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An experimental investigation of the kinetics and thermal properties of poly(ethylene) terephthalate and its related di-acid modified copolymers

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ABSTRACT

Title of Thesis : An experimental study of the kinetics and thermal
properties of Poly(ethylene) Terephthalate and its
related di-acid modified copolymers

Satish Baliga, Master of Science, 1984

Thesis directed by : Dr. Chen-Chong Lin

Poly(ethylene) Terephthalate , PET, is synthesized from purified Bis-hydroxyethyl Terephthalate,(BHET), in the presence of antimony oxide catalyst. Rate constant for the polycondensation reaction, based on a second order kinetic model is found to be 152.4/mol/hr.

A new modified polyester Polyethylene Adipic Terephthalate (PEAT) is synthesized from BHET and adipic acid. The effect of adipic acid content in the copolymer,on the rate of polycondensation is studied. Adipic acid is shown to improve the activity of the polymer chain ends thereby increasing the apparent reaction rate constants.

The modified polyesters are observed to melt at a lower temperature than PET. Moreover, the temperature of maximum crystallization is significantly decreased. This property of PEAT would allow a much lower mold temperature during processing and improve the crystallization rate.

AN EXPERIMENTAL STUDY OF THE KINETICS AND THERMAL PROPERTIES OF POLY(ETHYLENE) TEREPHTHALATE AND ITS RELATED DI-ACID MODIFIED COPOLYMERS

By

Satish Baliga

Thesis submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree of
Master of Science in Chemical Engineering
1984

APPROVAL SHEET

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I. INTRODUCTION

Poly(ethylene) terephthalate, PET, is a well known commercial polymer widely used as a fiber and film. PET fibers became available in the United States in 1953 and their production has expanded at an ever increasing rate so that they now constitute the fastest growing fiber on the North American continent. Although the fiber has a great diversity of end uses, blends with cotton comprise easily the largest single end use. PET films were intoduced to the market in 1954 and the versatility in its properties broadened its use spectrum into such diverse markets as decorative yarns, packaging, capacitors and magnetic tapes. In 1966 the first injection-molding grades of PET were introduced and subsequently extensive research was carried out to improve its thermal properties and mechanical strength.

PET has been manufactured commercially either by the direct esterification of ethylene glycol and terephthalic acid or by the trans-esterification route in which dimethyl terephthalate is reacted with ethylene glycol usually in the presence of a catalyst. Due to the complex nature of the reactions involved, there has been very little agreement between investigators regarding the kinetics of PET polymerization. Side reactions that may occur during the synthesis of PET have been shown to greatly affect its mechanical and thermal properties.

In the absence of nucleating agents and plasticizers, PET crystallizes slowly and performs best only in applications where strength and crystallinity can be increased through mechanical orientation.eg in biaxially oriented film, oriented fiber and soft drink bottles fabricated by stretch blow molding. PET processing requires mold temperatures well in the excess of 100 C to provide a commercially acceptable rate of crystallization. Improved crystallization rates can be acheived by blending PET with some other polymer or by the copolymerization of PET.

It has been generally agreed that the introduction into a polymer of units that differ chemically, stereochemically or structurally from the predominant chain repeating elements imposes restrictions on the crystallization and fusion process. Treatment of crystallization in polymers by statistical thermodynamical methods have yielded several relationships between the melting temperature and polymer constitution. The melting point-composition relationship for copolymers has been derived by Flory (1) to be analogous to the freezing point composition relationship for ideal mixtures of simple molecules. As predicted by this theory, investigators (2-4) have shown that the addition of co-units into a polymer chain causes a significant depression in the melting point and also affects its thermal properties. Moreover, in general the glass transition temperature and the temperature of maximum crystallization are lower for the copolymer than for the homopolymer. A low glass transition temperature for PET copolymers facilitates rapid crystallization at low mold temperatures, resulting in shorter mold cycles.

The work in this thesis can be divided into two broad sets of experimental investigations. In the first, PET was synthesized via a new route. As discussed before, PET is commercially manufactured by the direct esterification of ethylene glycol with terphthalic acid or by its transeterification with dimethyl terephthalate. In both these methods the polycondensation step involves a reactant mixture containing monomer as well as oligomer. However, in this work the PET monomer viz. Bis-hydroxyethyl terephthalate , BHET, was isolated and purified by the process of recrystallization from boiling water. The kinetics of polycondensation of PET starting from pure BHET was then investigated by studying the course of intrinsic viscosity change. A Differential Scanning Caloriemeter (DSC) was then used to determine the melting and crystallization temperatures of PET.

The second set of experimental investigations involved the synthesis of a modified polyester viz. PEAT. Adipic acid units were incorporated into the homopolymer chain by polycondensing it along with BHET.Due to the random sequence distribution of the resulting copolymer, a simplified model had to be proposed in order to predict its kinetics and molecular weight. The melting and crystallization temperatures of PEAT were measured using the DSC and compared to the values predicted by Flory's theory (1).

II. THEORETICAL CONSIDERATION

A. Polycondensation Reactions

Polycondensation reactions (5) are those which proceed by a propogation mechanism in which an active polymerization site disappears every time one monomer reactant reacts. In general, a polymerization process which proceeds by a reaction between pairs of functional groups with the formation of interunit functional groups not present in the monomer(s) will be regarded as a condensation polymerization.

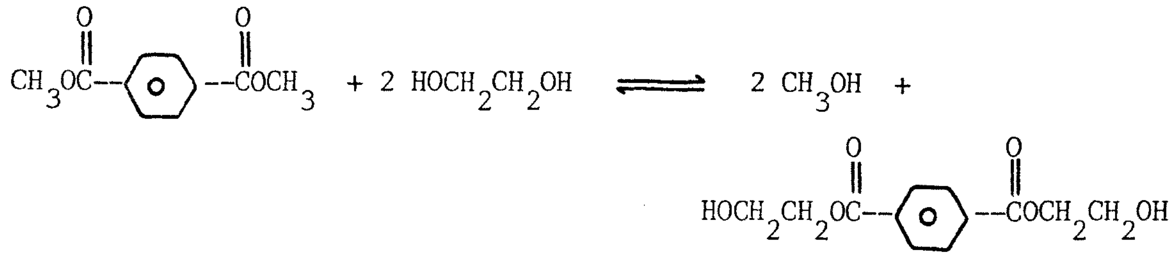
It is a general characteristic of polycondensation reactions that the number of growing chains decreases steadily with time, that the molecular weight distribution initially includes only a range of low molecular weight products which steadily increases in molecular weight and that the free monomer is largely consumed early in the reaction sequence.

B. Polyethylene Terephthalate Manufacture

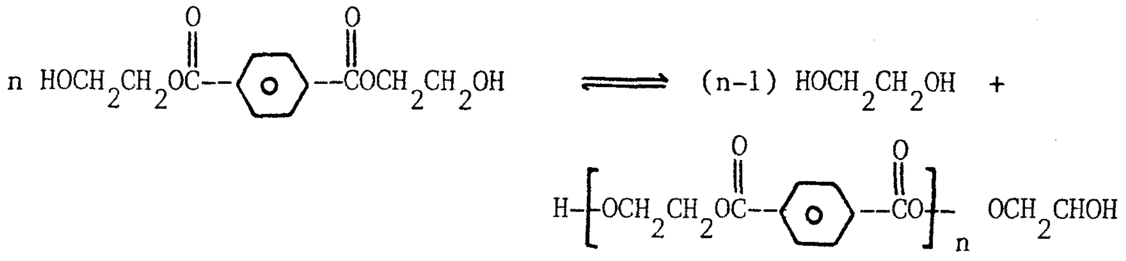
PET (6) for many years has been prepared commercially from ethylene glycol and dimethyl terephthalate. In recent years since terephthalic acid of high purity is available through air oxidation of p-xylene, its direct esterification with ethylene glycol is the preferred synthesis route because of higher reaction rates, the elimination of methanol as by-product and reduced catalyst requirements.

The polymerization essentially takes place in two steps:

(1) Ester Interchange or Transesterification

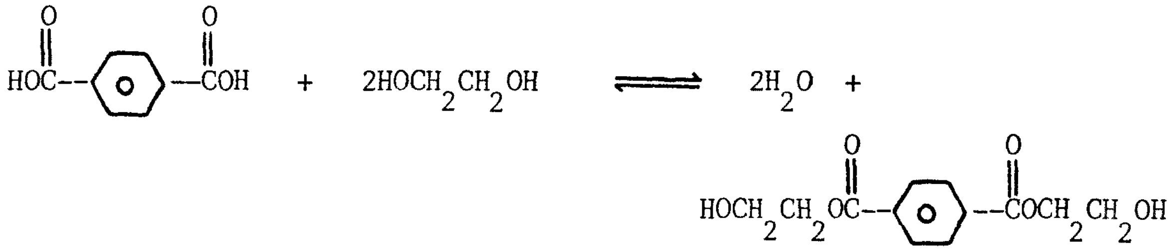


(2) Polycondensation



Monomer formation by the catalysed ester-interchange reaction between molten dimethyl terephthalate (DMT) and ethylene glycol takes place at 200 C. The product is a mixture of monomer, very low molecular weight polymer, and by-product methanol which distills at 150°C.

The alternative monomer formation system involves terephthalic acid instead of DMT and a direct uncatalysed esterification rather than ester interchange.



The monomer which is the same for both methods is polymerized in the presence of an antimony catalyst. Chain extension is promoted by the removal of excess glycol from the very viscous melt at 280°C until the desired degree of condensation is obtained.

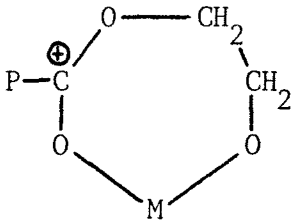
C. Catalysts and their effect

The choice of the best catalyst(s) is obviously of extreme importance in the commmercial preparation of PET. Rates of reaction must be fast as can be practically acheived , and color forming side reactions, degradation, or reactions that lead to the copolymerization of excessive amounts of diethylene glycol must be minimized.

(1) Transesterification Catalysts

In commercial practice, transesterification reaction between DMT and the glycol is catalysed by salts of manganese, zinc, calcium, cobalt or other metals. Transeterification catalysts are equally active in media that contain low or high concentrations of hydroxyl groups, but their catalytic activity is poisoned by small concentrations of carboxyl groups. At the end of the ester-interchange stage, when essentially all of the methanol has been evolved, the transesterification catalyst is converted to a catalytically inactive and substantially colorless form by reaction with a phosphorous compound such as triphenyl phosphate or phosphite.

Saunders and Dobinson (5) have discussed the effect of different catalysts on the characteristics of PET. Yoda (7) has shown that in a series of metal acetates , those salts of metals having an electronegativity lying between 1.0 and 1.7 ie calcium, manganese, zinc, cadmium, lead and cobalt, were most catalytically active. Yoda assumed that the metal compounds induce a positive charge on the carbonyl carbon atom of the ester group of DMT, facilitating attack of the glycol. In model reactions, catalysts (M) more strongly activated 2-hydroxyethyl esters, perhaps through the formation of a chelate :



P : Polymeric residue not taking part in the reaction.

(2) Direct Esterification or Polyesterification Catalysts

Direct esterification reactions may be catalysed by a second molecule of the carboxylic acid (self catalysis) or by an independent acidic catalyst. The presence of a catalyst can change the mechanism, rate and order of the esterification reaction. P-toluenesulphonic acid is an example of an acid catalyst used in simple esterification and polyesterification reactions.

(3) Polycondensation Catalysts.

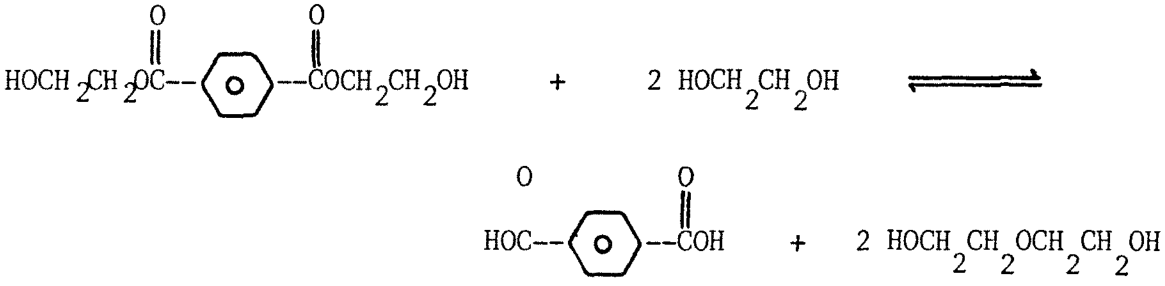
Sokolov (8) has illustrated the effect of various catalysts on the viscosity (molecular weight) of PET during polycondensation of BHET in the melt. Salts (acetates), oxides and hydroxides of certain metals (Iron, lead, aluminium, zinc etc.) are suitable catalysts of polycondensation in the melt. Kinetic investigations have shown that the viscosity of the polymer increases 1.5 to 2 times faster in the presence of catalyst. This is probably due to the fact that equilibrium has been attained more rapidly.

D. Side Reactions and their effect on PET

The effect of side reactions during the manufacture of PET include loss of functionality by decarboxylation of an acidic end group, thermal degradation of ester linkages, formation of ether linkages and cyclization reactions. In general, degradation is caused by hydrolysis, acidolysis and alcoholysis. In addition, two polyester chains may react resulting in transesterification.

A number of side products are formed in PET manufacture and these determine the quality and color of the product. Metal catalysts, which are commonly used in esterification and polycondensation reactions promote side reactions (9) which lead to the formation of diethylene glycol (DEG), acetaldehyde, acid end groups, vinyl end groups and water.

