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Studies of polymer-polymer interactions.

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STUDIES OF POLYMER-POLYMER INTERACTIONS

A Dissertation Presented

By

Ramon A. Neira Lemos

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

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September 1974

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STUDIES OF POLYMER-POLYMER INTERACTIONS

A Dissertation Presented

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STUDIES OF POLYMER-POLYMER INTERACTIONS

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Ramon A. Neira Lemos

ABSTRACT

THERMAL CRYSTALLIZATION OF ISOTACTIC POLYSTYRENE-
POLY (2, 6-DIMETHYLPHENYLENE OXIDE) BLENDS.

ABSTRACT

A new approach to the problem of polymer compatibility has been examined. Blends of isotactic polystyrene (iPS) and poly(2, 6-dimethyl - 1, 4 phenylene oxide)(PPO) have been prepared by precipitation from dilute solutions of the polymers in a common solvent. Crystallinity has been developed in these blends by isothermal annealing for several times. A variety of times, temperatures and blend compositions have been used. the degree of crystallinity is dependent on the conditions of crystallization and on blend composition. The percentage of crystallinity has been determined from DSC thermograms in two ways: one, by measuring heats of fusion and two, by evaluating the increase in C_p occurring at T_g . A reasonable agreement between these two techniques has been found. It suggest that within the experimental error iPS-PPO blends may be regarded to obey a two-phase additive model reasonably well, at least when the crystalline phase is iPS only.

The presence of relatively high degree of crystal-

linity is shown not to affect the blend compatibility.

Both amorphous and crystalline iPS-PP0 blends have a single composition-dependent glass transition temperatures as determined by DSC techniques. The crystallinity developed is a function of PP0 content. Blends containing 50 weight percent polymer display only traces of crystallinity after extended annealing. When the blend composition is less than 50 weight percent iPS, no crystallinity can be detected.

A melting point depression has also been observed which is composition dependent. The magnitude of the depression increases with increasing PP0 content. A discussion relating all of these facts to the level of miscibility of the polymers is given.

The multiple peaks observed in melting isotactic polystyrene and its blends are due not only to melting and recrystallization but also to the presence of different crystal size and/or defects.

SOLVENT INDUCED CRYSTALLIZATION OF IPS-PPO AND APS-PPO BLENDS

ABSTRACT

A study has been made on the solvent-induced crystallization behavior of poly(2, 6-dimethyl-1, 4-phenylene oxide)(PPO) and isotactic polystyrene(iPS) and their blends. Amorphous films of these materials have been exposed to methyl ethyl ketone (MEK) and/or acetone vapor at several controlled temperatures. Some aspects of the sorption behavior of the blends and the homopolymers have been investigated. Weight uptake as a function of time and equilibrium concentration of solvent in the polymer have been determined. The role of the solvent in the crystallization process is discussed.

Only iPS and iPS-rich blends crystallize at low temperatures. The degree of crystallinity increases with increase of temperature. The difficulty of completely removing entrapped solvent from the films without altering the thermal history of the material has been verified. Some residual solvent has affected the relative position of Tg's and Tm's, but a single composition dependent Tg has been found by DSC. By using combined

solvent plus thermal treatments the crystallization of PPO has been possible either pure or in its blends. IPS crystallizes under the same treatment. In addition by using atactic polystyrene-PPO blends, the crystallization of PPO, only, has been attained. The crystallization behavior of pure PPO has been investigated. Solvents with solubility parameters close to those of the polymers, and low molar volumes have been used. Upon removal of the solvent by heating the wet films above 90°C , crystallinity develops and a maximum degree of crystallinity is reached somewhere between 100 and 120°C . Kinetic rather than thermodynamic effects appear to control the crystallization at this stage of the process.

Cocrystallization of the two blend components has been carried out at 140 and 170°C . PPO crystallizes in its blends with either iPS or aPS as long as the composition by weight of PPO is 20% or higher. Analogously iPS crystallizes in blends containing less than 50 weight percent PPO. Cocrystallization occurs between these two compositions. A discussion on the possible existence of independent crystalline phases is presented.

Whether one or both polymers crystallize, the blends exhibit a single composition dependent T_g at locations displaced a few degrees with respect to those for the

amorphous blends of the same composition.

Degrees of crystallinity have been determined from DSC thermograms in two ways: one, by using enthalpies of fusion calculated from the areas under the melting peaks and two, by evaluating specific heat increases occurring at T_g on the assumption of the two-phase model. Considerable departure from this model is found as the content of crystalline PPO increases.

Melting point depressions and enthalpies of fusion appear to be composition dependent.

A exhaustive discussion on the feasibility of constructing a polymer a phase diagram is offered.

To my wife Betty, and my three children,
Julieta, Ramon Jr. and Camilo whose love,
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TABLE OF CONTENTS

Title page	i
Approval	ii
Acknowledgments	iii
Dedication	iv
Table of contents	v
List of Figures	viii
CHAPTER ONE	
INTRODUCTION	
Theoretical Aspects	1
Experimental Background	6
Thermal Transitions	7
Heats of mixing	8
Optical Homogeneity	10
Mechanical Integrity	12
Rheological Methods	14
Literature Review of the System PPO-PS	18
CHAPTER TWO	
THERMAL CRYSTALLIZATION OF ISOTACTIC	
POLYSTYRENE-POLY(2,6-DIMETHYLPHENYLENE OXIDE) BLENDS	
Abstract	24
EXPERIMENTAL	
Materials	26
Sample Preparation	26

Measurements	29
RESULTS	31
Glass Transition Temperature	32
Enthalpies of fusion and degrees of crystallinity	35
Specific-heat increases and degree of crystallinity	42
Isotactic Polystyrene: thermal history and melting temperature	51
DISCUSSION OF THE RESULTS	60
FIGURES (1. to 14)	66
CHAPTER THREE	
SOLVENT INDUCED CRYSTALLIZATION OF IPS-PPO AND APS-PPO BLENDS	
Abstract	80
Theory	83
Experimental	
Sample Preparation	87
DSC Measurements	89
RESULTS	
Solvent-Induced Crystallization of iPS-PPO blends	90
Glass Transition Temperatures	93
Enthalpies of fusion and degree of crystallinity	95

Crystallization of Poly(2, 6-dimethyl-1, 4 phenylene oxide) and its with polystyrene by combined solvent and thermal treatment	99
Glas Transition temperatures	105
Enthalpies of fusion and degree of crystallinity	108
Specific heat increases and degree of crystallinity	111
Melting temperatures	112
DISCUSSION OF THE RESULTS	121
SUGGESTIONS FOR FUTURE RESEARCH	134
Figures 15 to 36	137
BIBLIOGRAPHY	157

LIST OF FIGURES

FIGURE		PAGE
1.	Glass transition temperatures of amorphous and semicrystalline iPS-PPO blends, versus weight fraction of PPO, (W_1).	66
2.	Degree of crystallinity in terms of enthalpy of fusion of iPS-PPO blends annealed for 12 hours, versus annealing temperature.	67
3.	Degree of crystallinity in terms of enthalpy of fusion of iPS-PPO blends annealed for 24 hours, versus annealing temperature.	68
4.	Degree of crystallinity in terms of enthalpy of fusion of iPS-PPO blends annealed for 48 hours, versus annealing temperature.	69
5.	Degree of crystallinity in terms of enthalpy of fusion of iPS-PPO Blends annealed for 72 hours, versus annealing temperature.	70
6.	Specific heat increase (ΔC_p) versus weight fraction of PPO of semicrystalline blends annealed for 24 hours at the indicated temperatures(The dashed line corresponds to the linear interpolation between the two values found for pure polymers).	71

LIST OF FIGURES(Cont.)

FIGURE		PAGE
7.	Specific heat increase (ΔC_p) versus weight fraction of PPO of semicrystalline blends annealed for 48 hours at the indicated temperatures.	72
8.	Specific heat increase (ΔC_p) versus weight fraction of PPO of semicrystalline blends annealed for 72 hours at the indicated temperatures.	73
9.	Specific heat increase versus percent crystallinity (X) calculated by heat of fusion data for iPS.(The straight line presents the percent crystallinity calculated by equation 12).	74
10.	Specific heat increase versus percent crystallinity (X) calculated by heat of fusion data for 90/10 blends.	75
11.	Specific heat increase versus percent crystallinity (X) calculated by heat of fusion data for 75/25 blends.	76
12.	DSC thermograms of iPS annealed at 150°C (upper), 190 (middle) and 170°C (lower) for 24 hours.	77

LIST OF FIGURES (Cont.)

FIGURE		PAGE
13.	DSC Thermograms of iPS annealed at 210°C (upper), and 180°C lower.	78
14.	Melting temperature and area-to-weight ratio of semicrystalline iPS-PPO blends versus weight fraction of PPO (W_1).	79
15.	Glass transition temperatures versus weight fraction of PPO (W_1) of iPS-PPO blends crystallized by solvent treatment. (Dashed line corresponds to T_g values of completely dry samples).	135
16.	Weight fraction of acetone or MEK absorbed by iPS and PPO as a function of time.	136
17.	Degree of crystallinity in terms of enthalpy of fusion of iPS-PPO blends, crystallized by solvent exposure, versus temperature of crystallization (12 hours).	137
18.	Degree of crystallinity in terms of enthalpy of fusion of iPS-PPO blends crystallized by solvent exposure, versus temperature of crystallization (24 hours).	138
19.	Degree of crystallinity in terms of enthalpy of fusion of iPS-PPO blends crystallized	139

LIST OF FIGURES (Cont.)

FIGURE		PAGE
19.	by solvent exposure, versus temperature of crystallization (48 hours).	139
20.	Degree of crystallinity in terms of enthalpy of fusion of iPS-PPO blends crystallized by solvent exposure, versus temperature of crystallization (72 hours).	140
21.	Tg depression versus acetone content (weight percent) in PPO.	141
22.	Loss of solvent (Wt % acetone) versus time (hours) resulting from annealing PPO samples at 90 and 140°C.	142
23.	Enthalpies of fusion (ΔH_f) versus annealing temperature of PPO crystallized by solvent plus thermal treatment (24 hours) at indicated temperatures.	143
24.	Glass transition temperature of completely amorphous and crystallized blends of iPS-PPO versus weight fraction of PPO (W_1).	144
25.	Enthalpies of fusion versus composition of iPS-PPO and aPS-PPO blends crystallized by combined solvent plus thermal treatment at 140°C. (Dashed line corresponds to values	145

LIST OF FIGURES (Cont.)

FIGURE		PAGE
25.	calculated for ΔH_f of iPS by subtracting those corresponding to the full lines)	145
26.	Enthalpies of fusion versus composition of iPS-PPO and aPS-PPO blends crystallized by combined solvent plus thermal treatment at 170°C.	146
27.	Fractional crystallinity (X) versus weight fraction of PPO (W_1) of iPS-PPO blends crystallized by solvent plus thermal treatment at 170°C.	147
28.	Fractional crystallinity (X) versus weight fraction of PPO (W_1) of aPS-PPO blends crystallized by solvent plus thermal (140°C) treatments.	148
29.	Fractional crystallinity (X) versus weight fraction of PPO (W_1) of iPS-PPO blends crystallized by solvent plus thermal treatment at 140°C.	149
30.	Fractional crystallinity (X) versus weight fraction of PPO (W_1) of aPS-PPO blends crystallized by solvent plus thermal (170°C) treatments	150

LIST OF FIGURES (Cont.)

FIGURE		PAGE
31.	Specific heat increases (ΔC_p) versus weight fraction PPO (W_1) for iPS-PPO blends crystallized by solvent plus thermal treatment (140°C).	151
32.	Specific heat increases (ΔC_p) versus weight fraction PPO (W_1) for aPS-PPO blends crystallized by solvent plus thermal treatment (140°C).	152
33.	Specific heat increases (ΔC_p) versus weight fraction PPO (W_1) for iPS-PPO blends crystallized by solvent plus thermal treatment (170°C).	153
34.	Specific heat increases (ΔC_p) versus weight fraction PPO (W_1) for aPS-PPO blends crystallized by solvent plus thermal treatment (170°C).	154
35.	Diagram showing the various phases in the system iPS-PPO at different temperatures as a function of composition (Weight fraction of PPO, W_1).	155

LIST OF FIGURES (Cont.)

FIGURE		PAGE
36.	Diagram for determining crystalline and amorphous content of each component at a given composition of iPS-PPO blends. Where W_1 and W_2 are weight fraction of PPO and iPS respectively. (This illustration corresponds to blends crystallized by solvent plus thermal (140°C) treatments for 24 hours.	156

C H A P T E R O N E

INTRODUCTION

A number of both theoretical and experimental methods have been used to study the miscibility or compatibility of two or more polymers in the bulk phase and in solution.

These methods have provided different criteria to formulate not only a definition but also semi-quantitative approach of polymer compatibility.

Theoretical treatments⁽¹⁻⁵⁾ of the nature of polymer-polymer solutions have resulted in chemical and thermodynamic predictions of compatibility which fail to take into account characteristic features of the behavior of macromolecules.

On the other hand, many experimental methods have been successful in examining and evaluating various properties of the polymer mixtures but they have turned out to be inconclusive and ambiguous in the formulation of compatibility criteria because of having only a tenuous connection with polymer miscibility.

Theoretical Aspects.

One of the most widely quoted theoretical treatment of polymer-polymer interactions was developed by Scott¹ and Tompa² based on the Flory-Huggins theory of polymer solutions. They were able to conclude that the mixing of chemically different polymers would be favored only in the case the polymers have a negative heat of mixing. In fact, if it is assumed that a polymer mixture can be brought to thermo-

dynamic equilibrium, then such a conclusion lies in the usual free energy of mixing expression

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

in which ΔG_m , ΔH_m and ΔS_m are respectively the free energy, enthalpy and entropy of mixing per unit mass of polymer. Since there is a negligible change of entropy of mixing ΔS_m for blends of high molecular weight unless ΔH_m is negative, ΔG_m will be positive and mixing of polymer will not be favored. The conclusions from the Scott - Tompa treatment of polymer-polymer compatibility presume a $\Delta S_m \approx 0$ and a $\Delta H_m > 0$; however $T \Delta S_m$ is not $= 0$, but makes a finite contribution to ΔG_m , i.e. ΔG_m is not independent of temperature. Furthermore the quantities ΔH_m and ΔS_m are functions of domain size and, depending on the particular polymer-polymer interaction parameter, can result in a situation leading to maximum miscibility i.e. that in which $\Delta H_m \leq T \Delta S_m$ over all the range of domain sizes. The most common situation, however, is that where $\Delta H_m > T \Delta S_m$ for all domain sizes, and no miscibility occurs at all, although the case in which $\Delta H_m < T \Delta S_m$ for a partial region of the domain size does also exist; in this case a minimum in ΔG_m occurs for a partial intermediate cluster size. This means that the thermodynamic requirements for compatibility may be met over some scale larger than the extent of the individual segment.

Macknight et al⁸ point out an important feature of polymer miscibility. They state that there is a true spectrum

of miscibility ranging from the most intimate, at the polymer segment level, passing by an intermediate case in which the placement of the individual polymer molecule is randomized, to a coarser level where segregation into clusters or domains of polymer molecules occurs. Although the same authors are aware of the fact that an apparently compatible mixture cannot be assumed a priori, to be in thermodynamic equilibrium, they relate the free energy of mixing, ΔG_m , to a parameter s representing the level of mixing in terms of the average normalized size of the segmental clusters in the system.

If mixing occurs at a segmental level, then $s = 1/N \approx 0$, where N is the degree of polymerization. When the level of mixing corresponds to the polymer molecule itself $s = 1$; and phase separation takes place at $s \gg 1$. ΔG_m will be negative for all values of s if the heat of mixing $\Delta H_m < 0$, but the size of the average cluster sN , will depend also on the relative contribution of ΔS_m , the entropy of mixing. ΔS_m at first increases, as s decreases, as a result of the greater number of segments configurations available. However, ΔS_m eventually decline because of the increasing restrictions in the number of possible configurations imposed by the condition of contiguity of polymer segments in the range: $0 < s < 1$. These changes in ΔS_m make ΔG_m to become negative, with a minimum for $0 < s < 1$, even in the cases where ΔH_m is positive as long as it is not too large.

Turning back to the Scott's theoretical treatment, the following expression for the Gibbs free energy of mixing of two polymers was derived

$$G_{\text{mix}} = \frac{RTV}{V_r} \left[\frac{v_A}{x_A} \ln v_A + \frac{v_B}{x_B} \ln v_B + \chi_{AB} v_A v_B \right] \quad (2)$$

where V is the total volume of the mixture, V_r is a reference volume which is taken as close to the molar volume of the smallest polymer repeat unit as possible, v_A and v_B , x_A and x_B are in their order volume fractions and the degree of polymerization of polymer A and B respectively, and χ_{AB} is the interaction parameter between the two polymers.

For a binary system a critical point indicates the circumstance under which the system will just begin to separate in two phases i.e. the limits of the compatibility. Scott found such critical conditions: interaction parameter χ_{AB} , and volume fractions v_A and v_B as functions of the degree of polymerization of the two homopolymers. Scott noted using those relationships, that $(\chi_{AB})_{cr}$ would be very small for two homopolymers having appreciable degrees of polymerization, and that polymers of infinite molecular weight would be incompatible if there were any positive heat of mixing at all.

Scott also discussed the behavior of mixtures of two polymers in the presence of a solvent. He obtained equations

that led to a Gibbs free energy of mixing and the critical conditions for such a system.

These equations are exactly like those obtained for a binary mixture of polymers, as long as volume fractions and effective interaction parameter between the polymers in the presence of solvent are defined properly.

The interaction parameters, therefore, play a very important role in the study of polymer compatibility as they can be related to the enthalpy of interaction of the polymer units, each of molar volume V_r . In fact, the interaction parameter between molecules of comparable size can be written in terms of Hildebrand⁶ solubility parameters:

$$\chi_{AB} = \frac{V_r}{RT} (\delta_A - \delta_B)^2 \quad (3)$$

where δ_A and δ_B are solubility parameters for A and B respectively. When segment - segment interactions are nearly the same the interaction parameter is small or zero and the heat of mixing becomes negative as evaluated by equation 1.

In a recent review article, Krause⁵ presents a method of calculation for predicting compatibility of polymers. She asserts that calculated rather than experimental values of solubility parameters produce more accurate predictions. Consequently, solubility parameters can be evaluated by using the expression:

$$\delta = \frac{\rho \sum F_i}{M} \quad (4)$$

where ρ is the density of the polymer at the temperature of

interest, M is the molecular weight of the monomer unit in the polymer and $\sum F_i$ is the sum of all the molar attraction constants of all the chemical groups in the polymer repeat unit.

Values of molar attraction constants to use with Eq.4 have been revised and compiled recently by Hoy⁷.

With the aid of the solubility parameters the interaction parameter between two polymers χ_{AB} can be evaluated. Krause has made comparisons of the calculated values of χ_{AB} and of $(\chi_{AB})_{cr}$, the critical point on a phase diagram for a binary system, in order to predict compatibility of polymers and found that if χ_{AB} is greater than $(\chi_{AB})_{cr}$, the two polymers should be compatible at some percentage composition. The greater the difference between these two values, the smaller the range of composition in which the polymer will be compatible.

In another theoretical approach Pazonyi and Dimitrov⁴ calculated a value for which the heat of mixing, ΔH , is less than the entropy term, $T \Delta S$. They conclude that, if the difference between the cohesive energy densities of the two components is smaller than 0.016 cal/cm^3 , there exists the possibility of mutual solution, whatever the sign of the heat of mixing turns out to be.

Experimental Background.

To visualize clearly the experimental frame within

which studies of polymer compatibility have been developed, we will mention, briefly, the applicability of some of the experimental methods used and will describe the way the experimental results obtained, are interpreted to underlie and predict the corresponding criteria of compatibility.

So far, all the experimental research has been directed to elucidate criteria of polymer miscibility on the basis of

- a) Thermal - transition uniformity
- b) Thermodynamic changes upon mixing
- c) Optical homogeneity
- d) Mechanical Integrity
- e) Rheological behavior of blend melts and solutions.

