated.

Poly(butylmethacrylate)s

Although a great deal of work has been done on all aspects of the thermal and photolytic decompositions of poly(methylmethacrylate) an understanding of the general pattern of polymethacrylate degradations can only be obtained from similarly detailed studies of other polymethacrylate esters.

Grassie and MacCallum⁶ carried out a study of both the thermal and photolytic decomposition of the poly(n-butyl) and poly(t-butyl) members at 250°C and 170°C respectively. They showed that

poly(n-butylmethacrylate), like poly(methylmethacrylate) yields monomer as the predominating volatile product of thermal degradation at 250°C. Unlike poly(methylmethacrylate), however, which quantitatively yields monomer, poly(n-butylmethacrylate) only degrades to monomer to the extent of about 40%. Since traces of 1-butene were detectable in the volatiles and anhydride structures observed in the residue of poly(n-butylmethacrylate) it was postulated that competition between depolymerisation and ester decomposition to acid proceed simultaneously during the thermal degradation of this polymer.

They go on to make the important point that competition between these two processes is a general property of polymethacrylates with poly(methylmethacrylate) and poly(t-butylmethacrylate) representing the two extremes of behaviour. This interference by ester decomposition prevented quantitative comparisons of the thermal depolymerisation of the poly(alkylmethacrylates) but it was shown that, similar to poly(methylmethacrylate), poly(n-butylmethacrylate) degradation was end initiated.

Unlike the thermal reaction, the photochemically initiated depolymerisation to monomer at 170°C was quantitative for both poly(n-butyl) and poly(t-butylmethacrylate) which thermally undergoes almost quantitative ester decomposition. Preheating of poly(t-butylmethacrylate) at 170°C was found to inhibit the photodegradation. This was explained in terms of acid migration along the polymer chain so that intramolecular anhydride structures could be formed by the elimination of water between adjacent acid units. MacCallum⁷ carried out a more detailed study of the photolytic degradation of poly(n-butylmethacrylate) using conditions similar to those of Cowley and Melville.⁴ As this polymer has a much lower glass

transition temperature (22°C) than the methyl ester (105°C) it was hoped that some of the problems due to slow diffusion of monomer found by Cowley and Melville could be avoided. A plot of molecular weight as a fraction of the original versus per cent degradation⁹ implied end - initiation. However, hydrogenation of the unsaturated chain ends had no effect on the rate of depolymerisation, which indicates initiation does not occur solely at the chain ends. It was concluded that random initiation can take place. Since then MacCallum⁸ has shown through theoretical analysis that random initiation with complete unzipping can give the same sort of molecular weight - conversion to monomer relationship as had been predicted for end - initiation.⁹ Isaacs and Fox³¹ also studied the photodegradation of poly(n-butylmethacrylate) but at lower temperatures (50° to 100°C) and found 1-butene and n-butyl formate as well as monomer in the volatile product.

In the field of solution work, Maura³² irradiated 3% solutions of poly(methyl), poly(ethyl), poly(hexyl) and poly(n-butylmethacrylate) at room temperature with a ^{60}Co source and observed that molecular weight decreased with increased dose of radiation. He suggested that radiation caused the degradation of the macromolecules but increased their flexibility. The irradiated chains therefore showed a degree of extension larger than that of the non-irradiated molecules for the same molecular weight. He also said that the size of the side group altered the rate of degradation: the longer the group the more easily degraded was the polymer.

Using the technique of surface energy and contact angle quite well known in the field of U.V. degradation of polymers³³⁻³⁷ to determine the surface composition of a sample, Price and Fox³⁸ studied

the effects of 253.7 nm light from a medium pressure mercury lamp on films of poly(methyl) and poly(n-butylmethacrylate) at room temperature under vacuum and in inert atmospheres. From infrared studies of the degraded poly(n-butylmethacrylate) films it was observed that the products appeared to be acidic and compared to poly(methylmethacrylate) the smaller rate of change of contact angles against polar liquids reflected the presence of four-carbon chains in the surface. As degradation proceeds the chains will tend to "buffer" the surface as more polar groups appear in the products.

Some work has also been done on poly(t-butylacrylate) to determine the significance of the cis and trans isomers in the degradation process. Monahan³⁹ irradiated a thin film under Helium with 253.7 nm light and found that the only significant volatile product in the temperature range 20-110°C was isobutene. In a later analysis, Monahan⁴⁰ postulated a photoinduced rotational equilibrium between the cis and trans ester conformations with isobutene elimination occurring from the cis form.

Poly(ethylmethacrylate)

Relatively little work has been done on the photodegradation of this polymer either on its own or compared with other poly(methacrylates).

Lehrle and Robb⁴¹ studied the thermal degradation of poly(methylmethacrylate) and poly(ethylmethacrylate) by quantitative gas chromatography using techniques they developed from previous work⁴²⁻⁴⁵ to ensure high resolution for short time degradations. They found that both polymers degraded by the normal unzipping mechanism up to 500°C giving monomer as the only volatile product

but that above 650°C the sole volatile product was acetylene in the case of poly(methylmethacrylate). They also suggested that poly(ethylmethacrylate) and poly(methylmethacrylate) degraded via end initiation at low temperatures and random scission at higher temperatures (above 500°C).

Using thermal volatilization techniques⁴⁶⁻⁴⁸ McNeill studied the thermal decomposition of poly(methyl) and poly(ethylmethacrylate). He showed that while poly(methylmethacrylate) gives solely monomer as product, replacement of the ester methyl group by ethyl leads to a considerable difference in degradation behaviour. Whenever two or more carbon atoms are present in the alkoxy group there is a possibility that the ester decomposition reaction to give olefin plus poly(methacrylic acid) may occur. In a case such as poly(*t*-butylmethacrylate) this reaction occurs to the almost complete exclusion of the depolymerisation process.⁴⁹ For poly(ethylmethacrylate) however, monomer production is dominant and the formation of ethylene is secondary.

A thorough study of the photolytic decomposition of thin films of poly(ethylmethacrylate) under 253.7 nm light at temperatures between 140°C and 180°C was made by Schoff.¹⁰ Comparing results he obtained from poly(methylmethacrylate) he concluded that poly(ethylmethacrylate) degraded similarly by random scission followed by rapid depolymerisation. He also observed that the activation energy plots, both Arrhenius and log t versus 1/T, gave two straight lines that intersected, resulting in two activation energies. It was concluded that the degradations were viscosity controlled and a T_0 correction factor could be applied in the equation $K = Ae^{\frac{-Ea}{R(T-T_0)}}$,

the slope giving the true activation energy.

Observing the Tg's of the polymethacrylate esters it can be seen that poly(isobutylmethacrylate) has a Tg which is lower than either poly(methyl) or poly(ethylmethacrylate):-

<u>Polymethacrylate ester</u>	<u>Tg °K</u>
methyl	378
ethyl	338
propyl	328
n-butyl	293
iso-butyl	326

An analysis of the kinetics of the decomposition reaction of the isobutyl ester could be useful in assessing the significance of the To correction factor arbitrarily chosen by Schoff, leading to a better understanding of the viscosity controlled aspect of these photolytic decompositions.

Experimental

Preparation of polymer samples.

The monomer was 'Puriss' grade isobutyl methacrylate supplied by Koch-Light Ltd. It was washed four times with a dilute sodium hydroxide solution to remove the hydroquinone inhibitor. This was followed by four washings with distilled water and drying over anhydrous sodium sulphate for 12 hours. The purified monomer was then filtered and distilled under reduced pressure (b.pt. 59°C at 12mm of mercury). The purity of the distillate was tested by infrared, mass spectroscopic and gas - liquid chromatographic analysis and gave results all of which could be attributed to isobutyl methacrylate.

Polymerisations were carried out in sealed tubes at 60°C with two different concentrations of 2:2'-azobisisobutyronitrile (0.1% and 0.6% by weight) recrystallized from a chloroform/methanol mixture, as initiator. The tubes were evacuated and degassed several times after the addition of monomer and initiator and before polymerisation. Polymerisations were carried to around 15% conversion. The resultant polymer-monomer solution was dissolved in an excess of chloroform and precipitated from methanol in the ratio of approximately 0.5 litres chloroform solution added to 5 litres of methanol vigorously stirred. The monomer was obtained as a very fine 'snow' which tended to coagulate into rubbery lumps when stirring ceased. The product was filtered with suction and allowed to stand for one day in a dessicator. It was then left in a vacuum oven at room temperature for four days, ground to a fine powder and returned to the vacuum oven for a further three days.

Degradation Apparatus

The apparatus used to degrade the samples was essentially that

used for thermo-gravimetric analysis with adaptations for use in photodegradation at various constant temperatures. The basic apparatus was a Stanton MF-L5 Thermobalance as shown in Fig. 2. Work by Tanner⁵¹ details the problems involved in using this model and suggests methods for improving the machine's performance.

After several experiments had been done to investigate the most efficient and convenient methods of determining the rate of photolytic degradation of the samples four basic alterations were made to the thermobalance.

1. The tall narrow silica boat used to carry the sample in the original balance was replaced by a brass boat of inside diameter 3.10 cm, internal depth 0.65 cm and weighing 4.56g. This boat was so designed as to be of the smallest possible weight and largest possible surface area which could just fit into the glass tube, and yet be light enough to maintain the sensitivity of the balance mechanism. To ensure that the boat remained on top of the rise arm and in a central position, a saucer type lip was cut out of the base such that the rise arm top plate fitted neatly into the recess created.

2. The standard sealed glass tube supplied by Stanton was replaced by a longer open ended tube sealed by a Silica window fixed with 'Araldite' and with a side arm near the top. Light from the U.V. source could therefore be directed down onto the heated sample through this window.

3. Since the pressure detection equipment in the original balance was very near the pumping system but far away from the sample, a Pirani head was mounted in the side arm close to the sample to measure the pressure as close to it as possible.

4. Several trial experiments led to observation of a strange unreported phenomenon. When a sample was irradiated at a high temperature an initial sudden weight increase was recorded by the balance. Depending upon the size of the sample and the intensity of the light, this effect varied between a 0.5 mg and 4 mg initial weight increase. It was also observed that when the U.V. lamp was switched off after a short run a sudden weight decrease occurred as shown in Fig. 3. The only type of weight increase reported in the thermogravimetric analysis field was of a buoyancy type, observed to occur at much higher pressures and to be of a much smaller magnitude. The observed effect was called the "thrust" effect and was explained as follows. When the sample is exposed to U.V radiations decomposition begins almost instantaneously and is relatively fast in the initial stages. The reaction involves the breaking up of polymer molecules into monomer which is volatile under the low pressure conditions. The monomer thus evaporates in an upward direction with considerable momentum, the resultant downward reaction causing the weight of the boat and sample to apparently increase. The "thrust" effect is therefore a localised pressure effect with the sample and boat being subjected to a higher pressure above than below from the volatile monomer molecules produced in the reaction. If an average example of 2.5 mg apparent weight increase is considered the pressure differential required above and below the boat can be calculated approximately as shown.

$$\begin{aligned}\text{Apparent weight increase} &= 2.5 \text{ mg.} = 2.5 \times 10^{-6} \text{ Kg} \\ \text{Area of boat} &= \pi (1.55)^2 \text{ cm}^2 = 7.54 \times 10^{-4} \text{ m}^2 \\ \text{Pressure exerted on boat} &= \frac{2.5 \times 10^{-6} \times 9.81 \text{ Kg m}^{-1} \text{ sec}^{-2}}{7.54 \times 10^{-4}} \\ &= 3.25 \times 10^{-2} \text{ Nm}^{-2} \\ \text{But 1 atmosphere} &= 1.013 \times 10^5 \text{ Nm}^{-2} \\ &= 760 \text{ torr} \\ \text{Pressure differential} &= \frac{3.25 \times 10^{-2}}{1.013 \times 10^5} \times 760 \text{ torr} \\ \text{around boat} &= 3.2 \times 10^{-3} \text{ torr}\end{aligned}$$

As can be seen from this calculation, large weight increases can be observed for very small pressure gradients. There is also weight increase due to the normal buoyancy effect of the boat in the localised monomer atmosphere but this would be very small compared to the weight increase due to the "thrust" effect.

Two possible ways exist of minimising this problem. To stop the degradation product escaping at high speed from the sample surface and imparting momentum to the boat a new boat was constructed with holes in the side and a quartz window fixed over the top to ensure that the monomer molecules lost most of their momentum within the boat before escaping into the rest of the tube. This boat however proved to be too heavy to maintain the sensitivity of the balance and did little to reduce the weight increase effect.

The other way of reducing this thrust, which proved very successful, was to reverse the molecular flow in the tube by resorting to pumping

out through the top of the apparatus rather than through the bottom as with the original design. By closing the isolation valve above the pumping system but below the sample and pumping out through the top side arm the local pressure gradient around the boat is reduced since the mean free path of the monomer molecules upward away from the boat is increased thus considerably reducing the chances of molecules returning to the locality of the boat. An added advantage of the overhead pumping method is that the pumping rate is increased and any sudden pressure changes can be easily observed since much of the dead volume within the balance itself is left out. These alterations to the balance are represented schematically in Fig. 4.

Preparation and running of samples

Polymer samples were irradiated in the form of films of thickness 4×10^{-4} cm to 1×10^{-3} cm. which were cast directly onto the brass boat used as an irradiation vessel. The films were prepared by placing a weighed amount of polymer powder (10 - 25mg) in the boat, dissolving the powder in a very small quantity of 'Analar' solvent and allowing the solvent to evaporate in air.

The runs were done by first evacuating the sample to approximately 0.07 torr (91 Nm^{-2}), heating the furnace to between 140°C and 180°C and letting the U.V. lamp heat up for 45 minutes with a cover over the end of the silica window in the sample tube. When the pressure had stabilised, the balance was released and the weight changes recorded until constant weight readings were obtained. The cover was then removed and the weight changes noted up to a percentage degradation of about 30%.

The light source

The light source was a G.E.C. Osram 125 watt H.B. low pressure

mercury arc lamp with envelope removed, fed through a choke and condenser. According to Hanovia literature⁵² approximately 90% of the radiation given off by a typical low pressure lamp is of wavelength 253.7 nm. Since longer wavelength radiation is not significantly absorbed by the films used and energy emitted at shorter wavelengths (principally 185 nm) is absorbed by the quartz window, the 253.7 nm radiation was assumed to be the only photolytically active energy in this work. To get suitable rates of degradation (20% degradation in 20-60 minutes), the lamp was placed approximately 120 cm above the sample with a 50 cm tube used to prevent any stray light escaping.

Molecular weight measurements

The apparatus shown in Fig. 5 was used to prepare samples for molecular weight change measurements and to check the validity of the runs on the thermobalance. Samples were run for a short time, weighed and re-run, weighed and re-run etc. to obtain plots of time against percent degradation for comparison with those obtained from the same samples under similar conditions in the thermobalance. The results were found to agree, showing that the adapted thermobalance was suitable but much faster than the normal reweigh - rerun technique.

To measure molecular weight changes, samples were run in this apparatus for varying short lengths of time (5 - 50 minutes), then removed, made up into solutions of known concentration for viscometry. Although viscometry is not absolute as in osmometry or light scattering,⁵³ it is a rapid method with relatively few sources of experimental error.

Before going further, the following definitions should be made:⁵⁴

$$\text{relative viscosity (viscosity ratio)} = \eta_{\text{rel}} = \frac{\eta}{\eta_0} \approx t/t_0$$

where t_0 is the flow time of the solvent through a viscometer and t is the flow time through the same viscometer of a dilute solution of

polymer.

$$\text{specific viscosity} = \eta_{sp} = (\eta_{rel}) - 1 \approx \frac{t - t_0}{t_0}$$

$$\text{reduced viscosity} = \eta_{red} = \frac{\eta_{sp}}{C}$$

where C is the concentration of the polymer solution in gm/100ml

$$\text{inherent viscosity} = \eta_{inh} = \frac{\ln \eta_{rel}}{C}$$

$$\text{intrinsic viscosity} = [\eta] = \lim_{C \rightarrow 0} \left(\frac{\eta_{sp}}{C} \right) = \lim_{C \rightarrow 0} \left(\frac{\ln \eta_{rel}}{C} \right)$$

The determination of intrinsic viscosity requires the preparation of dilute solutions of the polymer in a suitable solvent. The viscosities of the solutions are then measured relative to that of the solvent. The intrinsic viscosity is obtained by extrapolation to zero concentration of a plot of either reduced viscosity or inherent viscosity. A correlation between intrinsic viscosity and molecular weight for linear polymers is achieved through the Mark-Houwink equation^{54,55} where M is molecular

$$[\eta] = KM^a$$

weight, K and a are constants for a particular polymer-solvent system. The constants K and a are determined by the intercept and slope, respectively, of a log-log plot of intrinsic viscosity and molecular weight. The molecular weights used in such a plot are determined by one of the absolute methods such as osmometry or light scattering. The value of a will be in the range 0.6 to 0.8 for most systems.

An equation has been developed for determining intrinsic viscosity by a single point determination for dilute solutions⁵⁶ but according

$$[\eta] = \left[\frac{(2)}{C} \right] (\eta_{sp} - \ln \eta_{rel})^{\frac{1}{2}}$$

to Bovey et al⁵⁵ the inherent viscosity of a single sufficiently dilute

solution ($c \approx 0.1\text{gm}/100\text{ml}$) is frequently taken as approximately equal to intrinsic viscosity.

The molecular weight changes due to degradation for the poly (isobutylmethacrylate) samples were estimated from the intrinsic viscosities of acetone solutions at 25°C using the equation⁵⁷

$$[\eta] = 0.199 \times 10^{-5} M^{0.94}$$

based on weight average molecular weights obtained from light scattering data. Intrinsic viscosities were determined by dilution in a suspended level BS/IP/S2 viscometer (Volac 1933) having a flow time of about 118 secs for acetone at $25.0 \pm 0.1^{\circ}\text{C}$. There is a great tendency for the solutions to pick up dust so the viscometer was charged, cleaned and dried through a sinter at all times.

Results

Molecular weight determination

The molecular weights of the two samples used were determined by viscosity measurements of dilute solutions in acetone. Using solutions of 0.05%, 0.10%, 0.15% and 0.20% polymer concentration, the sample polymerised with 0.1% "bisto" was found to have a molecular weight of 2.71×10^6 . Using solutions of 0.20%, 0.40%, 0.60% and 0.80% polymer concentration, the sample polymerised with 0.6% bisto was found to have a molecular weight of 3.09×10^5 . Figs. 6 and 7 show the graphical determination of $[\eta]$.

Analysis of kinetic data

a) Order of Reaction with respect to weight.

The order n of a reaction can be determined from t/P versus t plots, using a method devised by Williamson⁵⁸ based on the equation

$$\frac{1}{K} + \frac{nt}{2} = \frac{t}{P}$$

derived from the general rate equation $\frac{-dw}{dt} = kw^n$ written as

$$\frac{-d(1-P)}{dt} = K(1-P)^n \quad \text{where } P = \text{fractional conversion.}$$

Plotting t/P versus t gives a straight line with a slope of $n/2$ and an intercept of $\frac{1}{K}$.

By applying the criterion put forward by MacCallum⁸ that an order of 0 to 1 indicates end initiation while 1 - 2 indicates random scission it is therefore possible to define the initial mechanism of the reaction from the apparent order calculated from one series of runs of different sample weights at different temperatures.

The apparent order can be checked using the integrated rate

equation to give

$$\frac{1}{n-1} \left(\frac{1}{w^{n-1}} - \frac{1}{w_0^{n-1}} \right) = kt$$

derived from $-\frac{dw}{dt} = kw^n$

Values for $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} - 1 \right]$ are plotted against t for each of the runs in the series. If the result is a series of straight lines, it can be assumed that the average order calculated would be a good approximation to the true order.

b) Rate constants

The rate of a reaction is given by $-\frac{dw}{dt} = kw^n$. In both reactions it is necessary for the k to have the units of a first order rate constant (time^{-1}). The rate equation becomes $-\frac{dw}{dt} = \frac{Kw^n}{w_0^{n-1}}$ where $K = kw_0^{n-1}$ has units of time^{-1} and can be considered to be a true rate constant. The slope of a plot of

$$\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} - 1 \right] \text{ versus } t \text{ is } K$$

$$\text{since } \frac{1}{n-1} \left[\frac{1}{w^{n-1}} - \frac{1}{w_0^{n-1}} \right] = kt = \frac{K}{w_0^{n-1}} t$$

c) Overall Activation Energy

The experimental activation energy, E_a , is usually defined by the Arrhenius equation. $K = Ae^{-E_a/RT}$ where $A =$ a constant, $R =$ gas constant and $T =$ temperature in $^{\circ}\text{K}$. A graphical solution for E_a may be obtained from the slope of a plot of $\log K$ versus $\frac{1}{T}$.

10, 15, 20 and 25mg of poly (isobutylmethacrylate) of molecular weight 2.71×10^6 were cast as films from chloroform, methylene chloride and benzene and degraded at 140, 150, 160, 170 and 180 $^{\circ}\text{C}$ on the adapted thermobalance. The information obtained of weight

loss against time was analysed as indicated above giving results as shown in tables 1, 2 and 3. A similar analysis was carried out on 10, 20 and 25 mg of poly(isobutylmethacrylate) of molecular weight 3.09×10^5 cast as films from chloroform and degraded at 150, 160, 170 and 180°C. The results obtained are shown in table 4.