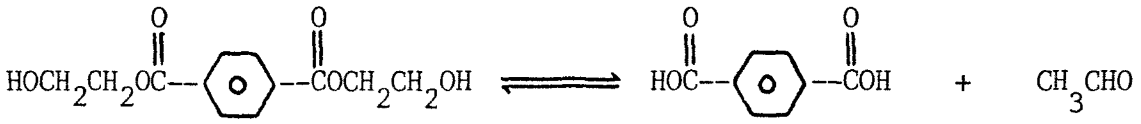
(1) Diethylene Glycol



Terephthalic acid (DEG)

DEG is not likely to be removed from the reaction mixture by distillation because of its rather high boiling point (245 °C). DEG will enter the polyester chain through a polycondensation reaction. The melting point of PET decreases by about 5 °C for every 1 percent DEG incorporated in the polymer chain and the PET chain then becomes more susceptible to degradation at ether linkages, therby adversly affecting the properties of PET. An Increased amount of DEG also increases the dyeability of PET at the expense of other properties, such as, melting point, tensile strength, etc. However, the dye take-up of PET yarn will not be uniform if the DEG units are not uniformly distributed.

(2) Acetaldehyde



Acetaldehyde formed during the reaction can react with itself and many other compounds. Polyenaldehydes formed from acetaldehyde are responsible for color formation in PET. Recent tests indicate that it may produce off-taste in a cola product at levels as low as 50 parts per billion.

(3) Acid end groups

Acid end groups, formed due to side reactions, can further participate in the polymer chain growth as long as the concentration of the hydroxyl is high as compared to acid end groups. If the acid end group formation rate is very high, then the final degree of polymerization decreases. Acid content in PET is crucial for thermal stability.

(4) Water

Water is formed in the reaction mixture due to esterificatioin reactions involving acid end groups. Any water present in the PET can promote hydrolytic degradation.

E. Polycondensation Copolymers

Copolycondensation, like copolymerization, makes it possible to vary considerably the properties of the polymer products. For this reason, polycondensation copolymers have found extensive applications both in the laboratory and in the industry. Coplymers obtained by polycondensation display a number of properties typical of all copolymers : lower melting point than homopolymers, higher solubility, lower degree of crystallinity etc.

The problems involved in the crystallization and melting of copolymers cannot be uniquely formulated. This arises from the fact that when a copolymer crystallizes, participation in the transformation by all the differing chain elements is not an apriori requirement. A wide variety of possibilities exist. These depend on the crystallization conditions, the concentration of the different chain units present and their sequence distribution.

(1) Theory of Melting Point Depression

The regularity of the copolymer structure strongly affects their melting point. Regular polymers obviously have a higher melting point. In case of irregular copolymers, the dependence of the melting point on the composition of the copolymer may be represented by a curve with a minimum (8). The minimum appears on the curve as aresult of the impaired regularity of the polymer chain and, cosequently , of the decrease in the number of intermolecular links per unit legth of polymer chain.

A common situation encountered with synthetic polymers and simpler type of chain molecules is that in which only the units that occur in major proportion crystallize. Specific cases exist, however where the other chain units present enter into the same crystal lattice.

Flory (10) developed a theory to predict the melting point depression in copolymers. The component which brings about the depression may be a constituent of the polymer itself. In a copolymer consisting of A units which crystallize and B units which do not, with the two units occuring in random sequence along the chain, it has been shown (1) that the latter should depress the melting point of the former according to the equation :

$$1/T_m' - 1/T_m = -(R/\Delta H_m) \ln N_A$$

where N_A is the molefraction of A units in the random copolymer, ΔH_m is the enthalpy of fusion, and T_m and T_m' are the melting points of the homopolymer and copolymer respectively. For an ordered or block-type copolymer, characterized by the crystallizable units occuring in very long sequences, the depression of the melting temperature is not as great as for random copolymers. For alternating copolymers in which the abundance of long sequence of crystallizable units is reduced, a greater depression of melting temperature is observed.

The melting temperature-composition relations for some representative copolyesters and copolyamides have been illustrated by Mandelkern (11). Copolyamides of this type, whose units crystallize independently of one another, display certain characteristic features. The melting temperatures depend only on composition and are independent of the co-ingredient that is introduced. This observation is consistent with wide angle X-ray observations, which indicate that only one of the units participates in the crystallization. As the concentration of the added ingredient is sufficiently increased, it can itself undergo crystallization at the expense of the other component. The melting point-composition relations for this component follow an independent curve, so that a eutectic-type minimum results at the intersection of the two curves. This is typical behaviour of random copolymers when studied over the complete composition range. If the comonomers are isomorphous, ie., capable of replacing each other in the crystals, the melting point may vary smoothly over the composition range. An example is the copolymer of hexamethylene terephthalamide and hexamethylene adipamide (12).

(2) Effect of Copolymerization on the Glass Transition Temperature (T_g)

The glass transition temperatures of random copolymers usually fall between those of the corresponding homopolymers, T_g for the copolymer often being a weighted average given by

$$a_1c_1(T_g - T_{g1}) + a_2c_2(T_g - T_{g2}) = 0$$

where $T_{g1}$and T_{g2}refer to the homopolymers , $c_1$and $c_2$are the weight fractions of monomer 1 and 2 in the copolymer, and a and a depend on the monomer type.

The contrast between this behaviour and the common depression of T_m by copolymerization is not surprising, since the changes at T_g do not require fitting a structure into a crystal lattice, and in consequence structural irregularity does not affect T_g as it does T_m.

F. Kinetic Study

(1) Kinetics of PET polycondensation by catalysed transesterification

The kinetics of catalytic transesterification has received the attention of several investigators, but little agreement has been reached even as to the order of the reaction. Skwarski (13) first reported on the polycondensation kinetics and found the catalysed reaction to be third order. Griehl and Schnock (14) investigated the kinetics of both the steps, precondensation and polycondensation, and reported each reaction to be first order with respect to ester group alone, although the the rate of reaction was proportional to catalyst concentration.

Experimental investigations conducted by Fontana (15) have shown that the polycondensation reaction involving DMT and ethylene glycol to be third order in the presence of zinc acetate catalyst. Large volume changes in the PET system made it necessary to take into account the changing catalyst concentration and the third order rate constant was obtained from

$$K_{111} = (dm_t / dt) V^2 / R_m (ROH) C_m$$

where (dm_t / dt) is the rate of methanol generation in moles per second, V is the volume of the melt in liters, C_m is the catalyst amount in moles and (ROH) is the general hydroxyl group reactivity given by

$$(ROH) = 2g + 1/2 R_g$$

where g is the moles of glycol and R_g is equivalents of half esterified glycol.

It was observed that experiments with zinc catalysts gave third order rate constants that were not always consistent between different runs or even within the same run. In some runs considerable drop in catalyst activity was noted near the end of the ester interchange. In one run with excess zinc acetate , methyl acetate was identified in the condensation product. Five runs, however, did yield a fairly consistent set of third order constants given by the equation

$$\log K_{111} = -3290/T + 6.15$$

where T is the reaction temperature in K.

Stevenson and Nettleton (16) assumed the polycondensation of PET in the presence of antimony trioxide to be a reversible second order reaction. When BHET trimer was polycondensed at 251°C in the presence of 0.025 weight % of Sb_2O_3 ,an equilibrium constant of 0.363 was obtained corresponding to a forward reaction rate constant of 0.28 lit/mol/hr. On the basis of derived activation energy of 29 Kcal., this corresponded to a rate of 1.28 lit/mol/hr.

(2) Kinetics of PET polycondensation by polyesterification

Several authors have postulated that in the absence of an added catalyst, one of the reaction groups functions as a catalyst and the polyesterification reaction would therefore follow third order kinetics. According to Flory (17), in the absence of catalyst, the following third order rate equation would hold :

$$-d(COOH)/dt = k_1(COOH)^2(OH)$$

In the presence of an acid catlyst the rate equation would reduce to :

$$- d(COOH)/dt = k_2(COOH)(OH)$$

In recent publications (18-20), Lin proposed the following rate equation for uncatalysed polyesterification :

$$-d(COOH)/dt = k'_1 (COOH)(OH)$$

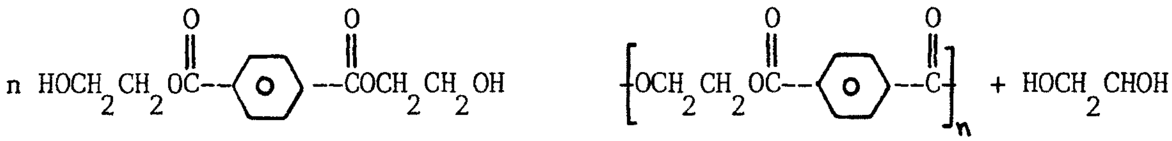
In the presence of an added catalyst, the rate equation based on a diffusion control mechanism reduces to :

$$-d(COOH)/dt = k'_2 (COOH)$$

Kemkes (21), assumed second order kinetics for the esterification reaction between DMT and terephthalic acid at 260°C. He has reported a value of the rate coeffecient of 4.31×10^{-4} kg/eq/sec.

(3) Kinetics of PET polycondensation from purified BHET monomer

In this work, the kinetics of PET poycondensation from BHET was studied in the presence of Sb_2O_3 catalyst (250 ppm) at 278°C and 1.5 mm Hg pressure.



(BHET) (PET)

A simplified kinetic model was proposed based on these assumptions :
(1) The polycondensation reaction is almost completely irreversible.

This assumption is justified by the fact that ethylene glycol is distilled off under reduced pressure, therby causing the equilibrium to shift to the right.

(2) The reaction is second order with respect to BHET alone

(3) The effect of side reactions on the rate equation can be neglected assuming that only minimal amounts of side products are formed.

(4) Volume of the polymer melt can be assumed to be almost constant.

Based on these assumptions, the rate equation for monomer consumption can be written as :

$$-dB/dt = 2k_2B^2$$

where B is the number of moles of particles having $-CH_2CH_2OH$ end groups. Integration from initial to final condition yields

$$\bar{P}_n = B_o/B = 1 + 2k_2B_ot$$

where $\bar{P}_n$ is the degree of polymerization and B_o is the initial number of moles of BHET. Multiplying the above equation by M_o(192), the molecular weight of the repeating unit, and assuming that the polymer is sufficiently high molecular, we obtain

$$\bar{M}_n = 2k_2M_oB_ot$$

As discussed before, the molecular weight of PET is related to its intrinsic viscosity in tetrachloroethane-phenol (1:1 vol) at 25°C by

$$[\eta] = 2.1 \times 10 \ (\bar{M}_n)$$

Combining the above two equation yields :

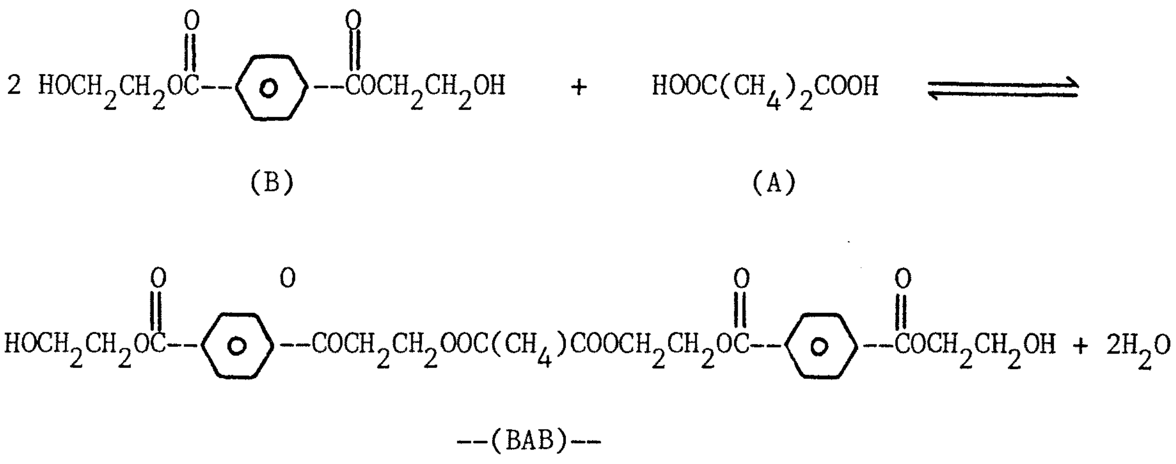
$$\log[\eta] = -3.678 + 0.82 \log(2k_2M_oB_o)^{0.82} + 0.82 \log t$$

If the second order model assumption is valid, then a plot of $\log[\eta]$ versus logt should yield a straight line whose intercept on the y-axis is used to calculate the reaction rate constant k_2 (Appendix A).

(4) Kinetics of Polyethylene adipic terephthalate (PEAT)polycondensation

The kinetics of PEAT polycondensation have been dicussed by Chou (22) for the case where the molar ratio of BHET and adipic acid is 2:1. Chou assumed that the polycondensation step was preceeded by a pre-polymerization reaction, during which, most of the monomer was consumed. End group analysis of pre-polymer with NaoH showed that the pre-polymer end end groups were not acidic. Hence the pre-polymer was assumed to be of the type : ---BAB--- or ---BABAB---

(1) Pre-polymerization



(2) Polycondensation

$$n \text{ --(BAB)--} \rightleftharpoons \text{PEAT} + (n-1)\ HOCH_2CH_2OH$$

The polycondensation reaction was assumed to be irreversible and second order with respect to the pre-polymer. Neglecting the formation of any side products, the rate equation was written as :

$$-dC/dt = 2k_2'C^2$$

where C is the number of moles of particles having $-CH_2CH_2OH$ end groups. Integration from initial to final condition yields :

$$\bar{P}_n = C/C = 1 + 2k_2'C_o t$$

where $\bar{P}_n$ is the degree of polymerization and C_o is the initial number of moles of pre-polymer present in the system. Multiplying the above equation by M_o', the molecular weight of the repeating unit, and assuming that the copolymer is high molecular, the following equation was obtained :

$$\bar{M}_n = 2k_2'M_o C_o t$$

The molecular weight of PEAT is related to its intrinsic viscosity in sym. tetrachloroethane-phenol (1:1 vol) at 25°C by :

$$[\eta] = K\,\bar{M}_n^{\,a}$$

where the values of 'K' and 'a' are unknown . Combining the above two equation yields :

$$\log[\eta] = \log\ K(2k_2'M_o'C_o) + a\log t$$

If the assumption of second order kinetics is valid, the plot of $\log[\eta]$ versus logt should yield a straight line. The slope of this line can be used to predict the value of 'a' and the intercept would give an approximate value of the rate constant k_2' , for a given value of 'K'.