Although interrelations exist among these groups of properties of polymer blends, they represent in our concept, well defined and separated areas on which almost all the effort of investigators has been centered to examine the phenomenon .

Thermal Transitions.

A polymer blend is said to exhibit thermal uniformity within a range of compositions if it does not show the individual thermal transitions of its components within that range.

Commonly, differential calorimetry has been used to determine thermal behavior of polymer blends and the

presence of a single glass transition temperature (T_g), which is, of course, composition dependent has been taken as a criterion for the compatibility of the blend.

Mixtures which exhibit a single composition - dependent T_g appear to obey expressions of the type

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \quad (5)$$

Where W 's and T_g 's stand for the weight fraction and glass transition temperatures of polymer A and B.

Almost all the methods used in the determination of T_g of homopolymers may and, indeed, have been employed to measure the T_g of blends. The different methods produced somewhat different and in some cases⁸ clearly separated the individual T_g 's of the blend components in contrast with single values obtained by differential calorimetry for the same blend. This indicates that the sensitivity of different measuring techniques toward the glass transitions in mixtures depends on the physical dimensions of the phases. Thus, dynamic mechanical measurements can apparently detect smaller phases than differential calorimetry as concluded by Macknight et al.

Heat of mixing.

Although the concept of a positive heat of mixing has been accepted as the driving force for the general rule of incompatibility of polymer pairs soluble in a common

organic solvent, relatively few direct measurements of this quantity have been reported⁽⁹⁻¹¹⁾. Slonimskii and coworkers utilized Hess' law of the independence of heat effects on the particular path chosen for the mixing process to obtain

H_m values for a number of polymer pairs. All pairs existing as homogeneous solutions had exothermic heats and the behavior of two mixtures which had exothermic heats of mixing and still phase - separated in solution was explained in terms of a volume change on mixing. All the pairs with endothermic heats of mixing displayed phase separation in solution.

Recently Ichihara et al¹¹ has followed a identical procedure to measure the enthalpy of mixing of a blend of poly (methyl - methacrylate and poly(vinyl acetate)).

Briefly, the method is an indirect determination of heats of mixing from the difference between heats of solution of pure homopolymers and blend of them assuming Hess' law holds. If ΔQ_1 is the heat of solution for simultaneous dissolution of nonblended a grams of polymer A and b gms. of polymer B in a given volumen of solvent, and ΔQ_2 is the heat of solution of (a+b) grams of the blended sample of A and B in the same volume of the solvent, then, according to Hess' law, the heat of blending ΔQ_b (cal/gm) is given by

$$\Delta Q_b = (\Delta Q_1 + \Delta Q_2) / (a+b) \quad (6)$$

Using as basis the magnitude as well as the sign of the

heat of mixing a degree of compatibility can be inferred. The heat of mixing may be taken as an approximation of the free energy of mixing like it has been suggested by Scott and Tompa.

Optical Homogeneity.

The optical appearance is an important feature in the characterization of polymer blends as it reflects the level of molecular interaction among the various components of the blend.

In the bulk, compatible polymers form transparent films which exhibit no heterogeneity under considerable magnification. High transparency in blends of polymers with different refractive indices, reveals that the magnitude of the microphase dimension is at least comparable to the wavelength of the visible light. However, ambiguities may appear in practice because i) visible clear films of polymer mixtures may have phase-separated domains too small to be detected visually and, ii) even incompatible polymers form transparent films when they have the same or similar refractive index or, if the refractive indices are different, they may form two layered films which appear transparent when a solution of the polymers is evaporated¹². To overcome these ambiguities further magnification is necessary and staining techniques¹³ may be used to allow observation

of particles even where the refractive indices of the constituent polymers are the same.

The so-called technique, phase contrast microscopy may yield clear evidence of the existence of phase domains as small as 0.1μ . Phase contrast microscopy has been useful in demonstrating the multiphase structure of some polyblends¹³ in the form of dark-to-bright contrast image. The brighter areas seen under the dark contrast condition are assigned to domains of that component possessing the lowest optical density. When better levels of molecular interaction are found, the phase contrast pictures become blurred and ill-defined even with the finest section preparation as thin as 2 to 3 microns owing to the fact that the structural units involved may be near or below the limit of resolution of light microscopy.

Under favorable circumstances electron microscopy can be used to detect size of domains comparable to molecular dimensions and even smaller¹³. However attempts to study the bulk structure of some polymer blends have encountered a number of difficulties. These include awkwardness in cutting ultrahigh thin sections, susceptibility to electron beam damage and shortage of image contrast owing to the usual slight difference in the electron optical density between blend-component microphases.

Mechanical Integrity.

Mechanical integrity is a term employed to denote the degree of retention or otherwise improvement of the mechanical properties of a polymer blend as compared to those of its individual components. Indeed, a major interest in the preparation of blends rests on the ability of some of such mixtures to improve desirable mechanical properties of their components.

Both dynamic¹⁴⁻¹⁸ and static¹⁹⁻²⁰ mechanical measurements have been carried out on polymer mixtures in order to test the response to applied stresses which is suggestive of the function of each polymer in its new environment.

Measurements such as tensile strength, elongation at break, impact strength etc. have been intended to characterize both compatible and two-phase blends. In particular, a two-phase system where a rubbery polymer is dispersed in a glassy matrix can result in a significant increase in impact strength, with a slightly lower modulus than the glassy component alone, and a yield point below the ultimate tensile strength of the glass, followed by ductile deformation up to its point of failure. In such a system the improvement of properties is reached without a great sacrifice of other properties as would be obtained through ordinary internal plasticization. This means that in order to obtain a successful two-phase impact plastic a certain optimum level of compatibility must be achieved; great

enough to provide the necessary adhesion at the glass-rubber interface, yet not so great that the discrete impact-absorbing phase is destroyed by solubility.

In brief, there is no well defined relationship between blend composition and mechanical properties as measured by state methods. However, in practice, it is common to interpret the achievement of the desired mechanical properties of the blend as a degree of mechanical integrity within a given range of compositions and thereby a somewhat relative concept of compatibility may be associated with the polymer blend.

On the other hand, dynamic mechanical properties have been performed on polymer blends to the end of observing the relaxational behavior and examining the intensity of the loss peaks. Binary mixtures in which the two components are miscible in one another give single damping peaks, although sometimes broader¹⁴. The damping peaks occur at a temperature between the damping peaks of the pure components.

Dynamic mechanical measurements are particularly sensitive for investigation of very fine domain sizes in mixtures of partially compatible polymers. Two-phase systems with relatively small cluster size show two well defined damping peaks. Furthermore systems that appear compatible as tested by differential calorimetry exhibit the two peaks characteristic of their components in curves of dynamic mechanical loss as a function of temperature

Hickman and Ikeda¹⁹ have found, however a good agreement between T_g values determined by both dynamic mechanical and calorimetry methods on compatible and incompatible blends. They have reported shear modulus and internal friction data for a series of compatible blends. In all cases there appear to be only one glass transition for each blend as indicated by the single relaxation peak and the accompanying sharp drop in modulus. These T_g values shift with the composition in a monotonic fashion. On the other hand the modulus-temperature curve assumes a clear step character and the loss data show maxima for each transition for incompatible binary blends.

Additional information was obtained with DSC. The series of compatible blends exhibit single glass transitions and the T_g values fit well with those calculated by using eq. 5. In contrast, thermograms for the incompatible blends displayed the step character indicating the individual component glass transitions, in agreement with the mechanical results.

Rheological Methods.

A blend is said to be rheologically compatible if its rheological behavior maintain close analogy to that of a pure polymer. In fact, linear viscoelastic response was found to be characteristic of compatible blends, just

as it is for a pure homopolymer²². In general two-phase systems exhibit a nonlinear viscoelastic behavior²³. Viscoelastic response of polymer melts are controlled mainly by the monomeric friction factor (ζ_0) and the average molecular weight between entanglements (M_e), the former is a measure of the local resistance to motion of a polymer chain segment and the latter represents intermolecular interactions. Both ζ_0 and M_e are constant for a given polymer. Therefore, a compatible blend melt is expected to have a monomeric friction factor essentially independent of composition because in order for segmental miscibility to occur the energy of mixing must be very small and hence segment-segment interaction are nearly the same.

Furthermore, the relationship between zero-shear viscosity and the 3.4 power of the weight average molecular weight, which is valid for high molecular weight homopolymers, at equal free volumes, extends its validity to a compatible polymer-blend melt and predicts the composition dependence of the iso-free volume zero-shear viscosity for the blend, provided that the Bueche's assumption, that the critical molecular weight is twice the molecular weight between entanglements of each component, be taken into account.

Boeng²⁴ have found a linear relationship between logarithm of dynamic viscosity of a compatible polymer-

blend melt and the weight fraction of each component in the blend. When a second viscous phase appears the effective viscosity of the mixture tends to increase in an amount proportional to the volume fraction of this second phase. This is the reason for the existence of a decreasing slope in the loss-modulus versus frequency curve for two-phase systems as reported by Hill and Maxwell²¹. These authors found no maximum in the loss modulus as a function of composition for two phase systems.

What all the above mentioned criteria denote, with more or less adequacy and accuracy, is the degree of molecular interaction between the components of a polymer mixture. During the process of blend formation and depending upon the kinetic and the thermodynamic equilibrium such interactions make different polymer molecules to seek a favorable environment. The molecules may aggregate as regions whose sizes are ultimately a consequence of how strong those interactions are.

The polymer compatibility becomes optimum when monomer units of the distinct components contact one another so intimately as to reduce the size of the microphase to the dimension of a few monomer units. Therefore, if a more absolute concept of polymer compatibility were to be formulated the average size of the microphase should be evaluated. However, it is

practically inaccessible in the case of good compatibility and only approximate direct estimation of the phase dimensions may be obtained by means of the above mentioned optical methods.

Calorimetry, mechanical, dielectric and rheological techniques make, after all, an indirect measure of the average size of the microphases.

Literature Review of the System:

Poly(2, 6 -dimethylphenylene oxide)-Polystyrene.

The system poly(2,6-dimethyl-1,4 phenylene oxide)(PPO) Polystyrene (PS) has been the subject of several investigations over the past few years.

Different experimental techniques have been used to study the properties of this blend over the entire range of compositions. The physical properties of the PPO-PS blends determined through the above experimental techniques, may be summarized as follows:

- a) The mixture exhibits a single heat capacity discontinuity corresponding to a single composition dependent glass transition temperature (T_g) intermediate between those of the pure components when examined by differential scanning calorimetry (DSC)²⁵.
- b) The thermomechanical response of the PPO-PS blends shows also a single T_g and a single-step rubbery plateau that falls between the response of the individual components²².
- c) PPO-PS blends display two partially merged relaxation peaks in the vicinity of the DSC T_g as examined by dynamic mechanical experiments¹⁵.
- d) Dielectric relaxation studies reveal a single peak corresponding to single composition dependent T_g ⁸. However, composition dependence is not the same as observed by either DSC or dynamic mechanical techniques.

- e) The blends possess optical transparency and no evidence of phase separation is observed^{15,22} even when prepared by melting the bulk mixing of the powders.
- f) The PPO-PS blends show linear viscoelastic behavior and the monomeric friction coefficient remains approximately independent of composition²². Furthermore, the compositional dependence of the zero shear viscosity may be predicted by the iso-free volume zero shear viscosity-composition relationship derived by Berry and Fox²⁶, provided that the ratio of the critical molecular weights be assumed equal to the ratio of the entanglement molecular weights. this latter determined by measuring the equilibrium modulus in the entanglement plateau of the blend melt²².

All of these experiments have been performed using atactic polystyrene (a-PS). From the analysis of the above described results it has been concluded⁸ that PPO and a-PS are compatible but probably not on a segmental basis.

In this work we have examined the behavior of the system PPO - isotactic polystyrene (i-PS) under different thermal treatments. Previous experiments in this laboratory have shown that considerable crystallinity can be readily developed in PPO-i-PS blend by thermal annealing at appropriate temperatures and blend compositions. It is expected that the use of crystallizable

polymers can provide not only additional information about polymer-polymer interactions but also , broaden and supplement the information we have on individual polymers. A few studies have been published recently on the effects of noncrystallizable polymer diluents on the properties of crystallizing polymers.

Keith and Padden²⁷ and Boon and Azcue²⁸ reported that at given temperature, dilution of isotactic polystyrene with noncrystallizable atactic polystyrene depresses the maximum spherulite growth rate in proportion to the amount of diluent added, but there is a discrepancy in the degree of depression, probably owing to differences in molecular weights of both constituents or tacticity of the crystallizable polystyrene used by the two groups of investigators.

Yeh and Lambert²⁹ have studied the crystallization kinetics, morphology and melting behavior of isotactic polystyrene in blends with various molecular weight atactic polystyrenes over a wide range of concentrations. they found that spherulitic growth rates are uniformly depressed with increasing amounts of atactic diluent and that these growth rates decreased with increasing the molecular weight of the added polystyrene. However, growth rates displayed a sudden increase at certain values when increasing the molecular weight of the

diluent. In addition, morphological observations revealed an increase in coarseness of the spherulites with increasing molecular weight of the atactic polystyrene.

Natov et al³⁰ have studied the morphology and melting behavior of blends consisting of one crystallizing and one amorphous polymers. These authors concluded that, the crystals formed in polymer mixtures containing polar substitutes in their molecules turned out to depend not only on the nature of the crystallizing polymer, but also on the content, nature, and molecular weight of the amorphous component. However, the effect of the amorphous component on super-molecular structures is insignificant in mixtures with no polar substitutes. The observations of the same authors on the melting behavior of the blends show that three kinds of crystal mixtures may be formed: mixtures in which the melting point changes proportionately to the composition; mixtures whose melting point is constant and does not depend on the composition; and those whose melting point depends on the composition only within a certain interval. For the case where the melting temperature of the crystals in the blends drops in proportion to the content of noncrystallizable polymer, the assumption is made that this component occupies the defective areas in the crystal grating. In general, there seems to be no clear correlation between melting point

depression and the level of compatibility of the polymers, which may be drawn from the latter observations.

Thermodynamic considerations employing conventional mixture theories which account for the reduction in chemical potential that occurs on mixing³¹, show that a miscible diluent produces a depression in the equilibrium melting temperature T_m , given by

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u} \frac{V_u}{V_1} (v_1 - \chi_1 v_1^2) \quad (7)$$

which relates the depression of the melting point by the diluent with respect to the melting point T_m^0 of the pure crystalline polymer, to the volume fraction v_1 of the diluent. In addition, the melting temperature drop depends on the heat of fusion ΔH_u per repeating unit, on the ratio of the molar volumes of this unit and the diluent, and, on the interaction parameter χ_1 . In particular, according to equation 7 the melting point depression by diluent is inversely proportional to the molar volume of the diluent molecule; if the latter is a high molecular weight polymer, essentially no lowering is observed.

Nevertheless, if we consider polymer-polymer miscibility at levels between the mixing of individual polymer molecules and the most intimate segmental mixing,

it becomes apparent that the effective size of the diluent molecule may range from the highest submolecule order to that of a few monomer units of noncrystalline polymer per monomer unit of crystallizable polymer. Under these circumstances the molar volume ratio may become significant and the melting point depression as given by equation 7, is no longer negligible. Of course, a combination of this latter effect and a morphological one might also be possible.

On the other hand, Bohn³² has pointed out that a compatible mixture of one crystalline polymer with any other polymer is unlikely because of the elevated heats of crystallization, which must be adverse heats of mixing for a molecular mixture with restricted crystallization.

In view of the above, further studies concerning the compatibility of crystalline polymers and the ability to crystallize and melting behavior of these polymers in binary blends turns out to be of great importance.

THERMAL CRYSTALLIZATION OF ISOTACTIC POLYSTYRENE-
POLY (2, 6-DIMETHYLPHENYLENE OXIDE) BLENDS.

ABSTRACT

A new approach to the problem of polymer compatibility has been examined. Blends of isotactic polystyrene (iPS) and poly(2, 6-dimethyl - 1, 4 phenylene oxide)(PPO) have been prepared by precipitation from dilute solutions of the polymers in a common solvent. Crystallinity has been developed in these blends by isothermal annealing for several times. A variety of times, temperatures and blend compositions have been used. the degree of crystallinity is dependent on the conditions of crystallization and on blend composition. The percentage of crystallinity has been determined from DSC thermograms in two ways: one, by measuring heats of fusion and two, by evaluating the increase in C_p occurring at T_g . A reasonable agreement between these two techniques has been found. It suggest that within the experimental error iPS-PPO blends may be regarded to obey a two-phase additive model reasonably well, at least when the crystalline phase is iPS only.

The presence of relatively high degree of crystal-

linity is shown not to affect the blend compatibility.

Both amorphous crystalline iPS-PPO blend have a single composition-dependent glass transition temperatures as determined by DSC techniques. The crystallinity developed is a function of PPO content. Blends containing 50 weight percent polymer display only traces of crystallinity after extended annealing. When the blend composition is less than 50 weight percent iPS, no crystallinity can be detected.

A melting point depression has also been observed which is composition dependent. The magnitude of the depression increases with increasing PPO content. A discussion relating all of these facts to the level of miscibility of the polymers is given.

The multiple peaks observed in melting isotactic polystyrene and its blends are due not only to melting and recrystallization but also to the presence of different crystal size and/or defects.

C H A P T E R T W O

THERMAL CRYSTALLIZATION OF ISOTACTIC POLYSTYRENE-
POLY (2, 6-DIMETHYLPHENYLENE OXIDE) BLENDS.

EXPERIMENTAL

Materials.

The isotactic polystyrene used in this study was purchased from Polysciences Inc., Warrington, Pa. The material was received as a crystalline white powder and high tactic content with less than 2.38% solubility in boiling methyl ethyl ketone. The intrinsic viscosity of the polymer was measured in toluene at 30°C and yielded a value of 1.10g/dl, which corresponds to a molecular weight (\overline{M}_v) of 3.3×10^5 in accord with an equation given elsewhere³².

Additive free PPO manufactured by the General Electric Co. was used in this work. The polymer in the form of pellets was characterized by viscometry with the aid of Barrales-Riends and Peppers viscometric equation³³.

$$[\eta] = 5.74 \times 10^{-2} \overline{M}_n^{0.69} (\text{cm}^3/\text{g}) \quad (1)$$

The intrinsic viscosity of the polymer in its toluene solution at 25°C was 60.5 ml/gm and according to equation (1) a viscosity-average molecular weight of 2.3×10^4 was estimated.

Sample Preparation.

Blends of i-PS and PPO were prepared by dissolving

previously weighed amounts of both polymers in a measured volume of boiling toluene. Concentrations from 1.5 to 2.5 g. total polymer weight in 100 ml of solvent were commonly used.

In addition to toluene, o-dichlorobenzene and chlorobenzene were used as solvents in order to prepare larger amounts of the blends, by heating the solution at about 120°C.

Although the solubility of iPS in toluene was improved by melting and quenching the powdered polymer, concentrations were kept as low as 2 g./100 ml. in order to facilitate diffusion and molecular interpenetration of the polymers in a relatively low viscous medium.

While most of the blends were prepared in toluene solutions, the effect of the other solvents on the blend compatibility appeared to be the same. In fact, in all cases the samples after going through the same preparation procedure resulted in transparent films with indistinguishable thermal properties.

In all cases solutions were heated, while stirring, for times as long as 24 hours until the dissolution was completed. Upon cooling to room temperature, no phase separation was observed. The solutions were subsequently filtered in sinterized glass to eliminate dust or other impurities.