Molecular weight changes

25 and 50 mg of both samples of poly(isobutylmethacrylate) were degraded at 160°C and 180°C and the molecular weights of the samples determined by viscometry after varying times of irradiation. The results are shown in Fig. 31.

Preheating of samples

It was observed that if a sample was heated for a prolonged period in vacuum before U.V. degradation was allowed to begin, the rate of degradation was substantially reduced. Various tests were made using different combinations of the possible variables which might effect the rate of degradation i.e.

- 1). The length of time the sample is evacuated.
- 2). The length of time the sample is heated.
- 3). The solvent used to cast the film. The results of these tests are shown in Fig. 32 and table 5.

FIGURE 2

STANTON THERMOBALANCE (UNALTERED)

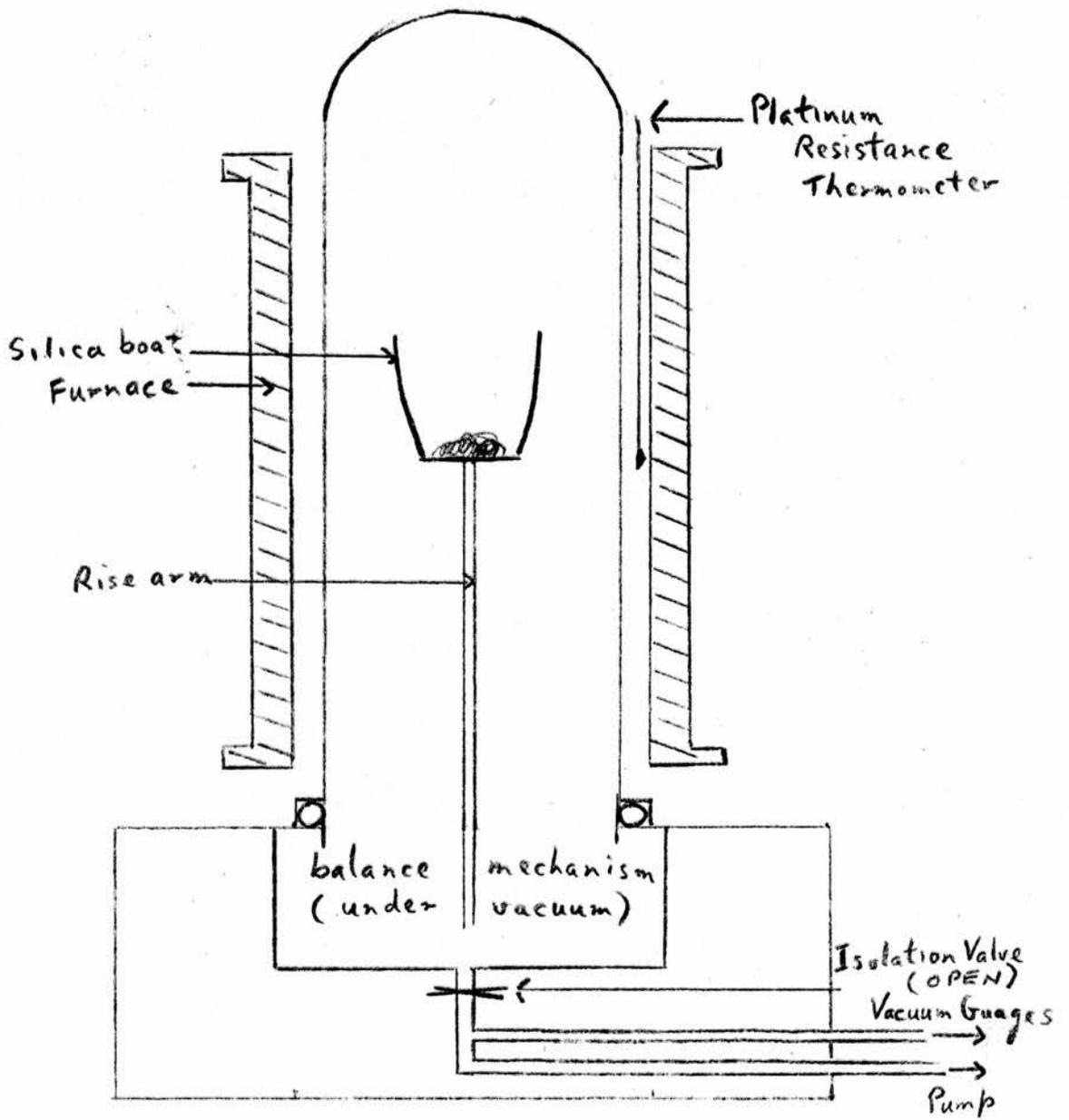


FIGURE 3

TYPICAL THERMOBALANCE RUN

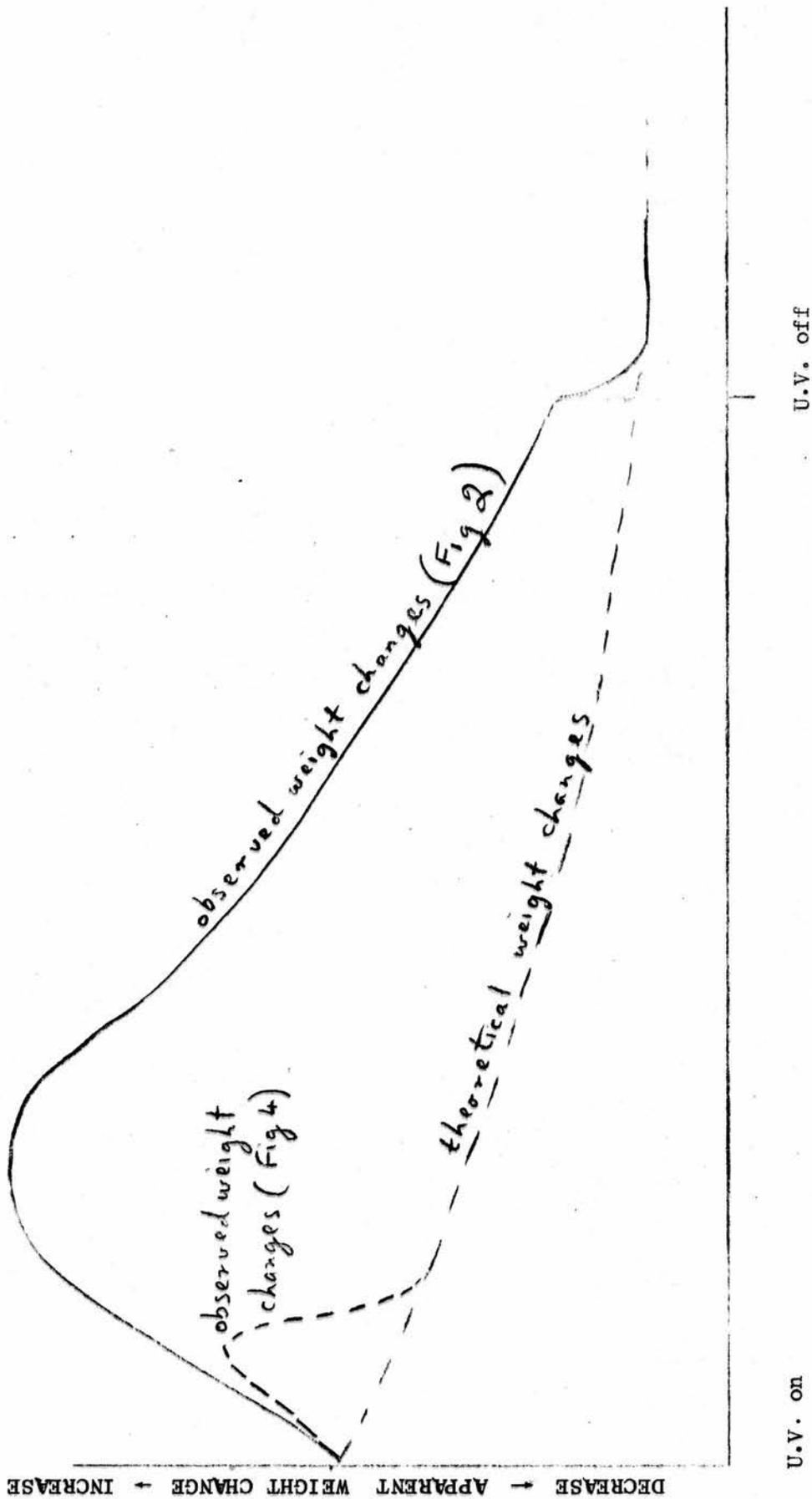
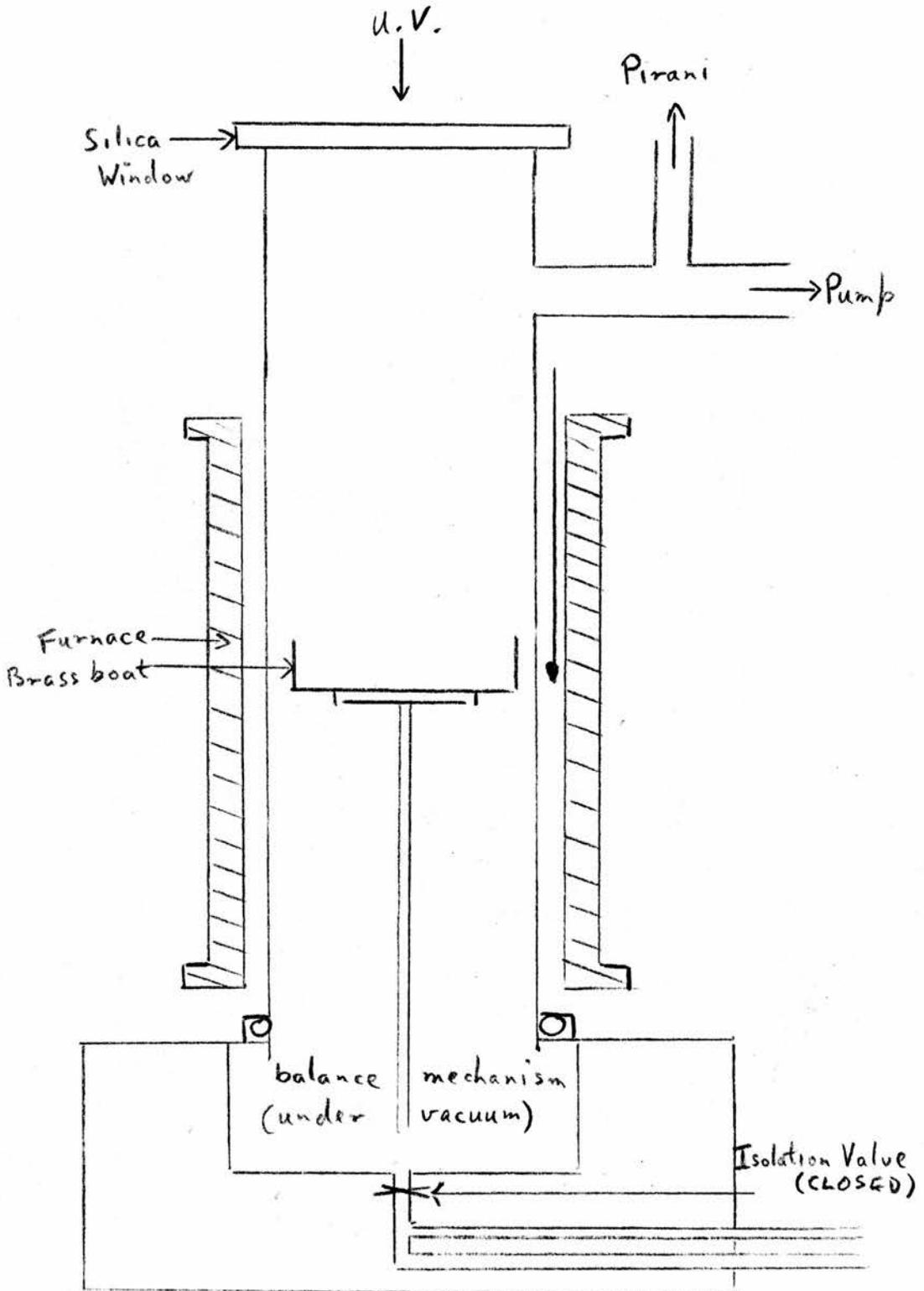


FIGURE 4

STANTON THERMOBALANCE (CONVERTED)