For the case where the BHET monomer is in large excess, the sequence distribution of the copolymer becomes very random and it becomes very difficult to predict the exact structure of the pre-polymer and repeating unit. A number of complex end group analysis would have to be performed to determine the same.

In this work, an hypothetical model is proposed, based on some simplifying assumptions. This model would enable one to predict the kinetic rate constants of PEAT polycondensation and estimate the average molecular weight. The following assumptions were made :

(1) The pre-polymer was assumed to contain BHET and adipic acid units in the same ratio in which they were added to the reaction vessel.

(2) The reaction is second order with respect to the pre-polymer and almost completely irreversible.

(3) The equilibrium molecular weight of PEAT will be in the same range as that of PET.

(4) The molecular weight of the repeating unit will equal that of the pre-polymer minus the amount of ethylene glycol and water distilled off during the reaction.

Computations of the reaction rate constant and molecular weight for PEAT, based on experimental values of intrinsic viscosity are shown in the Appendix B.

G. Theory of Crystallization

In the crystallization of high polymers, there is much evidence which makes it clear that the process, is one of birth (crystal nucleation) and growth (spherulite growth).

When high polymers crystallize, the single crystals are arranged in spherically symmetric arrays called spherulites. The crystals exist only within these arrays. The spherulites nucleate on adventitous surfaces (usually dust particles) in the melt and enlarge radially. The spherulites are only partially crystalline and are comprised of numerous single crystals which are all about the same size. Consequently, new crystals must be continuously nucleated as the spherulite develops. The new crystals nucleate near the old, the latter being the catalyst for the process. There is strong evidence that the process by which existing crystals grow is also controlled by a nucleation mechanism. Thus, the nucleation of new intraspherulitic crystals is controlled by nucleation processes near or on the surface, the entire course of crystallization is controlled by these heterogeneous nucleation mechanisms.

In most practically encountered polymer crystallizations, nucleation is heterogeneous. For instance, in many polymers, spherulites appear in the same positions in successive meltings and crystallizations (23). This shows that once the samples are sufficiently melted, remnants of polymer crystalline order are destroyed and nucleation starts on insoluble heterogenities, which, because of the high viscosity of the melt, cannot move.

(1) Degree of Crystallinity

The concept of crystallinity arises quite naturally from the observation that many properties of polymers are intermediate between those expected of a purely crystalline and of a purely liquid material. For instance, observed densities are normally higher than those estimatimated for polymer liquids but rarely as high as those calculated from X-ray studies.

Mayhan and Bosch (24) studied the degree of crystallinity of PET from density measurements. The degree of crystallinity can be directly related to density if knowledge of the densities of the amorphous and the 100% crystalline polymer are known. The density of the amorphous polymer was measured by the gradient method to be 1.333 g/cm^3 at 25 °C and that of the completely crystalline polymer was obtained from X-ray diffraction data as 1.455 g/cm^3 at 25 °C. Degree of crystallinity (DOC) of PET could then be calculated using the following expression :

DOC = Density of PET sample / Density of 100% crystalline PET

(2) Kinetics of Crystallization of PET

The transformation of an amorphous crystallizable polymer into a semicrystalline material is not instantaneous even under the most favorable thermodynamic conditions. Several investigators have studied the crystallization of PET from the melt using various analytical methods.

Lin (25) studied the rate of crystallization of PET by differential scanning calorimetry (DSC). An expression for the maximum crystallization rate was developed using the Avrami equation (26). It was found that the rate of crystallization decreased with increasing molecular weight of PET. Moreover, a study of isothermal crystallization showed that in the vicinity of the melting temperature, the crystallization rate is very slow. As the temperature is lowered, the rate progressively increases and eventually passes through a maximum. At crystallization temperatures below the maximum, the overall rate of crystallization becomes small again. The temperature (175°C) at which this maximum occured was found to be the same for PET samples having different molecular weights. Furthermore, a study of the course of crystallization showed a secondary crystallization transition at which the Avrami constant n changed from a value of 3 to 1.5. The only conclusion that was drawn from the values of n was that the crystallites favored linear growth during the primary stages of crystallization. Microscopic examination of crystallizing systems have shown tha transformation from primary to secondary crystallization occurs when a massive impingment of spherulite takes place. Thereafter, the rate of crystallization decreases rather abruptly and a very slow transformation process takes place.

Jackson and Longman (27) have investigated the factors that affect the rate of crystallization of PET and its related copolymers. Based on their study the following conclusions can be made :

(a) Increasing molecular weight decreases the rate of crystallization.

(b) Where random copolymerization gives a lower T_m , the rate of crystallization decreases with increasing co-unit and also the crystallization temperature at which the maximum rate is observed, decreases similarly.

(C) Where random copolymerization gives a higher T_m , the rate of crystallization is lower but the temperature of maximum crystallization rate increases. Moreover, the temperature range over which the crystallization occurs is much narrower.

(d) Efficacious nucleating agents increase the rate of crystallization and the maximum rate occurs over a wider range of temperature.

(e) Previous history of PET is not destroyed unless the melt is heated to atleast 280 C.

H. Thermodynamics of Fusion and Crystalline Melting

The fusion of polymeric systems can be classified as a first order transition (11). In the theoeretical limit of a homogeneous polymer of infinite molecular weight forming a perfectly crystalline phase, melting should occur sharply at a well defined temperature. The finite length of any real polymer chain introduces a certain element of disorder into the system, namely the chain ends. If the chain ends are not tolerated by the lattice, melting cannot be sharp even under the most ideal conditions of crystallization and annealing. Thus the process of fusion in actual crystalline high polymers will invaribly take place over a range of temperatures. However, the last vestiges of crystallinity should disappear at a well defined temperature known as the equilibrium melting temperature T_m. It represents the melting temperature of the hypothetical perfect crystal and is given by the equation :

$$T_m = \Delta H_m / \Delta S_m$$

where ΔH and ΔS are the enthalpy and entropy of fusion per repeating unit of the polymer.

Aliphatic polyesters melt at a lower temperature than polyethylene, in analogy with the melting temperature of monomeric chain esters as compared with the corresponding hydrocarbons. A general decrease in T_m is noted as the proportion of ester groups in the chain increases (28). Polyesters that contain an odd number of CH_2 sequences melt at lower temperatures than those containing even number of sequences. ΔH_m for polyesters containing an odd number of units is slightly less than for the even numbered polymers. This may be the explanation for the difference in melting temperatures between the two types. The introduction of ring structures into the chain gives rise to substantially higher melting temperatures when compared with the corresponding aliphatic polymers. This may be a result of lowered entropy of fusion.

The enthalpies of fusion and melting points of several polymers has been discussed in literature. These values vary significantly depending on the method of determination. Mandelkern (11) reports for PET an enthalpy of fusion of 5500 cal/mole corresponding to a melting point of 267°C and entropy of fusion of 10.2 cal/deg/mol . This estimate of ΔH_m was based on caloriemetric measurements of pure polymer. Roberts (29) has compared the values of ΔH_m obtained from different methods and reports a value of 5600 cal/mole based on the melting point depression produced by dibutyl phthalate diluent in PET.

III. EXPERIMENTAL

A. Synthesis of BHET

(1) Transesterification

A round bottom flask (fig .1) was charged with 48.5 g of dimethyl terephthalate (DMT), 186 g of ethylene glycol and 0.1467 g of zinc acetate catalyst. 0.1579 g of chloroacetic acid was added in order to inhibit the formation of catalyst inhibiting substances. From this reaction mixture , methanol (boiling point 64.7°C) was removed by distillation until the head temperature of the column rose to 150 C. Distillation was stopped and the reaction product consisting mainly of BHET monomer and oligomer was allowed to cool down to room temperature.

(2) Removal of unreacted glycol

To the solid mixture, 0.5 liters of distilled water was added . The mixture was thoroughly agitated and then filtered through a #1 filter paper using a bucchner funnel and aspirator bottle. Unreacted glycol which is very soluble in water was thus removed from the reaction product. The white residue consisting of only BHET monomer and oligomer (both insoluble in water at room temperature) was then vacuum dried in an oven at 70°C for 24 hours. The dried residue was found to weigh 57.2g indicating that the reaction had gone to only 90% completion.

(3) Purification

The residue was then added to 1 liter of distilled water which was brought to boil. The solution was filtered through a #1 filter paper and the oligomer (insoluble in water even at 100°C) was thus seperated. The mother liquor was cooled to room temperature and crystals of BHET were recovered by filteration. The BHET monomer purified in this manner was vacuum dried in an oven at 70°C for 24 hours. It was found to weigh 44.65 g corresponding to an ultimate yield of 70.3 %.

(4) Melting point

A polarizing microscope was used to determine the melting point of BHET monomer and residual oligomer mixture. The pure monomer was observed to melt in the temperature range 107-109°C whereas the oligomer mixture melted between 170-175°C.

B. Synthesis of PET by catalytic polycondensation

8g of BHET was taken in a test tube and 2 mg (250 ppm) of antimony oxide (Sb_2O_3) was added to it . The test tube was immersed in the salt bath maintained at 278°C. As a safety precaution, the test tube was sheilded by a metallic gauze. A slow stream of nitrogen gas was bubbled through the melt for a period of 1.5 hours. Nitrogen gas was then discontinued and the pressure was decreased to 1.5mm Hg using a vacuum pump. Polycondensation was then continued for 8 hours with simultaneous removal of glycol and other volatiles by distillation. A sample of the polymer was removed every two hours to study the course of polymerization by viscosity measurement. During sampling, the polymer was first allowed to cool to room temperature under nitrogen in order to prevent degradation by oxidation.

C. Synthesis of PEAT by catalytic polycondensation

8g of BHET was taken in a test tube and 0.42 g (8.4 mol %) of adipic acid and 2.1 mg (250 ppm) of Sb_2O_3 was added to it. Polycondensation was then carried out as before at 278°C first in a nitrogen atmosphere and then under vacuum. The copolymer was sampled every two hours for viscosity measurement. This procedure was then repeated using 16.2 mole % and then 23.5 mole % of adipic acid. These copolymers were also sampled every two hours to study the course of copolymerization.

D. Solution viscosity and molecular weight

Dilute solution viscosity of the polymer was measured by using a Ubbelohde viscometer. The advantage of using this viscometer is that the measurement is independent of the amount of solution in the viscometer and measurement at a series of concentration can easily be done by successive dilutions.

(1) Preparation of polymer solution

The polymer sample was accurately weighed and dissolved in a known volume of symmetric tetrachloroethane-phenol (1:1 vol.). The solution was maintained at 130°C for 20-25 minutes to ensure the complete dissolution of the polymer into the solvent. The solution was then cooled to room temperature and filtered through a 0.45 micron cellulose filter paper.

(2) Experimental set-up and procedure

The Ubbelohde viscometer (#1C) was cleaned with acetone and dried by passing clean, dry filtered air through the instrument to remove the final traces of solvent. The viscometer was now charged with the pure solvent and then placed in a constant temperature water bath at 25 °C (±0.2 °C) for approximately 20 minutes. The efflux time of the solvent was measured (85 sec). The solvent was then replaced by the polmer solution and its efflux time was measured to the nearest 0.1 second. The solution was then successively diluted and the efflux time at each dilution was determined. The solution concentration was restricted to the range that gave relative viscosities between 1.1 and 1.5.

(3) Intrinsic viscosity

Viscosity data as a function of concentration was extrapolated to infinite dilution by means of the Huggins equation (30) :

$$\eta_{sp}/C' = [\eta] + K'[\eta]^2 C'$$

where K' is a constant for a sereis of polymers of different molecular weights in a given solvent. The intrinsic viscosity $[\eta]$ is independent of concentration by virtue of extrapolation to $C' = 0$, but is a function of the solvent used. The values of intrinsic viscosity for PET and PEAT are recorded in table 1 and their variation with reaction time are shown in fig.3 and fig.5 respectively. In table 5 the logarithmic values of intrinsic viscosity and rection time for PET and PEAT are recorded.

(4) Molecular weight

The molecular weight of PET was determined (table 2) by using the following equation (31) :

$$[\eta] = 2.1 \times 10 \ (\bar{M}_n)$$

E. Melting and Crystallization temperatures of PET and PEAT

(1) Experimental set-up and procedure

A Perkin-Elmer Differential Scanning Caloriemeter (DSC-1B) was used for all thermal scans. Each sample was weighed (0.015-0.025g) into the standard aluminium dish , covered and placed in the left-hand sample holder. Nitrogen gas was flushed through the system at a rate of about 10 ml per minute and the system was allowed to stabilize for atleast 30 minutes. Any previous mechanical and thermal histories were considered to be erased by the first step in the experimental sequence, in which the sample was taken up to 290 °C and held there for 10 minutes. The sample was then allowed to cool to 50 °C at 40 °C/minute. The chart recorder speed was set at 20 cm/hr., the range at 16 and the sample was thermally scanned at the rate of 10 °C.

(2) Interpretation of Data

The peak maximum of the recording of a transition by the DSC-1B indicates the temperature and time at which the transition is proceeding at a maximum rate. It was observed that crystallization transitions, which are exothermic in nature, were recorded as downscale deflections. Melting transitions, which are endothermic in nature, were recorded upscale. The crystallization and melting temperatures of PET and PEAT were thus recorded (tables 3-4).