The filtered co-solutions were then precipitated at room temperature by adding dropwise to a vigorously stirred large excess of methanol. A ratio 8 to 1, methanol to polymer solution, (on a volume basis) was found optimum to obtain the clearest filtrate. Ethanol was employed for chlorobenzene solutions in a ratio 10/1. The precipitated material was then dried in a vacuum oven at ca. 100°C for 48 hours. After this, the samples displayed a cotton-like appearance irrespective of the composition. The dried fluffy material was then compression-molded in the following way: the material was put in a brass mold sandwiched between aluminum plates and the assembly placed on the hot press at about 150°C and heated up to a temperature in the vicinity of 270°C. Both PPO and iPS showed to be unstable at temperatures higher than 290°C . Degradation was counteracted by using nitrogen flowing into the sample assembly. PPO-rich blends were darker the higher the molding temperature. An appropriate temperature for molding PPO-rich blends is 250°C. When the press has reached a temperature between 250 to 280°C the sample is allowed to stand without further heating for 20 minutes after which a 5000 psi pressure is applied. Under these circumstances the sample is left for 10 minutes, removed while clamping together the two

aluminum plates and immediately quenched by immersion in an ice-water bath.

Transparent films, approximately 0.33 to 0.45 mm thick, were obtained in that manner. Small disk-shaped specimens suitable for DSC measurements were cut from the films and encapsulated in $\frac{1}{4}$ " diameter aluminum pans. In order to obtain the highest possible crystallinity, the samples corresponding to seven different compositions, were annealed from the glassy state in vacuum oven and subsequently quenched by placing them on a plate immersed in dry ice.

A variety on annealing times and temperatures were investigated.

Measurements.

A Perkin-Elmer differential scanning calorimeter model DSC-2 was used for all thermal analytical determinations reported here. The instrument was calibrated previously and every 28 runs on the basis of the melting temperatures and enthalpies of known amounts of high-purity Indium and Tin. Enthalpies of fusion were determined by graphical integration of the melting peak with an accuracy of 3 - 5% in most cases, always depending, mainly, upon the accuracy of the base line and the peak area measurements.

Sensitivities of 2 to 5 mcal./sec. were used in accord with the sample weights. Most experiments were carried out at heating rate of $10^{\circ}\text{K}/\text{min}$. but the effect of using lower and higher heating rates was studied. In particular, the changes in specific heats occurring at the glass transition temperatures were scanned at a heating rate of $20^{\circ}\text{K}/\text{min}$, in order to increase the length of the ordinate deflections.

Finally, a Perkin-Elmer digital autobalance, model AD-2, capable of reading to 0.001 mg. was used for weighing all the samples. The weights of the samples examined range between 5 and 12 mg.

Reproducibility of the data was checked by doing at least two runs on each composition subjected to a particular treatment.

RESULTS

Table I shows the compositions of the samples of iPS-PP0 blends prepared in the way described previously.

TABLE I

Summary of weight compositions of the iPS-PP0 blends.

<u>Sample Identification</u>	<u>iPS in blend, Wt. %</u>
iPS	100
90/10	90
75/25	75
50/50	50
25/75	25
10/90	10
Pure PP0	0

With the exception of iPS, which was treated at additional temperatures, samples of all above indicated compositions were annealed for 12, 24, 48 and 72 hours at the following temperatures: 120, 135, 150, 180, 200 and 220°C. This temperature set includes approximate upper and lower limits out of which no thermal induced crystallinity was encountered even for times as long as a week.

From the analysis of the DSC thermograms obtained for each sample the following determinations have been made:

- a) Glass transition temperatures.
- b) Degree of crystallinity measured by two independent

methods. The first involves the determination of enthalpies of fusion by graphical integration of the curves of heat flow rate (dq/dt) vs time, whereas the second simply measures the specific heat increase ΔC_p at the glass transition temperature, which has proved to be significantly crystallinity dependent.

c) The melting characteristics of iPS and crystallizable iPS-PPO blends as well as the composition-dependent melting point reduction.

Glass transition Temperatures.

The DSC thermograms for the annealed samples were extended through the glass transition region. A relatively sharp single T_g was encountered for all compositions. The magnitude of the discontinuity in specific heat, C_p , associated with T_g , was clearly dependent on the degree of crystallinity but the location of the transition appeared only slightly changed for the different thermal histories in the iPS-rich blends. An increase in T_g , for blends containing 90 and 75 weight percent iPS, appears as a result of the relative change in the composition of the amorphous phase, which becomes richer in PPO.

The glass transition temperature in this work is taken as the temperature corresponding to the midpoint of the discontinuity in C_p .

The results are summarized in table II

Annealed samples were scanned at $10^{\circ}\text{K}/\text{min}$. heating rate from 340°K up to above the melting temperature, then cooled at the same rate and run again to observe the effect of the absence of crystallinity on the location of T_g . Crystalline melting of the iPS was detected in the first run, in mixtures with a iPS content larger than 50%. However no melting peak was observed in subsequent runs which is in agreement with previous experiments²⁷, accounting for the slow crystallization of iPS. Each amorphous sample was then scanned two to three times under similar conditions to ensure the existence of significant effects of the thermal history on both T_g and specific heat increase. The glass transition temperatures listed in table II are, thus, the average of several additional scans made at the same experimental conditions and were reproducible to $\pm 1^{\circ}\text{C}$. Since T_g values appeared only slightly dependent of the degree of crystallinity, we report here those corresponding to samples of highest crystallinity.

In addition amorphous iPS-PPO samples were run at a heating rate of $20^{\circ}\text{K}/\text{min}$. Consistently, higher values of T_g (2 to 3°C) were found for the entire range of compositions. However the most interesting feature of increasing the heating rate was to expand the magnitude of the discontinuity in C_p which will be useful for other

purpose later on in this work.

Tg values obtained at 20°K/min. heating rate are also included in table II.

The Tg data are plotted as a function of composition in figure 1. The resulting curve shows the typical composition dependence for Tg, displayed by compatible blends. Furthermore, the data agree reasonably well with those calculated by theoretical equation of Fox³⁵ as indicated by the dashed line in figure 1.

TABLE II

Glass transition temperatures of partially crystallized (T_{g1}) and amorphous (T_{g2} , T_{g3}) iPS-PPO blends.

<u>Blend Composition</u>	$T_{g1}^{(a)}\text{ }^{\circ}\text{C}$	$T_{g2} \text{ }^{\circ}\text{C}$	$T_{g3}^{(b)}\text{ }^{\circ}\text{C}$
Pure iPS	103	98	103
90%"	110	106	109
75	119	114	118
50	139	138	141
25	178	178	181
10	198	199	202
Pure PPO	216	217	220

a. Samples annealed at 180°C for 24 hours.

b. Tg measured at 20°K/min.

Enthalpies of fusion and Degree of Crystallinity.

Enthalpies of fusion of the crystalline samples were determined by graphical integration of the melting peaks on the DSC thermograms. These thermograms are curves of heat flow rate dq/dt versus time. When a crystalline polymer is heated through its melting range, dq/dt goes through a maximum and falls as the crystalline material is melted out. The area A , under this peak is proportional to the heat input during the phase transition, Q_f , and is given by:

$$Q_f = (dq/dt)dt = KA \quad (2)$$

in which K is a constant calculated from,

$$K = \frac{cS}{mV} \quad (3)$$

where c is a calibration constant of the calorimeter, S is the full range of the power in millical sec^{-1} inch^{-1} , m is the mass of the sample and V is the chart speed in inch sec^{-1} .

The constant c was determined by calibrating the calorimeter with known amounts of high purity Tin and Indium. The calibration was made prior to the experiments and periodically every 28 runs. A mean value of 11.45×10^{-2} for c was found by averaging 20 values obtained for Tin and 20 for Indium with a standard deviation of 0.14×10^{-2} .

The accuracy of the measurements of the heat of fusion depends, mainly, on the precision on evaluating peak areas and on the choice of the appropriate baseline.

The enthalpies of fusion calculated in the manner just described are recorded in tables III to VI.

From these values of ΔQ_f , a percentage of crystallinity X_c can be evaluated by the relation

$$X_c = \frac{\Delta Q_f}{H_f} \times 100 \quad (4)$$

where ΔH_f is the enthalpy of fusion of completely crystalline polystyrene which has been found to be 80.3 joules g.⁻¹ ³⁶ quite close to that of 86.3 joules g.⁻¹ reported by Danusso and Moraglio³⁷. Both values were determined by using melting point depression data of the polymer with different concentrations of a diluent. In our calculations we use an intermediate value of 20.0 cal g.⁻¹ (83.72 joules g.⁻¹) which is nearly the arithmetic mean of those values. The percent crystallinity data are also shown in tables VII to X, for the different blend compositions and pure iPS.

The degree of crystallinity is markedly dependent on the PPO content in the blends, decreasing as the iPS/PPO ratio decreases. No crystallinity was found under any annealing conditions for blends containing more than 50% in weight of PPO. These facts are illustrated in figures 2 to 5, in which the degree of crystallinity in terms of enthalpy of fusion

are plotted against crystallization temperature for all the crystallizable samples for each annealing time.

TABLE III

Enthalpies of fusion in joules g.⁻¹ of pure iPS resulting from annealing at the temperatures and time indicated.

Temperature, °C	Time (Hours)			
	12	24	48	72
120	-	-	-	1.05
135	6.20	9.13	16.12	21.43
150	15.78	20.34	22.44	24.15
170	23.61	30.81	30.64	31.98
180	25.33	28.42	30.98	32.06
190	22.10	24.07	27.38	29.85
195	17.58	20.26	23.78	27.92
200	14.65	16.53	20.09	25.74
210	11.64	15.28	18.08	20.51
220	-	1.67	3.27	6.07

In the following tables appropriate correction has been made for taking into account only the weights of iPS present in each blend sample.

TABLE IV

Enthalpies of fusion in joules g^{-1} of 90/10 iPS/PPO blends resulting from annealing at temperatures and time indicated.

Temperature $^{\circ}\text{C}$	Time (Hours)			
	12	24	48	72
135	1.80	6.17	7.95	13.40
150	14.31	16.49	21.16	22.81
180	19.51	26.14	27.84	29.15
200	9.50	13.98	16.66	19.97
220	-	-	1.80	3.62

TABLE V

Enthalpies of fusion in joules g^{-1} of 75/25 iPS/PPO blends resulting from annealing at the temperatures and time indicated.

Temperature $^{\circ}\text{C}$	Time (Hours)			
	12	24	48	72
135	-	-	1.54	3.45
150	10.36	11.68	13.79	16.32
180	15.71	16.95	19.88	23.60
200	6.56	7.47	9.69	11.84
220	-	-	1.47	3.55

TABLE VI

Enthalpies of fusion in joules g.⁻¹ of 50/50 iPS/PP0 blends resulting from annealing at the temperatures and time indicated.

Temperature °C	Time (Hours)			
	12	24	48	72
150	-	-	1.59	2.39
180	-	2.09	3.72	5.94
200	-	-	1.84	2.30

TABLE VII

Percent crystallinities calculated from data of enthalpy of fusion of iPS resulting from annealing at the temperatures and time indicated.

Temperature °C	Time (Hours)			
	12	24	48	72
120	-	-	-	1.2
135	7.4	10.9	19.3	25.6
150	18.8	24.3	26.8	28.9
170	28.2	36.8	36.6	38.2
180	30.3	33.9	37.0	38.3
190	26.4	28.7	32.7	35.7
195	21.0	24.2	28.4	33.4
200	17.5	19.7	24.0	30.7
210	13.9	18.2	21.6	24.5
220	-	2.0	3.9	7.2

TABLE VIII

Percent crystallinities calculated from Data of enthalpy fusion of 90/10 iPS/PPO resulting from annealing at the temperatures and time indicated.

Temperature °C	Time (Hours)			
	12	24	48	72
135	2.1	7.2	9.5	16.0
150	17.1	19.7	25.0	27.2
180	23.3	31.1	33.2	34.7
200	11.3	16.7	19.9	23.8
220	-	-	2.1	4.2

TABLE IX

Percent crystallinities calculated from Data of enthalpy fusion of 75/25 iPS/PPO resulting from annealing at the temperatures and time indicated.

Temperature °C	Time (Hours)			
	12	24	48	72
135	-	-	1.7	4.0
150	12.2	14.0	16.3	19.5
180	18.6	20.2	23.7	28.2
200	7.6	8.8	11.4	13.9
220	-	-	1.6	3.0

TABLE X

Percent crystallinities calculated from data of enthalpy of fusion of 50/50 iPS-PPO blends resulting from annealing at the temperatures and times indicated.

Temperature °C	Time (Hours)			
	12	24	48	72
150	-	-	1.95	2.81
180	-	2.80	4.56	7.07
200	-	-	2.37	2.63

Specific heat increase and degree of Crystallinity.

At the glass transition temperature, T_g , a discontinuity in specific heat, C_p of the amorphous part of the material takes place. For semicrystalline polymers the magnitude of this increase in specific heat ΔC_p , is directly related to the amorphous content of the material, i.e. it can be taken as a measure of the degree of crystallinity of the polymer³⁸. This assertion presupposes the validity of the additive two phase behavior for the amorphous and crystalline components in the sample. In this respect isotactic polystyrene adheres very closely to the two phase model³⁹. As a matter of fact polystyrene appears to follow most of the experimental findings on which the two-phase model is based³⁸, namely:

- a) In atactic and isotactic samples no difference have been experimentally found among the specific heats, measured below the glass transition and above the melting point.
- b) Both atactic and amorphous polymers display the same increase in specific heat at T_g .

In addition, as we have previously shown, the glass transition temperature is not basically altered by the crystalline phase.

It follows that, in general, the per cent crystallinity of a semicrystalline polymer may be determined by

measuring ΔC_p occurring at the glass transition, provided that the variation of the whole amorphous polymer is known.

Thus, let C_{pg} and C_{pr} be the heat capacities of the polymer before and after T_g . By analogy with other expressions the degree of crystallinity, x , of the polymer, may be described in terms of the heat capacities by

$$x = \frac{C_{pr}'' - C_{pr}'}{C_{pr}'' - C_{pr}^*} \quad (5)$$

Where the upper prime, double prime and the asterisk denote the completely amorphous, the semicrystalline and the perfectly crystalline forms of the polymer respectively.

Since the specific heats are assumed to be alike below T_g , equation 5 may be written:

$$x = \frac{(C_{pr}'' - C_{pg}'') - (C_{pr}' - C_{pg}')} {(C_{pr}'' - C_{pg}'') - (C_{pr}^* - C_{pg}^*)} \quad (6)$$

the differences within parenthesis are in their order:

ΔC_{pA} , ΔC_{pS} and ΔC_{pC} , which represent the increases in C_p at T_g of the whole amorphous, semicrystalline and completely crystalline polymer respectively. Since no change at all can be observed for an entirely crystalline polymer at T_g , ΔC_{pC} vanishes and equation 6 becomes

$$x = \frac{\Delta C_{pA} - \Delta C_{pS}}{\Delta C_{pA}} \quad (7)$$

On the other hand from the basic thermodynamics we can write the heat flow rate, dQ/dt in cal/sec, into a sample of mass m gm. and specific heat C_p in cal $\text{gm}^{-1} \text{ } ^\circ\text{K}^{-1}$, as follows

$$\frac{dQ}{dt} = m C_p \frac{dT}{dt} \quad (8)$$

where dT/dt is the heating rate in $^\circ\text{K}/\text{sec}$.

From DSC theory, it is known that the heat flow rate is directly proportional to the ordinate deflection, L caused by the changes in the instantaneous specific heat of the sample. Thus, if S is full scale value of the power (sensitivity) in millicalories $\text{sec}^{-1} \text{ inch}^{-1}$, the heat flow rate is given by:

$$\frac{dQ}{dt} = SL \quad (9)$$

and by equating eqs. 8 and 9 and letting L be the fractional increase in the ordinate at the transition, the increase in the specific heat can be evaluated by:

$$C_p = \frac{S L}{m(dT/dt)} \quad (10)$$

now, if L_S and L_A are the ordinate-deflection increase due to semicrystalline and completely amorphous polystyrene respectively and as long as the experimental conditions are

maintained in both determinations the following relationship is readily obtained

$$\frac{\Delta C_{pS}}{\Delta C_{pA}} = \frac{m_A \Delta L_S}{m_S \Delta L_A} \quad (11)$$

Where the symbols and both suscripts, A and S, have the same meaning as given above.

An expression for the degree of crystallinity may be derived from equations 7 and 11:

$$x = 1 - \frac{m_A}{m_S} \frac{L_S}{L_A} \quad (12)$$

Both equations, 10 and 12, are used in our calculations of the magnitude of the increase in C_p and the per cent crystallinity respectively, of the pure iPS and its blends with PPO.

$\Delta C_{p'S}$ for amorphous blends and homopolymers were calculated from thermograms run in duplicate at the same experimental conditions as used for annealed samples. Heating rates of 20°K/min and sensitivities of 5 mcal/sec. were used in all cases.

As expected no significant difference in $\Delta C_{p'S}$ was found between atactic and amorphous isotactic polystyrene.

For crystalline blends and pure iPS, the percent crystallinity was calculated by equation 12. Quite consistently, whenever crystallinity was absent in the samples, no change in ΔC_p was observed. However low degrees of crystallinity as indicated by small melting peaks are undetectable by measuring ΔC_p 's because the decrease of the magnitude of the ordinate displacement caused by the crystallinity sample turns out to be within the experimental error in the measurements of ΔL .

After running the crystalline samples, additional scans were made on the samples cooled quickly from above the melting point. No change in ΔC_p was observed consequently with the disappearance of the whole crystallinity.

The values of ΔC_p and percent crystallinity reported here were averaged on at least three different measurements of ΔL . The ΔC_p values for pure iPS and PPO agree excellently with those reported by Karasz et al³⁹⁻⁴⁰, which were determined by means of an adiabatic calorimeter. Results are summarized in tables XI to XVII. In tables XV to XVII are shown percentages of crystallinity determined in two ways; x_f corresponds to those values found from the data of heat of fusion via equation 4, and x_c represents percent crystallinity as evaluated from the data of specific heat increase through equation 7, assuming that

the samples follow the two phase model . The values of ΔC_p are plotted versus blend composition for amorphous and semicrystalline blends at constant annealing time, in figures 6 to 8.

Finally in figures 9 to 11 the variation of ΔC_p with crystallinity is illustrated for each blend composition. The straight line corresponds to the ideal two phase behaviour.

TABLE XI

Specific-heat increases of amorphous blends and homopolymer.

<u>Composition</u>	<u>C_p joules $^{\circ}K^{-1} g.^{-1}$</u>
Isotactic PS	0.298
Atactic PS	0.296
90/10	0.292
75/25	0.287
50/50	0.281
25/75	0.265
10/90	0.256
PPO	0.242

TABLE XII

Values of specific heat increase, ΔC_p in joules $\text{deg}^{-1} \text{g}^{-1}$ for semicrystalline iPS resulting from annealing at the temperatures and time indicated.

Temperature $^{\circ}\text{C}$	Time (Hours)		
	24	48	72
135	0.276	0.228	0.219
150	0.215	0.217	0.206
180	0.187	0.186	0.177
200	0.244	0.224	0.198

TABLE XIII

Values of specific heat increase, ΔC_p , in joules $\text{deg}^{-1} \text{g}^{-1}$ for semicrystalline 90/10 iPS/PPO blends resulting from annealing at the temperatures and time indicated.

Temperature $^{\circ}\text{C}$	Time (Hours)		
	24	48	72
135	0.260	0.250	0.250
150	0.227	0.213	0.209
180	0.193	0.190	0.172
200	0.229	0.222	0.197

TABLE XIV

Values of specific heat increase, ΔC_p in joules $\text{deg}^{-1} \text{g}^{-1}$ for semicrystalline 75/25 iPS/PP0 blends resulting from annealing at the temperatures and time indicated.