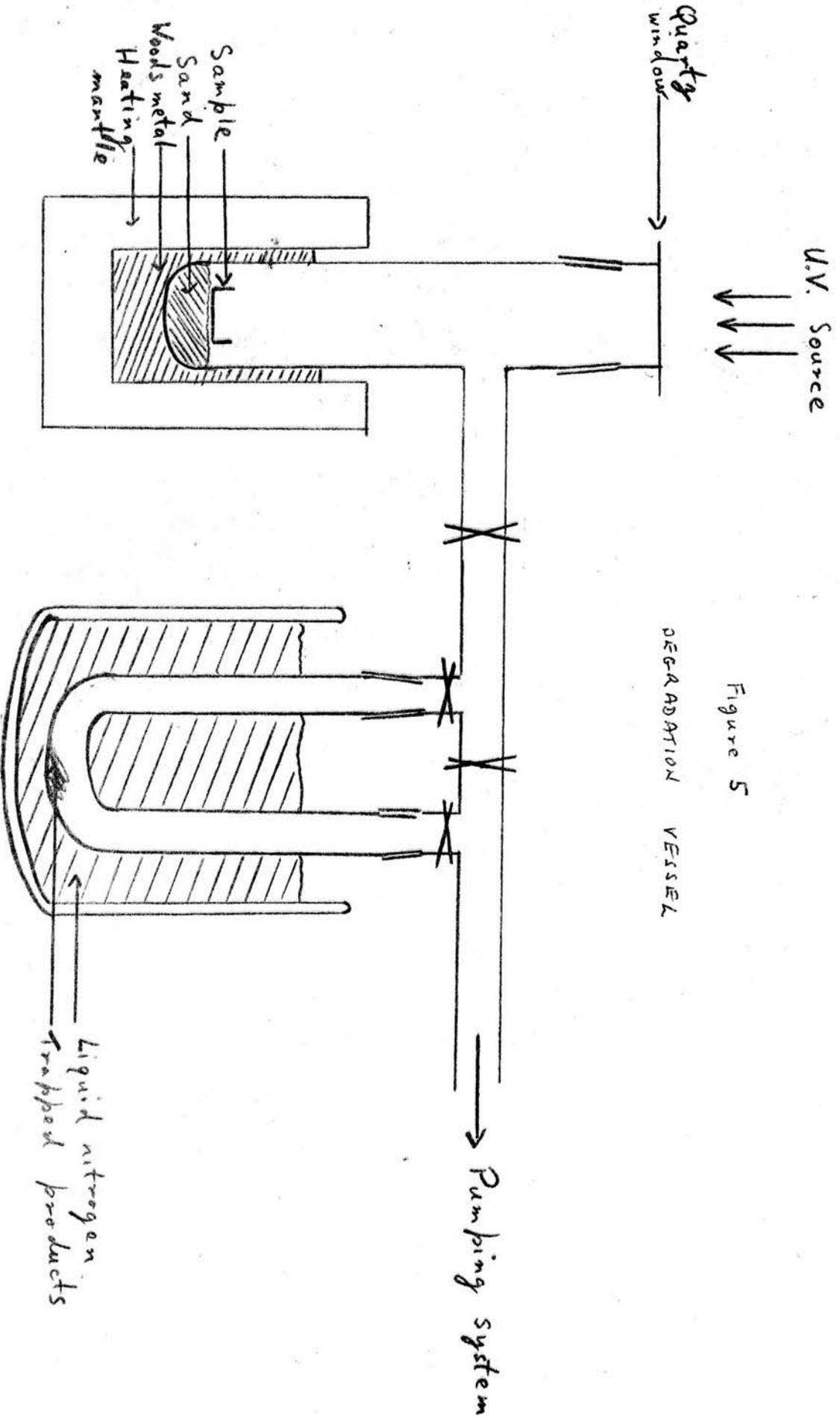


Figure 5

FIGURE 6

INTRINSIC VISCOSITY DETERMINATION FOR SAMPLE PIBMA 1

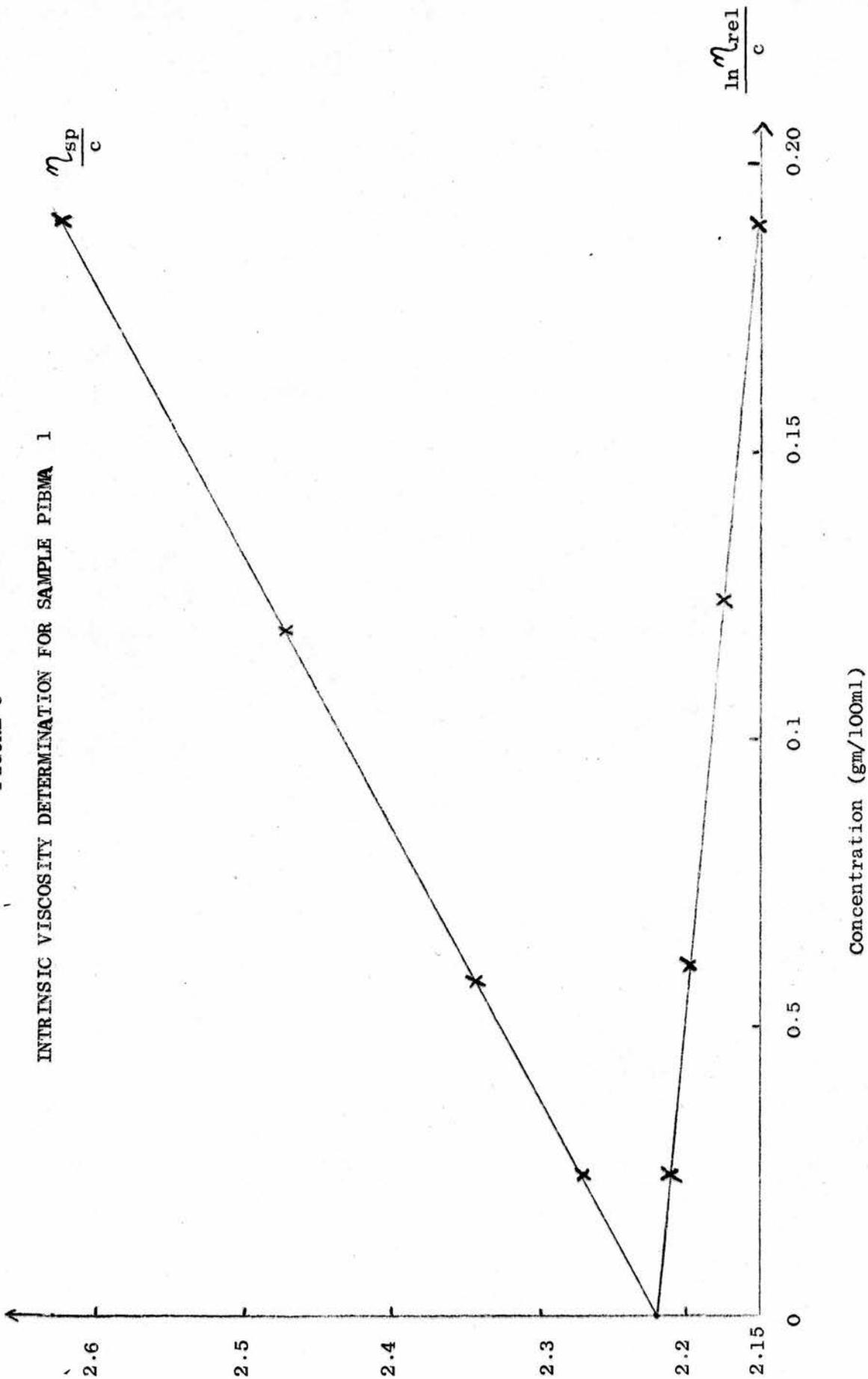


FIGURE 7

INTRINSIC VISCOSITY DETERMINATION FOR SAMPLE PIBMA 2

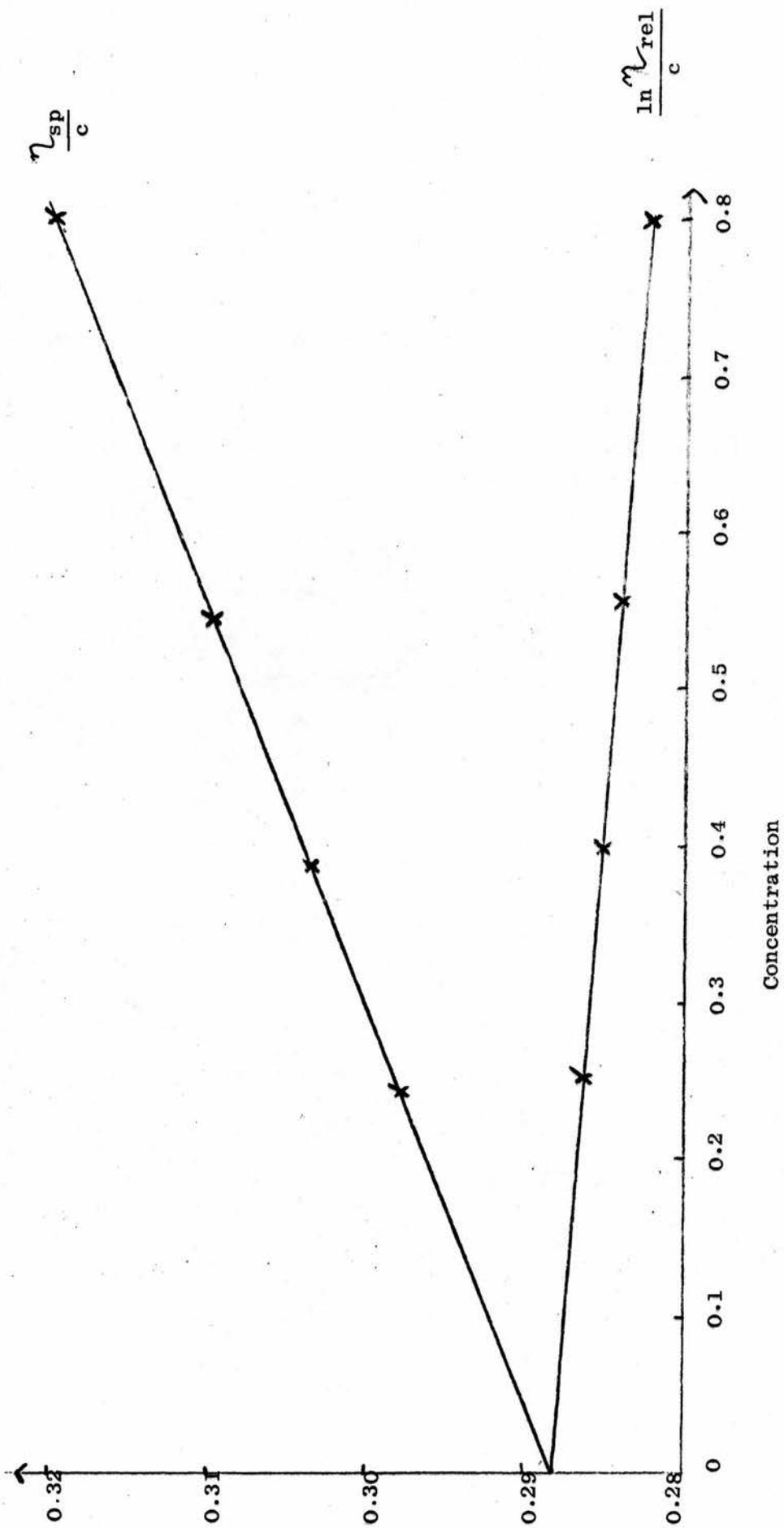


FIGURE 8

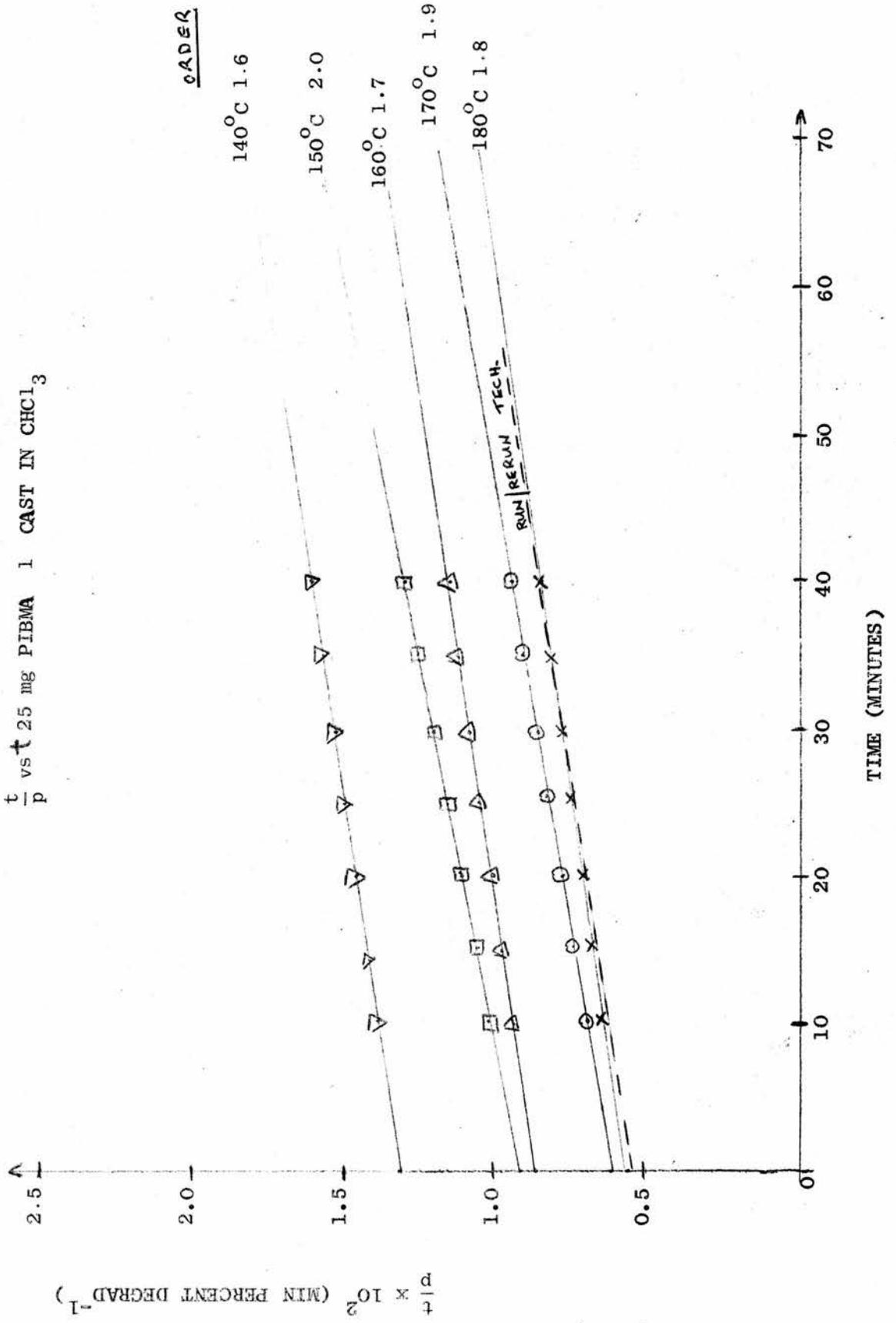


FIGURE 9

$$\frac{1}{0.9} \left[\left(\frac{w_0}{w} \right)^{0.9} - 1 \right] \text{ vs } t \text{ 10 mg PIBMA 1 CAST IN CHCl}_3$$

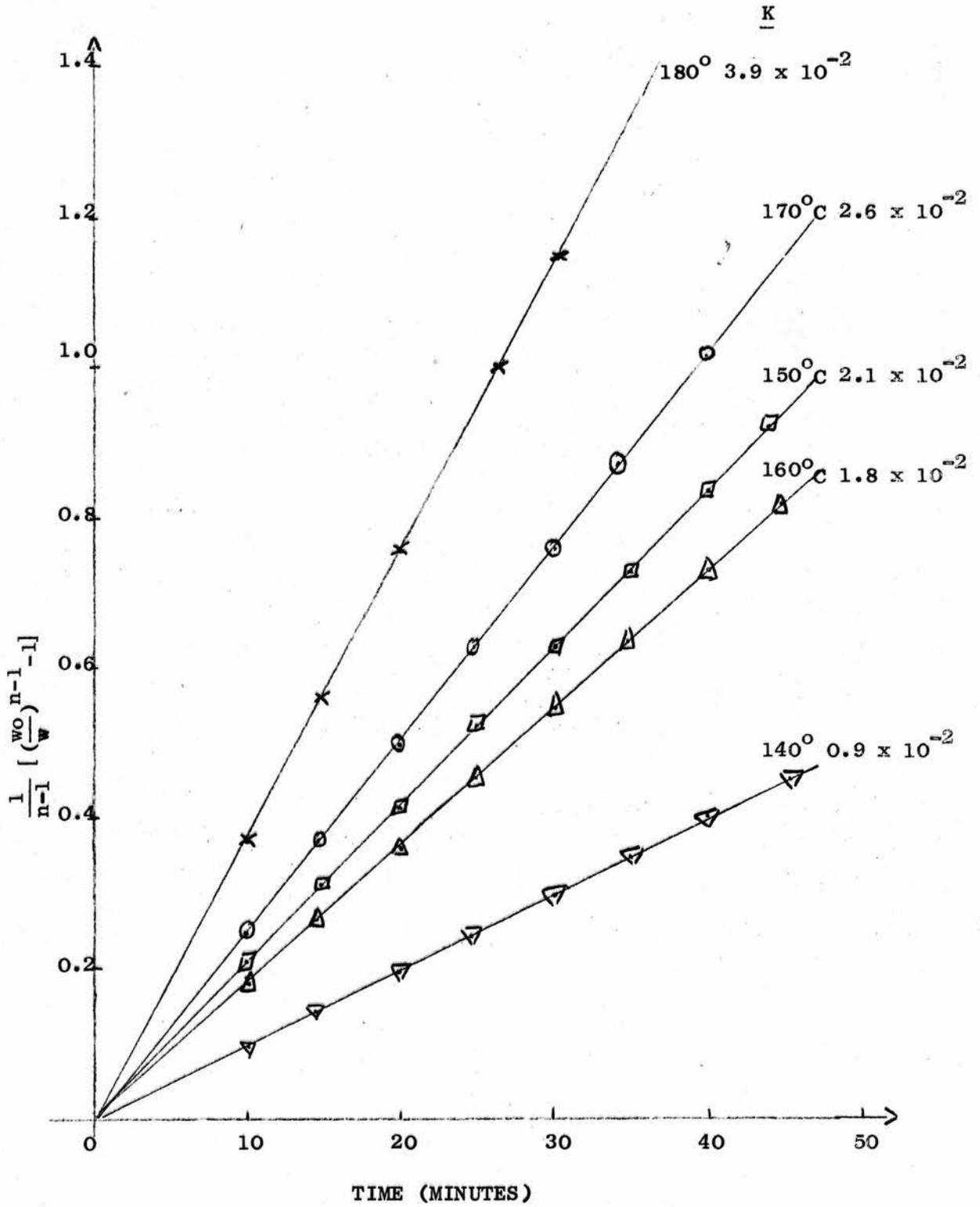


FIGURE 10

$\frac{1}{0.9} \left[\left(\frac{w_0}{w} \right)^{0.9} - 1 \right]$ vs t 15 mg PIBMA 1 CAST IN CHCl_3

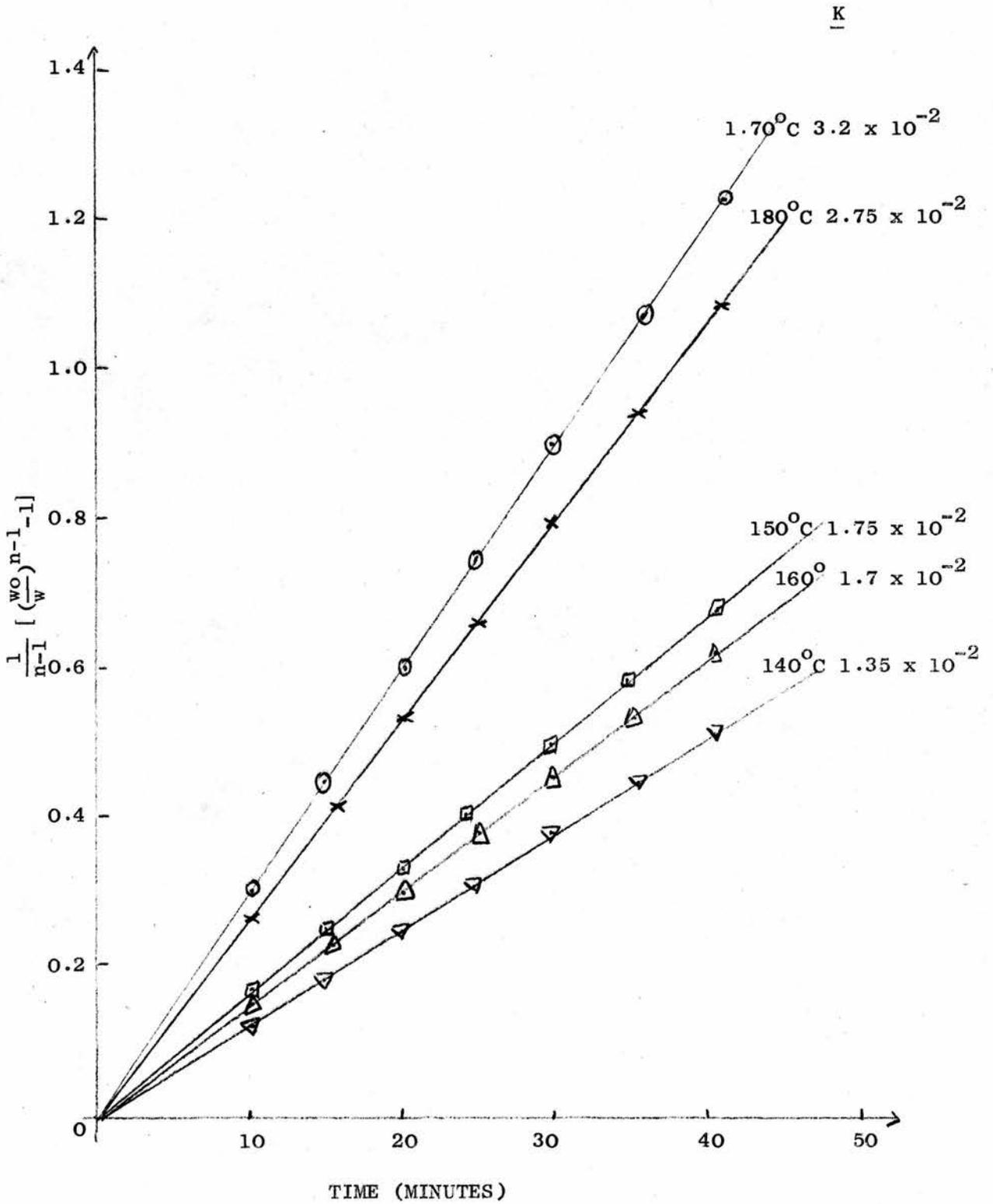


FIGURE 11

$\frac{1}{0.9} \left[\left(\frac{w_0}{w} \right)^{0.9} - 1 \right]$ vs t 20 mg PIBMA 1 CAST IN CHCl_3

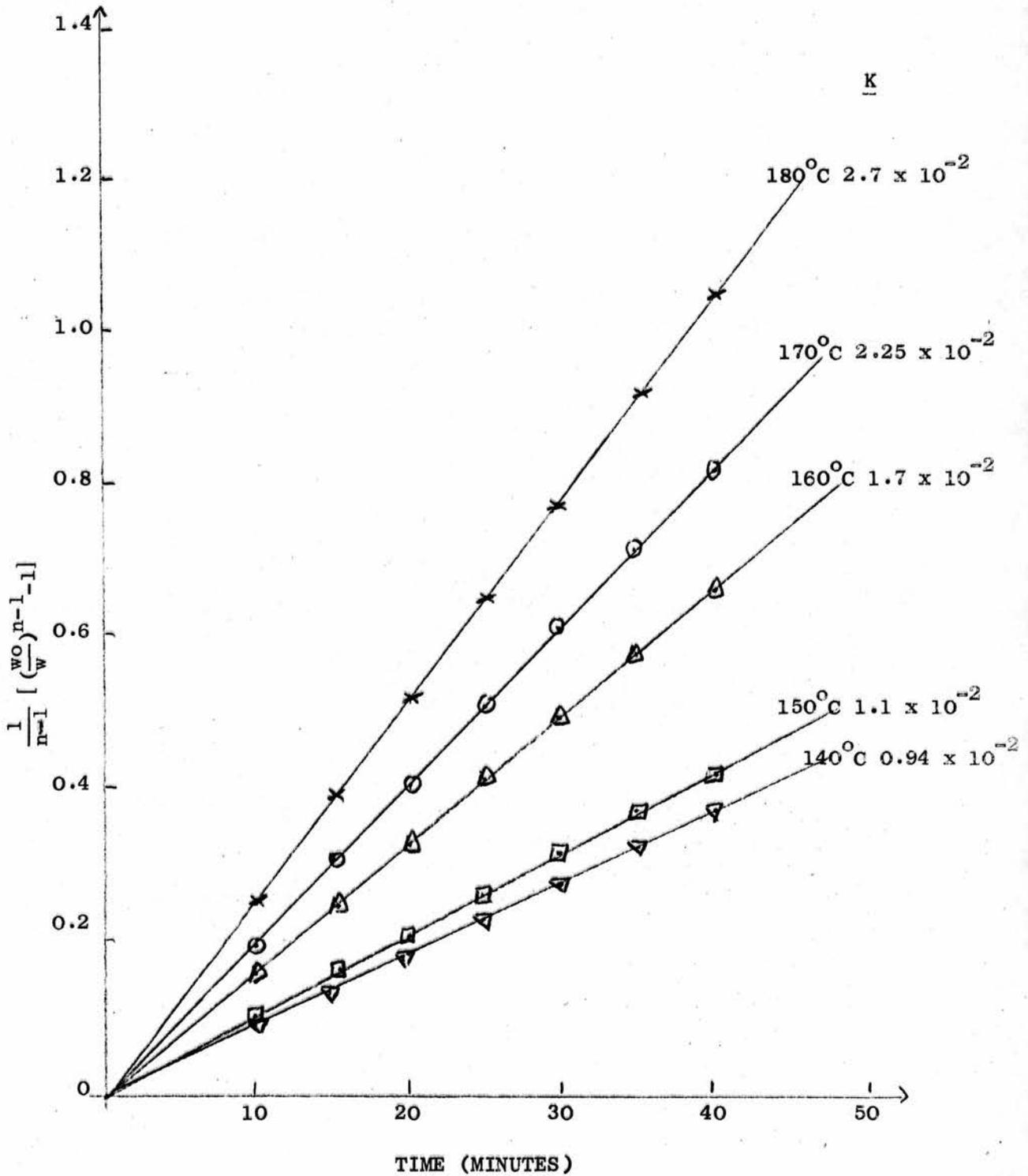


FIGURE 12

$\frac{1}{0.9} \left[\left(\frac{w_0}{w} \right)^{0.9} - 1 \right]$ 25 mg PIBMA 1 CAST IN CHCl_3