IV. RESULTS AND DISCUSSIONS

A. Intrinsic viscosity and molecular weight of PET

Intrinsic viscosity of PET was observed to increase with reaction time (Fig.3). At the end of 8 hours of reaction, an intrinsic viscosity of 0.5369 dl/g was obtained. This corresponds to a number average molecular weight of 14312 and a degree of polymerization of almost 75 as shown in Appendix A. It is assumed, that at high viscosities, polycondensation reactions are diffusion controlled ie the growth rate of macromolecular chains is determined by the rate of diffusion of the terminal active sites towards one another. Since, in this experiment, a conversion of 98.6% was obtained, one can assume that the molecular weight obtained is almost equal to the ultimate molecular weight. As shown in fig.4, the molecular weight is observed to increase linearly with reaction time.

B. Intrinsic viscosity and molecular weight of PEAT

As shown in fig.5, by increasing the amount of adipic acid in the copolymer, the intrinsic viscosity increases. Moreover, the rate of increase in viscosity also shows a slight improvement. There could be a number of possible explanations for this phenomenon :

(1) The presence of adipic acid has a catalytic effect which causes an increase in the activity of the polymer chain ends. It is highly likely that the activity between the end groups of BHET and adipic acid is much higher than the activity between two BHET endgroups. However, since the activity between two adipic acid end groups is zero, hence an excess of adipic acid as a co-unit, could posibbly inhibit the polymerization.

(2) The presence of adipic acid could affect the flexibilty and hydrodynamic volume of the molecule and therby alter the viscosity.

Since the sequence distribution of BHET and adipic acid is essentially random, hence it is very difficult to obtain the values of molecular weight based on intrinsic viscosity measurements. In Appendix B, the molecular weights of PEAT copolymer are predicted based on a simplified kinetic model. As shown in table 7, the molecular weight of PEAT is predicted to increase, with increasing amounts of adipic acid co-units.

C. Melting and crystallization temperatures of PET and PEAT

The melting point , T_m , of PET was recorded on the DSC-1B as an endothermic deflection corresponding to a temperature of 262°C. This value is around 8°C lower than that reported in literature (31). There are two posible explanations for this :

(1) The molecular weight of the PET obtained in the laboratory could be lower than that of commercial PET.

(2) The melting point of PET decreases by nearly 5°C for every 1% of diethylene glycol incorporated in the polymer chain. Thus, it is possible that about 1.6% of diethylene glycol is present in the polymer chain due to presence of side reactions.

The temperature of maximum crystallization rate, T_c , of PET was recorded as an exothermic peak corresponding to a temperature of 174 °C. The ratio T_c / T_m (temperatures in °K) equalled 0.835 and is consistent with values reported in literature (11).

As predicted by Flory's theory of melting point depression in copolymers, the incorporation of adipic acid co-units in PET causes a significant decrease in its melting point (table 4, fig.8). The melting point is observed to decrease by about 1.4 C for every mole% of adipic acid co-unit present.

There is a fairly large discrepancy between the melting point depression predicted according to Flory's theory and that obtained from the experiment (table 9, fig.12). As stated by Flory, alternating type copolymers have a larger depression in their melting point compared to random copolymers. Since BHET is in large excess over the adipic acid units, the PEAT copolymer may in fact be a mixture of the following chains which could cause a greater depression in melting point :

(1) Chains containing two or more BHET units alternating between adipic acid units.

(2) Chains containing only BHET units

(3) Chains containing BHET and adipic acid units distributed randomly.

The crystallization temperature , T_c , of PEAT as measured by the DSC-1B, was not perfectly reproducible. The sharpness of the exothermic peak was observed to vary slightly with the amount of sample used and the scanning rate. Average T_c exhibited a sigmoidal behaviour with respect to the concentration of adipic acid co-units (table 3, fig.7). As the adipic acid concentration is increased to 23.5 mole % , the crystallization temperature drops down to 136 °C. If the adipic acid concentration was to be greatly increased, it is very likely that the adipic acid units would begin to crystallize independent of the PET units and the crystallization temperature of PEAT would approach that of adipic acid alone.

D. Prediction of rection rate constants for PET and PEAT condensation

The plot of log versus logt (fig.9) for PET gave a straight line of slope 0.8099 and an intercept on the y-axis of -1. The slope, which corresponds to the exponent 'a' in the viscosity-molecular weight relationship, compared favorably with the value of 0.82 stated in literature. This validates the assumption of second order kinetics for the polycondensation of PET. The intercept was used to estimate the reaction rate constant as shown in Appendix A. A value of 0.945 lit/mol/hr was obtained for PET.

The reaction rate constant obtained in this study was observed to be slightly lower than that obtained by Stevenson and Nettleton (16), for the polycondensation of linear ethylene terephthalate trimer. On the basis of the derived activation energy of 29 Kcal., the authors predicted a reaction rate constant of 1.28 lit/mol/hr.

One explanation for the lower reaction rate constant obtained in this work could be based on the theory given by Stevenson and Nettleton that the Sb_2O_3 catalyst is deactivated in the presence of pure BHET. Challa (32), has distinguished the reactivity of BHET endgroups from the reactivity of BHET endgroups with polymer endgroups, the latter in turn is different from that of polymer endgroups with polymer endgroups. The polycondensation of polymer endgroups is found by Challa to be 1.8 times as fast as the polycondensation of polymer endgroups with BHET endgroups. The latter reaction is 1.8 times as the fast as the polycondensation of two BHET endgroups.Though this theory may not hold good perfectly, it may be a possible explanation for the lower reaction rate obtained.

Another point to be noted is that the rate constant obtained by Stevenson and Nettleton, took into account the reversible nature of the polycondensation reaction. However, in this work, the second order kinetics was developed on the assumption that the reaction was irreversible. This assumption could be erroneous due to the fact that during the experiment, small amounts of glycol could be seen refluxing on to the melt. A sufficiently high concentration of glycol could lead to a reverse reaction (glycolisis) and cause the formation of diethylene glycol. Therefore, the rate constant estimated in this work may represent a value significantly less than the true forward rate.

For PEAT, it was observed that the relationship between log and logt (fig.10) was linear. This validates the assumption of second order kinetics for PET polycondensation.The procedure for predicting the rate constants for the PEAT copolymers is shown in Appendix B and the values are listed in table 8. It was observed that the incorporation of 8.4 mole% of adipic acid in PET caused a lowering of the rate constant in comparison to the value for pure PET polycondensation. However, a further increase in the adipic acid concentration caused a significant improvement in the values of rate constant. The latter could be explained based on the hypothesis that the presence of acid groups catalyses the polycondensation rate. It was assumed that the activity of adipic acid endgroups and BHET endgroups is greater than the activity of two BHET endgroups and therfore the polycondensation rate is enhanced.

The decrease in the reaction rate of PEAT having 8.4 mol% adipic acid caused a lowering of the predicted molecular weight from a value of 14312 for pure PET, to a predicted value of 13838 . This behaviour is found to be rather anamalous as compared to the behaviour of PEAT copolymers having higher adipic acid concentrations. It has been shown in this work, that the kinetics of polycondensation is very sensitive to the amount of catalyst used. Since the amount of catalyst used in these experiments was very small (250 ppm), inaccuracies in weighings (due to the limitations in the sensitivity of the balance used),could have caused a very high percent error in catalyst concentration and therby led to unpredictable behaviour in the kinetics. A detailed study of the effect of adipic acid on the flexibility and hydrodynamic volume of the polymer molecule and its effect on the activity of the chain ends would have to be made, before a satisfactory explanation could be offered.

E. Effect of catalyst on the rate constant of PEAT polycondensation

Figure 12 shows a plot of log$[\eta]$ versus logt for PEAT (adipic acid concentration: 16.2 mol%), both in the presence and absence of catalyst. The plot shows that the two lines are nearly parrallel, indicating that the value of 'a' (corresponding to the slope) in the viscosity-molecular weight relationship (Ch.III) is nearly the same. This validates the theory that the exponent 'a' is a function of only polymer structure , solvent and temperature, and independent of the catalyst used. However, the different values of the intercept on the y-axis shows that the kinetics are greatly altered in the presence of catalyst. The reaction rate constant (Appendix B) is shown to increase from a value of 140.5 /mol/hr to 181.6 /mol/hr with the addition of 250 ppm Sb_2O_3 catalyst.

V. CONCLUSIONS

1. Inspite of the initial deactivation of Sb_2O_3 catalyst, the kinetics of polycondensation of PET from purified BHET is shown to be comparable to the kinetics stated in literature for the polycondensation via other routes.

2. Incorporation of adipic acid in the polymer, increases the reaction rate significantly. Moreover, there is a substantial decrease in the melting and crystallization temperatures of the copolymer PEAT, with increasing adipic acid contents.

3. In general, PEAT copolymer melts are more viscous than PET polymer melts, and would be more suitable for film and textile fiber applications.

4. PEAT would have superior processing characteristics as compared to that of PET. A lower crystallization temperature would possibly improve the crystallization rate at low mold temperatures, resulting in shorter mold cycles.

VI. RECOMMENDATIONS

1. Since the sequence distribution of the copolymer PEAT was considered to be random, a number of simplifying assumptions were made for the sake of mathematical convenience . The prepolymer of PEAT was assumed to contain BHET and adipic acid units in the ratio in which they were added to the reactor. However, in reality, this assumption may not be valid. Hence, it is recommended that a more detailed study of the actual sequence distribution be made with the help of titrations and end group analysis.

2. Since the values of'K' and 'a' in the viscosity - molecular weight relationship are not known in literature for PEAT, the molecular weights should be determined by more absolute methods viz. light scattering, memberane osmometry etc.

3. The polycondensation of PET from purified BHET should be performed in the presence of catalysts other than Sb_2O_3 which may not be deactivated by the monomer. This may result in higher rates of polycondensation.

4. The rates of crystallization of PET and PEAT should be determined using the DSC-II. The quenching rates of the DSC-1B are not high enough to permit the study of isothermal crystallization rates.

VII. GLOSSARY

a	:	Dimensionless constant which is a function of solvent and polymer type
a_1, a_2	:	Dimensionless constants which depend on monomer type
B_o		Initial number of moles of BHET monomer
B	:	Number of moles of polymer particles having -CH CH OH end groups
c_1, c_2	:	Weight fractions of homopolymers
C'	:	Concentration of polymer solution (g/dl)
C	:	Catalyst amount in moles
C_o	:	Initial number of moles of prepolymer present
C	:	Number of moles of copolymer particles having -CH CH OH end groups
g	:	Moles of glycol
ΔH_m	:	Enthalpy of fusion of polymer cal / mol
K	:	Dimensionless constant which is a function of solvent and polymer type
K'	:	Dimensionless constant for a sereis of polymers of different molecular weight in a given solvent
K_{111}	:	Third order rate constant (g equiv/lit) (sec)
k_1, k_1',	:	Third order reaction rate constants (mole) (sec)
k_2, k_2',	:	Second order reaction rate constants (mole) (sec)
M_o, M_o'	:	Molecular weight of repeating unit of PET and PEAT resp.
M_A, M_B	:	Molecular weight of adipic acid and BHET respectively

$\bar{M}_n$: Number average molecular weight
M_{pp} : Molecular weight of prepoymer
m : Moles of methanol generated
n : Avarami constant (dimensionless)
$[\eta]$: Intrinsic viscosity of polymer solution (dl/g)
η_{sp} : Specific viscosity of polymer solution (dimensionless)
$\bar{P}_n$: Number average degree of polymerization

R : gas constant cal.mol °K
R_m : Equivalents of methyl ester
R_g : Equivalents of half esterified glycol

ΔS_m : Entropy of fusion of polymer cal/mol / °K
T_m : Melting point of homopolymer °K
T'_m : Melting point of copolymer °K
T_c : Temperature of maximum crystallization °K
T_g : Glass transition temperature of copolymer °C
T_{g1}, T_{g2} : Glass transition temperature of homopolymer °C
V : Volume of polymer melt (litres)
$\bar{X}_n$ Degree of conversion

VIII. APPENDIX

A. Prediction of reaction rate constant and molecular weight of PET

(a) Molecular weight of BHET monomer :

$M_B = 254$

(b) Molecular weight of repeating unit :

M_o = 254 - molecular weight of ethylene glycol

$= 254 - 62$

$= 192$

(c) Initial number of monomer units :

B_o = Initial weight of monomer / Molecular weight of monomer

$= 8/254$

$= 0.031496$ moles

(d) Number average molecular weight of PET at time t equal to 8 hours :

$$= K\,(\bar{M}_n)^a$$

$$0.5369 = 2.1 \times 10^{-4}\,(\bar{M}_n)^a$$

Molecular weight = 14312

(e) Degree of poloymerization :

$\bar{P}_n = 14312/192$

$= 74.5$

(f) Degree of conversion

$\bar{X}_n = (\bar{P}_n - 1) / \bar{P}_n = 0.986$

(g) Reaction rate constant

From fig.9, intercept = -1

$$= \log K(2k_2 M_o B_o)^a$$

where $K = 2.1 \times 10^{-4}$, $M_o = 192$, $B_o = 0.031496$, $a = 0.82$

Substituting the above values yields

$k_2 = 152.4$ /mol/hr

Assuming that the volume of the polymer melt remains nearly constant throughout the reaction at 0.0062 litres, the rate constant can also be expressed as

$k_2 = 0.945$ lit/mol/hr.