Temperature $^{\circ}\text{C}$	Time (Hours)		
	24	48	72
150	0.225	0.221	0.216
180	0.210	0.195	0.185
200	0.238	0.226	0.223

TABLE XV

Percentage of crystallinity for iPS calculated:

- a) from data enthalpy of fusion (x_f) and
- b) from specific heat increases at T_g (x_c) ; resulting from annealing at the conditions shown:

Temp. $^{\circ}\text{C}$	Time (Hours)					
	24		48		72	
	x_f	x_c	x_f	x_c	x_f	x_c
135	10.9	7.4	19.3	23.5	25.6	26.5
150	24.3	27.9	26.8	27.2	28.9	30.9
180	33.9	37.3	37.0	37.6	38.3	40.4
200	19.7	18.1	24.0	24.8	30.7	33.5

TABLE XVI

Percentage of crystallinity for 90/10 iPS/PP0 blends calculated:

- a) from data of enthalpy of fusion (x_f) and
 b) from specific heat increase at T_g (x_c); resulting from annealing at the conditions shown:

Temp. °C	Time (Hours)					
	24		48		72	
	x_f	x_c	x_f	x_c	x_f	x_c
135	7.2	11.0	9.5	12.3	16.0	14.4
150	19.7	22.3	25.0	27.1	27.2	28.4
180	31.1	33.9	33.2	34.9	34.7	41.1
200	16.7	21.6	16.9	24.0	23.8	32.5

TABLE XVII

Percentage of crystallinity for 75/25 iPS/PP0 blends.

Where x_f and x_c have the same meaning as above.

Temp. °C	Time (Hours)					
	24		48		72	
	x_f	x_c	x_f	x_c	x_f	x_c
150	14.0	21.6	16.3	23.0	19.5	24.7
180	20.2	26.8	23.7	32.1	28.2	35.6
200	8.8	17.1	11.4	21.3	13.9	22.3

Isotactic Polystyrene: thermal history and melting characteristics.

At this point, we will discuss some observations made on the melting behavior of isotactic polystyrene and its crystallizable blends with PPO.

Considerable crystallinity is readily developed in pure iPS and iPS-PPO blends containing more than 50% in weight of iPS by thermal treatment. We have explored the whole temperature range between 120° and 220°C at different intervals.

Typical thermograms are shown in figures 12 and 13. The presence of multiple melting peaks, whose magnitude and location are dependent on crystallization conditions, is clearly observed in those thermograms.

These experiments confirm the findings made previously by other investigators^{41, 42}. However, we have found some differences which suggest that the phenomenon needs to be studied more rigorously, both theoretically and experimentally.

When samples of iPS are scanned at 10°K/min, three peaks appear as long as the temperature of crystallization, T_c , is 180°C or lower. The onset of the first peak (I) is evident at temperatures as low as 140°C as T_c is 135°C (Thermogram A Fig. 12). In general the onset of the first peak is observed at temperatures 3 to 5°C higher than T_c .

Moreover, the temperature corresponding to the transition between the first (I) and second (II) peak, although somewhat diffuse, seems to lie between 180 and 185°C independently of the annealing temperature. In fact, in samples annealed at T_c higher than 180°C the first peak is not observed any more. Similarly the transition between second and third peaks lies between 195 and 200°C. Consequently, if T_c is chosen between 180°C and 200°C, two peaks can be seen and at T_c beyond 200°C only one peak appears. (fig. 12). It should be noticed that the end of the last peak shifts only slightly (1 to 2°C) toward higher temperatures as T_c is increased from 135 to 210°C.

In brief, what we have observed in our experiments is that the onset of the melting process increases linearly with crystallization temperature T_c , and it lies approximately 4 or 5°C above T_c . Moreover the temperature at which the whole melting process ends, is essentially unaltered whatever T_c is. This suggests that the peak III, which represents the fusion of larger and more perfect crystallites, always appears irrespective of the thermal treatment as illustrated in figure 12 where the three peaks are clearly distinguishable although very close to one another. The difficulty arises in assigning the true melting temperature of the system. One can think that the temperatures corresponding to the maxima of the three

peaks increase linearly with different slopes up to a common intersection at the equilibrium melting point, depending upon the crystallization conditions.

Actually, what one can see is the intersection of the characteristic peak with the extrapolations of the melting temperatures of the other peaks.

The presence of a single, two, or three peaks is subordinated to the annealing treatment. Evidently, when the sample is annealed at temperatures higher than that one corresponding to the melting of smaller or less perfect crystallites, represented by the peak I, and subsequently quenched from that temperature none of such crystallites can be developed because of the very known low growth rate of spherulites of the polystyrene. The same effect is seen when the sample is annealed above the melting temperature of the crystallites represented by the peak II. This is supported by the presence of a single sharp peak in samples annealed at 210°C (fig. 13).

So far, all of these facts have been explained in two ways: one suggesting that multiple peaks are caused by the presence of morphologically different crystal structures⁴¹ and the more recent one showing that multiple peaks originate from melting and recrystallization during the scanning⁴²⁻⁴³. The latter, apparently, gives account for many of the facts observed. Although the exact mechanism

of the recrystallization is not yet clear in the case of iPS, it has been assumed to be a continuous process in which the melting of the primary crystalline structure enables the polymer chain to rearrange into more perfect crystals upon further heating. If this is the case, such a recrystallization process is not complete and a considerable amount of crystallites giving account for the presence of peaks I and II, are destroyed. The precedent statement is made in view of the results of some of our experiments.

In fact, we subjected some iPS samples to identical thermal treatments (annealing at 160°C for 24 hours). Under these conditions the samples exhibit the three peaks. Initially, several samples were run and the areas under the peaks measured and normalized in accord with the sample weight. A quite consistent value of $1.853\text{cm}^2\text{ g}^{-1}$ was found for the whole area. A new sample (similarly treated) was run up to a temperature (190°), at which only the first peak appeared, and cooled down as quick as possible at room temperature. (It took only 30 sec to reach equilibrium temperature, 330°K , in the DSC). then the sample was rerun all the way up to above the melting of the last peak. Now, the area under the two peaks turned out to be $1.740\text{ cm}^2\text{ g}^{-1}$. Since the first peak represents

about 10.3% of the total crystallinity, less than a half of the crystalline fraction represented by the first peak has been incorporated into the region of larger and/or more perfect crystallites. A second experiment is more illustrative; if the samples are heated up to 202°C, where the two first peaks appear, followed by a similar cooling as in the first experiments and finally rerun up to well above of the melting of the last peak, a value of 1.496 cm² g⁻¹ is now found for the single peak. This means that 19.3% of the originally crystallized material is destroyed upon melting of smaller or less perfect crystallites.

Furthermore, since the largest peak represents about 57.8% of the total crystallinity in the original samples, it is clear that recrystallization also takes place but it is not the only reason for the presence of multiple peaks. The experiments just mentioned were performed at a heating rate of 20°K/min, but at lower rates the same effect was observed although the recrystallized fraction increased. In addition, a decrease in the specific heat change at T_g, also indicates a decrease in the degree of crystallinity in the samples where either the first or the two first peaks have been suppressed in the way just described.

As a result of these experiments one comes to the conclusion that multiple melting is partially due to

melting and recrystallization when the sample is scanned at low enough heating rates and partially due to the presence of different crystal sizes and/or defects. At reasonable heating rates some of these crystallites are destroyed completely and do not contribute any more to the total crystallinity of the sample.

This is not surprising if one realizes that kinetic factors can prevent some crystallites from reorganizing to more perfect higher melting crystals during scanning.

In addition, since melting of crystallites and recrystallization are two opposite processes from the thermodynamic point of view, the location and the intensity of each peak must reflect the net heat effect of the changes taking place. This means that the fraction of material which is found to recrystallize might, actually, be lower.

Further investigations should be directed to determine the melting behavior of iPS at considerably lower heating rates. The more likely to occur is that recrystallization is complete at a certain very low heating rate.

We have also studied the effect of the heating rate on the melting temperature, T_m , of iPS. Table XVIII shows the several heating rates used and the corresponding values of T_m . Here, the melting temperature is taken as

the temperature at which the last trace of crystalline material disappears which may be experimentally determined by finding the intersection of the baseline with the extrapolated post-maximum side of the last melting peak.

TABLE XVIII

Melting points of iPS determined at the indicated heating rates.

<u>Heating Rate</u>	<u>Melting Point</u>
(°C/min)	°C
20	230
10	231
5	233
2.5	234.5
1.25	236
0.62	237
0.31	237

These measurements were performed on samples of iPS annealed at 180°C for 24 hours.

As it can be seen an increase in T_m with decreasing heating rates has been found, which is again an indication of recrystallization.

In spite of the previous results all the melting

temperatures reported in this work have been determined at a heating rate of $10^{\circ}\text{K}/\text{min}$ and no attempt will be made to correct these values by taking into account the heating rate effect.

As discussed earlier some irregularities have been found in the melting behavior of pure iPS and its blends owing to recrystallization and variation in the crystal structure which result in multiple melting peaks, as well as the change in both location and relative intensity of these peaks when the crystallization temperature is changed. These irregularities are particularly noticeable when the samples are crystallized at temperatures equal to or lower than 180°C . However, at crystallization temperatures higher than 200°C . A single sharp melting peak, whose area and location are composition dependent, has been observed for all crystallizable samples. The position of these peaks does not displace significantly with changes in heating rates and it is completely reproducible. Such melting temperatures appear to be very close to the equilibrium melting point in good agreement with values previously reported.

In our measurements the samples were annealed at 200°C for 24 hours and scanned at $10^{\circ}\text{K}/\text{min}$. The melting temperatures were determined as described earlier and these values plotted against blend composition in

figure 14, and tabulated in table XIX.

Similar depressions in melting temperature, with increasing PPO content, are observed in blends annealed under different conditions.

TABLE XIX

Melting points of iPS-PPO blends with the highest crystalline content.

<u>Weight %</u>	T_m °C \pm 1°C
100	231
90	227
75	222
50	217

DISCUSSION OF THE RESULTS

The system PS-PPO has proved to be what might be defined as a typical compatible blend in the sense of the criteria enunciated in chapter one. This compatibility extends over the entire range of compositions regardless of the microstructure of the polystyrene and/or its degree of crystallinity. In fact, aPS-PPO blends, and amorphous and semicrystalline iPS-PPO blends, are characterized by single glass transition values which shift with composition in a monotonic fashion.

Although there appears to be no remarkable difference in the T_g values of these blends, an increase in T_g of crystalline blends containing 90 and 75 weight percent iPS is persistently observed. This is not surprising since the amorphous region becomes richer in PPO owing to the loss of iPS by crystallization.

Degrees of crystallinity of pure iPS and iPS-rich blends have been observed to depend upon crystallization conditions. For iPS-rich blends, the dependence is much the same as in pure polymers. Thus, the melting points of the blends increase with crystallization temperature, T_c , up to the equilibrium melting temperature. There is also an intermediate temperature between T_m and T_g at which maximum crystallinity is reached. Heats of fusion, which

are a measure of the degree of crystallinity, are dependent on T_c , decreasing in magnitude as either T_m or T_g is approached. In addition, the multiple peaks observed in melting pure iPS also appear when iPS-rich blends are melted. The first small peak is undetectable in the blends.

In figure 14, the area-to-weight ratios of the melting peaks of iPS are plotted as a function of composition. The plot shows a monotonic decrease as the weight fraction of PPO is increased. Blends containing about 45 weight percent or less iPS have no melting peak at all, which means that PPO does not crystallize by thermal treatment. The dashed line in figure 14 connects the observed area for pure iPS and zero for PPO. If it were not for amorphous PPO interfering with iPS crystallization one might expect constant area-to-iPS weight ratios. Such a case should occur if the polymer molecules do not interact at all. Moreover, even in cases where moderate interaction could exist, it would be reasonable to regard clusters or domains of iPS decreasing in size with increasing PPO content, but still containing enough material for crystallization to take place. Such a behavior might be represented by the dashed line. However, neither one is the case. Our experimental results show that strong polymer-polymer interactions occur upon mixing iPS and PPO.

The decrease in the levels of crystallinity with increasing PPO content can be explained by referring to figure 14. At low concentrations of PPO, there must be regions predominantly rich in iPS, even in the presence of strong molecular interactions. This is in agreement with the fit between the curve and the dashed line at compositions as high as 15% by weight of iPS.

At higher PPO concentrations the size of the iPS domains decreases considerably until a point is reached where the amount of crystallizable material is small enough so that no appreciable melting peak is observed, or perhaps, no crystallinity is developed at all. Quite notably, this point happens to be very near 50% weight composition, which is a further indication of the submolecular level of mixing, i.e. since there is no mass excess of one polymer over the other, there cannot be domains richer in one component, if a good degree of compatibility is to be expected. The same finding is reported by others for the case of a compatible blend⁴⁵.

Thus, the system iPS-PPO becomes one of the few systems reported as compatible mixtures of one crystalline polymer with any other one. Compatible blends of crystalline and amorphous polymers have been regarded unlikely except in the remotely possible case of mixed crystal formation by L. Bhon³².

The presence of a single T_g at approximately the same location in both amorphous and semicrystalline blends indicates that significant changes in the average mass content of the microphases do not occur upon crystallization.

The two-phase behavior of the mixture has also been studied. Changes in specific heat occurring at T_g were examined as a function of composition and degree of crystallinity. Our results lead to the conclusion that pure iPS closely obeys the two-phase model but the blends depart from the model proportionately as the content of PPO increases in the amorphous phase. Individually, PPO has shown considerable departure from the ideal two-phase behavior⁴⁰.

In crystallized iPS-rich blends, the crystalline phase consists of iPS crystallites with presumably some amorphous material occupying the defective areas in the crystal grating, whereas the amorphous phase may be visualized as a entangled mass of randomly intertwined molecules of the two polymer. This level of homogeneity in the amorphous phase can be assumed on the basis of the T_g values. For example, a blend containing 90 weight percent iPS and having about a 30 percent crystallinity exhibited a T_g of 110°C . For such a blend, the composition.

of the amorphous phase becomes approximately 86% by weight of amorphous iPS. The glass transition as found independently for a wholly amorphous blend of this composition is also around 110°C.

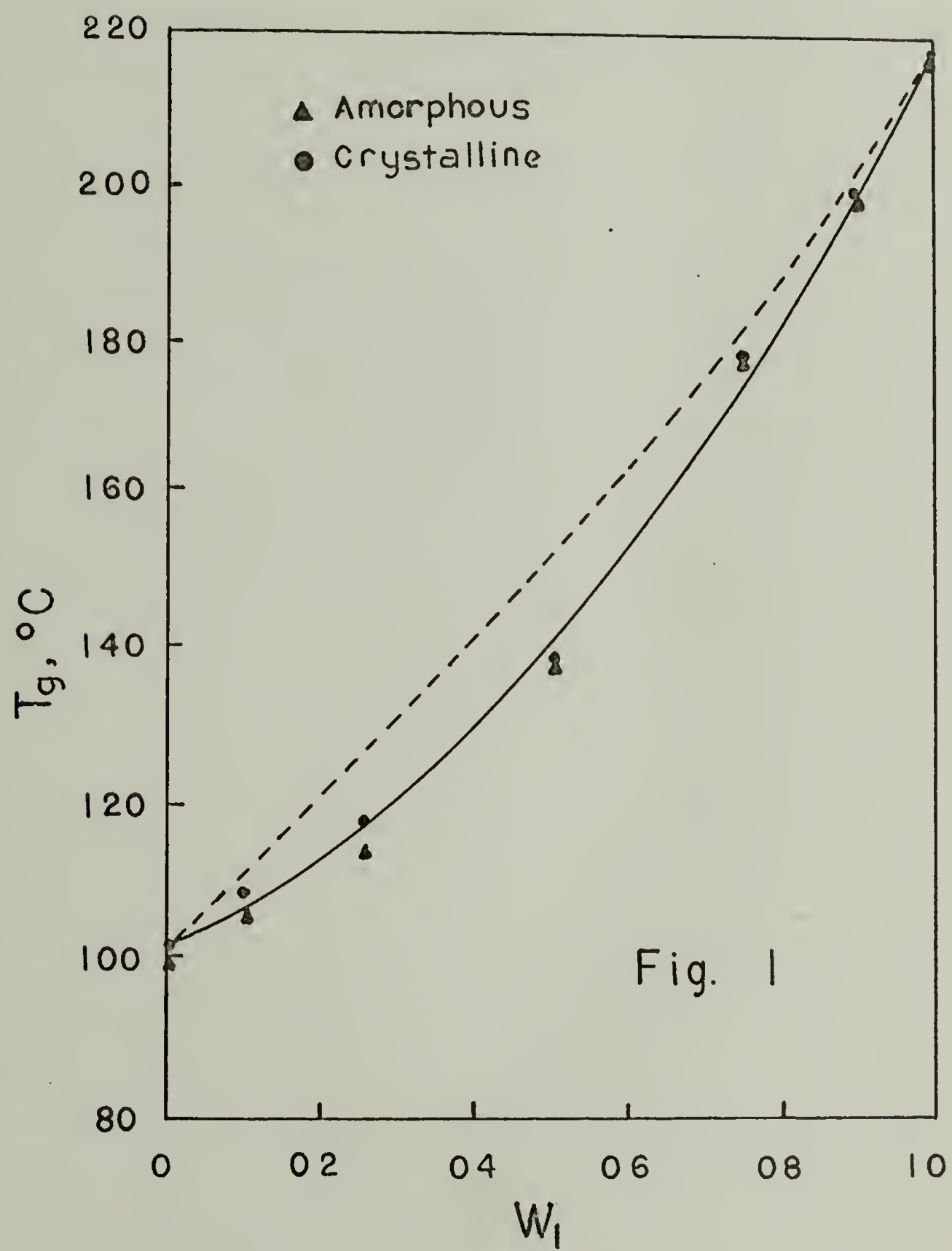
Moreover, as the degree of crystallinity calculated by specific heat increases, are compared to those calculated from enthalpies of fusion, one encounters that the former values are 15 to 20% higher than the latter ones. Our calculations of the percent crystallinity from heat of fusion data involved the assumption that the heat of fusion of a hundred percent crystalline iPS is of 20 cal/g. However, this value, cannot be obtained by direct calorimetric determination, but they are determined in conjunction with data of melting point depressions caused by diluents. Therefore, some corrections are necessary to adequate this value to a real polymer system. For real polymers factors contributing to the reduce melting temperature arise from the finite size of the crystallites, their degree of internal perfection and the interfacial and connecting regions. Actually, a real value lower than 20 cal/g. might be expected and this in turn, would increase the percent crystallinity determined by using heats of fusion. This discussion does not mean that the values determined by changes in specific heats can be assumed more reliable;

but instead the discrepancies are reduced not only because of departure from the two-phase behavior of the iPS-rich blends but also because of possible underestimated values of the degree of crystallinity using Q data.

The depression in the melting point of the blends can also be adduced as a proof of the considerable intimacy of the mixture. It might be contended that a high molecular weight diluent cannot produce a depression this large on the basis of the thermodynamic theory developed by Flory for solutions of polymers in low molecular weight diluents. However, this theory is not completely suitable to be applied to polymer-polymer mixtures, nor can the size of the entire molecule be considered to evaluate the molar volume of the diluent, at least not at high levels of miscibility of the polymers.