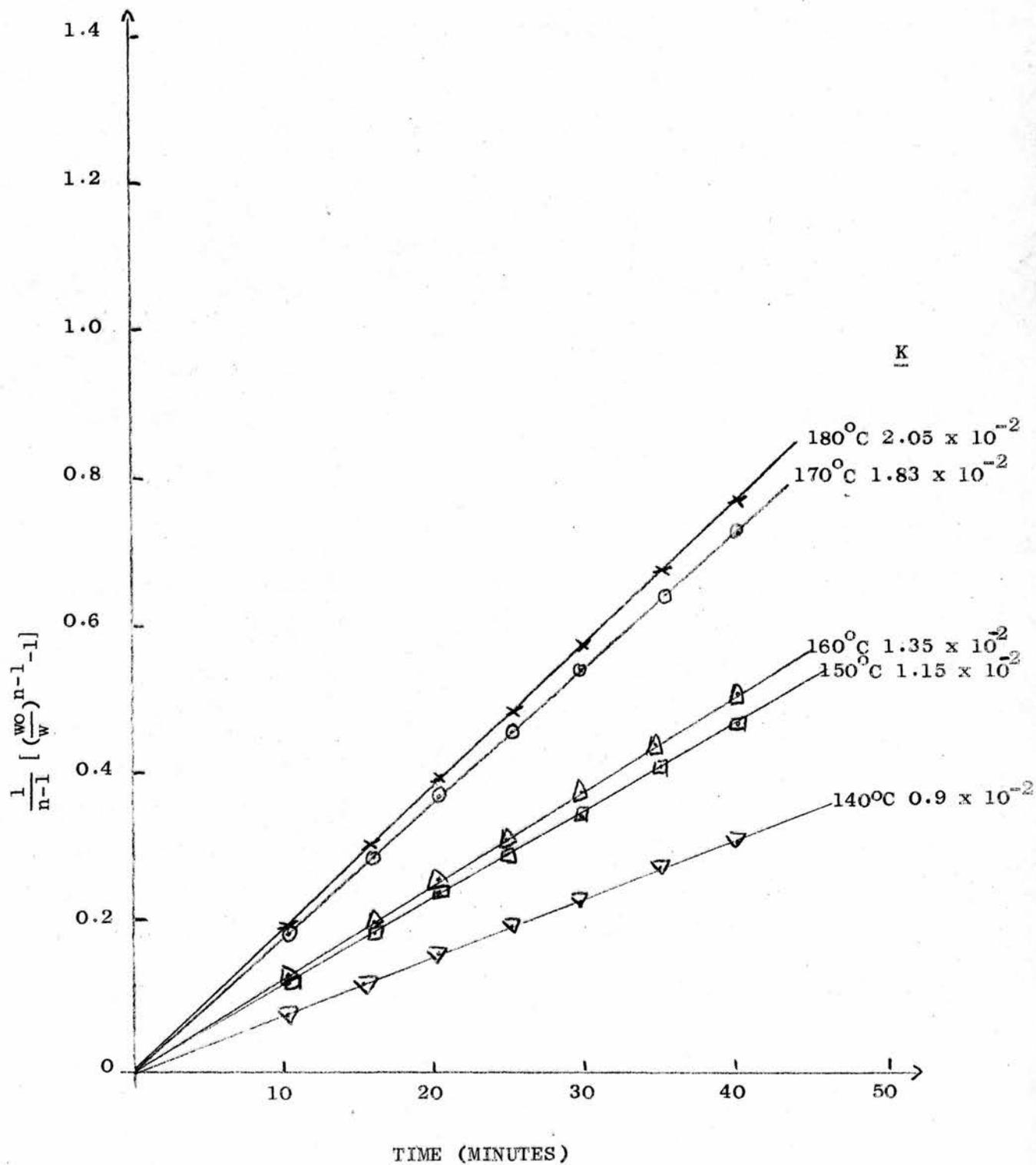


FIGURE 13

log K Vs $1/T$ 25 mg PIBMA 1 CAST IN CHCl_3

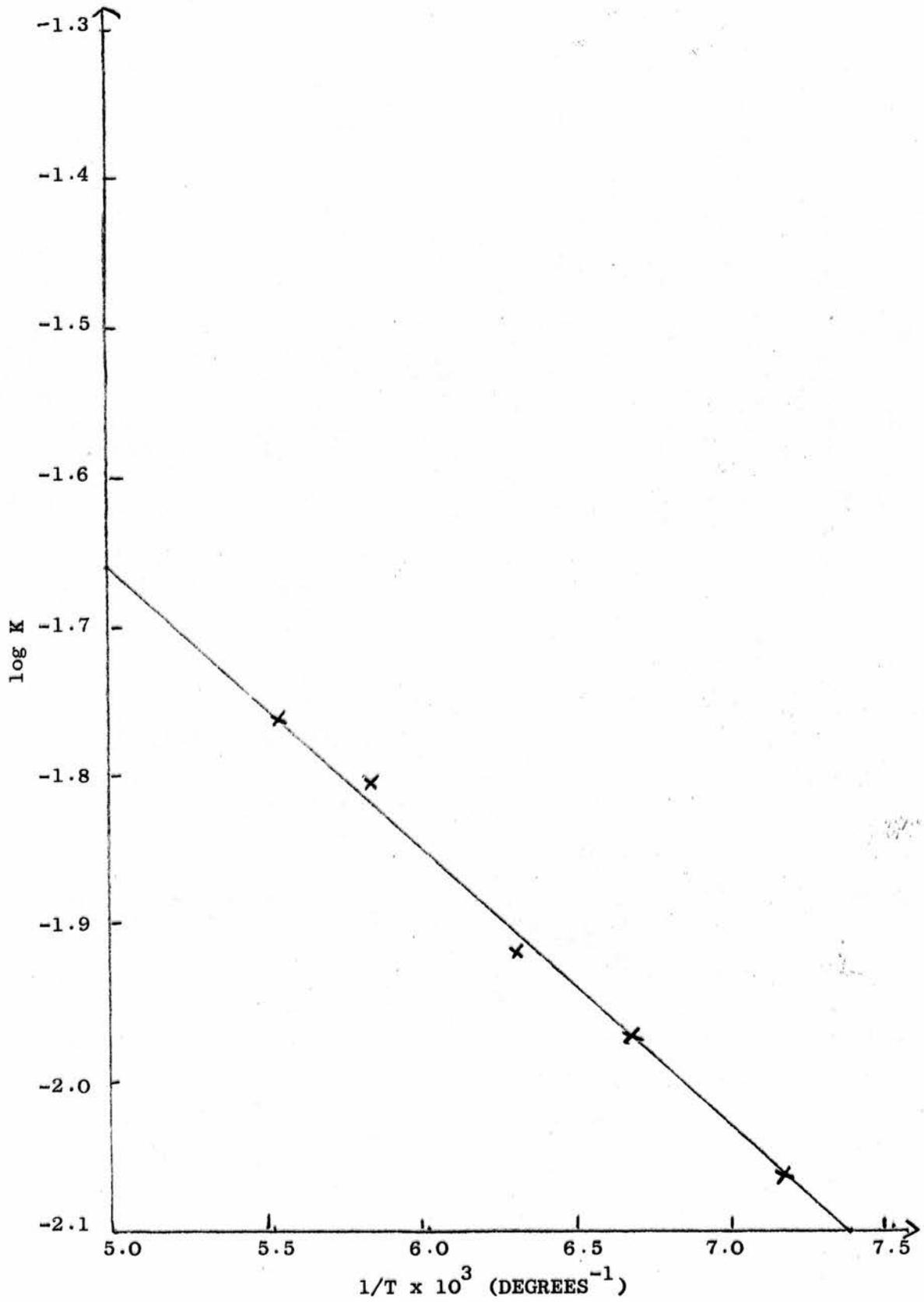


FIGURE 14

$\frac{t}{p}$ vs. t 20 mg PIBMA 1 CAST IN CH_2Cl_2

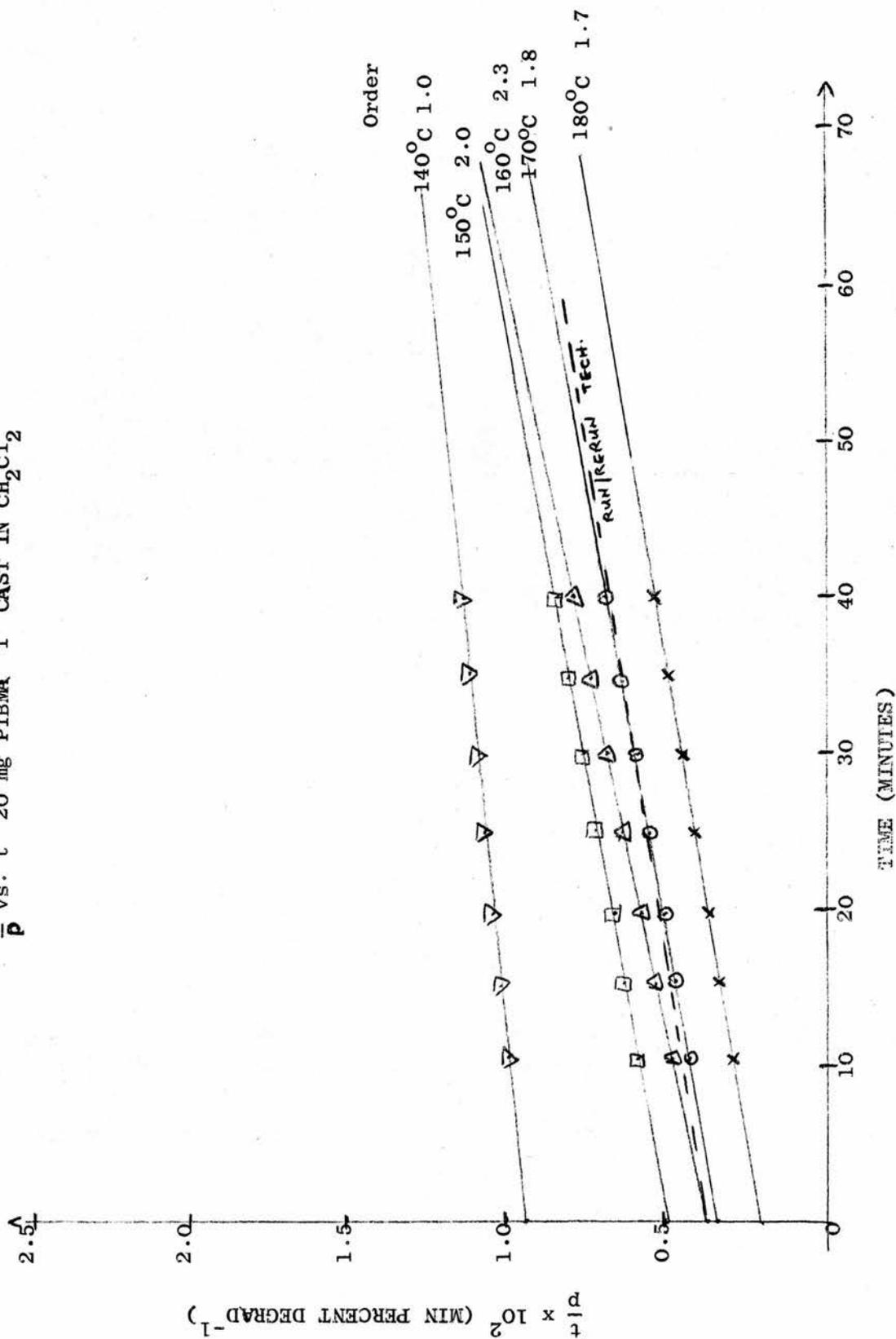


FIGURE 15

$\frac{1}{0.6} \left[\left(\frac{w_0}{w} \right)^{0.6} - 1 \right]$ vs t 10 mg PIBMA 1 CAST IN CH_2Cl_2

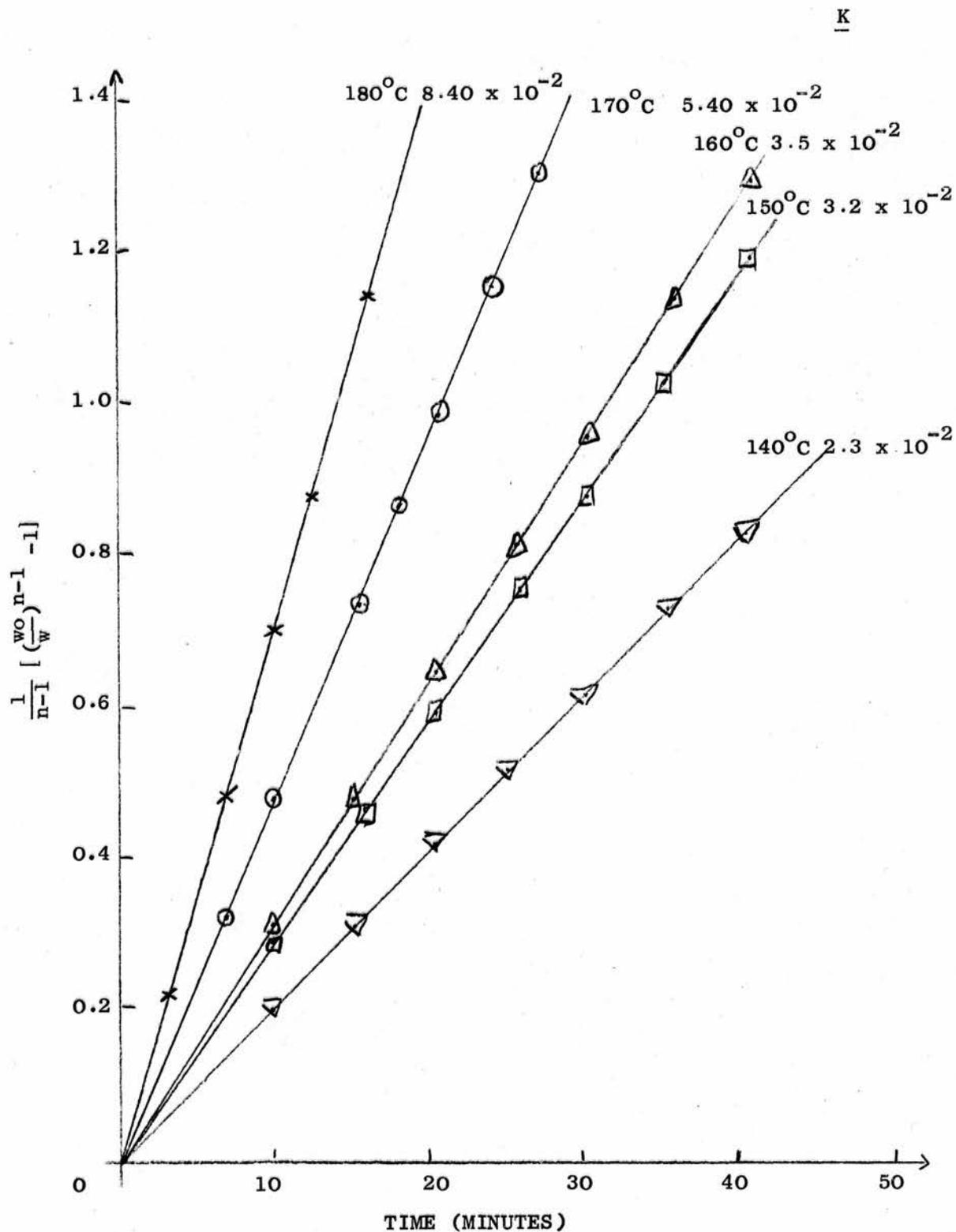


Figure 16

$\frac{1}{0.6} \left[\left(\frac{w_0}{w} \right)^{0.6} - 1 \right]$ vs t 15 mg PIBMA 1 CAST IN CH_2Cl_2

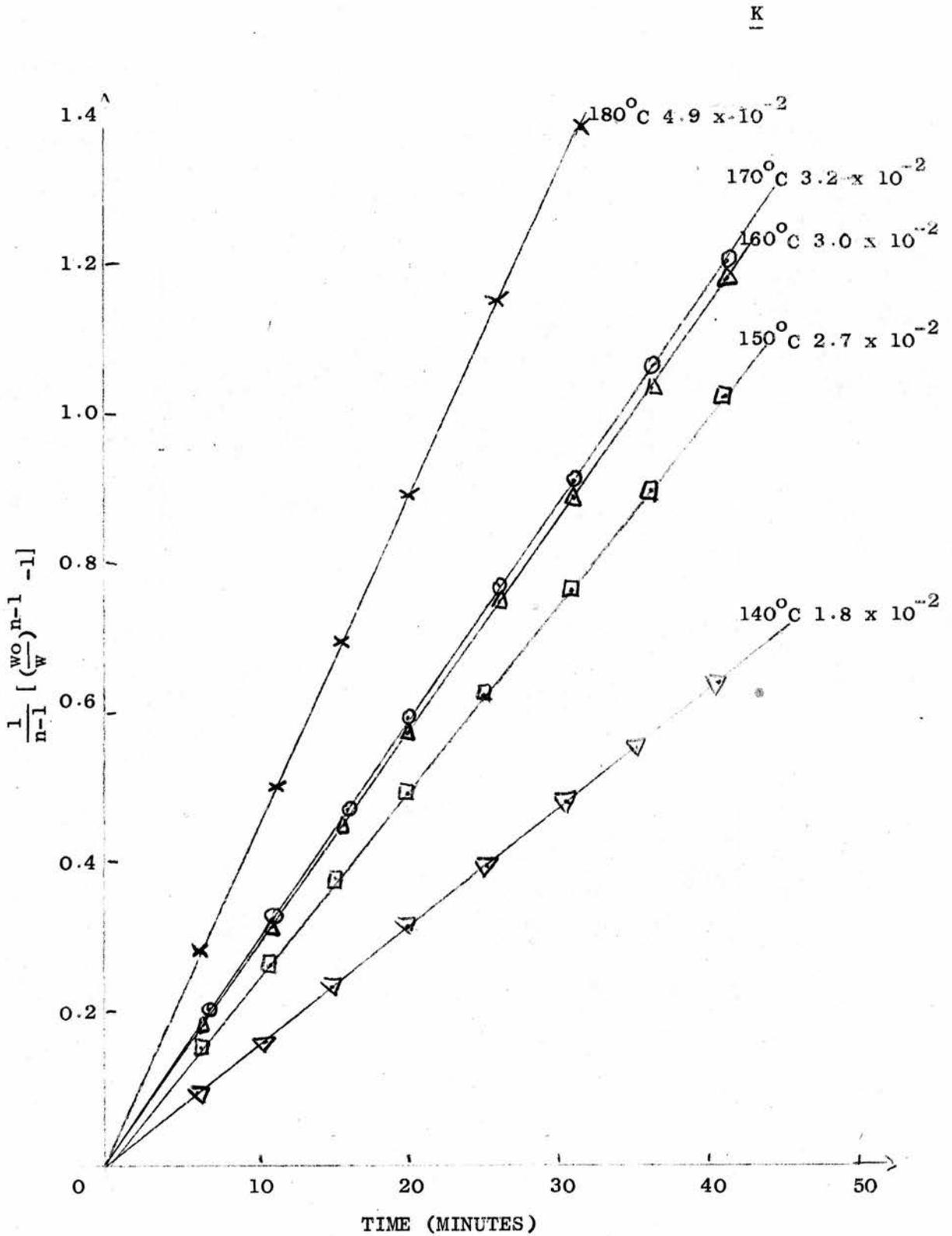


FIGURE 17

$\frac{1}{0.6} \left[\left(\frac{w_0}{w} \right)^{0.6} - 1 \right]$ vs t 20 mg PIBMA 1 CAST IN CH_2Cl_2

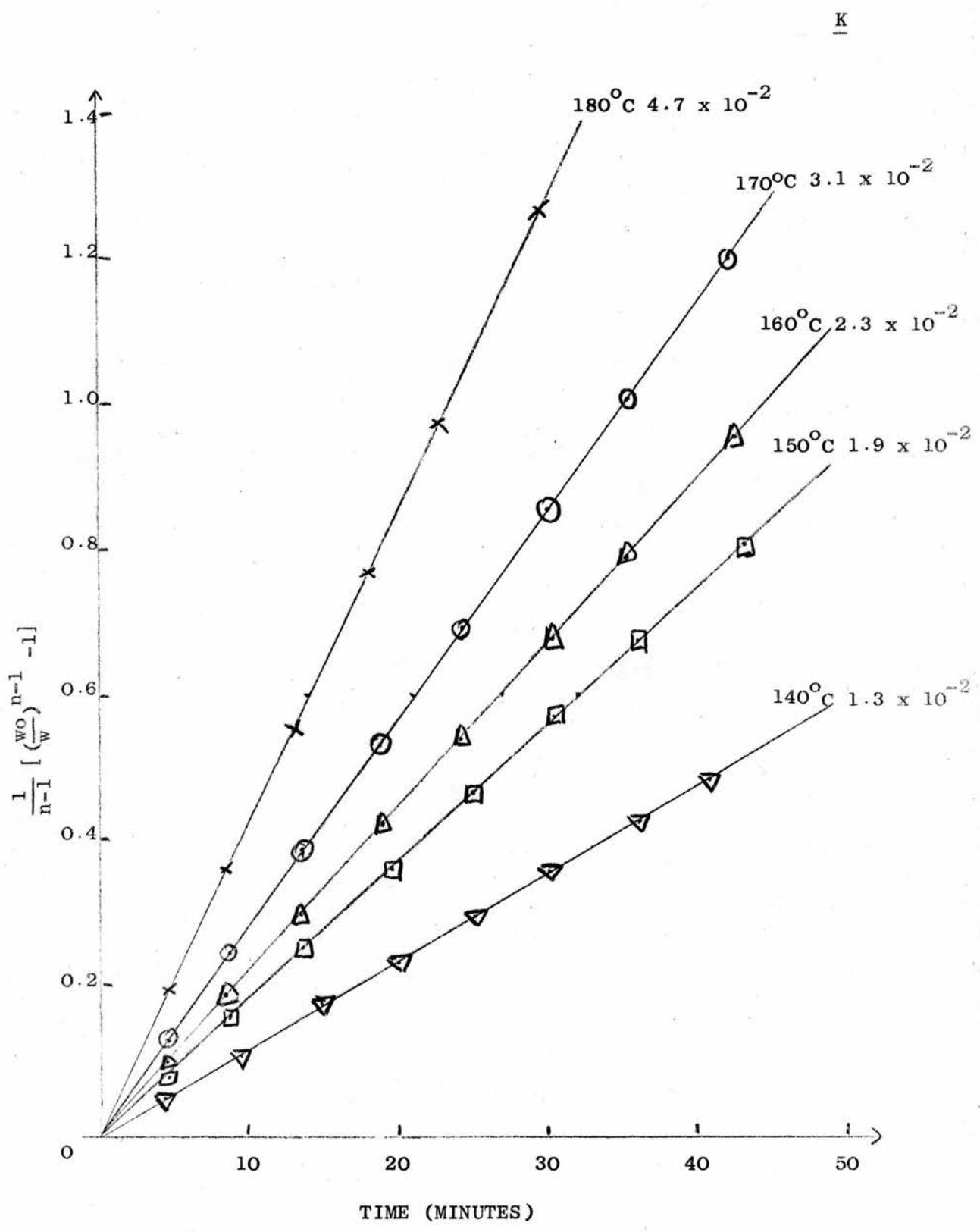


FIGURE 18

$\frac{1}{0.6} \left[\left(\frac{w_0}{w} \right)^{0.6} - 1 \right]$ vs t 25 mg PIBMA 1 CAST IN CH_2Cl_2