B. Prediction of rate constant and molecular weight of PEAT

Case I :

(a) Molar ratio of BHET : Adipic acid = $X_B : X_A$ = 91.6 : 8.4

(b) Molecular weight of prepolymer :

$$M_{pp} = X_B M_B + X_A M_A$$

$$= 0.916(254) + 0.084(146)$$

$$= 244.93$$

(c) Molecular weight of repeating unit

$$M_o' = M_{pp} - X_B(\text{molec. wt. of glycol}) - X_A(\text{molec. wt. of water})$$

$$= 244.93 - 0.916(62) - 0.084(18)$$

$$= 186.62$$

(d) Initial number of prepolymer units

$$C_o = \text{Initial weight of sample} / M_{pp}$$

$$= 8.42 / 244.93$$

$$= 0.034377$$

(e) Prediction of rate constant

The value of 'a' and 'K' in the viscosity-molecular weight relationship is not known for PEAT. The value of 'a' is obtained from the slope of the line shown in fig.10 and equals 0.4186. An approximate value of 'K' is generated by assuming that the molecular weight of PEAT is in the same range as that of PET.

$$0.3028 = K\ (14312)^{0.41864}$$

Therefore, $K = 5.51332 \times 10^{-4}$

From fig.10, intercept on the y-axis = -0.9056

$$= \log \; K(2k_2' M_o' \; C_o)$$

Solving for the rate constant we obtain,

$k_2' = 133$ /mol/hr

(f) Predicted number average molecular weight of PEAT at t = 8 hrs.

$$\bar{M}_n = M_o' \; (1 + 2k_2' C_o t)$$

$$= 186.62(1 + 2 \times 133 \times 343.77 \times 10^{-4} \times 8)$$

$$= 13839$$

(g) Degree of polymerization

$$\bar{P}_n = \bar{M}_n \; / \; M_o'$$

$$= 74$$

Case II

(a) Molar ratio of BHET : Adipic acid = 83.8 : 16.2

(b) Molecular weight of prepolymer :

$M_{pp} = 0.838(254) + 0.162(146)$

$= 236.5$

(c) Molecular weight of repeating unit :

$M_o' = 236.5 - 0.838(62) + 0.162(18)$

$M_o' = 181.628$

(d) Initial number of prepolymer units

$C_o = 6.6666 / 236.5$

$= 0.0281885$ moles

(e) Prediction of rate constant

From the slope of the line in fig.10, a = 0.05851

$0.4993 = K(\bar{M}_n)$

Therefore, $K = 1.84867 \times 10^{-3}$

The intercept on the y-axis = -0.8201

$= \log K(2k_2' M_o' C_o)$

Solving, we obtain $k_2' = 181.7$ /mol/hr

(f) Number average molecular weight for PEAT at t = 8 hrs.

$\bar{M}_n = 181.628 (1 + 2 \times 181.7 \times 281.885 \times 10^{-4} \times 8) = 15066$

(g) Degree of polymerization : $\bar{P}_n = 83$

Case III

(a) Molar ratio of BHET : Adipic acid = 76.5 : 23.5

(b) Molecular weight of prepolymer :

$M_{pp} = 0.765(254) + 0.235(146)$

$= 228.62$

(c) Molecular weight of repeating unit :

$M_o' = 228.62 - 0.765(62) - 0.235(18)$

$= 176.96$

(d) Intial number of prepolymer units

$C_o = 6.3530 / 228.62$

$=0.277884$ moles

(e) Prediction of rate constant

From th slope of the line in fig.10, $a = 0.6521$

$0.58 = K(14312)^{0.6521}$

Therefore, $K = 1.13054 \times 10^{-3}$

The intercept on the y-axis = -0.8105

$= \log \; K(2k_2' M_o' C_o)$

Solving, we obtain $k_2' = 191.8/$ mol/hr

(f) Number average molecular weight for PEAT at t = 8 hrs.

$\bar{M}_n = 176.96\ (1 + 2 \times 191.8 \times 277.884 \times 10^{-4} \times 8) = 15268$

(g) Degree of polymerization : $\bar{P}_n = 86$

Case IV

(a) Molar ratio of BHET : Adipic acid = 83.8 : 16.2

No Sb_2O_3 catalyst added during polycondensation

(b) Molecular weight of prepolymer :

$M_{pp} = 0.838(254) + 0.162(146)$

$= 236.5$

(c) Molecular weight of repeating unit :

$M_o' = 236.5 - 0.838(62) + 0.162(18)$

$= 181.628$

(d) Initial number of prepolymer units :

$C_o = 8.0555 / 236.5$

$= 0.03406$

(e) Prediction of rate constant

From the slope of the line in fig. 11, a = 0.5720

$0.3820 = K(14312)^{0.5720}$

Therefore, $K = 1.60325 \times 10^{-3}$

The intercept on the y-axis = -0.9415

$= \log K(2k_2' M_o' C_o)^{0.5720}$

Solving, we obtain $k_2' = 140.6$ /mol/hr

(f) Number average molecular weight for PEAT at t = 8 hrs.

$\bar{M}_n = 181.628\ (1 + 2 \times 140.6 \times 0.03406 \times 8) = 14098$

(g) Degree of polymerization : $\bar{P}_n = 78$

C. Tables

Table 1: Variation of intrinsic viscosity with reaction time for PET and PEAT having different adipic acid contents

Adipic Acid (mol%)	Catalyst (ppm)	reaction time (hrs)	Intrinsic viscosity (dl/g)
0	250	2	0.1749
0	250	4	0.3010
0	250	6	0.4245
0	250	8	0.5369
8.4	250	2	0.1715
8.4	250	4	0.2065
8.4	250	6	0.2684
8.4	250	8	0.3028
16.2	0	2	0.1708
16.2	0	6	0.3124
16.2	0	8	0.3820
16.2	250	4	0.3350
16.2	250	6	0.4490
16.2	250	8	0.4993
23.5	250	2	0.2409
23.5	250	6	0.5198
23.5	250	8	0.5800

Table 2 : Variation of Molecular weight with reaction time for PET

Reaction time (hrs)	Molecular weight
2	3645
4	7037
6	10747
8	14312

Table 3 : Variation of Crystallization temperature with adipic acid content for PEAT

Adipic acid content (mol%)	Crystallization temperature (°C)
0	174
8.4	163
16.2	140
23.5	136

Table 4 : Variation of Melting temperature with Adipic acid content for PEAT

Adipic acid content (mol%)	Melting temperature (°C)
0	262
8.4	249
16.2	239
23.5	228

Table 5 : Variation of logarithmic intrinsic viscosity with logarithmic reaction time for PET

$\log \eta$	logt
-0.7572	0.301
-0.5214	0.6020
-0.4245	0.7782
-0.5369	0.9031

Table 6 : Variation of logarithmic intrinsic viscosity with logarithmic reaction time for PEAT having different adipic acid contents

Adipic acid (mol%)	Catalyst (ppm)	$\log\eta$	logt
8.4	250	-0.7657	0.3010
8.4	250	-0.6850	0.6020
8.4	250	-0.5712	0.7782
8.4	250	-0.5187	0.9031
16.2	0	-0.7675	0.3010
16.2	0	-0.5053	0.7782
16.2	0	-0.4179	0.9031
16.2	250	-0.4749	0.6020
16.2	250	-0.3478	0.7782
16.2	250	-0.3016	0.9031
23.5	250	-0.6182	0.3010
23.5	250	-0.2842	0.7782
23.5	250	-0.2366	0.9031

Table 7 : Variation of predicted molecular weight of PEAT with Adipic acid content

Adipic acid (mol%)	Catalyst (ppm)	Molecular weight
0	250	14312
8.4	250	13839
16.2	0	14098
16.2	250	15066
23.5	250	15268

Table 8 : Variation of the predicted rate constant fot PEAT polycodensation with adipic acid content

Adipic acid (mol%)	Catalyst (ppm)	Rate constant $mol^{-1}hr^{-1}$
0	250	152.4
8.4	250	133
16.2	0	140.6
16.2	250	181.7
23.5	250	191.8

Table 9 : Comparison of experimental and theoretical variation** of melting point as a function of PET mole fraction X_A

X_A	$-\ln X_A$	$1/Tm \times 10^3$ °K^{-1}	
		Experimental	Theoretical
1	0	1.869	1.869
0.916	0.0877	1.9157	1.9027
0.838	0.1764	1.9531	1.9367
0.765	0.2679	1.9960	1.9720

** Flory's equation for melting point depression (Ref. 1) :

$$1/Tm' - 1/Tm. = -(R/\Delta Hm) \ln X_B$$

where Tm = 535°K

R = 1.987 cal /mol/°K

ΔH_m = 5184 cal/mol (Ref. 29)