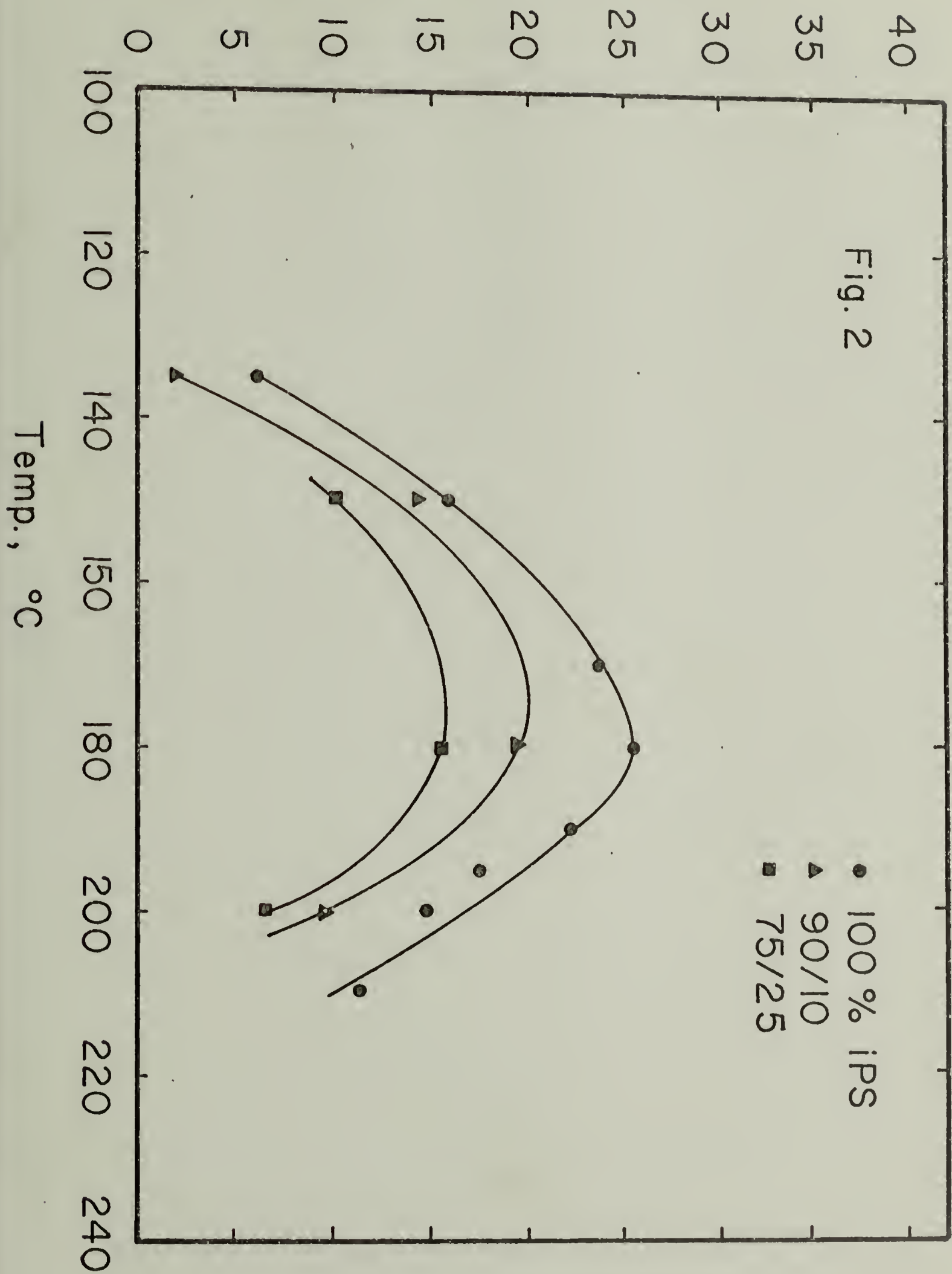
A more complete discussion on this topic is presented in a further report, but it is agreed here that both effective size of the diluent and more defective crystallinity with increasing diluent concentration are responsible for the depression in melting point.

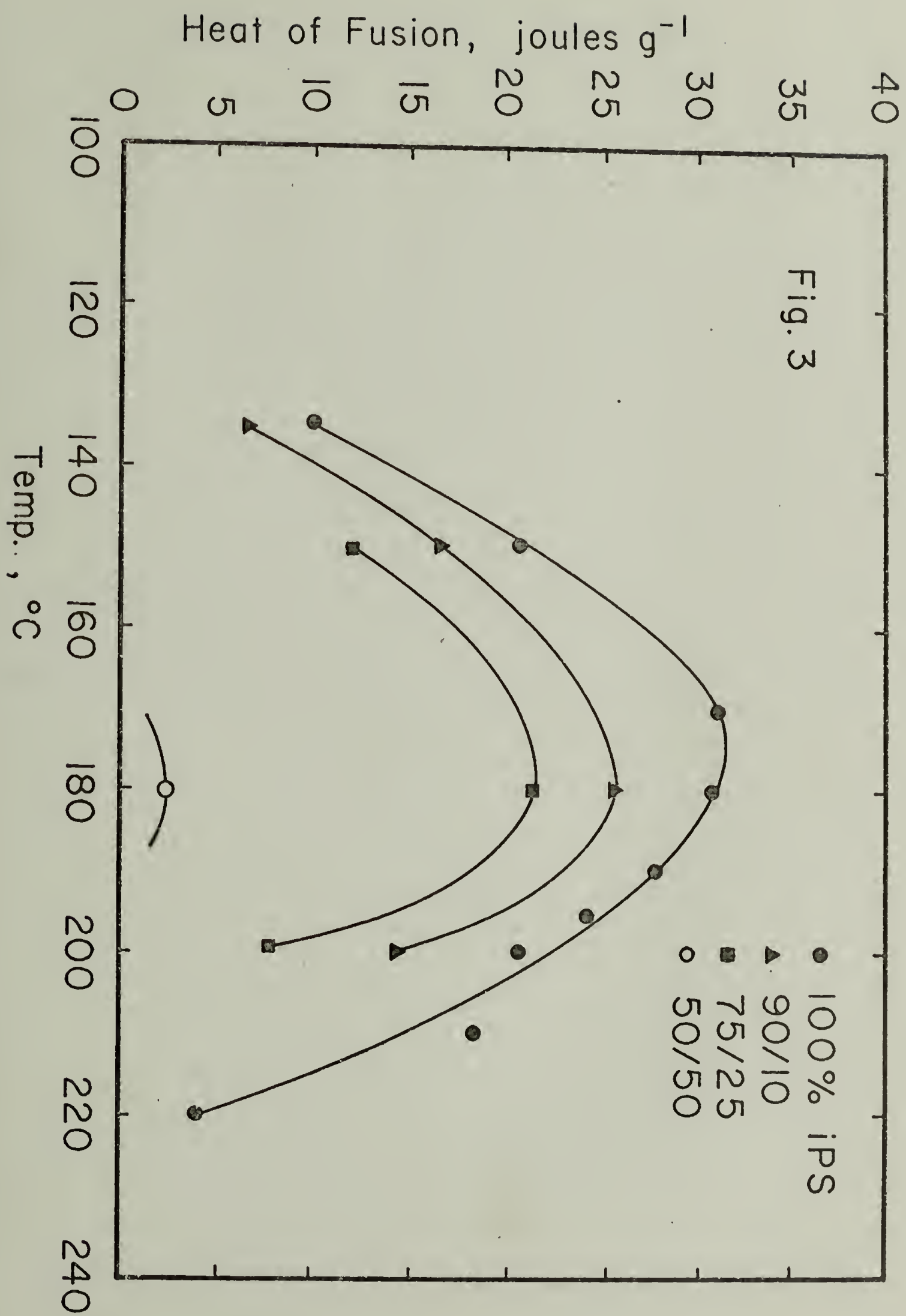
These two facts are perfectly interrelated. Thus, if the average effective size of the diluent reaches sub-molecular levels the development of crystalline regions meets physical barriers limiting both the growth rate and the size of the crystalline domains.