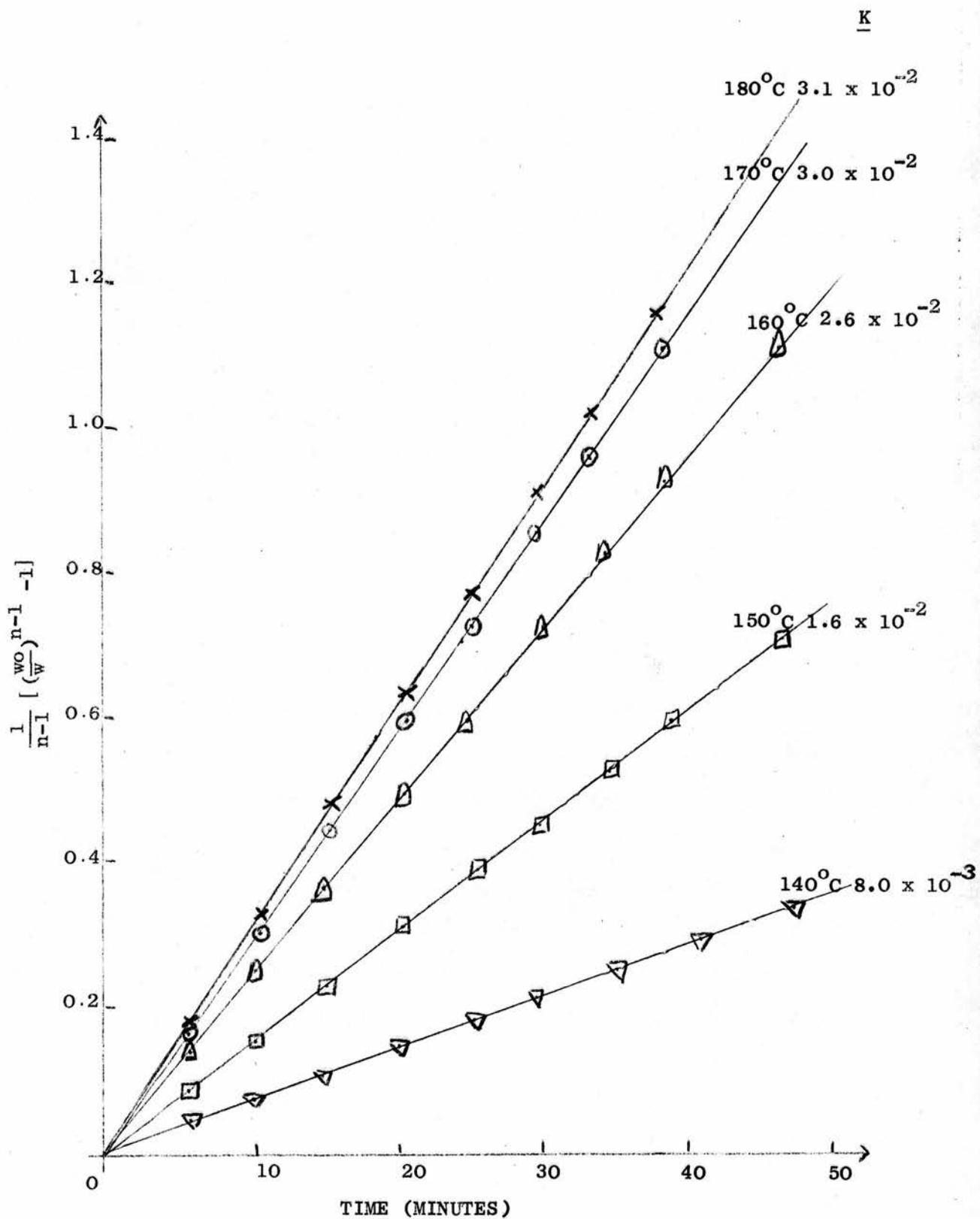


FIGURE 19

log K vs $1/T$ 20mg PIBMA 1 CAST IN CH_2Cl_2

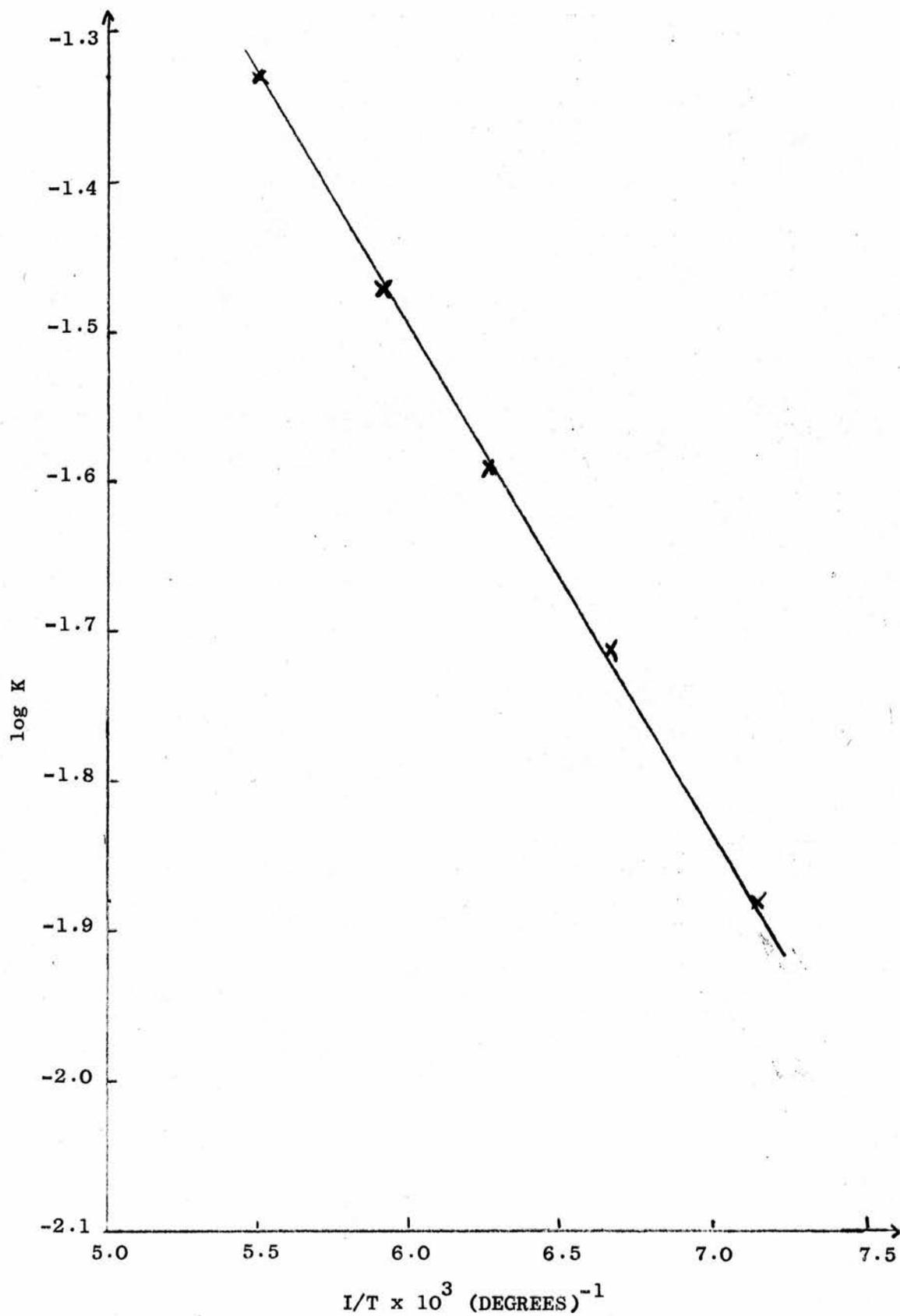


FIGURE 20

$\frac{t}{p}$ vs t 20 mg PIBMA 1 CAST IN BENZENE

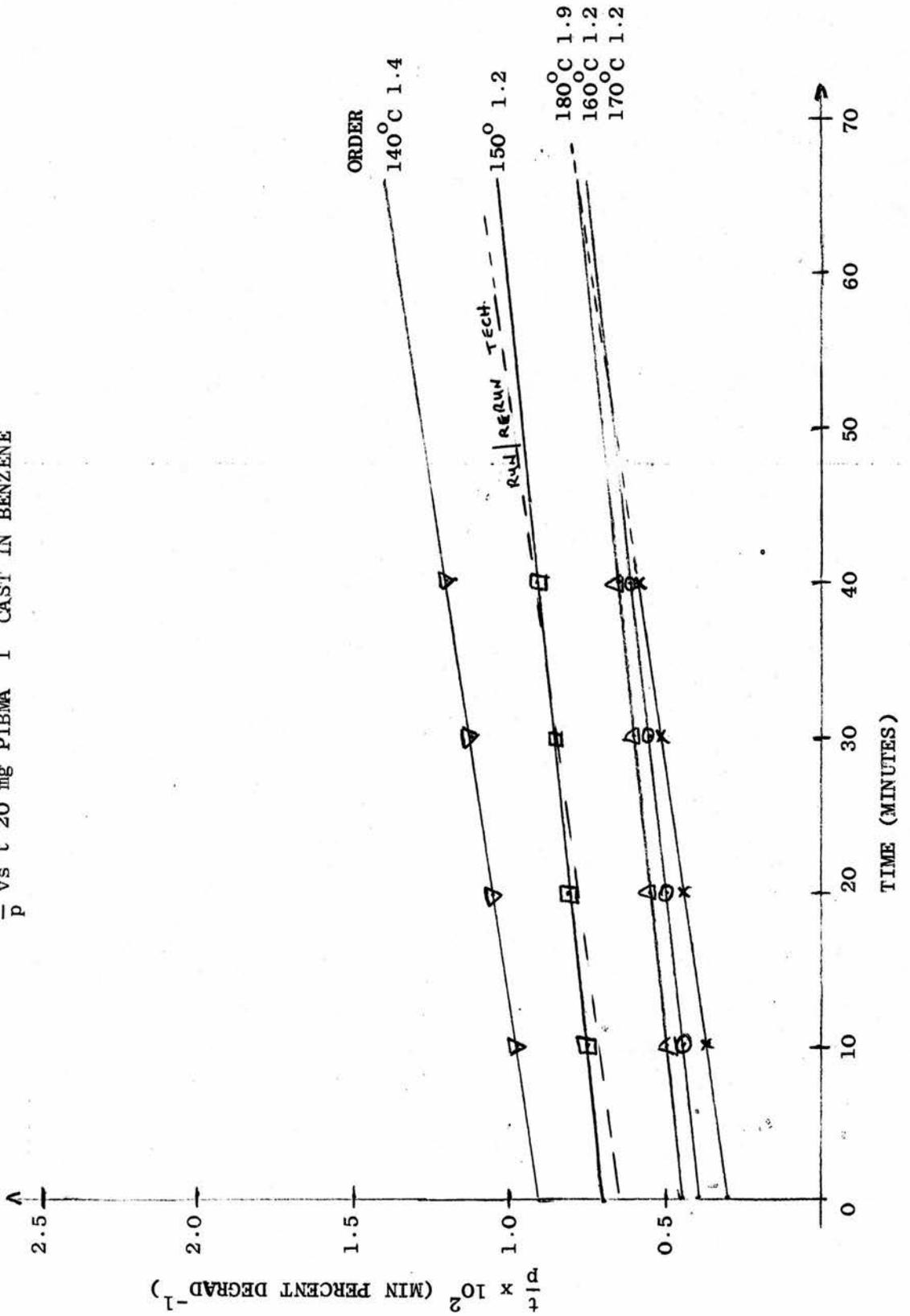


FIGURE 21

$\frac{1}{0.4} \left[\left(\frac{w_0}{w} \right)^{0.4} - 1 \right]$ vs t 10 mg PIBMA 1 CAST IN BENZENE

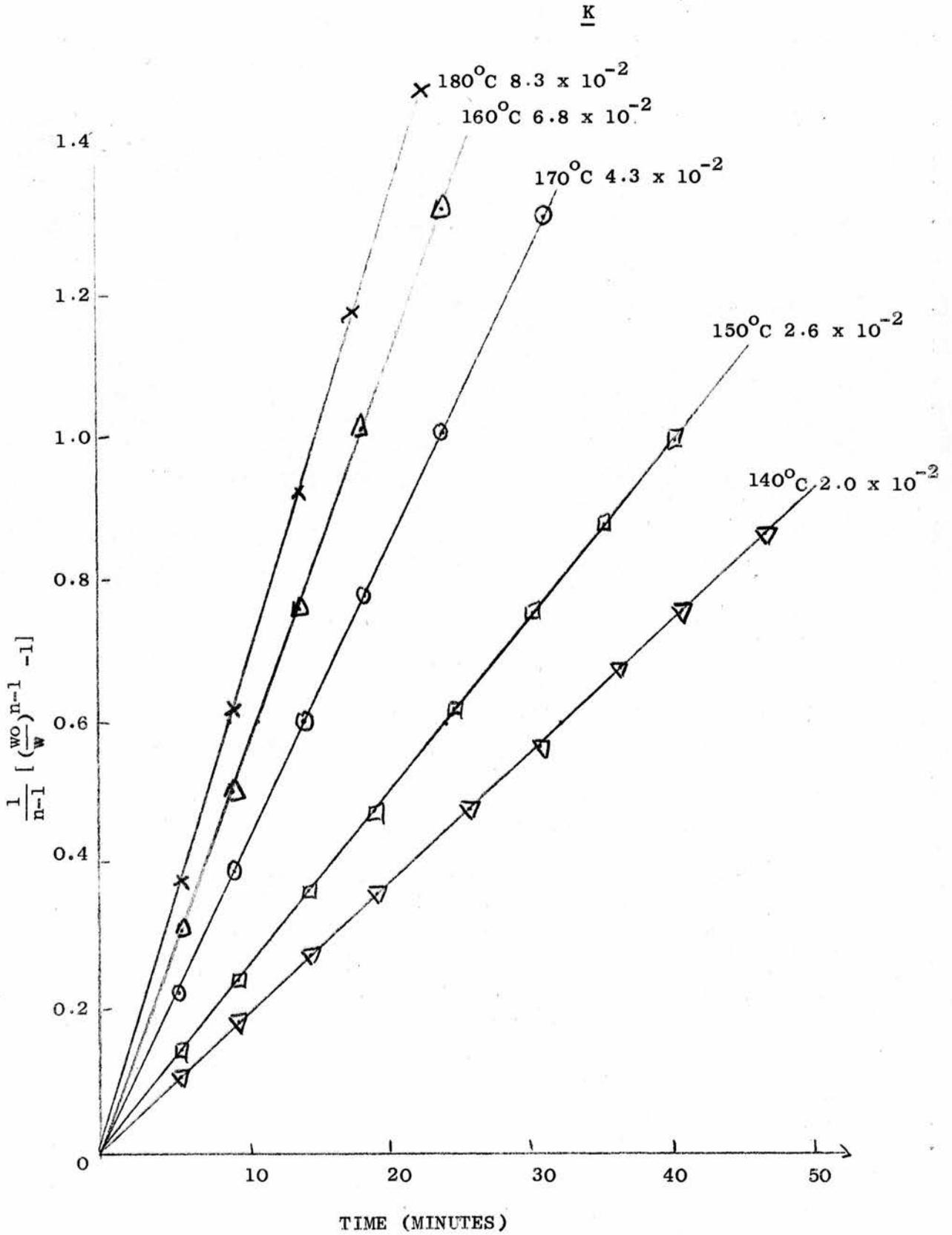


FIGURE 22

$\frac{1}{0.4} \left[\left(\frac{w_0}{w} \right)^{0.4} - 1 \right]$ vs t 15 mg PIBMA 1 CAST IN BENZENE

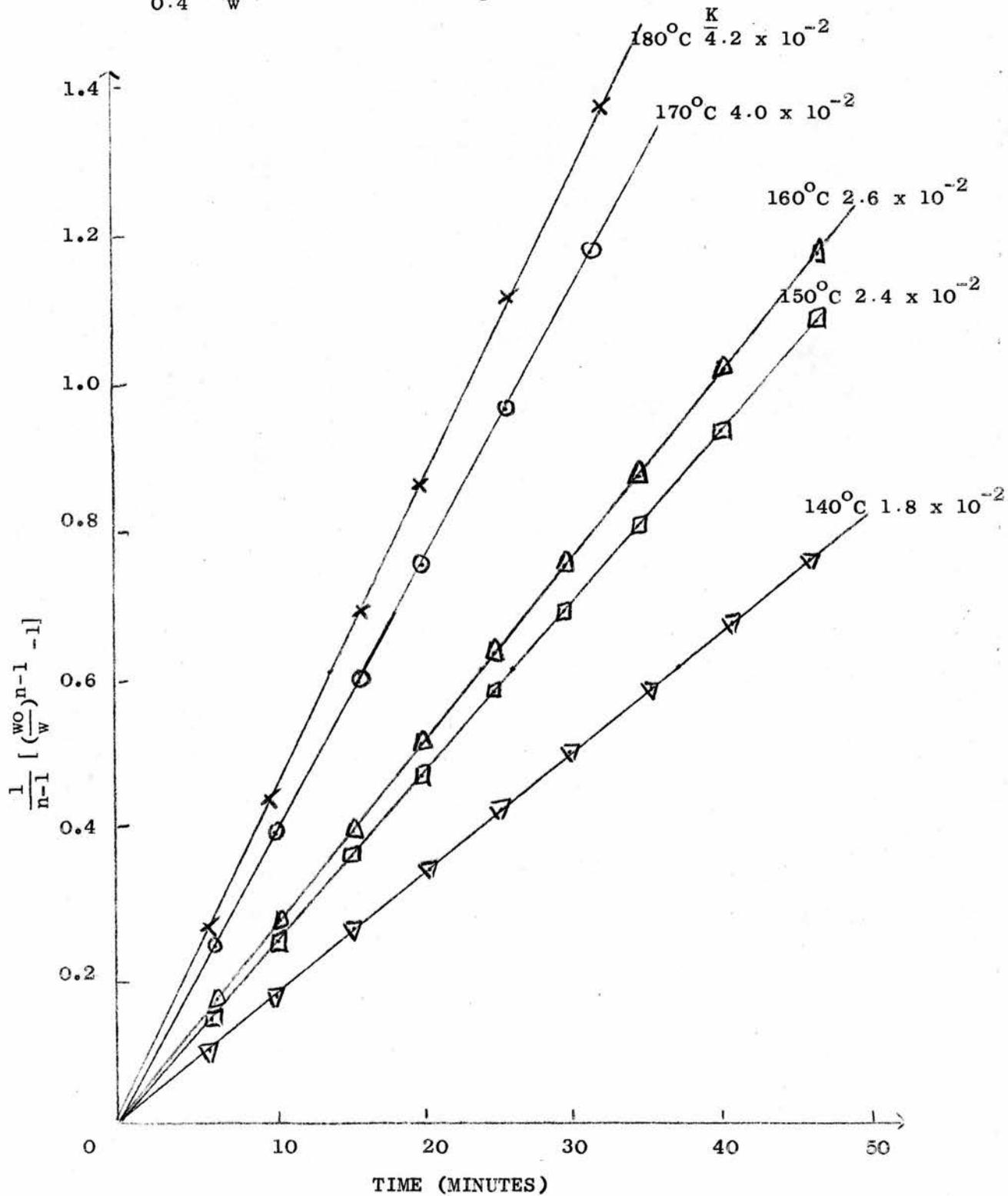


FIGURE 23

$\frac{1}{0.4} \left[\left(\frac{w_0}{w} \right)^{0.4} - 1 \right]$ vs t 20 mg PIBMA 1 CAST IN BENZENE $\frac{K}{K}$