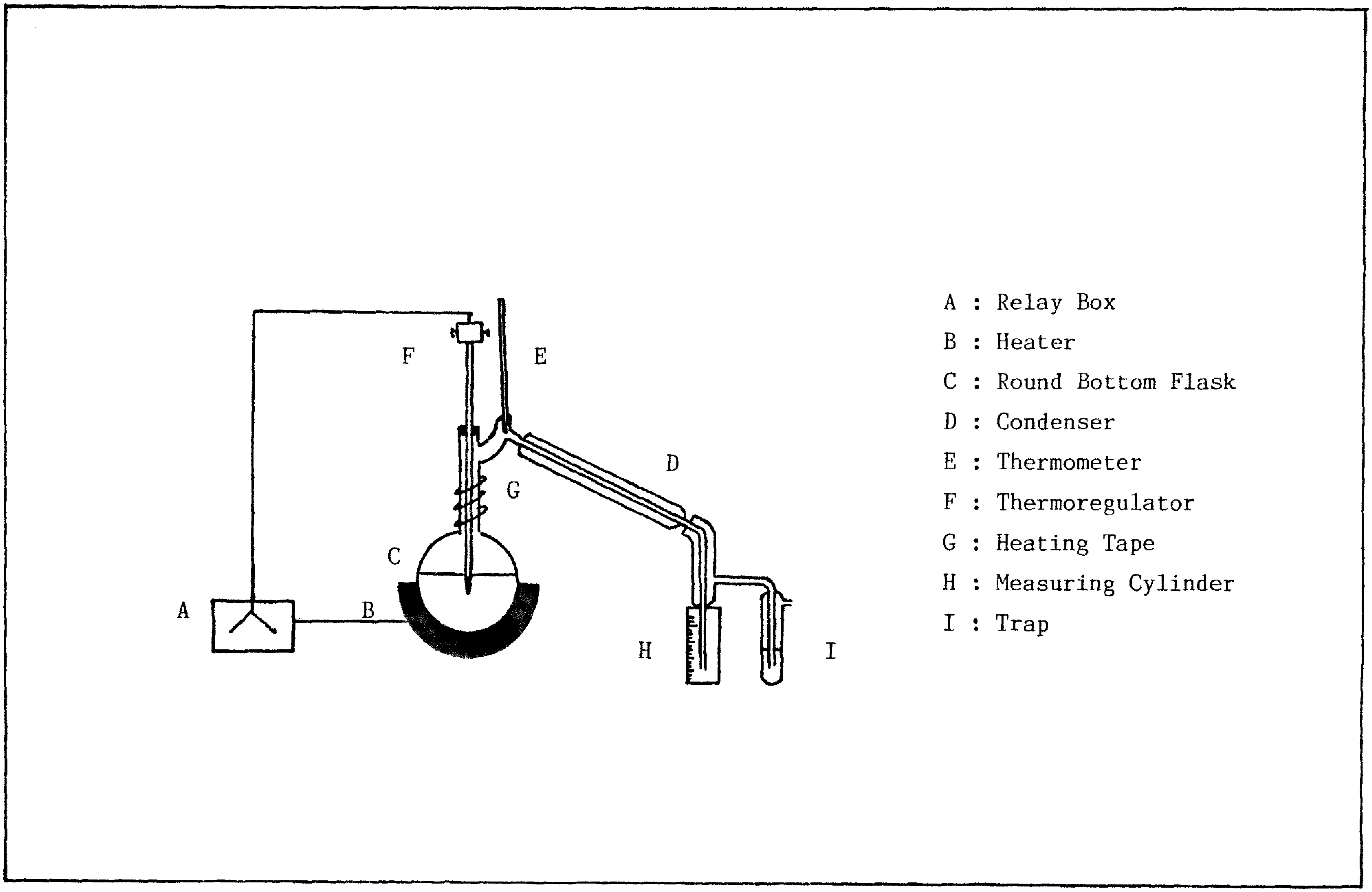


Figure 1 : Experimental Set up for BHET synthesis

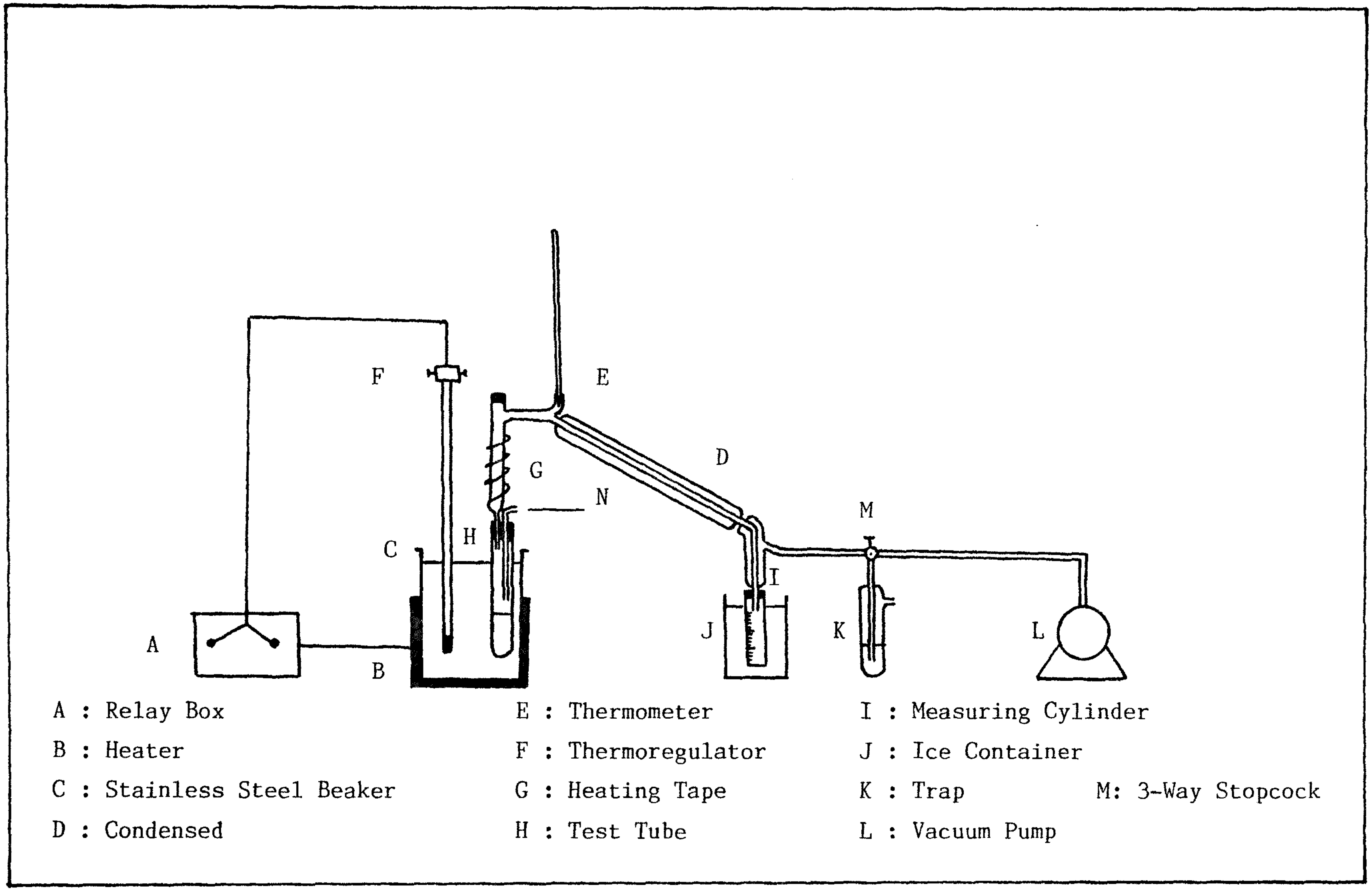


Figure 2 : Experimental set up for PET and PEAT synthesis

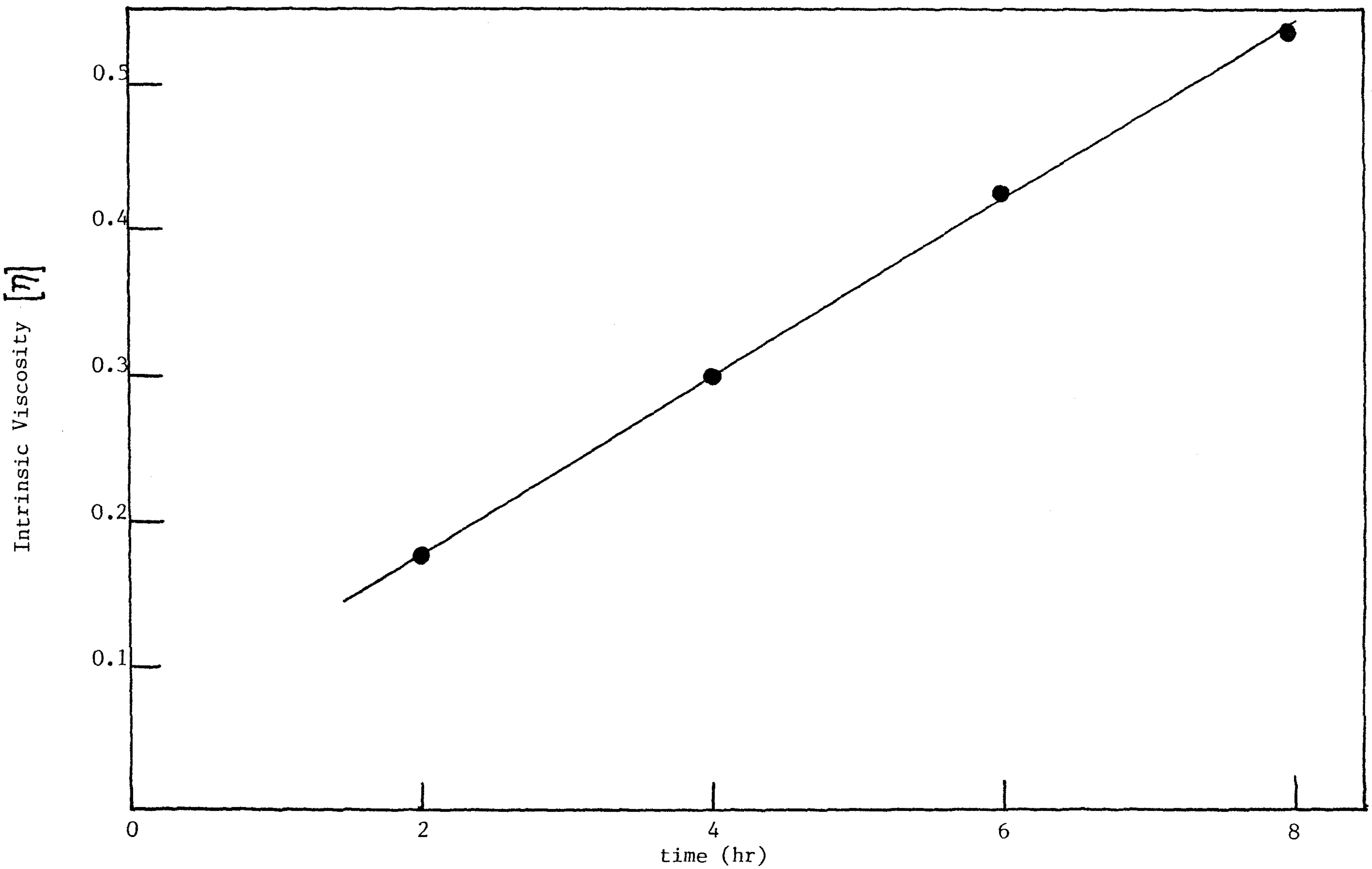


Figure 3 : Variation of Intrinsic Viscosity with Reaction Time for PET

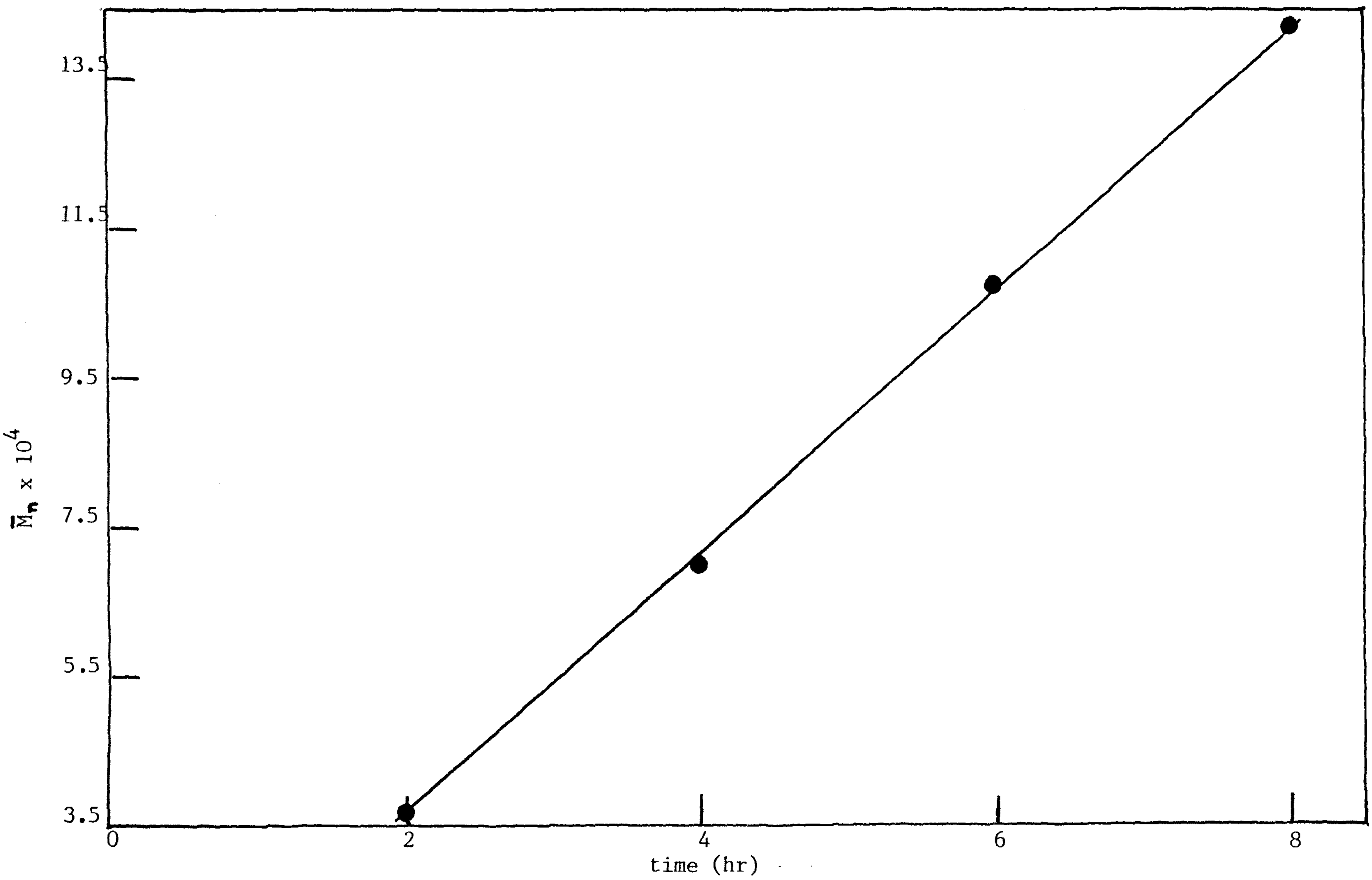


Figure 4 : Variation of Molecular Weight with Reaction Time for PET

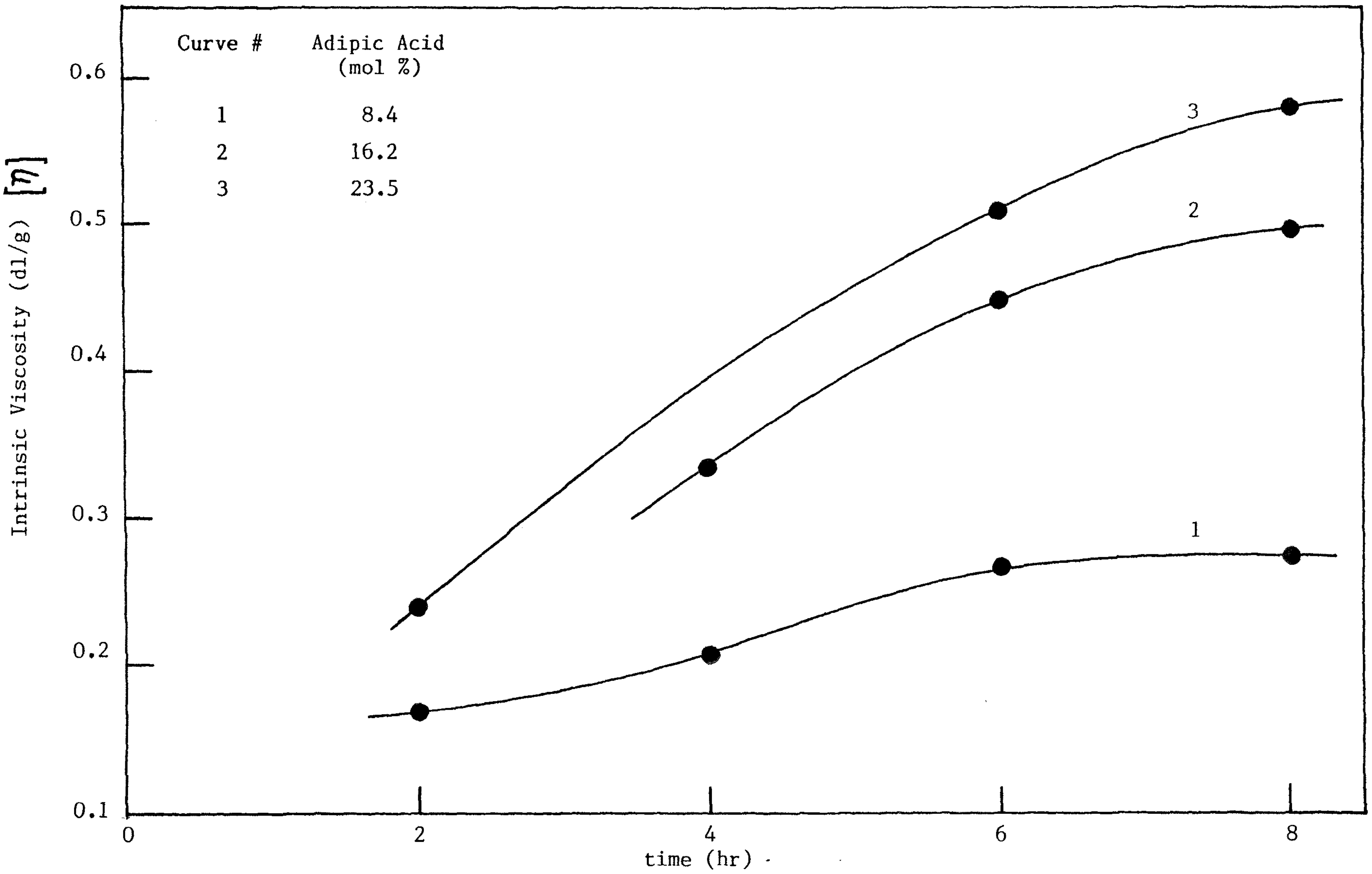