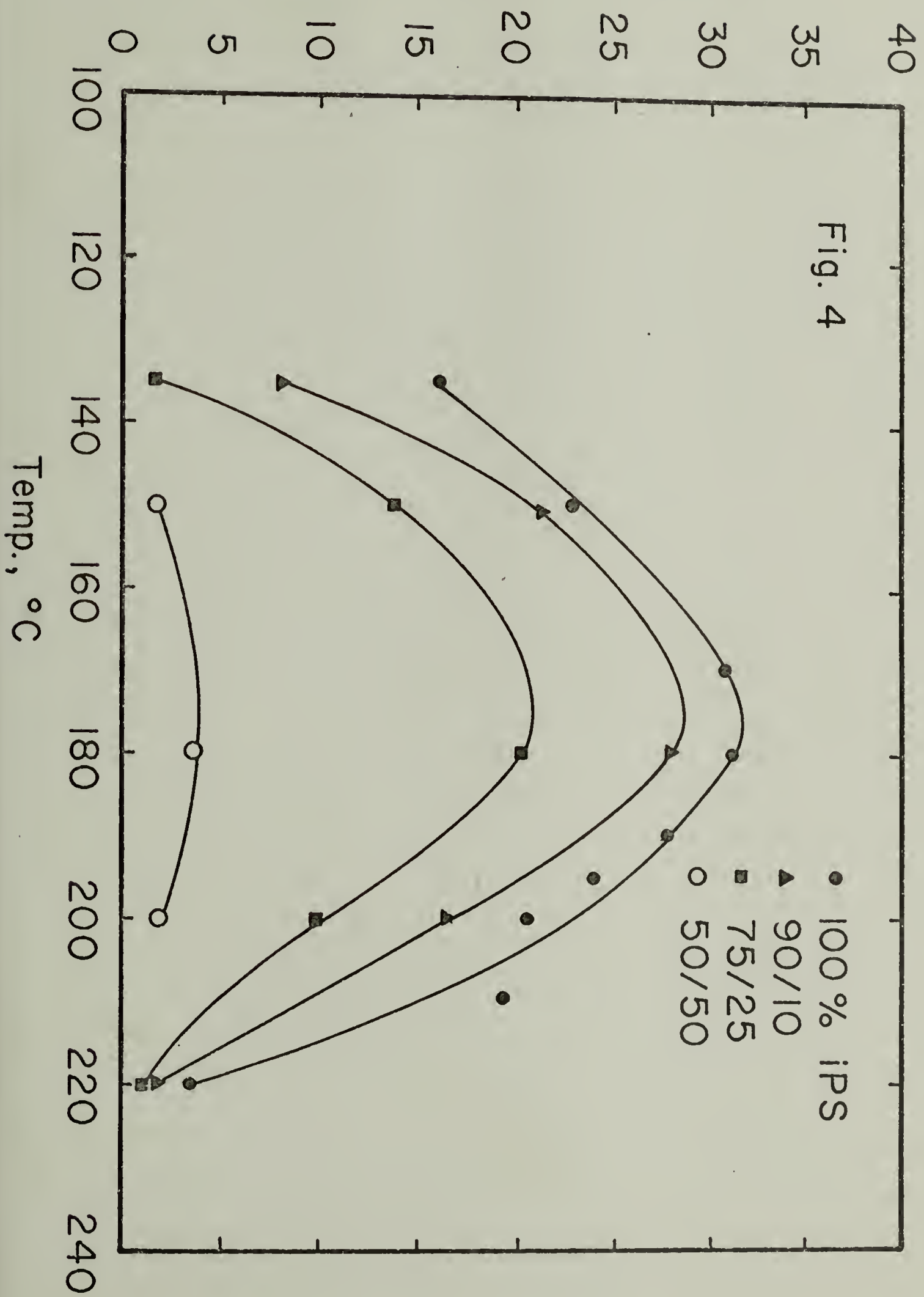


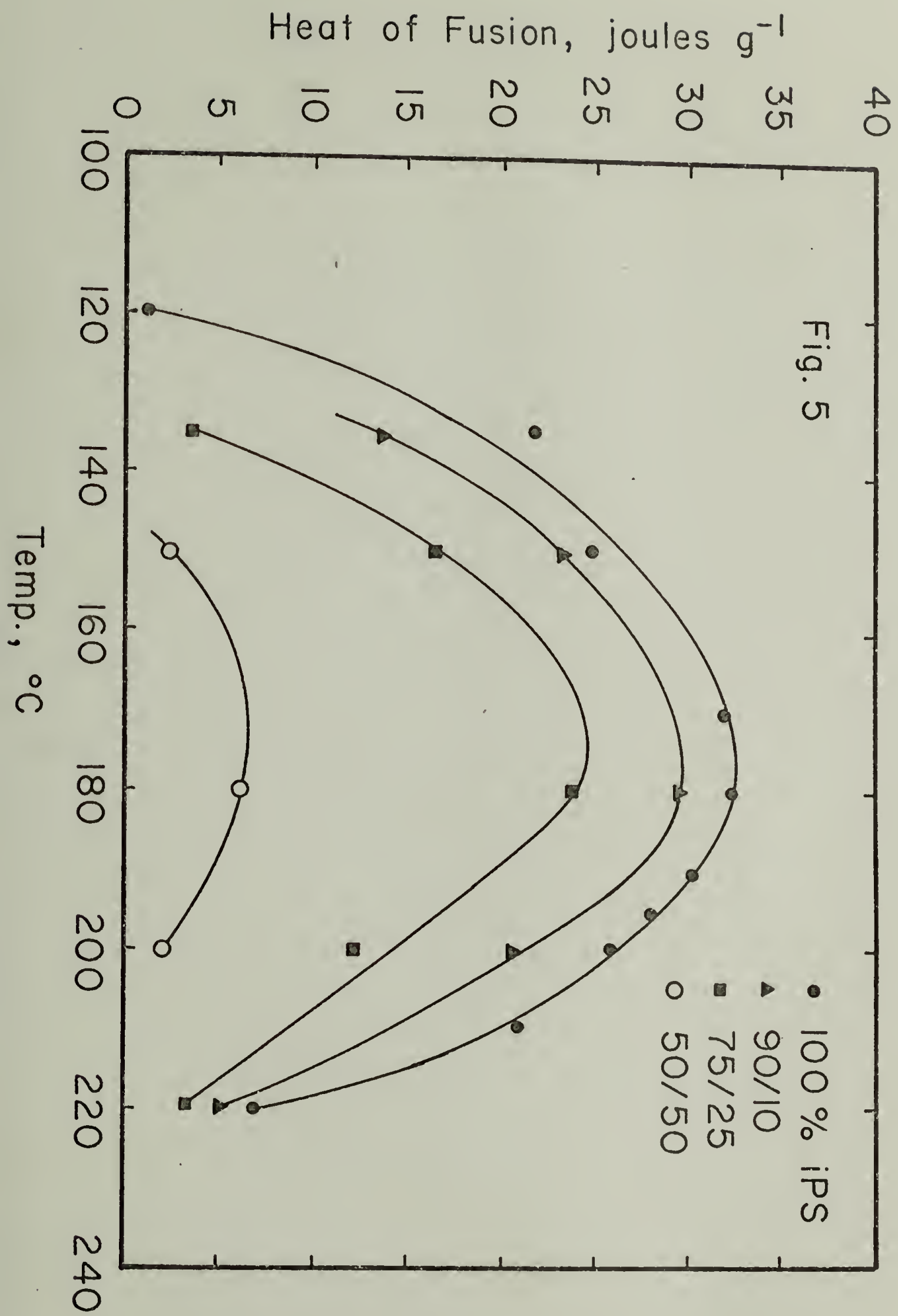
Heat of Fusion, joules g^{-1}

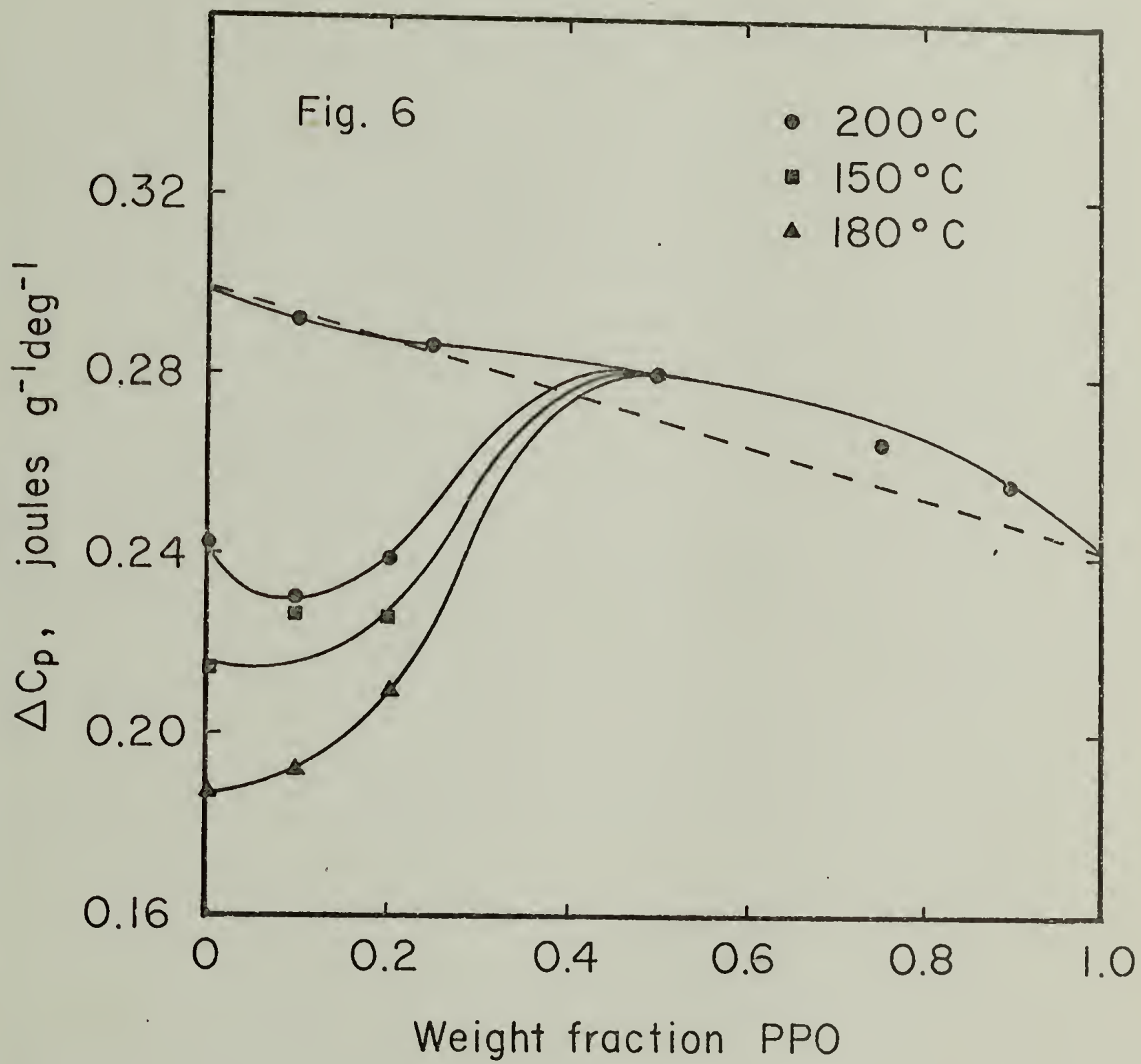
Fig. 2

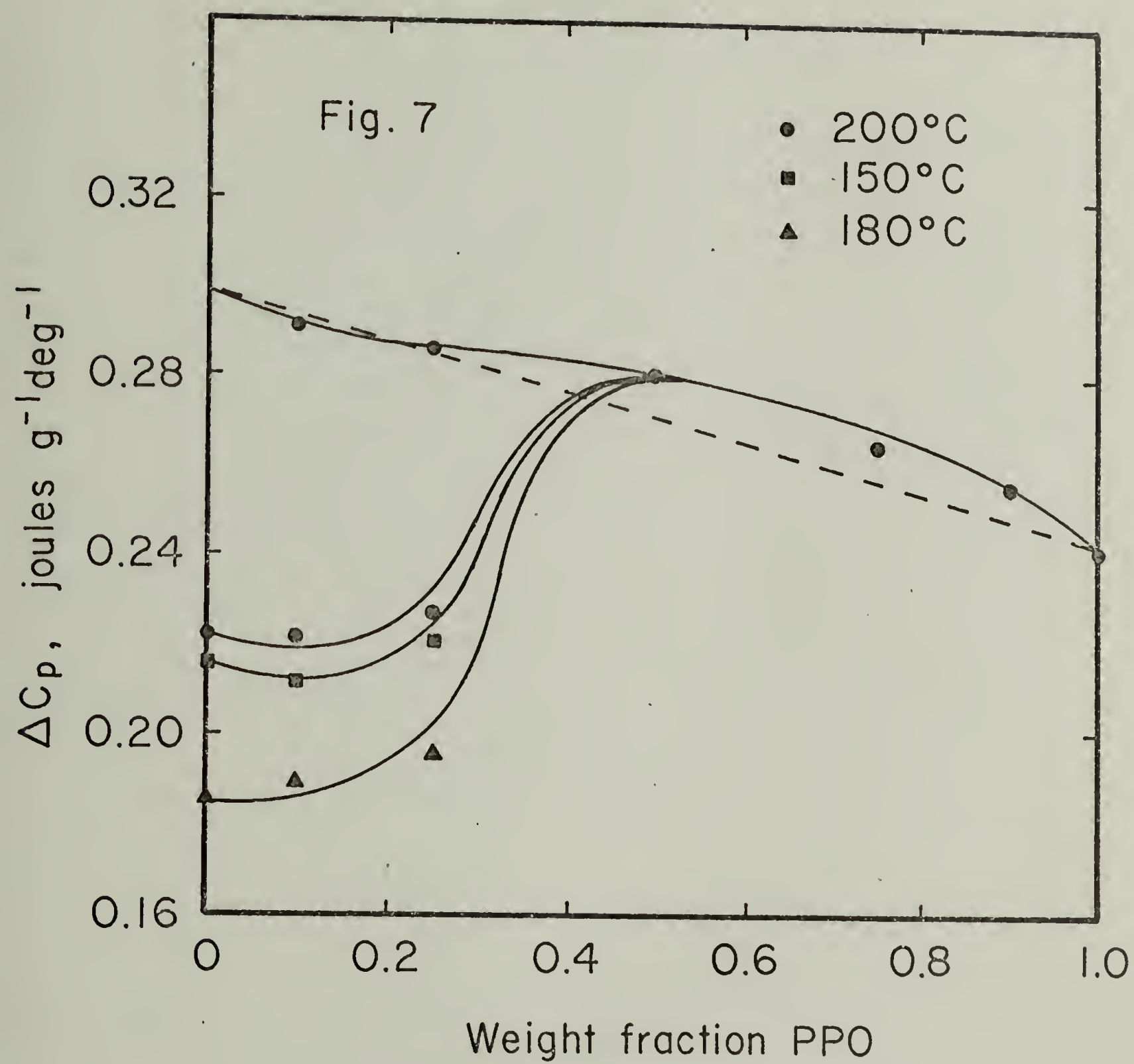


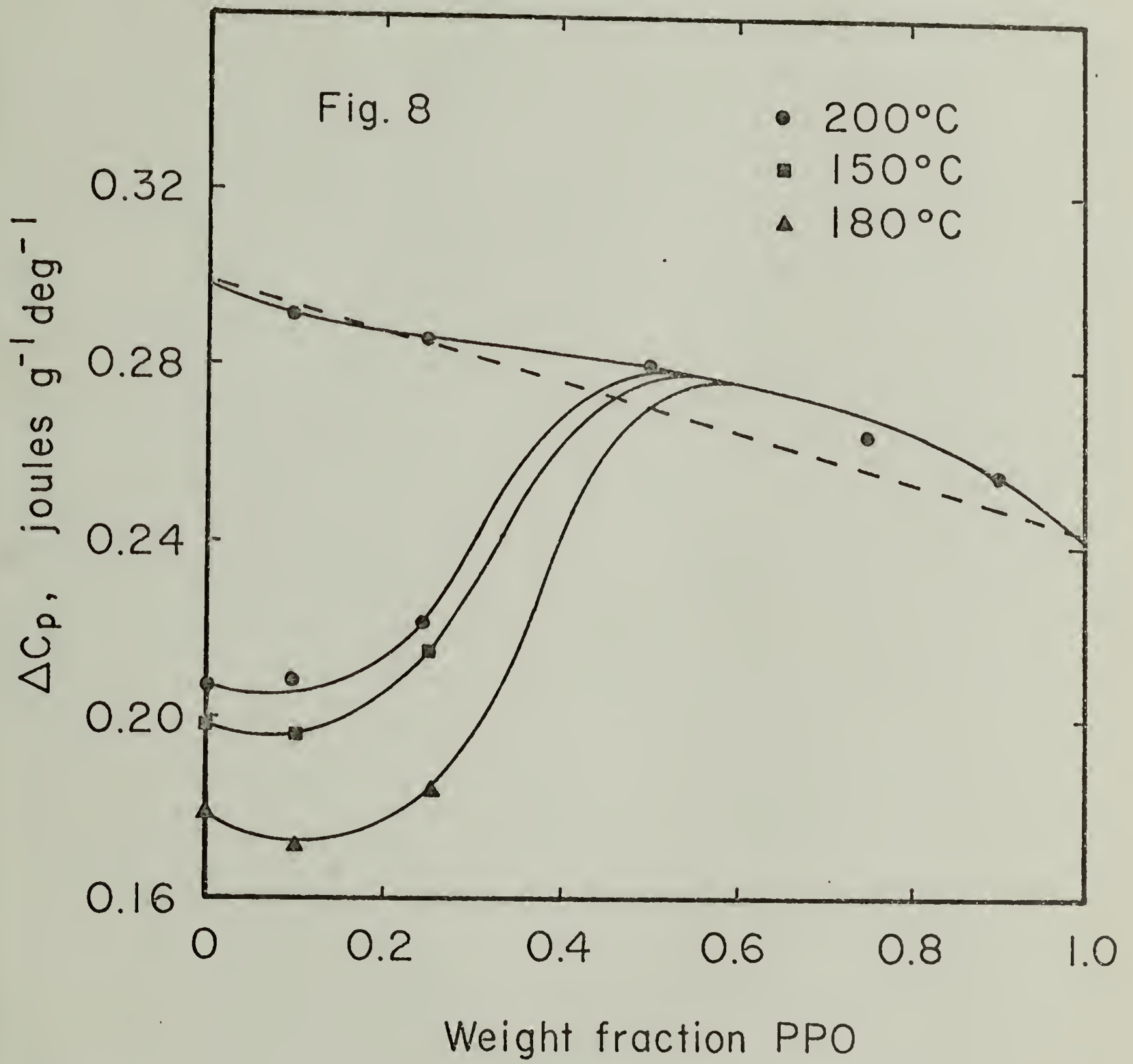


Heat of Fusion, joules g⁻¹









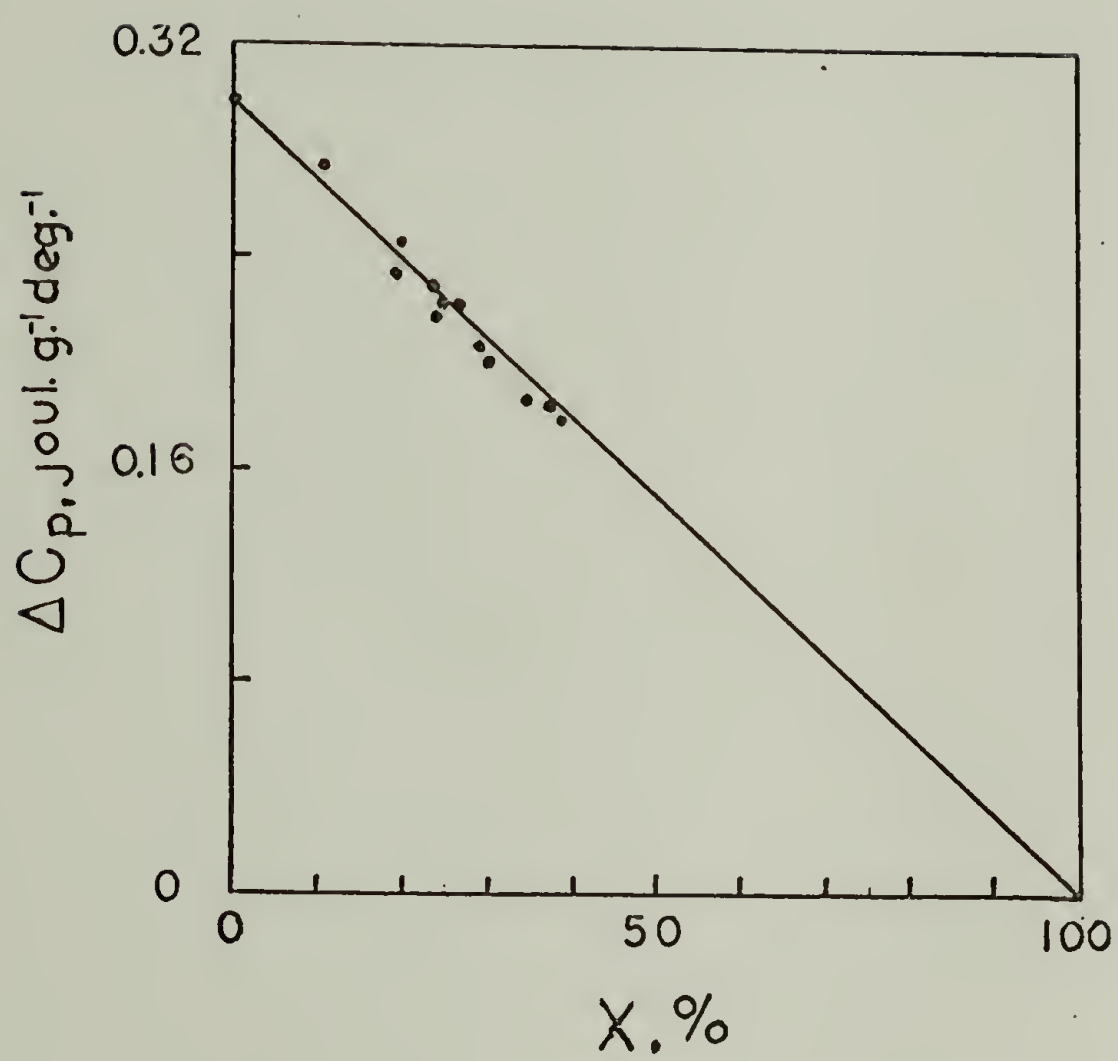


FIGURE 9

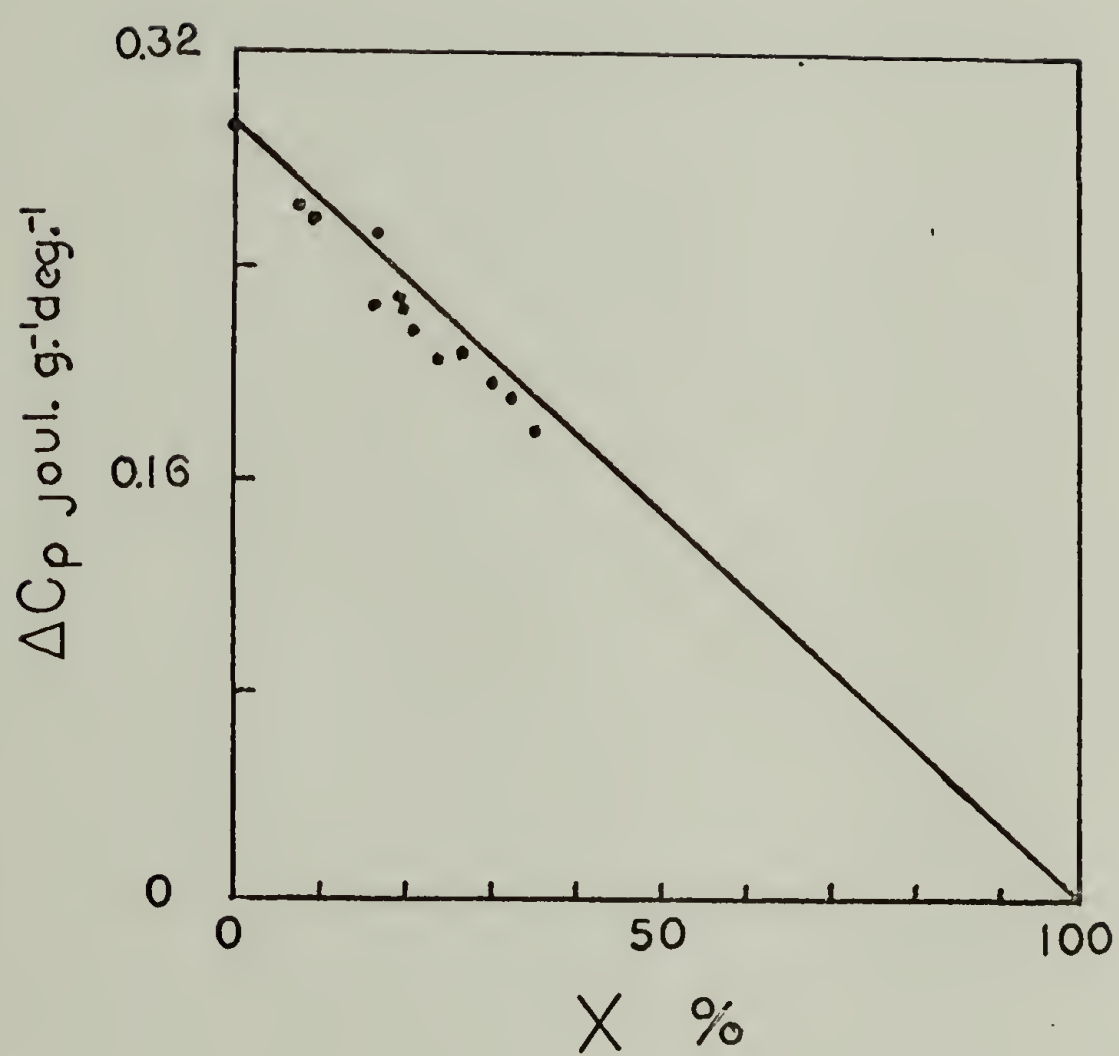


FIGURE 10

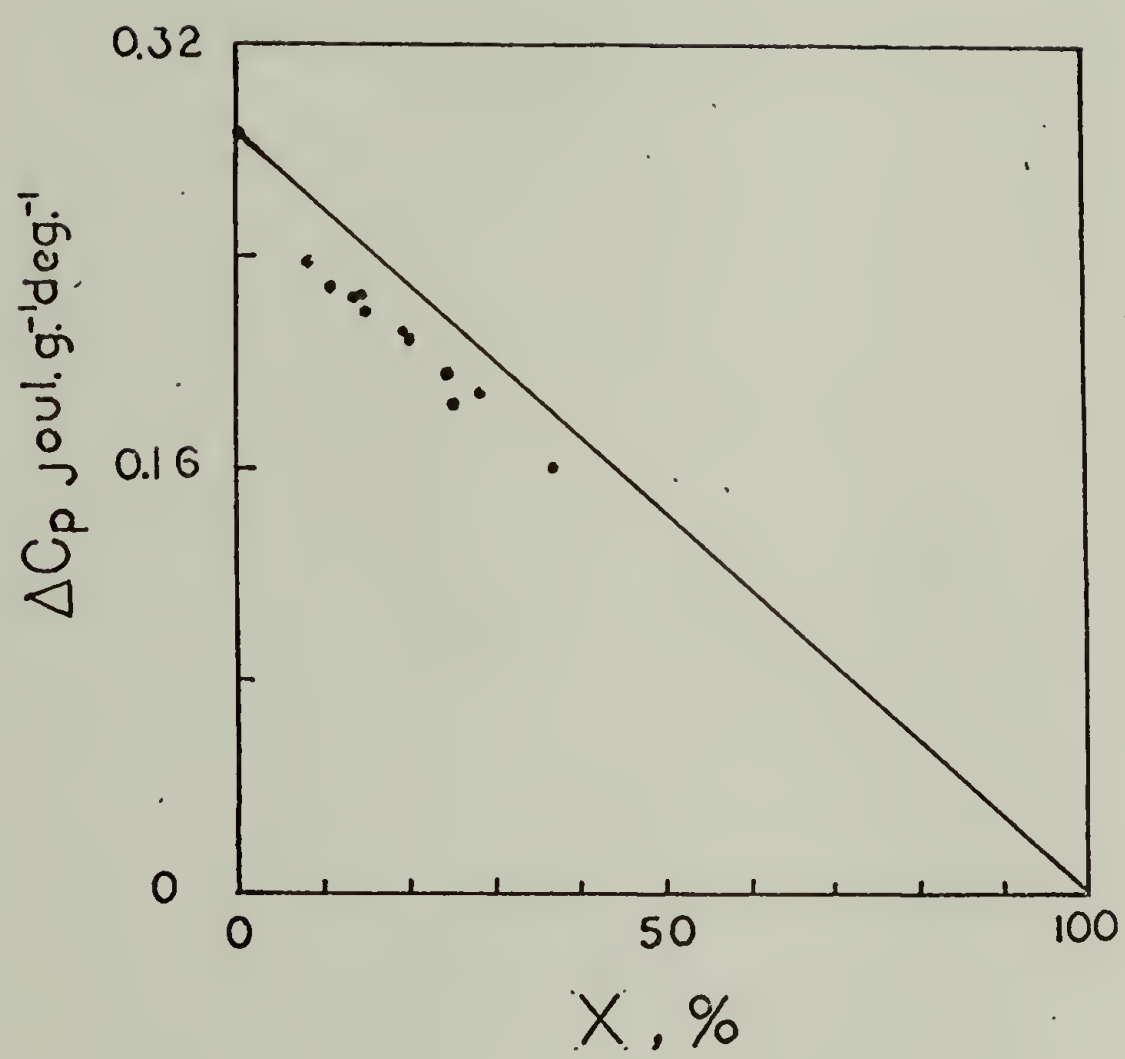


FIGURE II

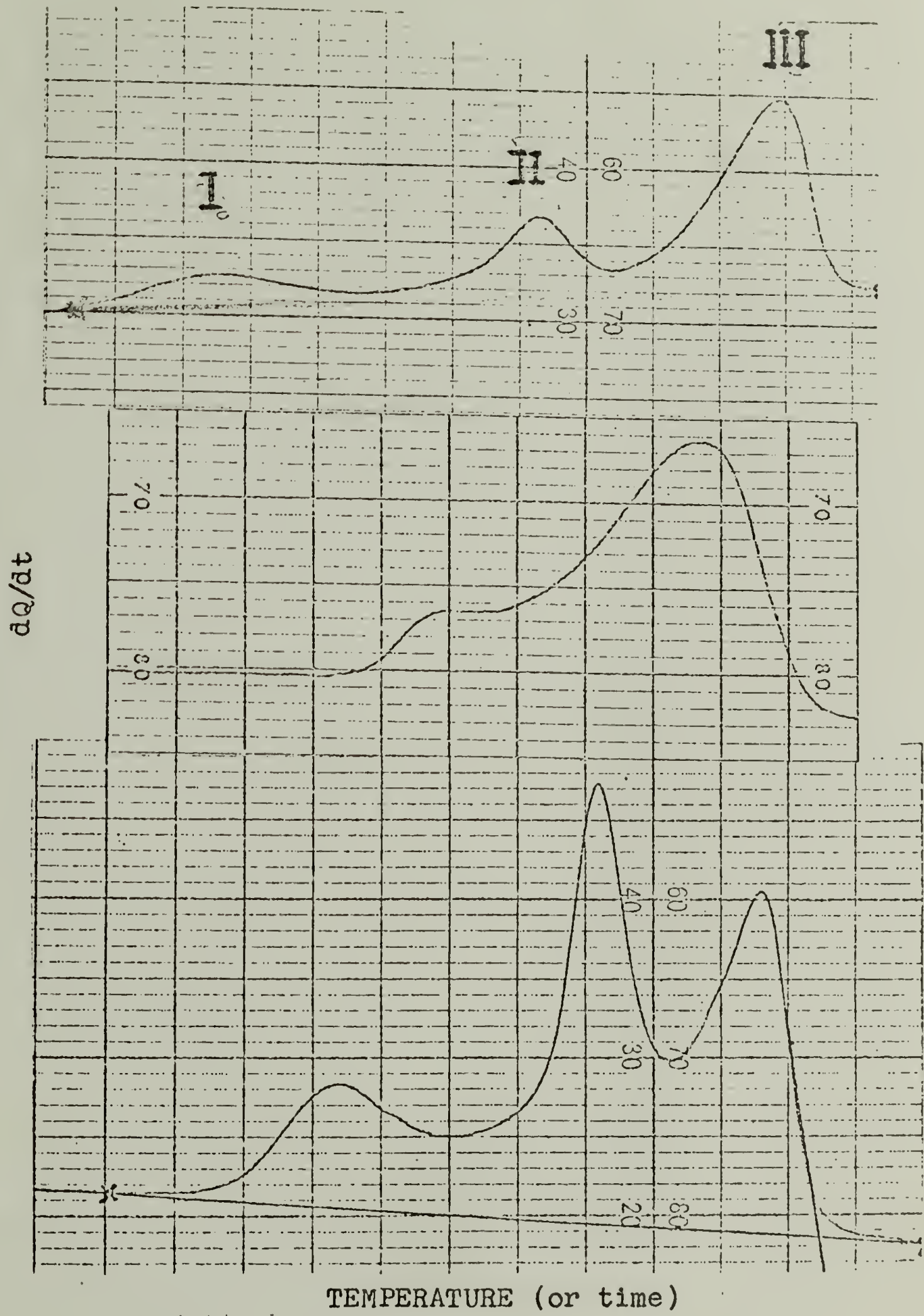


FIGURE 12

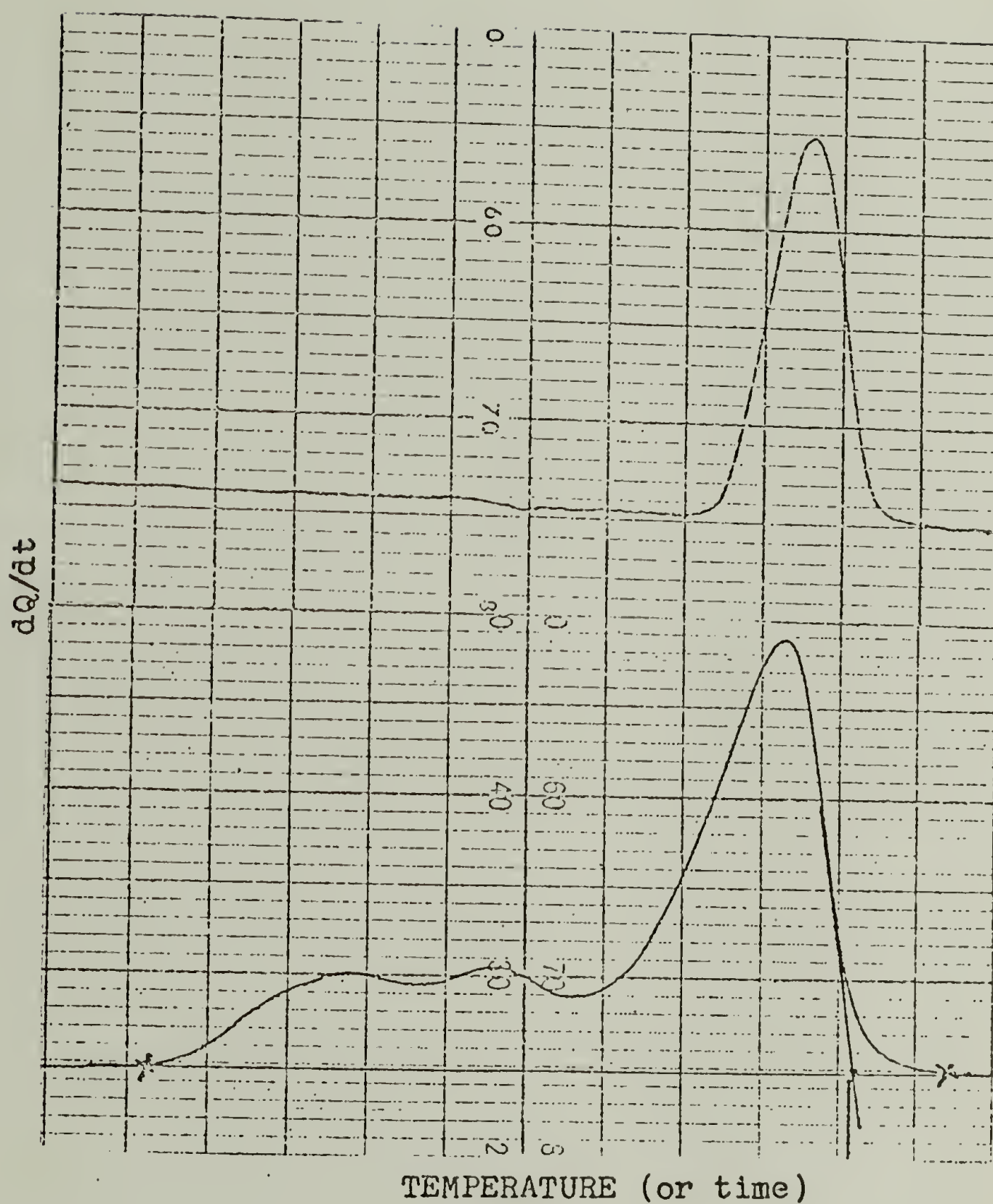


FIGURE 13

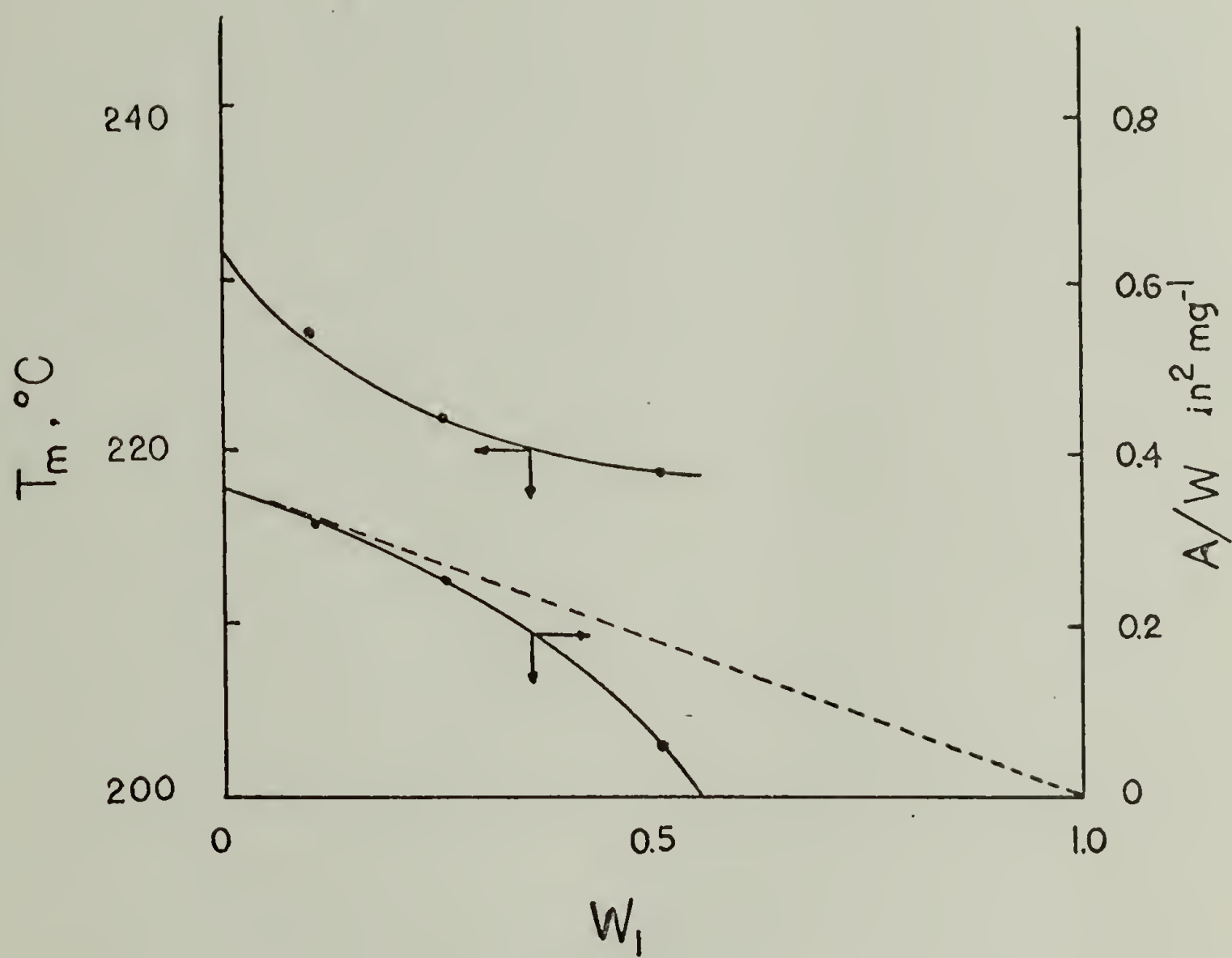


FIGURE 14

SOLVENT INDUCED CRYSTALLIZATION OF IPS-PPO AND APS-PPO
BLENDS

ABSTRACT

A study has been made on the solvent-induced crystallization behavior of poly(2, 6-dimethyl-1, 4-phenylene oxide)(PPO) and isotactic polystyrene(iPS) and their blends. Amorphous films of these materials have been exposed to methyl ethyl ketone (MEK) and/or acetone vapor at several controlled temperatures. Some aspects of the sorption behavior of the blends and the homopolymers have been investigated. Weight uptake as a function of time and equilibrium concentration of solvent in the polymer have been determined. The role of the solvent in the crystallization process is discussed.

Only iPS and iPS-rich blends crystallize at low temperatures. The degree of crystallinity increases with increase of temperature. The difficulty of completely removing entrapped solvent from the films without altering the thermal history of the material has been verified. Some residual solvent has affected the relative position of Tg's and Tm's, but a single composition dependent Tg has been found by DSC. By using combined

solvent plus thermal treatments the crystallization of PPO has been possible either pure or in its blends. IPS crystallizes under the same treatment. In addition by using atactic polystyrene-PPO blends, the crystallization of PPO, only, has been attained. The crystallization behavior of pure PPO has been investigated. Solvents with solubility parameters close to those of the polymers, and low molar volumes have been used. Upon removal of the solvent by heating the wet films above 90°C , crystallinity develops and a maximum degree of crystallinity is reached somewhere between 100 and 120°C . Kinetic rather than thermodynamic effects appear to control the crystallization at this stage of the process.

Cocrystallization of the two blend components has been carried out at 140 and 170°C . PPO crystallizes in its blends with either iPS or aPS as long as the composition by weight of PPO is 20% or higher. Analogously iPS crystallizes in blends containing less than 50 weight percent PPO. Cocrystallization occurs between these two compositions. A discussion on the possible existence of independent crystalline phases is presented.

Whether one or both polymers crystallize, the blends exhibit a single composition dependent T_g at locations displaced a few degrees with respect to those for the

amorphous blends of the same composition.

Degrees of crystallinity have been determined from DSC thermograms in two ways: one, by using enthalpies of fusion calculated from the areas under the melting peaks and two, by evaluating specific heat increases occurring at T_g on the assumption of the two-phase model. Considerable departure from this model is found as the content of crystalline PPO increases.

Melting point depressions and enthalpies of fusion appear to be composition dependent.

A exhaustive discussion on the feasibility of constructing a polymer a phase diagram is offered.

C H A P T E R T H R E E

SOLVENT INDUCED CRYSTALLIZATION OF IPS-PPO AND APS*-PPO
BLENDSTheory:

The phenomenon by which crystallization is induced by the action of a liquid or its vapor has been known for several years⁴⁶⁻⁴⁸.

However, unlike other methods, solvent induced crystallization (SIC) has been least investigated. Relatively very few data are available in the literature on the exact mechanism and the kinetics of this type of crystallization. Besides, the effects of the solvents on the final morphology and structure of the resultant crystallites are not well understood. Presumably the solvent induces some sort of relaxation which enables suitable juxtaposition of polymer chain units for crystallization to occur. Thus, the action of the solvent seems to be analogous to that of a plasticizer in the sense of giving the polymer internal lubricity as to facilitate movement of the macromolecules over each other. This behavior is governed by both, the inherent ability of the polymer chains to untangle and slip past one another in the absence of a solvent

* Atactic Polystyrene.

and by the polymer-solvent interactions. Depending on these two features the internal lubricity can be accompanied by an increase in the free volume of the system. As a result of the increase in both mobility and free volume the glass transition temperature is lowered considerably. Indeed, crystallization has been observed to develop in soaked amorphous polymers at temperatures well below those at which appreciable air or normal crystallization takes place. It occurs because T_g is reduced drastically but the melting point reduces only moderately, in that way increasing the undercooling as much as twice and sometimes more than that in the dry polymer.

It appears that the only role of the diluent is to widen the T_g - to- T_m interval. Since nucleation starts just a few degrees above T_g the process might become diffusion controlled.

In general, the rate of crystallization for a given polymer-solvent system at a fixed temperature will be dependent upon a number of variables. However, it is not clear to what extent established crystallization will affect further diffusion, nor at higher temperatures with suitable diffusing liquid what would be the influence of temperature alone. Thus, owing to the lack of adequate theory there is no basis to choose the proper parameters and conditions under which the process is

carried out most efficiently. However, it seems reasonable to select a suitable polymer-solvent system on the basis of the closeness of their solubility parameters, which assures strong polymer-solvent interactions. This is by no means a sufficient condition to attain an effective crystallization. Other factors such as temperature, residence time in the solvent (or its vapor) etc. should be chosen somewhat arbitrarily. Since some information is available on the dependence of the rate of solvent induced crystallization upon the thickness of the sample,⁴⁹ care must be taken to maintain thicknesses of the films as uniform as possible if comparisons are to be made.

An exhaustive study of the kinetics of the SIC process is outside the scope of this work. Our purpose is primarily to determine at what level and under what conditions, crystallization is induced in well known compatible blends.