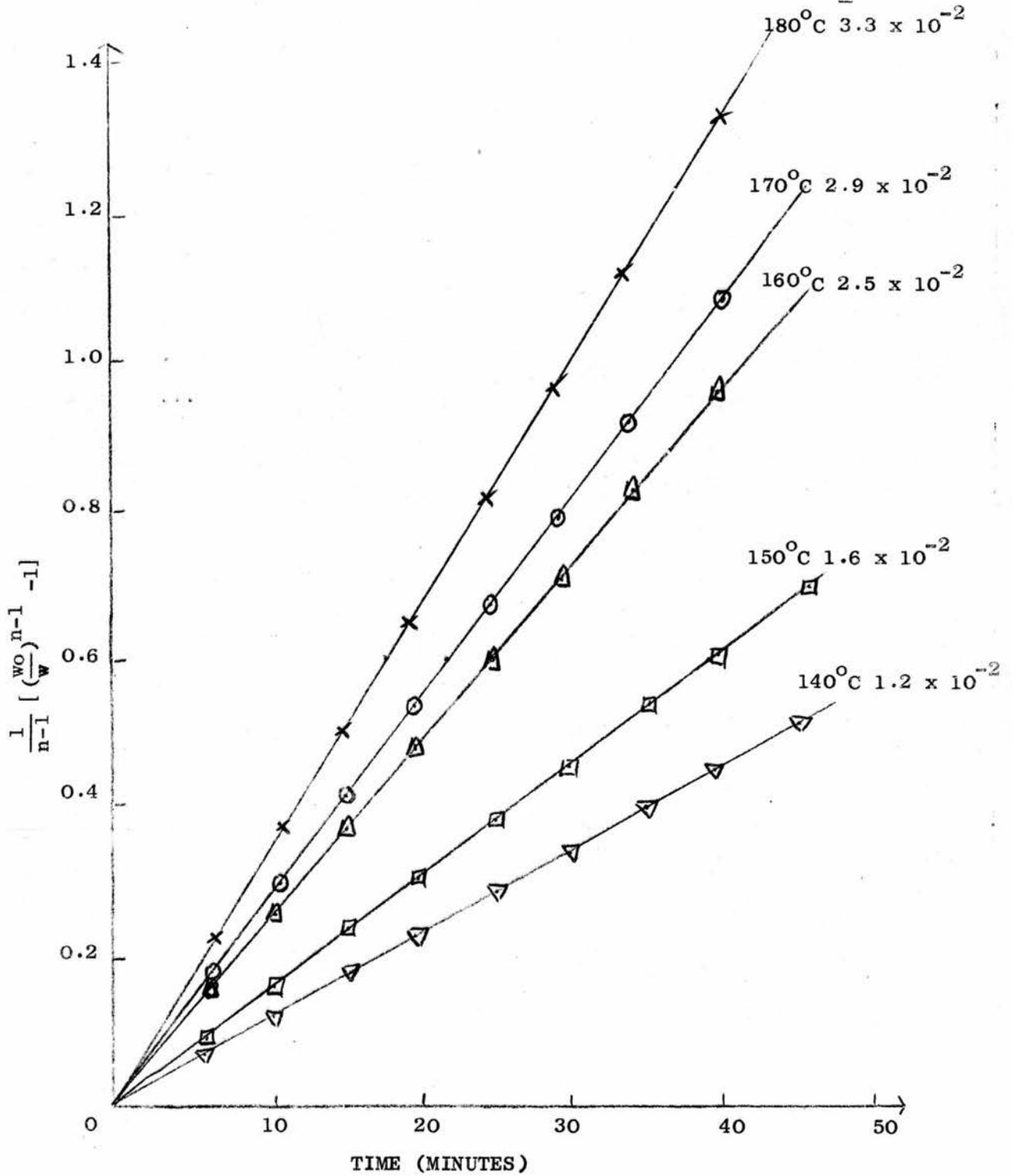


FIGURE 24

$\frac{1}{0.4} \left[\left(\frac{w_0}{w} \right)^{0.4} - 1 \right]$ vs t 25 mg PIBMA 1 CAST IN BENZENE

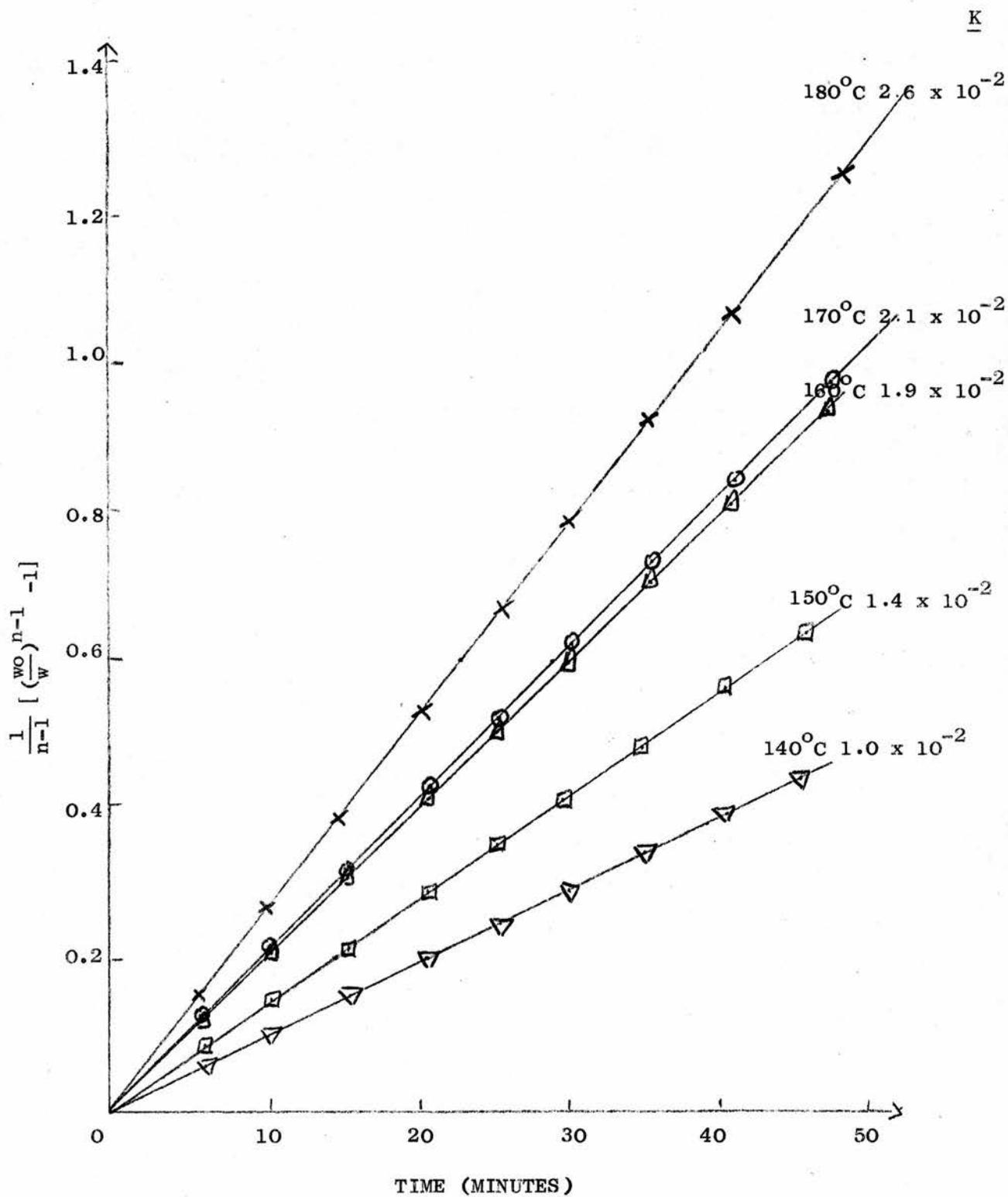
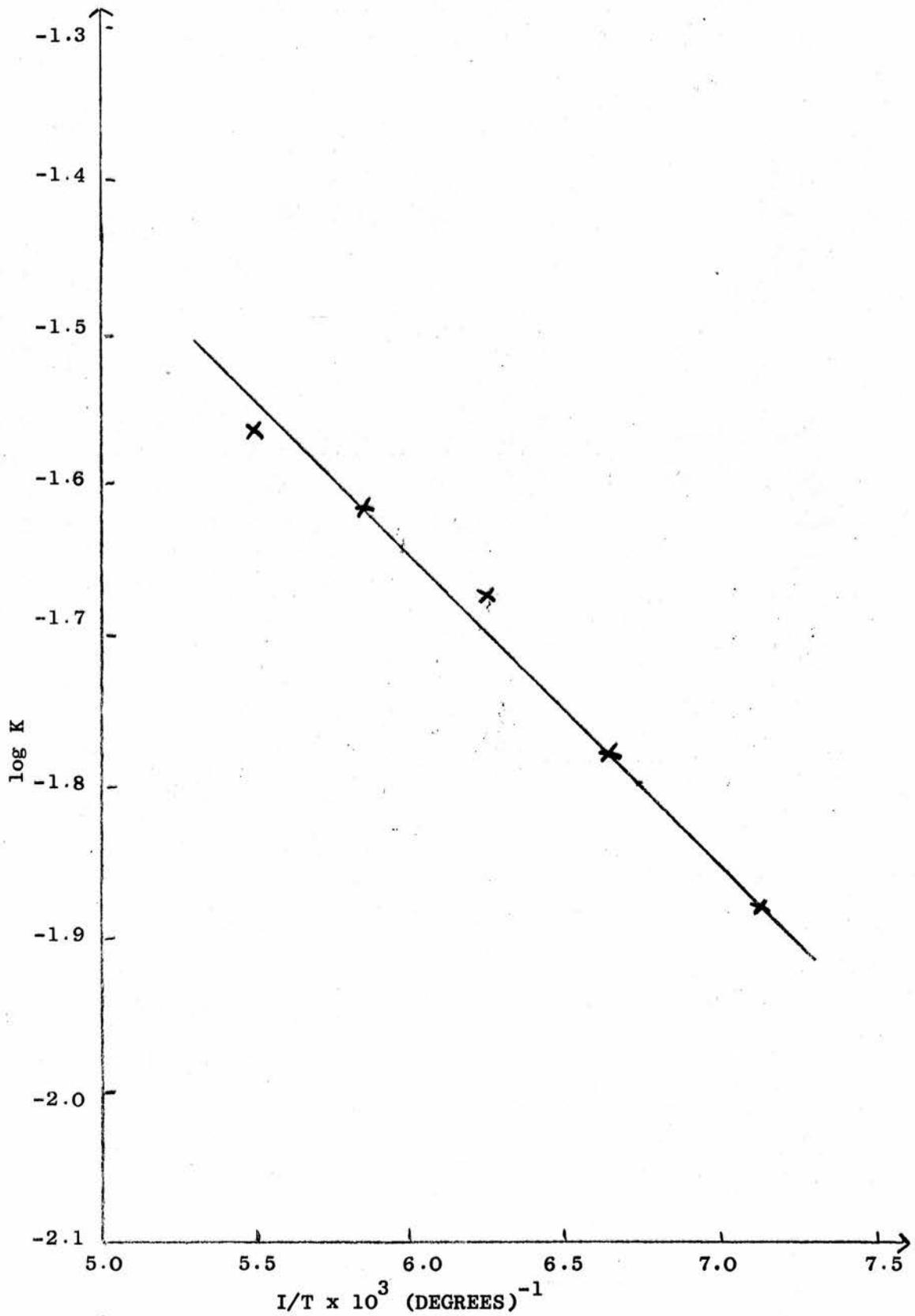


FIGURE 25

log K vs I/T 20mg PIBMA 1 CAST IN BENZENE



t/p vs t 20 mg PIBMA 2 CAST IN CHCl₃

Figure 26

t/p vs t 20mg PIBMA 2 CAST IN CHCl₃

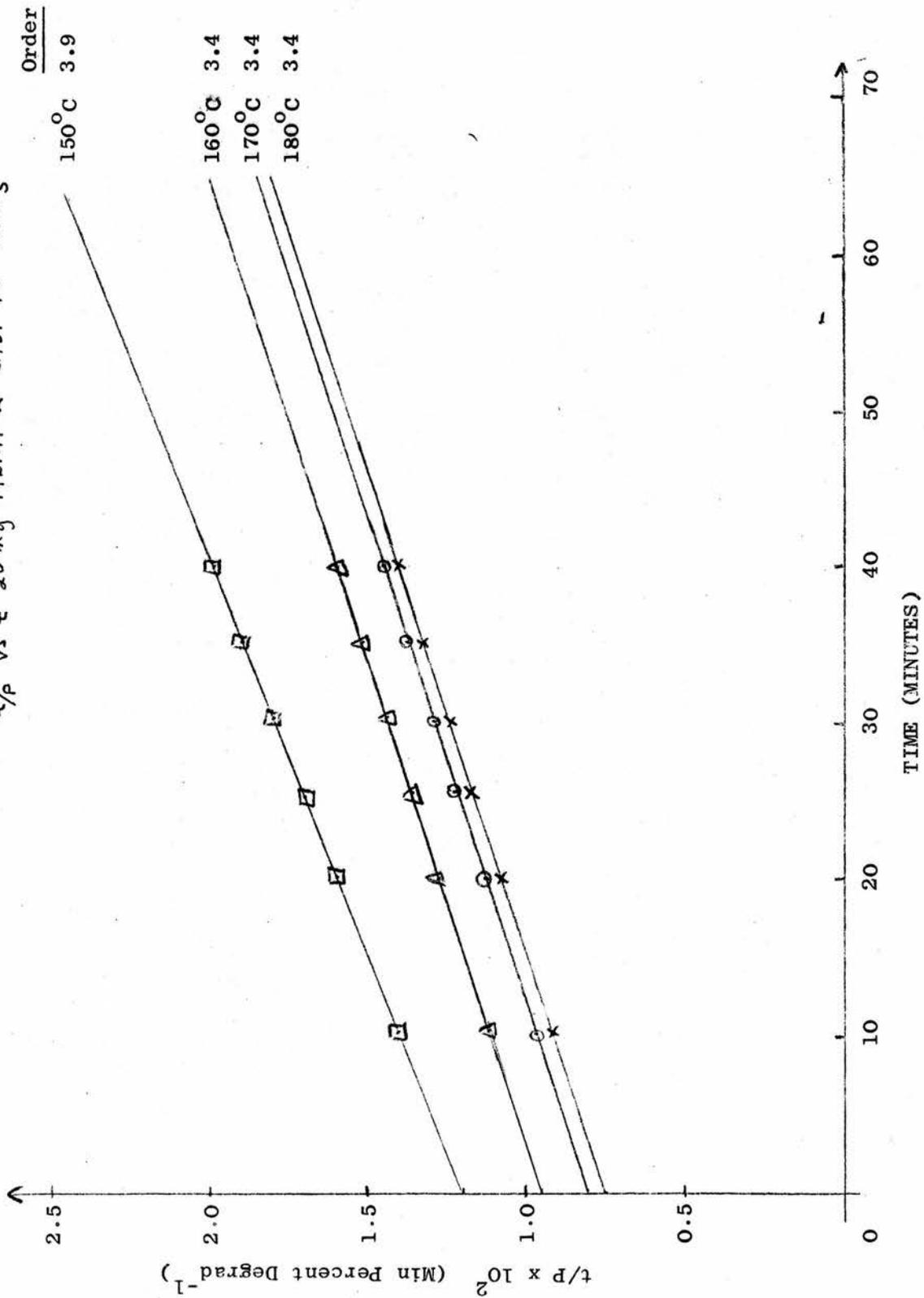


FIGURE 27

$\frac{1}{2.5} \left[\left(\frac{w_0}{w} \right)^{2.5} - 1 \right]$ vs t 10 mg PIBMA 2 CAST IN CHCl_3

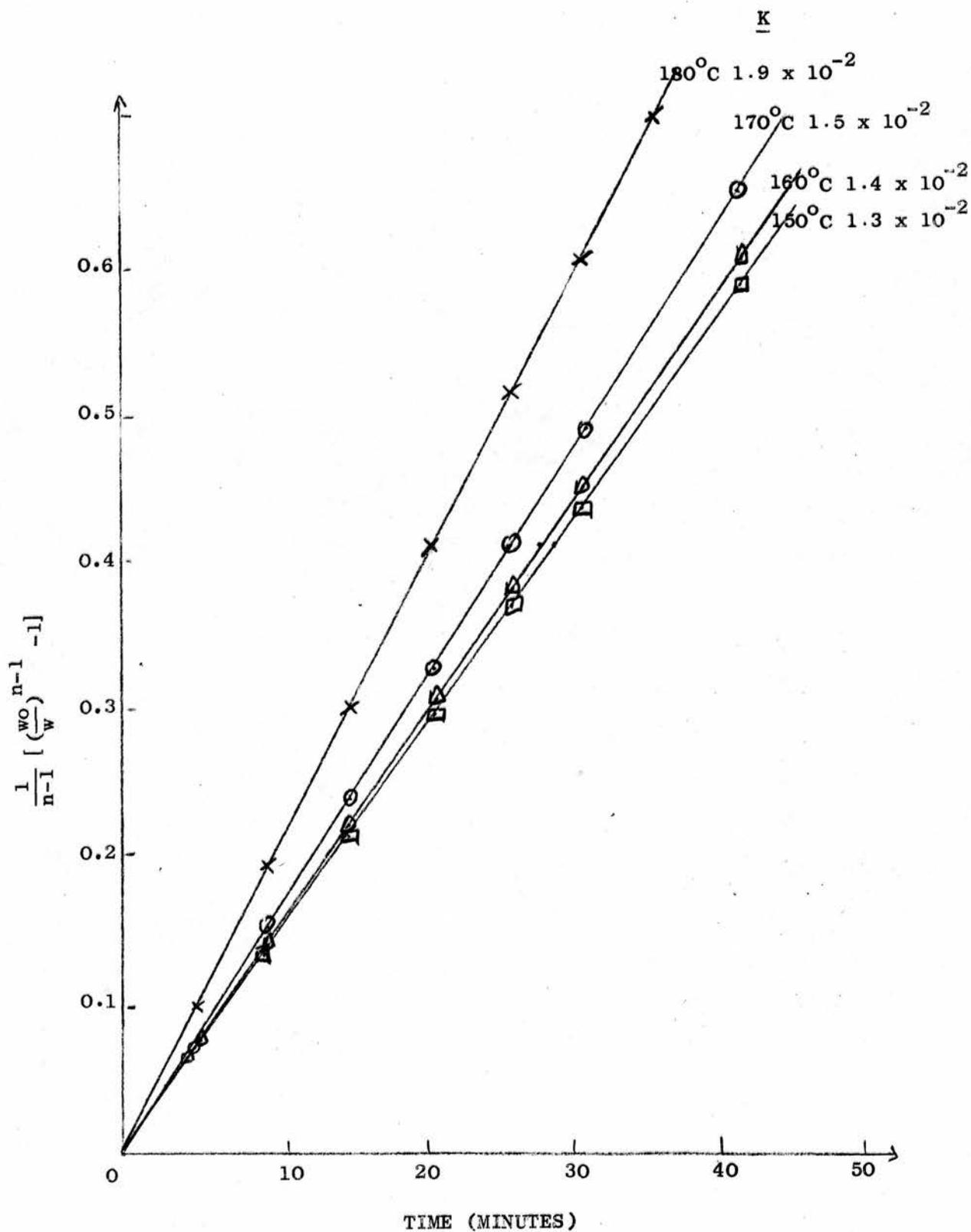


FIGURE 28

$\frac{1}{2.5} \left[\left(\frac{w_0}{w} \right)^{2.5} - 1 \right]$ vs t 20 mg PIBMA 2 CAST IN CHCl_3

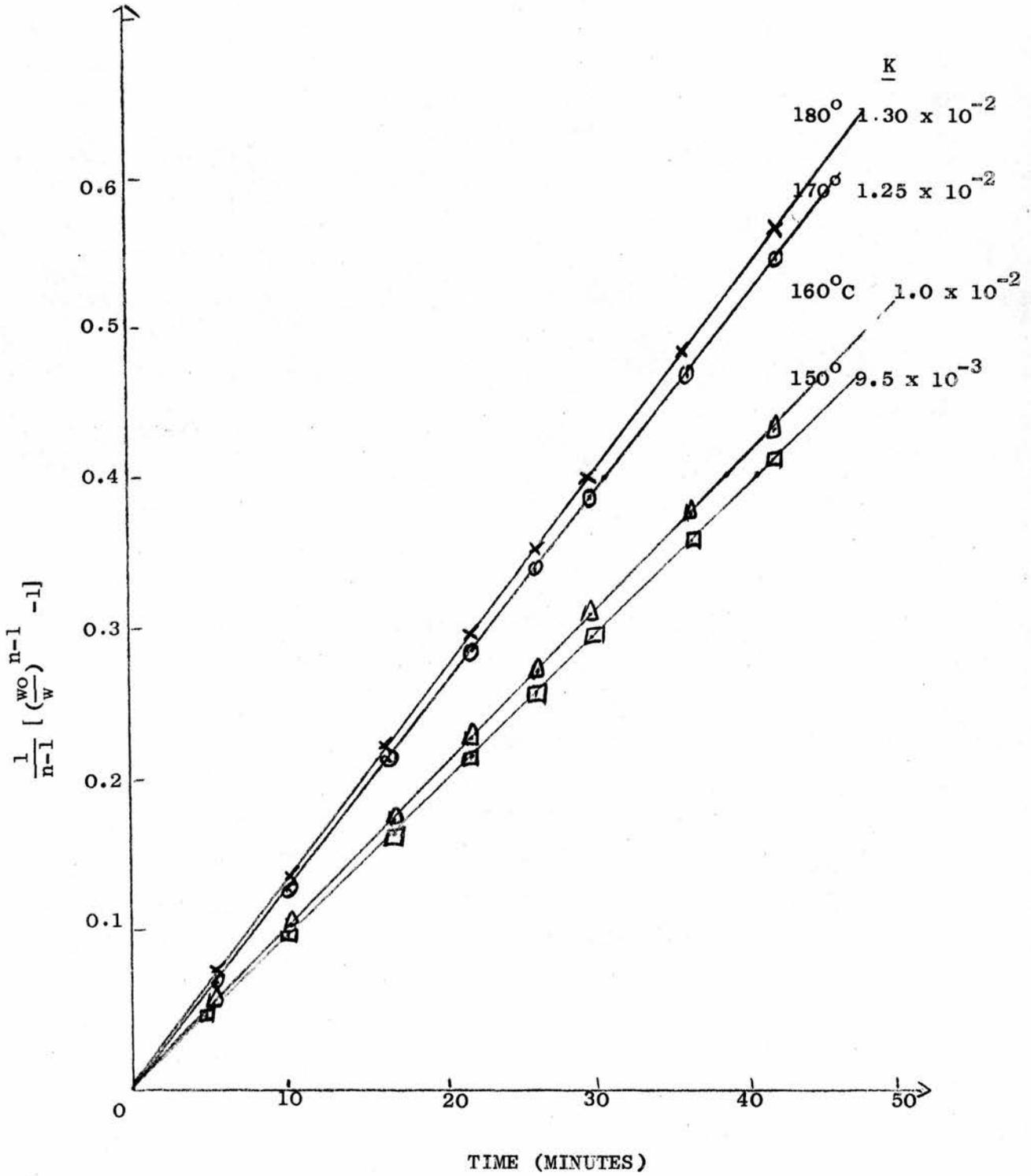


FIGURE 29

$\frac{1}{2.5} \left[\left(\frac{w_0}{w} \right)^{2.5} - 1 \right]$ vs. t 25 mg PIBMA 2 CAST IN CHCl_3