Figure 5 : Variation of Intrinsic Viscosity with Reaction Time for PEAT

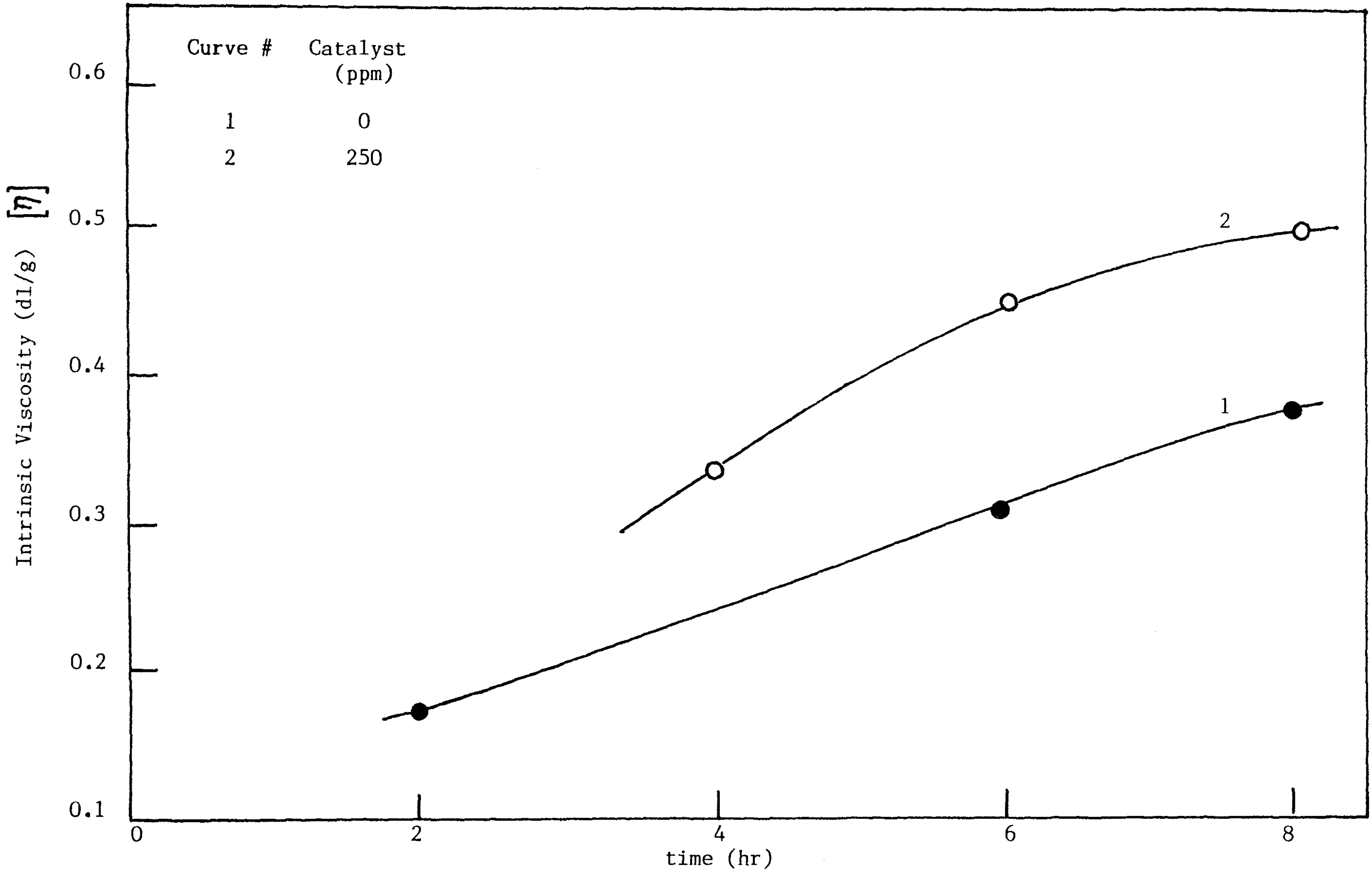


Figure 6 : Effect of Catalyst on the Intrinsic Viscosity of PEAT

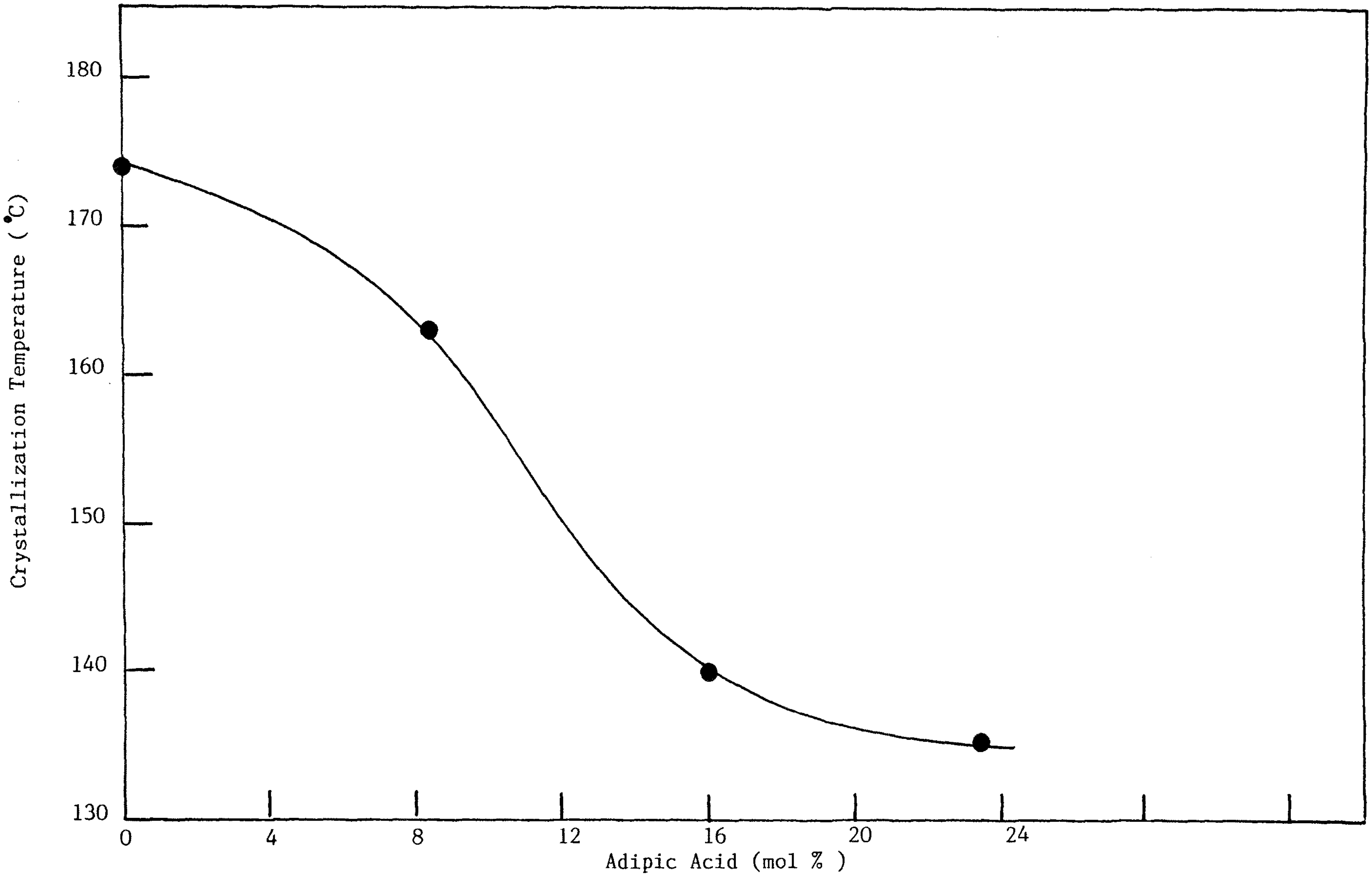


Figure 7 : Variation of Crystallization Temperature with Adipic Acid for PEAT

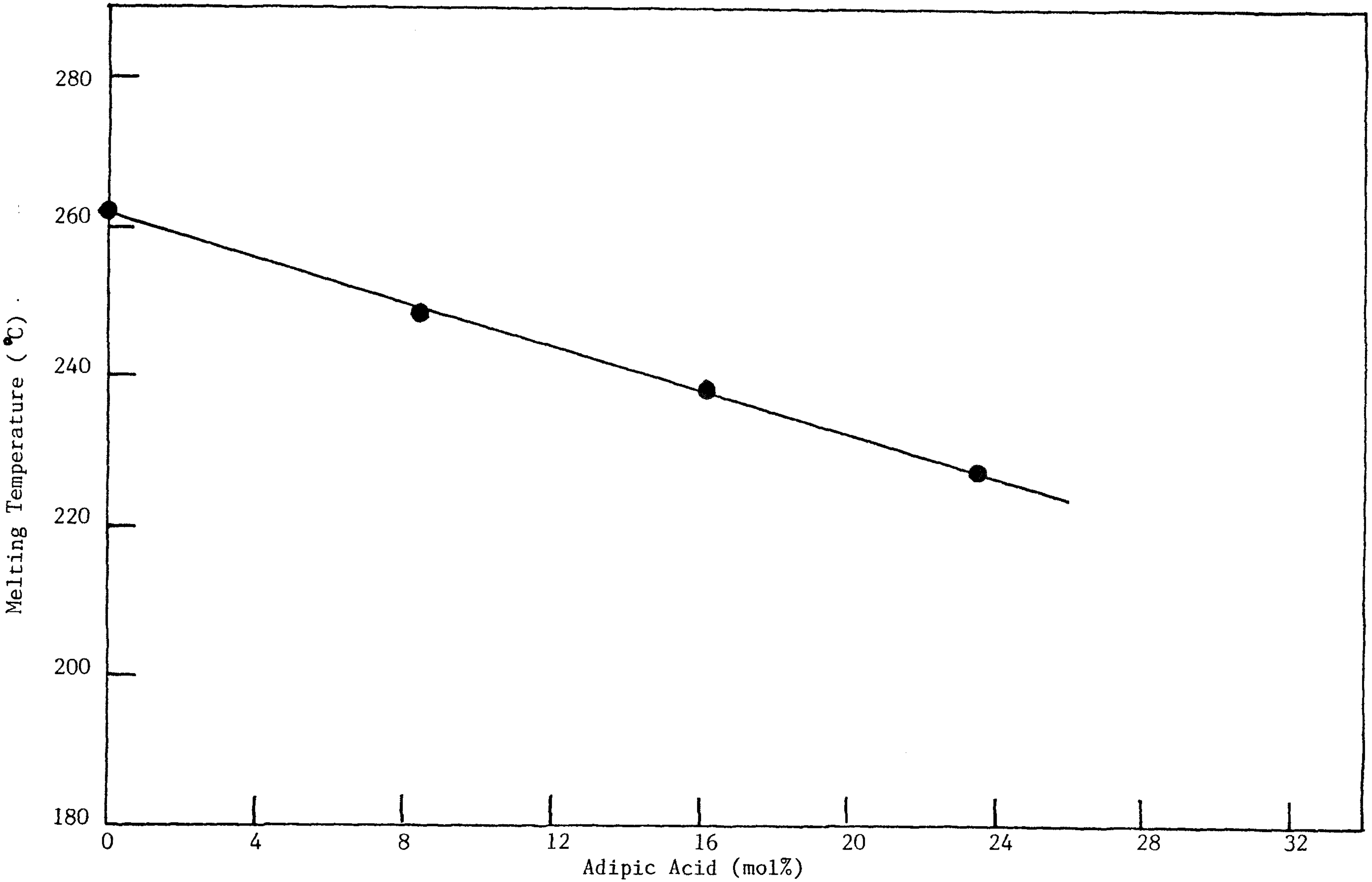


Figure 8 : Variation of Melting Temperature with Adipic Acid for PEAT

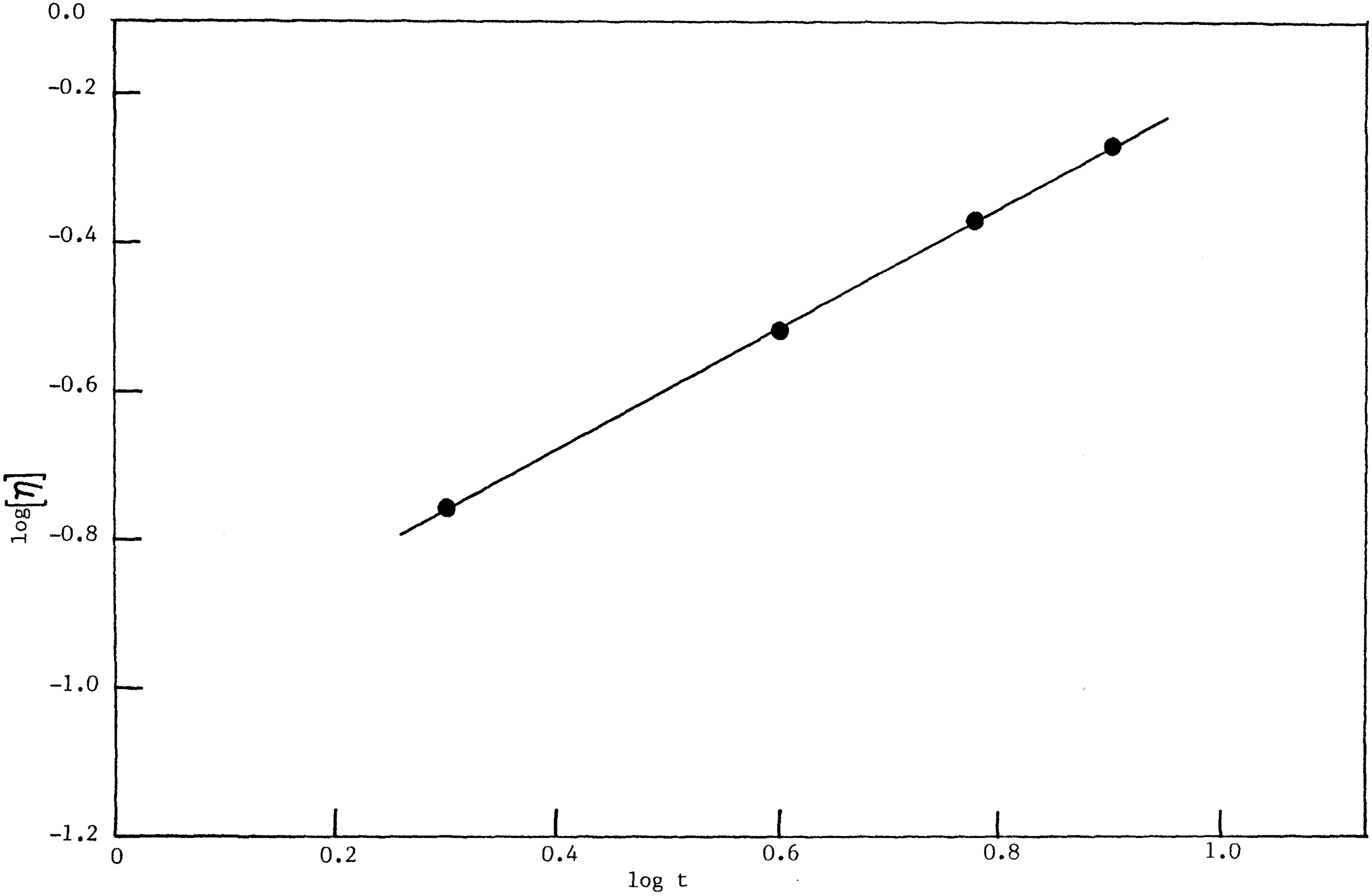