However, we have investigated indirectly some kinetic features of the process. In particular, thermodynamic aspects related to Tg depression has been observed as a function of solvent content of the blends. An equilibrium solvent concentration has also been determined for the individual blend components and the changes in solvent content have been followed after a diversity of solvent and combined solvent and thermal treatments.

On the other hand, the mere solvent treatment is insufficient to develop crystallinity in PPO. The reason is because PPO has a relatively high T_g (218°C) and although the solvent can lower it considerably, crystallization is not initiated, at least in an appreciable amount, at temperatures below the boiling point of the solvent. Accordingly, we have used a combination of solvent and thermal treatment in order to induce a good level of crystallinity in pure PPO as well as in PPO-rich blends. Of course, iPS crystallizes simultaneously in iPS/PPO blends under this combined solvent plus thermal treatment.

EXPERIMENTAL

Materials.

In addition to the polymer previously mentioned in chapter two, the following materials has been used: Atactic Polystyrene, aPS, which was an additive-free resin manufactured by the Monsanto Co. The molecular weight, as evaluated from intrinsic viscosity measurements in toluene at 25°C, was 1.9×10^5 .

Acetone (Fisher Scientific Co, reagent grade certified ACS) and methyl Ethyl ketone (Eastman Co., reagent grade) were used as diluents for inducing crystallization. The choice of this couple of solvents will be justified later.

Sample Preparation.

Both iPS-PPO and aPS - PPO blends were prepared in the manner described in chapter two . Only toluene was used as a solvent for the case of aPS-PPO mixtures.

During compression molding of the mixtures all effort was made in order to obtain the best thickness uniformity. Only films 0.44 ± 0.02 mm. thick were used in our SIC experiments. In all cases transparent films were obtained and cut into pieces of 1.5 cm in surface area. These pieces were weighed on a balance capable of reading to 0.001 mg.

Solvent treatment was then applied to the films as

follows:

Mixtures of iPS and PPO of the weight compositions tabulated in table 1 were introduced into test-tubes containing methyl ethyl ketone. The films were hung from the lid of the tubes and left in the vapor phase approximately 1 cm. away from the liquid surface. The test tubes in turn, were immersed in a thermostatically controlled bath at temperatures of 25, 50 and 75°C for 3, 6, 12, 24, 48 and 72 hours. Subsequently the films were removed, surface dried, and transferred to a dessicator where they remained for 1 hour before being reweighed. A constant solvent content in each sample after continued treatment for several hours, was then taken as the equilibrium concentration of the solvent in the blends.

In order to remove the solvent without modifying the degree of crystallinity by additional thermal treatment, it was necessary to place the films in a vacuum oven at ambient temperature for as long as 100 hours. The latter treatment was applied to films crystallized at 25°C. If the films were crystallized at 50 or 75°C they were allowed to dry in vacuum for 48 hours at 25°C plus 24 hours at 50°C. However, after this drying process the samples were not fully dried and they had to be run in the DSC with a small fraction of remnant solvent.

DSC Measurements.

A Perkin-Elmer Differential Scanning Calorimeter (DSC-2) was used to determine the glass transition, the melting point and the degree of crystallinity of the blend samples. The sampling and procedure were described earlier. The instrument was calibrated periodically with high purity Indium and Tin whose melting points covered the range 155 to 231.5°C. Thermograms were obtained at a 20°C.min heating rate and a sensitivity of 5 mcal/sec. The melting point, glass transition temperatures and heats of fusion were determined by the graphical methods previously described. Thermograms are converted to heat of fusion by standardization against Tin (14.45 cal/g.).

Degrees of crystallinity were derived from the heats of fusion and values of H_f for completely crystalline polystyrene of 83.7 joule g.⁻¹ and completely crystalline PPO of 41.8 joule g.⁻¹ 40.

RESULTS

Solvent Induced Crystallization.

Since crystallinity is accompanied by simultaneous whitening or opacity of the previously clear films, a visual observation of the developing of crystallinity can be easily done. The whitening of the films is seen to start at the end closer to the liquid surface and it moves upward to the other end. It is suggestive of the presence of a diffusion front. In the case of our iPS films complete whitening is reached after about 3 hours of MEK vapor exposure at 25°C. This fact is in agreement with the attainment of approximately a maximum weight uptake. In our case, although the time for attaining complete opacity was dependent of the film size, such an attainment was simultaneous with the onset of desorption of the solvent as determined by weight loss.

Since the data of solvent sorption versus time turn out to be dependent of the film size; films of identical size were used in order to obtain relevant information. This experiments was restricted to the case of pure homopolymers.

Films of iPS and PPO (0.044 cm x 1 cm x 2 cm) were employed. The partial pressure, p_i , of the solvents in the container were estimated by assuming the

system at an ambient pressure of 1 atmosphere. Values of p , calculated in this way at the various temperatures are given in table XX

TABLE XX

Partial pressures, p , calculated for MEK and acetone at 25, 50 and 75°C and ambient pressure of 1 atm.

Temperature °C	p_{MEK}	p_{acet}
25	0.127	0.263
50	0.367	0.715
75	0.914	-

For both iPS and PPO percentage of weight gain, W , due to MEK and acetone sorption at 25°C, for several times are listed in the table XXI. The data of W are also plotted as a function of time in figure 15.

TABLE XXI

Weight fraction of solvent in dry polymer (W) resulting from sorption of solvent by polymer at 25°C for the indicated times.

Time (Hours)	iPS		PPO	
	W_{ac}	W_{MEK}	W_{ac}	W_{MEK}
1	0.145	0.128	0.064	0.049

TABLE XXI (Cont.)

Time (Hours)	iPS		PPO	
	W_{ac}	W_{MEK}	W_{ac}	W_{MEK}
3	0.256	0.327	0.163	0.146
6	0.281	0.362	0.207	0.200
9	0.268	0.330	0.221	0.219
12	0.252	0.308	0.230	0.237
18	0.244	0.292	0.242	0.255
24	0.244	0.277	0.248	0.263
48	0.241	0.272	0.262	0.287
72	0.242	0.275	0.266	0.290

The results just tabulated are of great importance for understanding the mechanism of SIC process.

Moreover, the equilibrium concentration of solvent in the polymer given in terms of the weight of the solvent to the weight of dry polymer was encountered to depend on the blend composition and the temperature or more correctly on the partial pressure at which sorption and crystallization are held. This ratio also is independent of the size of the sample and within the experimental error the equilibrium concentration have been found to vary monotonically between those values determined for the pure components.

Glass transition temperatures.