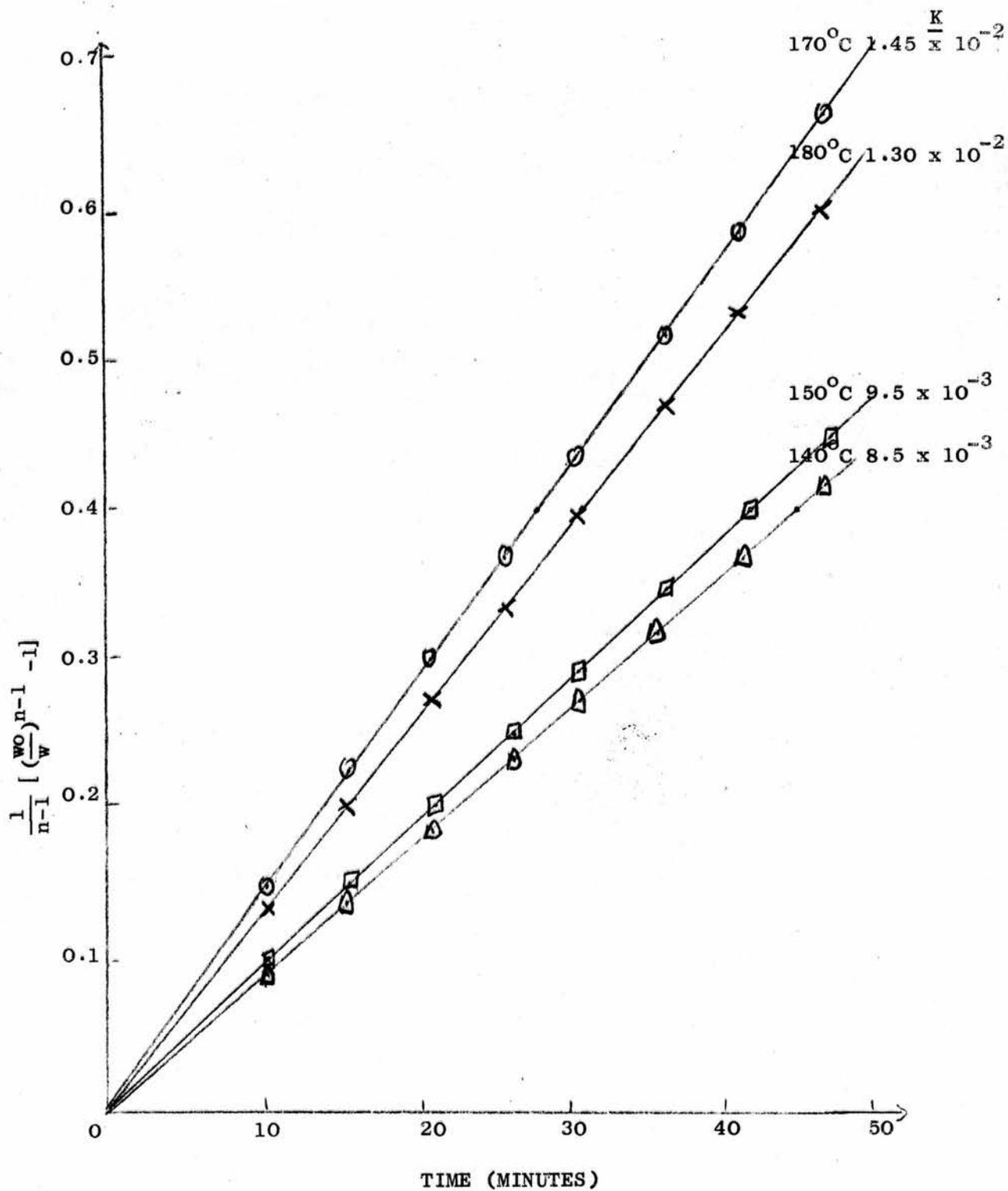


FIGURE 30

log K vs. $1/T$ 20mg PIBMA 2 CAST IN CHCl_3

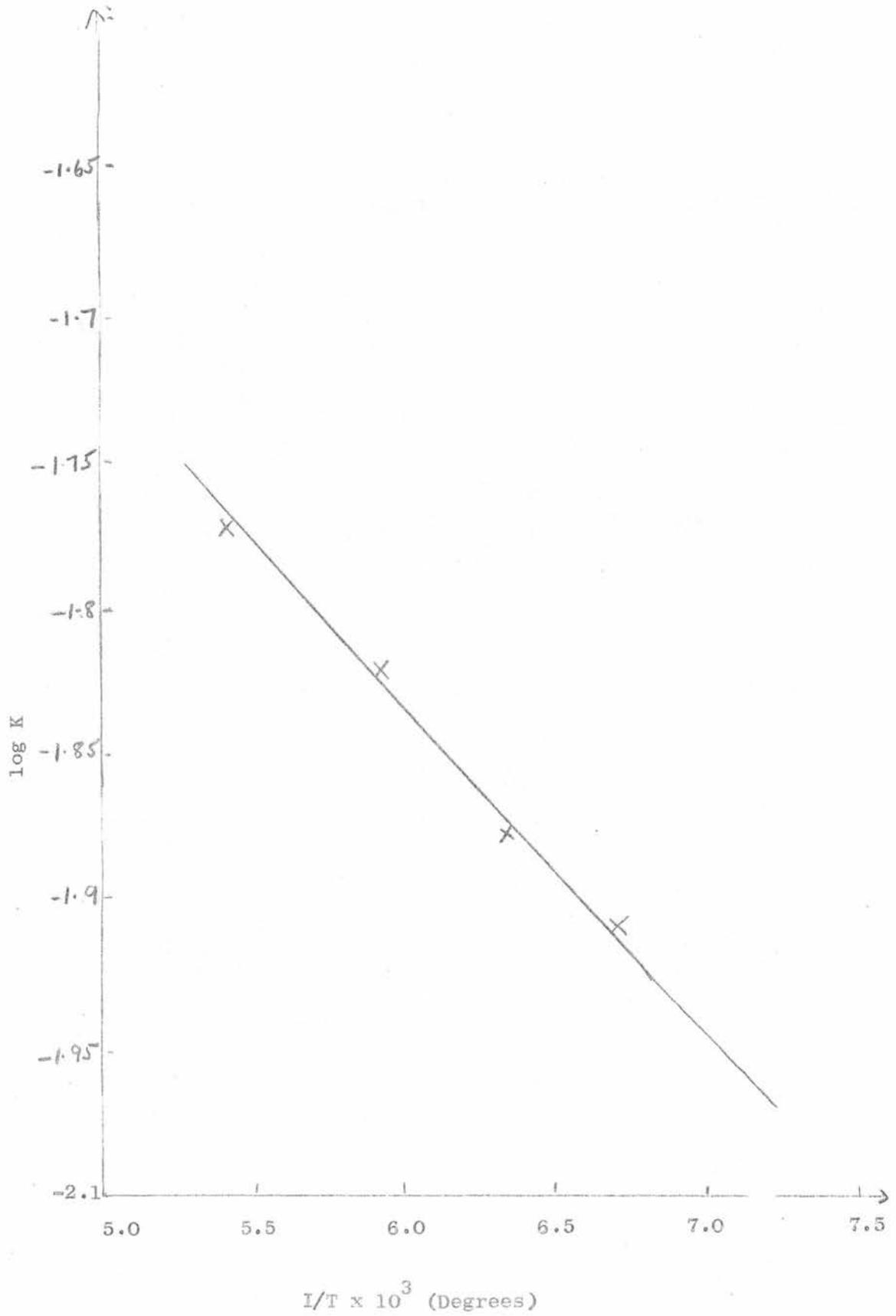


FIGURE 31

FRACTIONAL MOLECULAR WEIGHT VS. PERCENT DEGRADATION

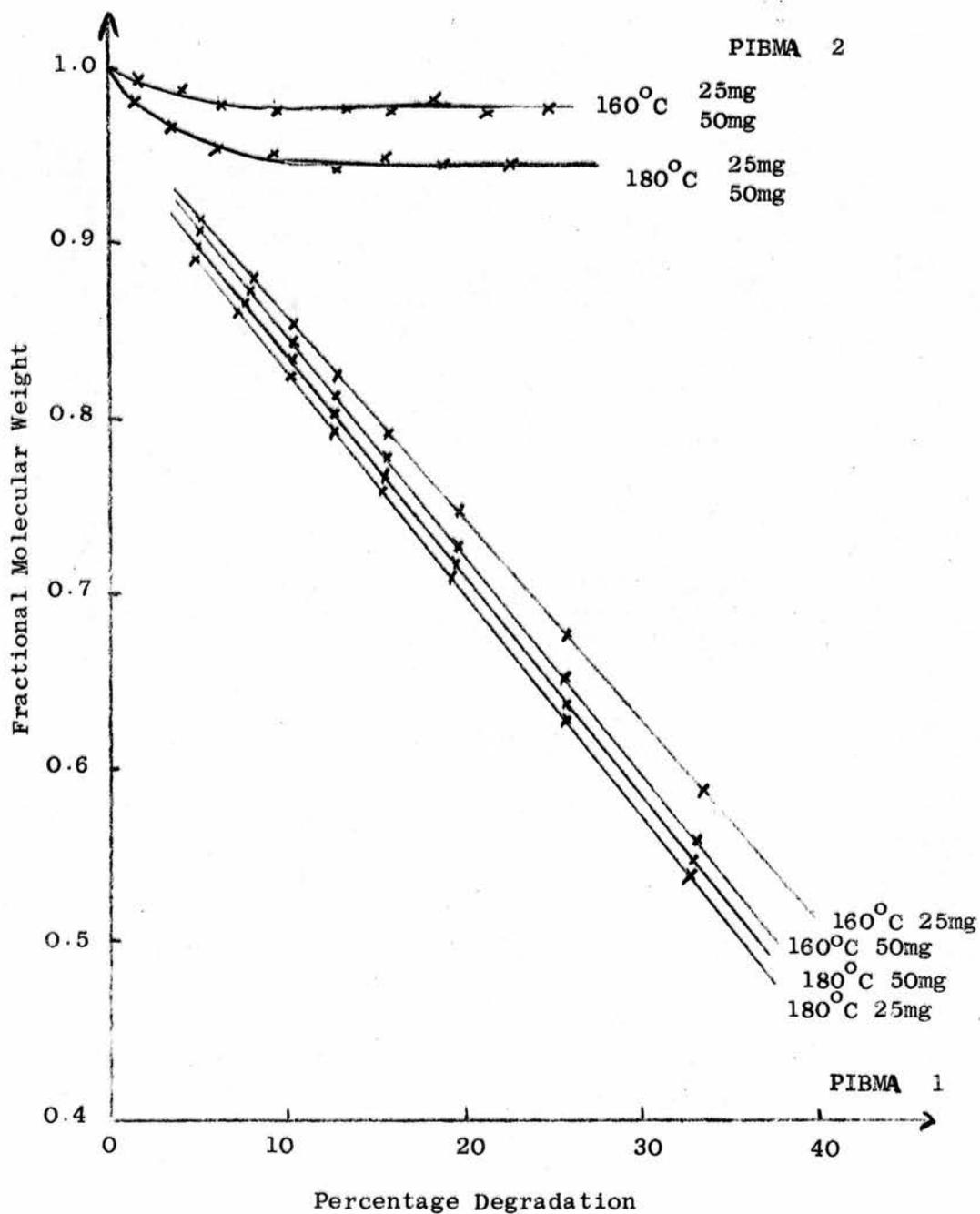


Fig 32

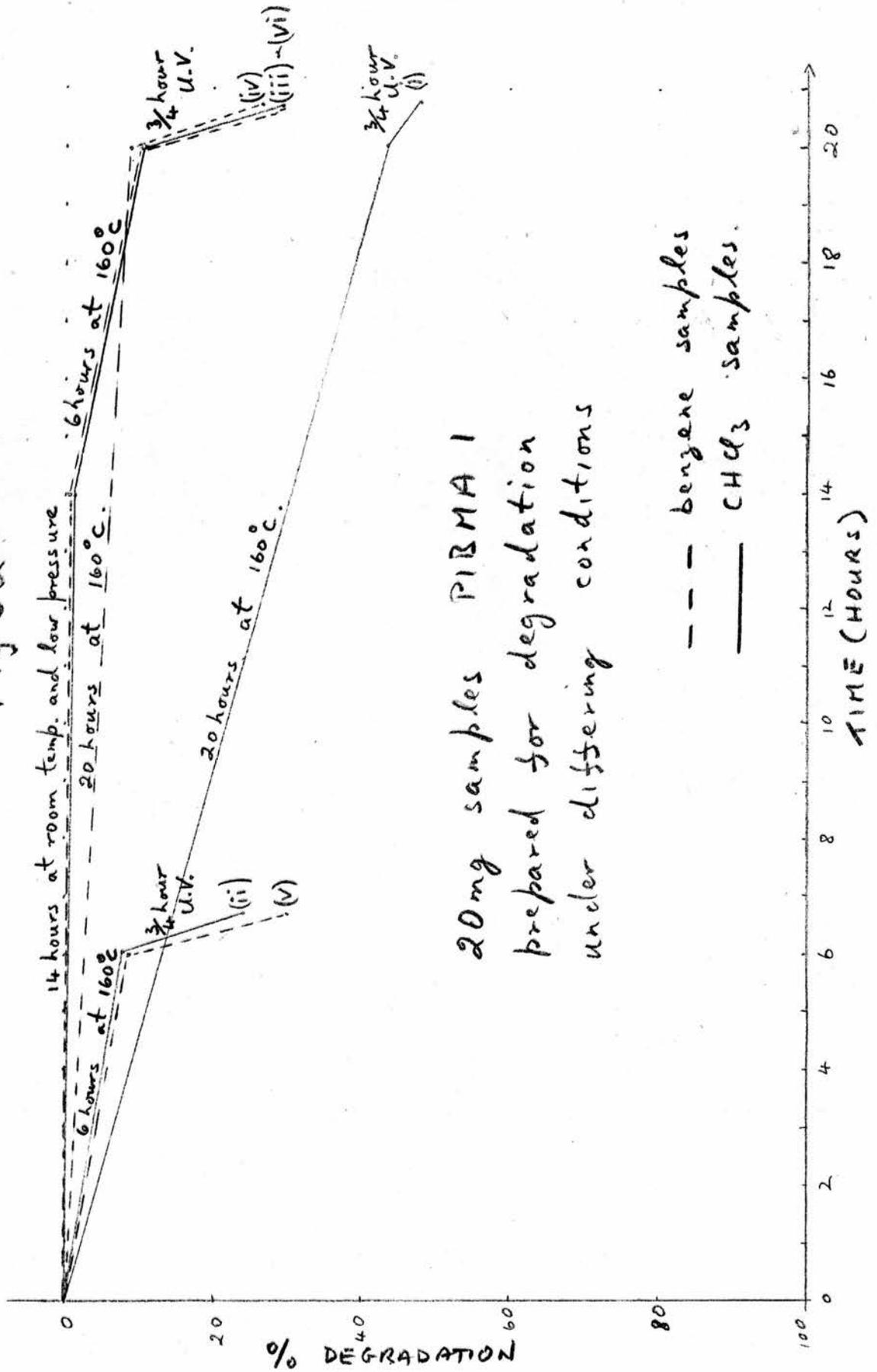


TABLE 1

Sample PIBMA
 Molecular weight 2.71×10^6
 Solvent $CHCl_3$

1.9 Example Fig. 8

T°C	140	150	160	170	180
wt. (mg)	10	15	20	25	
	9×10^{-3}	1.4×10^{-2}	9.4×10^{-3}	9×10^{-3}	
	2.1×10^{-2}	1.8×10^{-2}	1.1×10^{-2}	1.2×10^{-2}	
	1.8×10^{-2}	1.7×10^{-2}	1.7×10^{-2}	1.4×10^{-2}	
	2.6×10^{-2}	3.2×10^{-2}	2.3×10^{-2}	1.8×10^{-2}	
	3.9×10^{-2}	2.8×10^{-2}	2.7×10^{-2}	2×10^{-2}	

Fig. 9
 Fig. 10
 Fig. 11
 Fig. 12

Fig. 13

Average order from
 t vs $\frac{t}{p}$ checked as
 straight lines in
 $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} \right]^{-1}$

Values of K from
 slopes of t vs
 $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} \right]^{-1}$

Overall activation
 Energy from
 $\log K$ vs $\frac{1}{T}$

10 mg sample 48 kJMole⁻¹
 15 mg " 44 kJMole⁻¹
 20 mg " 41 kJMole⁻¹
 25 mg " 36 kJMole⁻¹
 Average
 42 kJMole⁻¹

TABLE 2

Sample
 Molecular weight
 Solvent

PIBMA
 2.71×10^6
 $\text{CH}_2 \text{Cl}_2$

1.6 Example

T°C	140	150	160	170	180
10	2.3×10^{-2}	3.2×10^{-2}	3.5×10^{-2}	5.4×10^{-2}	8.4×10^{-2}
15	1.8×10^{-2}	2.7×10^{-2}	3.0×10^{-2}	3.2×10^{-2}	4.9×10^{-2}
20	1.3×10^{-2}	1.9×10^{-2}	2.3×10^{-2}	3.1×10^{-2}	4.7×10^{-2}
25	8×10^{-3}	1.6×10^{-2}	2.6×10^{-2}	3.0×10^{-2}	3.1×10^{-2}

Average Order from
 t vs $\frac{t}{p}$ checked as
 straight lines in
 $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} \right]^{-1}$

Values of K from
 slopes of t vs
 $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} \right]^{-1}$

Overall activation
 Energy from
 $\log K$ vs $\frac{1}{T}$

10 mg sample 40 kJMole -1
 15 mg " 40 kJMole -1
 20 mg " 47 kJMole -1
 25 mg " 46 kJMole -1

Average

43 kJMole -1

Fig. 14

Fig. 15

Fig. 16

Fig. 17

Fig. 18

Fig. 19

TABLE 3

Sample
 Molecular weight
 Solvent

PIBMA
 2.71 x 10⁶
 Benzene

1.4 Example
 Fig. 20
 Fig. 21
 Fig. 22
 Fig. 23
 Fig. 24

T ^o C	140	150	160	170	180
wt (mg)					
10	2.0x10 ⁻²	2.6x10 ⁻²	6.8x10 ⁻²	4.3x10 ⁻²	8.3x10 ⁻²
15	1.8x10 ⁻²	2.4x10 ⁻²	2.6x10 ⁻²	4.0x10 ⁻²	4.2x10 ⁻²
20	1.2x10 ⁻²	1.6x10 ⁻²	2.5x10 ⁻²	2.9x10 ⁻²	3.3x10 ⁻²
25	1.0x10 ⁻²	1.4x10 ⁻²	1.9x10 ⁻²	2.1x10 ⁻²	2.6x10 ⁻²

Average Order from
 t vs $\frac{t}{p}$ checked as
 straight lines in
 $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} \right]^{-1}$

Values of K from
 slopes of t vs
 $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} \right]^{-1}$

Overall activation
 Energy from
 log K vs $\frac{1}{T}$

Average
 42 kJMole⁻¹

Fig. 25

TABLE 4

Sample PIBMA
 Molecular weight 3.09×10^5
 Solvent CH_2Cl_2

3.5 Example

Fig. 26

T ^o C	150	160	170	180
wt (mg)	1.4x10 ⁻²	1.4x10 ⁻²	1.5x10 ⁻²	1.9x10 ⁻²
	9.5x10 ⁻³	1.0x10 ⁻²	1.3x10 ⁻²	1.3x10 ⁻²
	9.8x10 ⁻³	8.5x10 ⁻²	1.5x10 ⁻²	1.3x10 ⁻²

Fig. 27

Fig. 28

Fig. 29

Fig. 30

Average Order from
 t vs $\frac{t}{p}$ checked as
 straight lines in
 $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} \right]$

Values of K from
 slopes of t vs
 $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} \right]$

Overall activation
 Energy from
 $\log K$ vs $\frac{1}{T}$

10 mg sample 43 kJMole⁻¹ Average
 20 mg " 27 kJMole⁻¹
 25 mg " 46 kJMole⁻¹ 39 kJMole⁻¹

DISCUSSIONThermobalance Technique - Assessment and Improvement.