Figure 9 : Logarithmic Intrinsic Viscosity versus Logarithmic Time for PET

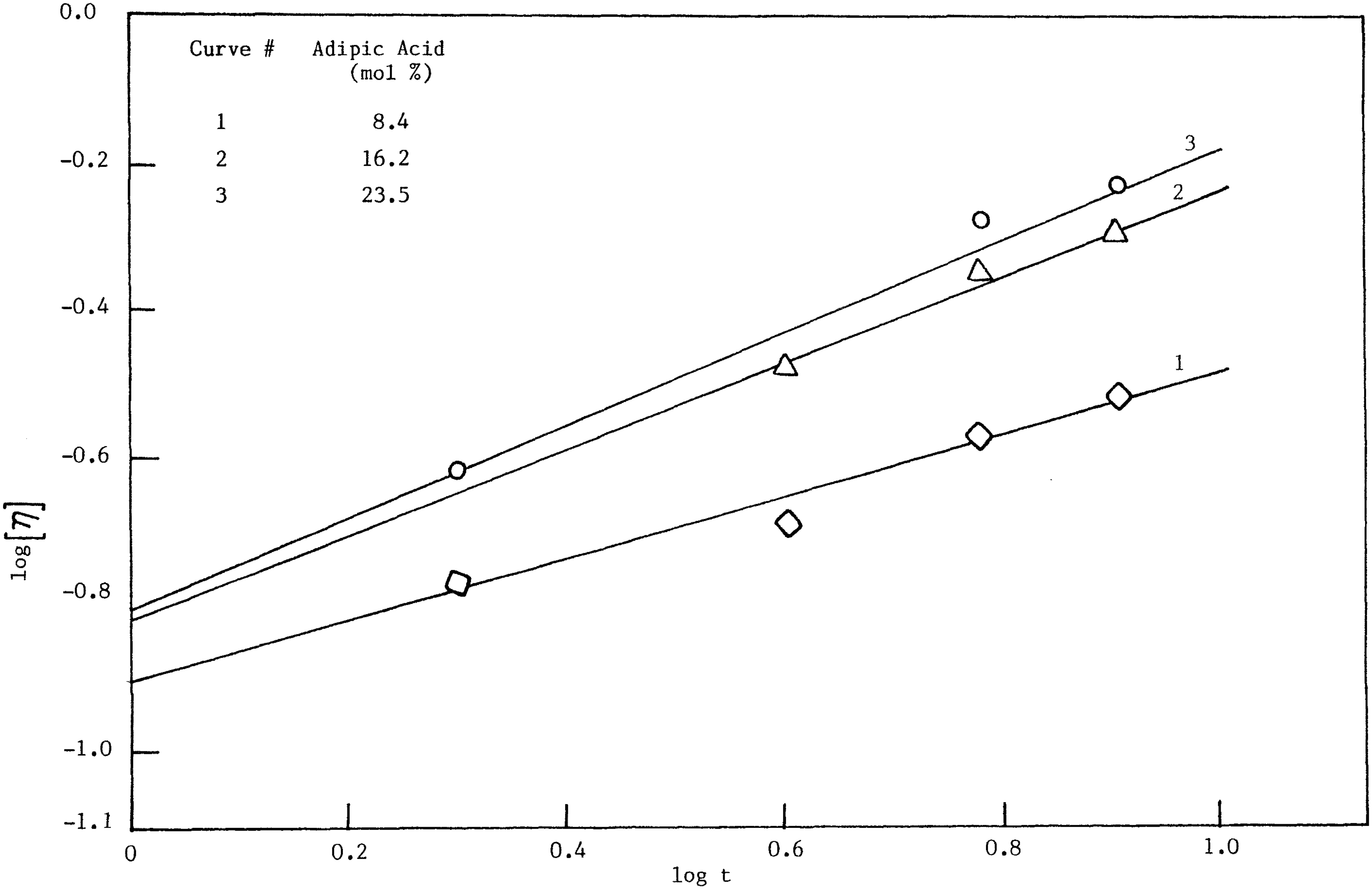


Figure 10 : Logarithmic Viscosity versus Logarithmic Time for PEAT

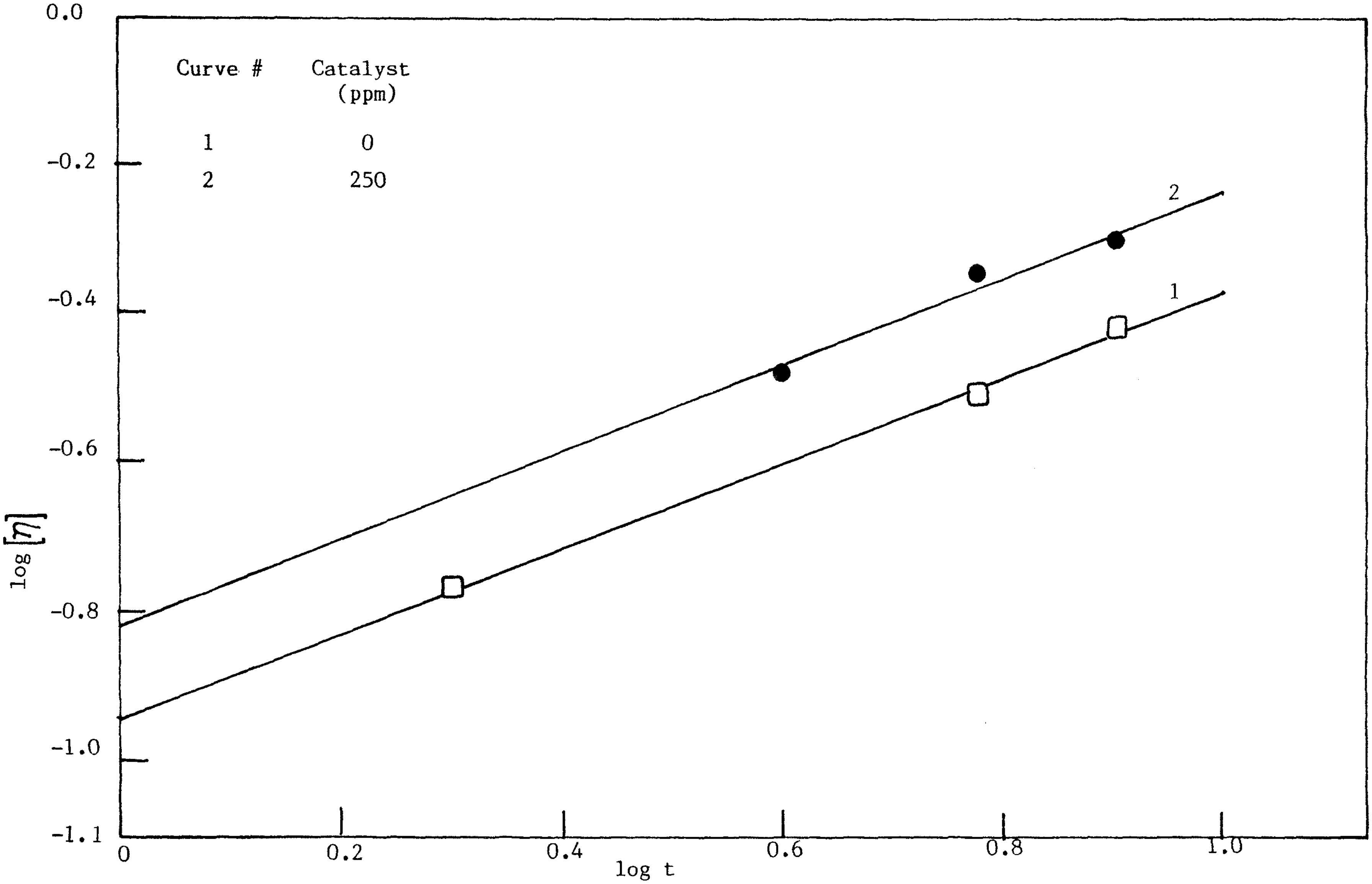


Figure 11 : Effect of Catalyst on the Logarithmic Viscosity of PEAT

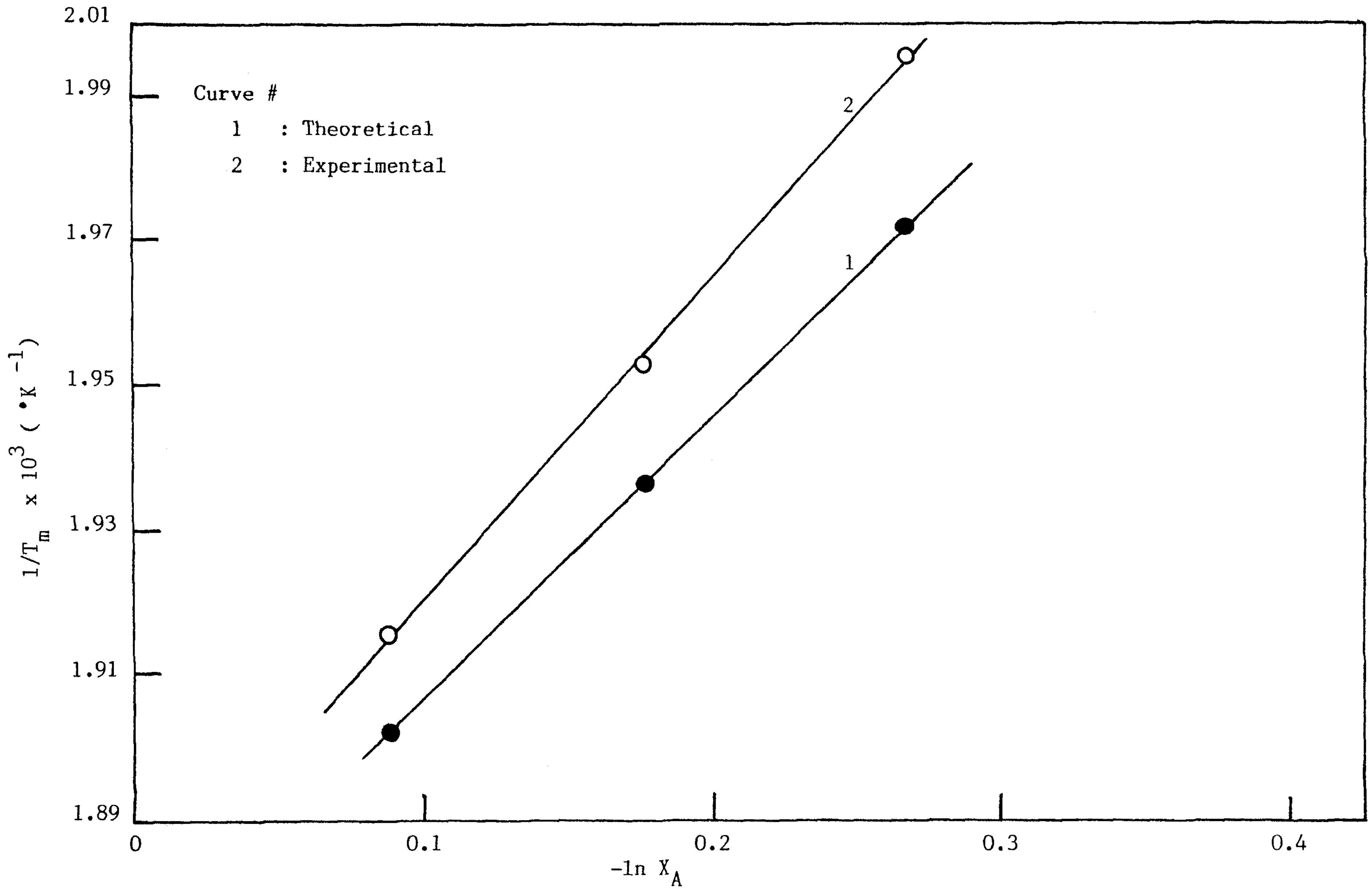


Figure 12 : Comparison of experimental and theoretical variation of melting point as a function of PET mole fraction X_A

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