From the experimental results obtained, it can be seen that from the point of view of throughput of data, the adapted thermobalance technique for measuring rates of ultra-violet degradation at constant temperatures is far superior to the commonly used method of running a sample for a short time, weighing and re-running etc. up to a suitable percentage degradation, on apparatus similar to that shown in Fig.5. As can be seen from t vs $\frac{t}{P}$ plots of samples run under similar conditions using the different techniques, random examples (Fig.8,14,20) show that, within experimental error, the techniques give similar results. The approximate preparation time from placing a cast film in the balance to beginning a run was 45 minutes and included evacuating, heating the sample to constant temperature, stabilising the balance mechanism and warming up the u.v. lamp to operating conditions. The runs themselves took a further 5 to 50 minutes, and, using two boats of almost identical weights, there was no waiting time between runs. A "series" of degradations of one particular sample cast in one particular solvent would require runs at 140-180°C in 10 degree intervals of samples of 10-25mg in 5mg intervals, averaging about 75 minutes start to finish for each one. Thus a series of 20 runs could be completed within 25 hours of continuous running.

Schoff¹⁰ working on the photodegradation of poly(methyl) and poly(ethylmethacrylate) over similar weight and temperature ranges, used a thermistor to measure the pressure of volatiles given off during degradation in an apparatus similar to that shown in Fig.5. His preparation time for

evacuating, bringing the u.v. source up to working temperature, heating the sample and allowing the thermistor guage to stabilise on zero at low pressure was at least 90 minutes and his degradation times varied from 30 minutes to 2 hours. Under these conditions a series of 20 degradations including a final weight measurement as a check at the end of each run would take approximately 50 hours, double the time required using the thermobalance technique.

Schoff's technique of using a thermistor guage to continuously measure the pressure of volatiles during the degradation is in fact a means of indirectly measuring the weight loss of a sample, and, although suffering from the uncertainty of indirect measurement, is infinitely quicker than the older technique of run, weigh, re-run, reweigh which involves pumping down and temperature stabilisation several times during one complete run.

Although the speed of measurement is a significant factor in the experimental procedure, the accuracy of the whole technique is of prime importance in assessing its usefulness. The great advantage of using a thermobalance in this type of degradation is that the kinetics of the reaction can be determined from direct weight measurement against time giving a continuous recording of weight change against time of irradiation. If the conditions of degradation are closely controlled and the weight measurement is accurate, the thermobalance technique would be ideal for many types of u.v. degradation reactions.

The converted Stanton thermobalance (Fig.4) gave weight change against time curves as in Fig.3, with the initial weight increase of the "thrust" effect clearly visible.

The accuracy of the system depends primarily on the accuracy of the weighing mechanism and the ability to eliminate or closely control the "thrust" effect. The balance registers sample weight differences against a counterpoise to an accuracy of $\pm 0.3\text{mg}$ allowing for the "noise" variation in the trace and the thickness of the pen line. Weight losses therefore have an accuracy of $\pm 0.6\text{mg}$ which is hardly sufficient even on the larger differences of up to 10mg and can range as high as 20% error in a 3mg weight loss run. Apart from obtaining the use of a balance of much higher sensitivity, the only other improvement that could be made in this area would be a substantial increase in sample size beyond the 25mg maximum imposed. Although little work has been on this problem, using samples of above 50mg introduces the problem of surface effects which distorts the kinetics of the degradation.

The boat used had an internal diameter of 3.10cm which was near the maximum size limits of the converted balance as shown in Fig.4. Removal of the internal sheath in the furnace and a reduction in the thickness of the glass tube would allow the internal diameter of the working area to be increased by 25 to 30%, increasing the maximum area of the boat by 55 to 80%. Within the confines of the Stanton balance, the further adaptations indicated and a corresponding increase in maximum sample size to 90mg would reduce the minimum percentage error with a weight loss of 40mg .

The "thrust" effect observed at the beginning of each degradation run is an interesting phenomenon which must be either eliminated or strictly defined in any future work of this nature. As explained on page 21, elimination of this

effect proved to be difficult, although reversing the molecular flow in the pumping system helped to reduce it to the measureable limits of Fig. 3. Several rough experiments to determine the size of the effect in relation to sample size and light intensity indicated that the initial weight increase was directly proportional to the size of the sample and ~~inversely~~ inversely proportional to the square of the distance of the u.v. source from the sample, within the accuracy of the balance as previously discussed. These results would seem to confirm the postulate that the magnitude of the "thrust" effect is directly proportional to the initial rate of the reaction. This idea opens up an interesting field of study into a means of measuring the "thrust" effect accurately enough to compare it with predetermined initial rates of reaction and thus determine the direct relationship between the two. Kinetic analysis of degradations involving different samples could be carried out using the information obtained as an alternative to that extracted by determining rate of reaction from order of reaction as explained on page 26.

Within the limits of accuracy of the Stanton balance as discussed, the accurate measurement of the "thrust" effect was extremely difficult. When the light source was placed a suitable distance away from the sample to obtain degradation runs of convenient percentage degradation with time, the "thrust" effect varied in size from 0.5 to 4mg dependent on sample size and temperature. As a weight difference the error in these values is extremely high and could only be reduced by choosing optimum light intensity conditions to maximise the effect at the expense of the subsequent degradation run. If the light source was placed close to the sample (60cm away instead of 120cm), initial weight increases of up to 10mg were observed

and, although no further work was undertaken in this area, greater increases in light intensity and sample size would very probably initiate accurately measurable "thrust" effects of up to 30mg.

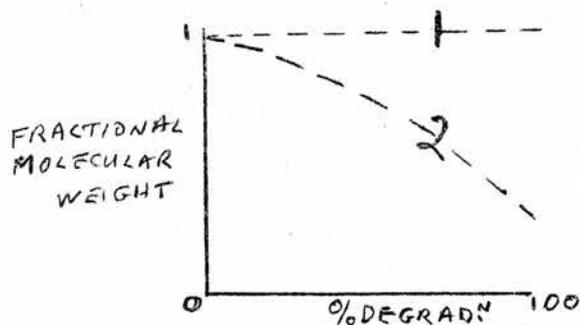
With reference to Figs. 9, 10, 21 and 29 and Tables I-4, deviations from a regular pattern of increased rate against increased temperature were observed. Although pre-heating and pre-treatment times were the same in all cases, several pairs of plots at different temperatures appeared to be transposed, but whether this is due to inaccuracy of measurement or true anomalies in the kinetics of the reaction is uncertain. If inaccuracy were the cause, serious doubt would be cast on the results obtained. If kinetic anomalies are to blame, further work could reveal hitherto unknown interesting new data and kinetic information.

The Kinetics of the Degradation of Poly(isobutylmethacrylate)

a) The order and type of the reaction.

With reference to the information obtained and shown in Tables I-4 and Fig. 31, it can be seen that the two polymer samples of very different molecular weights gave kinetic data of very different types. In the case of sample PIBMA 1, the average order of the degradation reaction determined from t vs $\frac{t}{P}$ plots checked as straight lines in $\frac{1}{n-1} \left[\left(\frac{w_0}{w} \right)^{n-1} - 1 \right]$ is 1.9 for samples cast in chloroform, 1.6 for samples cast in CH_2Cl_2 and 1.4 for samples cast in benzene. Sample PIBMA 2 however gives an order of 3.5 for samples cast in chloroform. Fig. 31 which shows plots of fractional molecular weight against percentage degradation also shows vast difference of behaviour between the two samples.

Some light can be shed on the meaning of these results if we consider MacCallum's progressive analysis of information in the kinetics of the photolytic decomposition of poly (n-butylmethacrylate) and the resulting theoretical calculations⁶⁻⁸. Plots of fractional molecular weight versus percentage degradation from two samples of poly(n-butylmethacrylate) of molecular weight 4.6×10^5 and 1.1×10^5 gave results almost identical to those obtained from PIBMA I&2. MacCallum⁶ deduced that these results indicated an end-initiated reaction with a kinetic chain length lying somewhere between the molecular chain lengths of the two samples. Subsequent theoretical calculations⁸ gave very different results. Dividing the depolymerisation initiation reaction into two main groups i) random initiation along the polymer molecular backbone and ii) chain end initiation followed by either no molecules lost by complete unzipping or all molecules unzipping completely once initiated, MacCallum calculated that a fractional molecular weight against percentage conversion plot for random initiation followed by complete unzipping would give a series of plots dependent on the breadth of distribution of molecular size in a sample.



In case 1 for example, the sample would be homodispersed with all molecules the same length and having an equal probability of undergoing scission. In case 2, the sample would have an exponential distribution of molecular sizes. Comparing these deductions with the plots obtained in Fig. 3I., it can be

that both samples of poly(isobutylmethacrylate) undergo random initiation. It would also appear that the sample PIBMA I also undergoes an unspecified termination reaction, while PIBMA 2 undergoes complete unzipping with behaviour close to that expected for the most probable distribution.

Returning to the problem of the different orders of reaction for the two samples, MacCallum also concluded that a randomly initiated degradation has an order of 1-2 whereas for end-initiation the order is in the range 0-1. In the case of sample PIBMA I this confirms the previous conclusion that the degradation mechanism is random initiated, because average orders of reaction of 1.9, 1.6 and 1.4 were observed for samples cast in chloroform, CH_2Cl_2 and benzene respectively. An observed order of 3.5 for samples of PIBMA 2 cast in benzene, whilst not negating a similar conclusion certainly does not come within the order range of 0-2 discussed by MacCallum. Until further work is done it would be impossible to establish a reason for this, but it is perhaps possible that the use of chloroform as a solvent in the film preparation of the far lower molecular weight samples sufficiently alters the molecular pattern of the film to give an unusually high order of reaction.

b) The energy of activation of the degradation reaction and possible viscosity effects.

As can be seen from Tables I-4, the energies of activation for the photolytic degradation of samples of PIBMA I cast in chloroform, CH_2Cl_2 and benzene, calculated from the slopes of $\log K$ vs $\frac{1}{T}$ plots were 42, 43 and 42 kJMole^{-1} respectively and for samples of PIBMA 2 cast in chloroform, 39 kJMole^{-1} . The error in these values averaged from values for each sample weight is extremely large, individual values ranging from

27 to 50 kJ Mole^{-1} and a reasonable estimate of accuracy for both samples of poly(isobutylmethacrylate) films cast from various solvents would give an energy of activation of $(42 \pm 8) \text{ kJ Mole}^{-1}$. This estimate compares favourably with the 20% error suggested in the accuracy with which the weight differences can be measured.

If this result is compared with the results obtained by Schoff¹⁰ on poly(methyl) and poly(ethylmethacrylate) some interesting comparisons can be made. The calculated energies of activation from the photolytic degradation of poly(methyl) and poly(ethylmethacrylate) at high temperatures were 41 and 43.3 kJ Mole^{-1} respectively the same as the energy of activation for poly(isobutylmethacrylate) within experimental error. Schoff also obtained plots of $\log K$ vs $\frac{1}{T}$ as not one but two intersecting straight lines giving two different activation energies dependent on temperature range. For poly(methylmethacrylate) his activation energy was 211 kJ Mole^{-1} below 175°C and 41 kJ Mole^{-1} above and for poly(ethylmethacrylate) 136 kJ Mole^{-1} below 135°C and 43.3 kJ Mole^{-1} above. Schoff's conclusion on this point was that the degradation was viscosity controlled at lower temperatures and that the T_g of the polymer played an important part in the kinetics of the degradation. With reference to the table of T_g 's on Pg. 17 it can be seen that poly(methylmethacrylate) has a T_g of 378°K , poly(ethyl), 338°K and poly(isobutylmethacrylate) 326°K . To obtain straight line $\log K$ vs $\frac{1}{T}$ plots, Schoff altered the Arrhenius equation $K = A e^{-\frac{E_a}{RT}}$ to $K = A e^{-\frac{E_a}{R(T-T_0)}}$ where T_0 was a factor of 140 degrees for poly(methylmethacrylate) and 100 degrees for poly(ethylmethacrylate) selected by trial and error. It is interesting to note that the value of T_0 in each case was 35 degrees above the listed value for the T_g .

The resultant activation energies were very low, being about $0.60 \text{ kJ Mole}^{-1}$ for poly(methylmethacrylate) and $0.65 \text{ kJ Mole}^{-1}$ for poly(ethylmethacrylate). Applying the same criterion in the case of poly(isobutylmethacrylate), a T_0 factor of 88 degrees should also give straight line $\log K$ vs $\frac{1}{T-T_0}$ plots of different slope to the $\log K$ vs $\frac{1}{T}$ plots already obtained, although these would not exhibit Schoff's intersecting lines behaviour since the range of measurement (140-180°C) is outwith the expected transition point of 123°C i.e. 12C.D. below the transition point for poly(ethylmethacrylate) and 52C.D. below the transition point for poly(methylmethacrylate).

In fact, data extracted from $\log K$ vs $\frac{1}{T-T_0}$ plots for poly(isobutylmethacrylate) with $T_0 = 88$ degrees gave curves rather than straight lines, and varying the T_0 factor between 40 and 140 gave no better results. It would appear in this case that Schoff's factor is unnecessary because the low T_g of poly(isobutylmethacrylate) puts the degradation reaction outwith viscosity control within the observation range 140-180°C.

c) The effects of varying conditions on the rate of reaction.

1) The length of time the sample is evacuated.

When two samples of PIBMA I cast in different solvents were evacuated at room temperature for 14 hours and reweighed ((iii) and (vi) Fig. 32) no loss of weight occurred and subsequent heating and u.v. degradation gave weight losses similar to other samples which had not been evacuated for such long periods.

Thus the rate of degradation of poly(isobutylmethacrylate) is independent of the length of time the samples are evacuated.

2) The length of time the sample is heated.

Samples of PIBMA I cast in chloroform and benzene were

evacuated, heated for 6 hours and 20 hours and subjected to 45 minutes of u.v. degradation ((i), (ii), (iv), and (v) Fig.32). The samples cast from benzene lost similar small amounts of weight during the 6 hour and 20 hour heating periods due to thermal degradation which would appear to occur mainly during a short initial period of heating, since the sample weight losses were very similar whether heating was applied for 6 or 20 hours.

A sample cast from chloroform and heated for 6 hours exhibited similar behaviour, although another sample cast from chloroform and heated for 20 hours showed marked thermal degradation ((i)).

3) The solvent used to cast the film.

Comparing runs (i) and (iv) it can be seen as above that prolonged heating of a chloroform cast film leads to 3 times the weight loss due to thermal degradation compared with a benzene cast sample. Weight loss was approximately proportional to the time of heating in chloroform cast film, suggesting that thermal degradation takes place at a uniform rate throughout the heating period of the sample, unlike benzene cast films which appear to degrade at a rate similar to chloroform cast films for a short period then cease thermal degradation completely.

It was concluded that within the limits of the new thermobalance technique which employs heating and pumping down periods of much shorter duration than above, solvent used, length of vacuuming down and length of heating of sample have little effect on the weight losses of the samples.

SUGGESTION FOR FURTHER WORK.

The general lack of sensitivity of the apparatus used to determine the kinetics of the photodegradation of poly (isobutylmethacrylate) was a serious problem in the assessment of the accuracy of the work. The principal of using a converted Stanton thermobalance is good in the respect that results are obtainable in a fraction of the time required using normal techniques.

Future work should be concentrated on increasing the sensitivity and accuracy of thermobalance technique such that small weight changes can be measured and the very interesting "thrust" effect quantified.

The kinetic data obtained suggests that poly(isobutylmethacrylate) fits into the pattern observed for other polyalkylmethacrylates but further studies at lower temperatures would be required to determine whether the degradation is viscosity controlled .

REFERENCES

- I. Netherlands Gov. Inst., India Rubber J., 54 688 (1917),
CA, 12, 322 (1918).
2. A. Van Rossem, Kolloidchem Beihefte, 10, 129 (1918);
CA, 13 2149 (1919),
3. J. Spiller, J.Chem.Soc., 18, 44(1865).
4. P.R.E.J. Cowley and H.W. Melville, Proc. Roy. Soc.,
A210, 461(1952); A211, 320(1952).
5. A. Charlesby and D.K. Thomas, Proc. Roy. Soc.,
A269, 104(1962),
6. N. Grassie and J.R. MacCallum, J. Polymer Sci.,
A2, 983(1964).
7. J.R. MacCallum, Polymer, 5, 213(1964).
8. J.R. MacCallum, Eur. Polymer J., 2, 413(1966).
9. N. Grassie, "Chemistry of High Polymer Degradation
Processes"; Butterworths, London, 1956.
10. C.K. Schoff, "A Study of the Photochemical Decomposition
of Polymethacrylates," University of St. Andrews 1970.
11. N. Grassie and I.C. McNeill, J. Chem. Soc.,
3929(1956).
12. N. Grassie and I.C. McNeill, J. Polymer Sci.,
27, 207(1958).
13. R.B. Fox, L.G. Isaacs and S. Stokes, J. Polymer Sci.,
A1, 1079(1963).
14. J.R. MacCallum, Makromol. Chem., 83, 129(1965).
15. N. Grassie and H.W. Melville, Proc. Roy. Soc.,
A199, 1,14,24,39(1949).
16. Quarterly Review, 61, 811(1958).
17. F.W. Billmeyer, "Textbook of Polymer Science"
Interscience, New York 1962.

18. R. Simha, J. Polymer Sci., 9 465(1952).
19. A. Votinov, B. Kobeko and V. Morei, J. Phys. Chem. (U.S.S.R.), 16 106 (1942).
20. M.I. Frolova and A.V. Riabov, Polymer Science(U.S.S.R.) 2 1(1961).
21. M.I. Frolova, L.V. Nevskii, A.V. Riabov, Vysokomol Soedin, 3 877(1961) in R.B. Fox, "Photodegradation of High Polymers," in "Progress in Polymer Science", Vol.I, A.D. Jenkins, ed., Pergamon Press London 1967.
22. A.R. Schultz, J. Phys. Chem., 65, 967(1961).
23. R.B. Fox, L.G. Isaacs, S. Stokes, and R.E. Kagarise J. Polymer Sci., A2, 2085(1964).
24. G. Oster, G.K. Oster and H. Moroson, J. Polymer Sci., 34, 671(1959).
25. R.B. Fox, L.G. Isaacs and F.H.M. Nestler, Org. Coatings and Plastics Chem. Div., Am. Chem. Soc., Preprints, 21(2), 405(1961); CA, 58, 12728d(1963).
26. A. Charlesby and D.K. Thomas, Proc. Roy. Soc., A269, 104(1962).
27. A. Charlesby and N. Moore, Int. J. Appl. Radiation and Isotopes, 15, 703(1964).
28. R.B. Fox and T.R. Price, Polymer Preprints, 5; 390(1964).
29. H.H. Jellinek and I.C. Wang, Kolloid-Z und Z-Polymere, 202, 1(1965).
30. J.R. Wilson, Pure and App. Chem., 30 No. I-2 (1972).
31. L.G. Isaacs and R.B. Fox, U.S. Naval Res. Lab., Rept. No. 6339(1965), in R. B. Fox, "Photodegradation of High Polymers" in "Progress in Polymer Science", Vol. I, A.D. Jenkins, ed., Pergamon, London (1967).
32. E. Maura., Ann. Chim. (Rome), 59, (7), 604 (1969).

33. W.A. Zisman, Record of Chem. Progress, 26 I3(I965) and Advances in Chem., Amm. Chem. Soc., Series 43(I964).
34. W.A. Zisman, R.B. Fox and P. Jarvis, Advances in Chem, Amm.Chem. Soc.,3I7(I964).
35. C. Jek, Z.Phys. Chem., 203, 309(I964).
36. N. Ehrenberg and P. Zimmer, Acta. Chem. Scand., 10 874(I956).
37. B. Jellinski, D. Hippe and C. Zurakowska, Orszagh Prezemysl Chem., 42, 356(I963).
38. R.B. Fox and T.R. Price, Organic Coatings and Plastics Chem. Div., Amm. Chem. Soc., 26, No. 2(I962).
39. A.R. Monahan, J. Polymer Sci., 4AI 238I(I966).
40. A.R. Monahan, J. Polymer Sci., 5AI 2333(I967).
- 4I. R. Lehrle and S. Robb, J. Gas Chrom.,89(I967).
42. T. Harms, Anal. Chem., 25,II40(I953).
43. P. Davidson, M. Slaney and W. Wragg, Chem. and Ind., I356(I954).
44. C. Madorsky and R. Strauss, Res. Nat. Bur. Stand., 40, 4I7(I948).
45. C. Barlow, R. Lehrle and S. Robb, Polymer, 2, 27(I96I)
46. I.C. McNeill, J. Polymer Sci., A4 2479(I966).
47. I.C. McNeill and T. Neil, "Thermal Analysis" p353, Academic Press, (I969).
48. I.C. McNeill, and T. Neil, "Thermal Analysis", p4I7, Academic Press.
49. N. Grassie and G. Grant, Polymer, I, 445(I960).
50. C.G. Hatchard and C. A. Parker, Proc. Roy. Soc, A220 IO4(I953).

51. J. Tanner, Ph.D. Thesis, University of St. Andrews
1966.
52. Engelhard Hanovia Lamps, Slough Bucks.
53. W. Moore, "Introduction to Polymer Chemistry" 1963.
54. P.J. Flory "Principles of Polymer Chemistry", Cornell
University Press, Ithaca, New York 1953.
55. F.A. Bovey, J.M. Kolthoff, A.I. Medalia and E.J. Mehan
"Emulsion Polymerisation", Interscience, New York 1955
56. O.F. Solomon and I.Z. Ciuta, J. Appl. Sci., 6, 683(1962)
57. R.J. Vallas, J. Polymer Sci., 3, 3853(1965).
58. J.G. Calvert and J.N. Pitts, "Photochemistry", John
Wiley & Sons New York (1966).