The measurements of the glass transition temperature have been unavoidably affected by residual solvent entrapped in the amorphous region or in the crystalline imperfections of the blends. The difficulty of completely removing entrapped solvent from the films, without altering either the crystalline content or the morphology, is illustrated by the following facts:

i) The samples crystallized at 25°C under the action of MEK were dried in vacuum at the same temperature for times ranging from 72 to 100 hours. The content of remnant solvent did not change significantly between 72 and 100 hours. The weight fraction of solvent in the blends dried for 100 hours are shown in table XXI, column 1, as a function of composition.

ii) The samples crystallized at either 50 or 75°C in MEK vapor, were dried in vacuum at 25°C for 48 hours followed by additional 24 hours at 50°C. After this drying treatment the weight fraction of residual solvent were found as reported in table XXI column 2.

TABLE XXII

Weight fraction of residual MEK in iPS-PP0 blends as determined after drying treatment thus

- 1) At 25°C for 100 hours.
- 2) At 25°C for 48 hours plus 24 hours at 50°C.

Composition	(1)	(2)
	W_1 Wt%	W_2 Wt%
Pure iPS	1.88	1.36
90/10	1.94	1.28
75/25	1.90	1.44
50/50	2.25	1.55
25/75	2.42	1.83
10.90	2.37	2.02
Pure PP0	2.56	2.17

According with the precedent analysis the T_g of the blends appeared reduced by a few degrees with respect to those values determined for dry blends. In table XXIII T_g values are listed for the several blend compositions. Those values are represented in figure 16 in which the curve for dry blends corresponds to the dotted line.

TABLE XXIII

Glass transition temperatures of iPS/PPO blends containing a weight fraction W of residual solvent (MEK)

Composition	Wt%	TG °C	W (Wt%)
iPS		88	1.88
90		95	1.94
75		107	1.90
50		133	2.25
25		160	2.42
10		183	2.37
PPO		198	2.56

Our experiments revealed that it is necessary to heat up the blends at temperatures as high as 140°C in order to attain an almost complete removal of the residual solvent. However at that temperature the crystallinity of the blends is surely affected.

Degree of solvent-Induced crystallinity.

The difficulty of completely removing the entrapped solvent from the blend films makes it inaccurate to evaluate degree of crystallinity from changes in specific heats at the glass transition.

In fact, for solvent-treated blends, we have found considerably larger specific heat increases as compared to those thermal-treated blends. These specific heat

increases appear larger as the PPO content increases and unlike the merely annealed blends, rich PPO mixtures greatly depart from the two phase behavior. Indeed,

ΔC_p 's for pure PPO become as large as twice with respect to value encountered for dry samples.

In view of the above, degrees of crystallinity induced by MEK in iPS-PPO blends will be determined by the heat-of-fusion technique only. This method was amply described in chapter two. Percentages of crystallinity are estimated by taking an value of $83.72 \text{ joules g}^{-1}$ as the enthalpy of fusion of completely crystalline iPS.

Figures 17 to 20 show curves of degree crystallinity as a function of temperature at a given time for pure iPS and 90/10 and 75/25 iPS/PPO blends. For 50/50 blends, well defined peaks were only observed at crystallization temperatures in the solvent of 75°C and for times longer than 24 hours. This would be represented as a single point in figures 19 and 20.

Results are summarized in tables XXIV to XXVI.

TABLE XXIV

Heats of fusion, ΔH_f in joules g.⁻¹ and percentage crystallinities, x_f , for pure iPS resulting from solvent treatment at the temperatures and time shown

Time (hours)	Temperatures, °C					
	<u>25</u>		<u>50</u>		<u>75</u>	
	H_f	x_f	H_f	x_f	H_f	x_f
12	11.79	14.1	17.57	20.0	22.41	26.8
24	13.40	16.0	17.30	20.6	22.85	27.3
48	14.81	17.7	19.66	23.5	23.53	28.1
72	16.54	19.8	22.48	26.9	29.86	35.6

TABLE XXV

Heats of fusion, ΔH_f in joules g.⁻¹ and percentage crystallinities, x_f , for 90/10 iPS-PPO blends, resulting from solvent treatment at the temperatures and time shown

Time (hours)	Temperatures, °C					
	<u>25</u>		<u>50</u>		<u>75</u>	
	H_f	x_f	H_f	x_f	H_f	x_f
12	9.56	11.4	14.17	16.9	16.59	18.3
24	11.62	13.9	16.31	19.5	18.11	21.6
48	12.39	14.8	17.33	20.7	18.94	22.6
72	15.86	18.9	19.87	23.7	20.75	24.8

TABLE XXVI

Heats of fusion, ΔH_f in joules g.⁻¹ and percentage crystallinities, x_f , for 75/25 iPS-PP0 blends, resulting from solvent treatment at the temperatures and time shown

Time (hours)	Temperatures, °C					
	<u>25</u>		<u>50</u>		<u>75</u>	
	H_f	x_f	H_f	x_f	H_f	x_f
12	5.97	7.1	10.65	12.7	12.25	14.6
24	8.13	9.7	11.66	13.9	13.45	15.6
48	11.34	13.6	15.45	18.5	17.94	21.4
72	14.08	16.8	15.93	19.0	18.10	21.6

CRYSTALLIZATION OF POLY(2, 6 - DIMETHYL - 1, 4 PHENYLENE
OXIDE AND ITS BLENDS WITH POLYSTYRENE BY COMBINED
SOLVENT AND THERMAL TREATMENT.

As far as we are aware, there are few published data on crystallization of PPO either in bulk or from dilute solution. Price et al⁵² have prepared single crystals of PPO from α -pinene solutions, and calculated the dimensions of the unit cell. These dimensions as well as the cell structure have been the subject of controversy, and it has been proposed the existence of different crystalline structures, depending on the solvent used to obtain the single crystals.

Recently, spherulites of PPO have been found to be formed by exposing a film to pinene or tetralin vapor³⁴. After drying, however, these spherulites, lose their birefringence, and the crystalline structure of the polymer also collapses. The role of the solvent in the crystallization of PPO has been more widely studied by Horikiri et al⁵³. These authors found that the morphology and the rate of crystallization are greatly dependent of the nature of the solvent. They observed that fibrillar spherulites are fastly developed at 35°C by exposing a PPO film to pinene vapor. At temperature above 40°C, however, the spherulites become banded rather than fibrillar. The number of spherulites formed increases

between 40 and 70°C and then decreases until finally above 110°C no spherulite can be observed.

Quite significantly the same authors found closely spaced banded spherulites formed at 36°C by tetralin vapor exposure. By using this solvent, spherulites cannot be formed above 50°C.

This facts indicate that the crystallization behavior of the PPO, and likely of the other polymers, depend, greatly, on the nature of the solvent.

In this work we have chosen solvents with solubility parameters close to those calculated⁷ for both PPO and PS. $(9.3 \text{ cal}^{\frac{1}{2}} \text{ cc}^{-\frac{1}{2}})^{50}$. Indeed, MEK and acetone are reported to have solubility parameters of 9.3 and 9.7 respectively⁵¹. This closeness in solubility parameters guarantee strong molecular interactions in the polymer-solvent system. In addition, those two solvents have a low molar volume. If the same factors affecting the melting point depression of the polymer are assumed to affect depression in T_g , then, the use of low molar volume becomes desirable. Molar volumes of MEK and acetone are quite smaller than those of α -pinene and tetralin. Under these circumstances, the crystallization was carried out in two steps. First, films of iPS-PPO blends and their pure components were exposed for 24 hours to the action of MEK vapor at a temperature

of 75°C (vapor pressure of MEK, 695 Torrs). Second, on removal of the films from the solvent, they were transferred to a vacuum oven where they were left at room temperature for 3 hours. Subsequently the temperature was raised up to 140°C and the films were allowed to remain for 24 hours at that conditions. The latter procedure was repeated at 170°C.

On the other hand, in order to make PPO crystallize without crystallizing its partner in the blends, atactic instead of isotactic polystyrene was blended with PPO. This changes seems reasonable on account of the compatibility of the blend is unaltered by the microstructure of the polystyrene. Films of aPS-PPO blends, similar in appearance and composition to those used in the precedent treatments, were placed in the vapor phase of acetone at 50°C for 24 hours. Acetone instead of MEK was employed in this case because atactic polystyrene is readily dissolved in the MEK vapor phase.

Excepting these differences in the solvent treatment of aPS-PPO blends, the rest of the procedure was identical to that followed with iPS-PPO blends just above described.

Since the process of exposing the polymer films to the action of a vapor to induce crystallinity has been discussed earlier, we will turn on the second step of

the combined solvent plus thermal treatment. On transferring the films to the vacuum oven and letting them remain for 3 hours at room temperature the weight fraction of solvent in the blends and homopolymers is about 12 to 15%.

For the case of pure PPO we have followed the entire path from that point through the heating at 90 and 140°C until the removal of the crystallized sample film.

This experiments was intended to understand at least partially the development of the crystallization in PPO.

Weight fractions of acetone content as low as 0.105 were necessary in order to obtain smooth enough DSC thermograms as to locate the glass transition temperature and the melting point if any. The glass transition temperature was observed to increase as the weight fraction of acetone was reduced, as illustrated in figure 21. A noteworthy aspect is that an appreciable melting peak was observed only after the films was heated up for at least 1 hour at 90°C. This means that at this temperature the rate of crystal growth becomes high enough as to induce significant crystallinity.

Acetone desorption in vacuum at 90 and 140°C was studied by determining the weight fractions at regularly spaced time intervals. These results are shown in figure 22.

As it can be observed from figure 22 the acetone

content in the samples annealed at 140°C becomes lower than 0.005, which assures essentially no effect of the solvent on either the glass transition or the melting behavior of the blends and the constituent homopolymers. This is the reason for using temperatures in the range 140 to 170°C for the complementary thermal treatment of the samples.

The sample films just removed from the solvent exposure, have a solvent content so high that it would make the scanning of the samples in the DSC troublesome and no well defined peaks could be observed. Further heating of the samples, causes solvent desorption and simultaneously crystallization of the material. Presumably, nucleation may have begun during the solvent treatment and perhaps some crystallinity might also be present. However, such a crystallinity turns out to be undetectable due to overlapping with solvent-desorption peaks.

High crystallinity in PPO, can be developed by heating the wet films at temperatures around 90°C and higher, whereas significant removal of the solvent takes place.

In figure 23, the degree of crystallinity of PPO films, in terms of the heat of fusion per gram, are plotted against the temperature of annealing.

These experiments were performed in air at temperatures in the range 90-170°C and the average values of the resulting heats of fusion are listed in table XXVII.

TABLE XXVII

Heats of fusion in joules g.⁻¹ of PPO, resulting from acetone exposure at 50°C for 24 hours followed by thermal annealing at the temperatures indicated for additional 24 hours.

<u>Temperature</u>	<u>Heat of Fusion, joules g.⁻¹</u>
90	19.562
100	20.412
110	21.167
125	19.164
140	18.266
155	17.385
170	16.577

From figure 23, the observation can be made that as the temperature is raised the degree of crystallinity increases slightly, passes through a maximum and then decreases. This curve shows a resemblance to those growth-rate type characteristic of semicrystalline polymers. Although kinetic rather than thermodynamic seem to be the controlling factors.

In fact, the effective times during which crystallization takes place are dependent on the temperature. As the polymer loses solvent the degree of undercooling reduces; since this loss is faster at higher temperatures, the effective time of crystallization becomes shorter when the temperature is increased. As a matter of fact, we have found that after 6 hours annealing at 140°C , the degree of crystallinity of PPO films have no appreciable change with further annealing. However, longer times are required for removing the remnant solvent.

A more rigorous discussion of this type of crystallization is left to be included in the section of conclusions.

In the next section we will present the results of the experiments carried out on samples of blends of PPO with either iPS or aPS. Films of these blends were crystallized in two steps, thus:

- a) Solvent exposure (MEK for iPS-PPO blends and acetone for aPS-PPO blends) at 50°C for 24 hours .
- b) Annealing in vacuum at 140 and 170°C for 24 hours.

Glass Transition Temperatures.

The inflection point in the DSC thermograms indicating the glass transition temperatures, appears not to be affected by the tacticity of the polystyrene. Both amorphous

iPS-PPO and aPS-PPO blends have essentially the same T_g values.

However, when either or both components become crystallized some changes take place. Thus, at moderate and high crystallinities, PPO displays no observable change in C_p at T_g . As a result a T_g value is difficult to assign for crystalline PPO. In addition, at lower crystallinities the transition becomes detectable and located 6 to 8°C above that corresponding to the amorphous sample. These facts suggest that crystallinity reduces considerably the free volume of the polymer as to increase the T_g beyond the onset of melting, giving rise presumably, to an overlapping between the T_g and the melting peak. Another possible explanation of the absence of a discontinuity in C_p for the partially crystalline PPO is based on the crystalline structure of the polymer. This may consist of numerous tiny spherulites interdispersed in the amorphous region as to make the size of the amorphous microphase unable to reflect the thermal effects occurring at T_g .

On the other hand, blends containing 90 and 75 weight percent PPO exhibit a T_g slightly lower than those of amorphous blends. This might be explained because the increase due to crystallinity cannot overcome a decrease

brought about by the increase of relative proportion of the more mobile PS molecules. At lower PPO concentrations, as iPS starts to crystallize, these two effects become balanced and are not reflected in changes in the Tg location.

In all cases, the blends exhibited a single composition dependent glass transition temperature whose values are given in table XXVIII. These values have been taken as the temperature corresponding to the midpoint of the transition and are given with a margin of $\pm 2^{\circ}\text{C}$ in order to include all the possible values. A plot of Tg versus composition is also shown in figure 24.

TABLE XXVIII

Glass transition temperatures of PS-PPO blends crystallized by combined solvent and thermal treatment .

<u>Composition</u>	<u>Tg</u>
Weight fraction of iPS	$^{\circ}\text{C}$
1.00	103
0.90	111
0.75	121
0.50	140
0.25	176
0.10	191
0.00	225

Enthalpies of fusion and degree of crystallinity.

Our experiments, using combined solvent and thermal treatments, have revealed that PPO crystallizes in its blends with either iPS or aPS as long as the composition by weight of PPO is 20% or larger. Analogously iPS crystallizes in blends with PPO if the weight percentage of the former polymer is greater or equal to 50%.

Consequently, in our series of blend compositions one can see a single melting peak corresponding to the melting of PPO, in 25/75, 10/90 iPS/PPO blends and pure PPO. In 50/50 and 75/25 iPS/PPO blends two partially resolved peaks are observed which correspond to each component. Finally, for pure iPS and 90/10 iPS/PPO blend the multiple peak characteristic of iPS appear.

On the other hand, the results obtained from crystallization and melting of aPS-PPO blends support the precedent observations. In fact melting peaks of nearly the same intensity and location are observed in pure PPO and aPS-PPO blends.

Where comparable, the areas under the melting peaks per unit weight appear 2-3% larger for aPS-PPO blends than those for the corresponding iPS-PPO blends.

aPS-PPO blends yield single melting peaks at weight fractions of PPO as low as 0.25. No melting is detected

in blends containing less than 20 weight percent PPO. Since crystallization of iPS alone is not possible, at least by following a similar solvent and thermal treatment, one can obtain indirectly the enthalpies of fusion of the iPS, in the blends where cocrystallization takes place, by subtracting the energy per unit weight corresponding to the fusion of PPO crystallites.

The validity of this procedure lies on the assumption of independent crystalline phases and negligible effects of tacticity and molecular weight differences between aPS and iPS. The small differences in the area-to-weight ratios of crystalline PPO in the mixtures, assure a reasonable degree of accuracy in this calculation.

The data of enthalpies of fusion in joules g.^{-1} for iPS-PPO and aPS-PPO blends of various compositions are listed in table XXVIII and XXIX for the two temperatures, 140 and 170°C, respectively.

these values of enthalpies of fusion are also plotted against weight fraction of PS in figures 25 and 26. The dashed line corresponds to the calculated differences in enthalpy of fusion in the way above mentioned. These differences are assigned to the heat of melting of iPS in the blends.

By observing the curves in figures 25 and 26, one

might think of the assumption of independent crystalline phases as being correct. In fact in the regions where only one of the two components crystallizes there seems to be superposition of the curves. There is also a smooth continuity between the dashed line and the full line, which is suggestive that the calculated values follow a reasonable course. The region where crystallization occurs is that enclosed within the full and dashed lines and it can be clearly delimited. In addition the heats of fusion calculated for iPS appear not to be very different from those obtained in crystallizing iPS by a thermal treatment even for times as long as 48 hours.

The degree of crystallinity of the iPS-PP0 blends and their constituents homopolymers is determined from the data of enthalpies of fusion, ΔQ_f , just tabulated.

The fractional crystallinity, x , of the polymers and their mixtures can be defined by the quantity

$\Delta Q_f / \Delta H_f$, where ΔQ_f has been calculated by graphical integration and ΔH_f is the enthalpy of fusion of the (hypothetical) completely crystalline polymers. These values has been taken from references 39 and 40 as being: 83.72 and 41.86 joules g^{-1} for iPS and PP0 respectively.

On the other hand, the fractional crystallinity may be defined in terms of specific heat changes occurring at T_g , by the expression

$$x = 1 - \Delta C_p / \Delta C_{pA}$$

where ΔC_p and ΔC_{pA} are the specific heat increases at T_g , for crystalline and completely amorphous polymer respectively. These value have been calculated in the manner described in chapter two.

The values of ΔC_{pA} for the system aPS-PPO show an excellent agreement with those found for the system iPS-PPO (table XXXI).

However, when PPO crystallizes in the blends or unmixed it becomes increasingly departed from the two-phase behavior and ΔC_p for PPO rich blends result, accordingly, very small or vanish.

Values of ΔC_p are listed in table XXXII for both iPS-PPO and aPS-PPO blends subjected to annealing at 140 and 170°C.

By using the experimental values for ΔC_p and ΔC_{pA} tabulated previously, curves of ΔC_p versus composition may be drawn in order to observe the deviation of the systems from the two-phase behavior. This is shown in figures 31 to 34. In these curves are also represented

ΔC_p values calculated by using the experimental fractional crystallinities estimated from ΔQ_f data. The dashed line representing the variation of these ΔC_p values with blend composition parallels that corresponding to the changes in ΔC_p for the completely amorphous samples. What this means is that if the two-phase model were obeyed along the entire range of compositions, the experimental

ΔC_p values would lie in the vicinity of this line. This is approximately true for PS-rich mixtures and pure PS, which is in agreement with the reported two-phase behavior of the semicrystalline polystyrene 39.

The melting points of PPO in its blends appear largely depressed as the composition of PPO decreases. The depression is slightly larger when blended with atactic PS at the same compositions, probably because of the lower molecular weight of the atactic PS. IPS, in turn, shows T_m depressions also, whether PPO crystallizes or not, although such depressions are smaller than those shown by PPO. Melting points of each component in the blends are plotted in fig. 35 as a function of composition. These melting point values have been determined from DSC thermograms as the temperatures at which the last trace of crystalline material disappears, and are measured by intersecting the baseline with the extrapolated post-maximum side of the melting peak. These values are listed in table XXXV.

Three basic differences between low and high molecular weight prevent us from depicting the behavior of a polymer system by the usual phase diagram.

High molecular weight systems have a more or less broad T_m rather than a sharp single one. There is no known polymer being completely crystalline, but have not only partial crystallinity but also crystals with a variety of sizes and defects.

In addition, polymers exhibit rubbery and glassy phases, which are absent in low molecular weight systems.

In order to describe the behavior of our system in a comprehensive way a double chart is at least required. This is illustrated in two separate figures (35 and 36). Fig. 35 shows both melting points and glass transition temperatures of the mixture as a function of composition. Whereas figure 36 gives the degree of crystallinity (fractional crystallinity) of each component as a function of blend composition.

We are aware of the fact that the representation of the melting points by means of a single line is a gross simplification made solely for the purpose of clarity in the diagram. Nevertheless, figure 35 is useful to describe the changes occurring upon heating or cooling the mixtures from a theoretical standpoint.

On the other hand, since only a part of the polymer

in the mixture is crystalline, there is need to know the the crystalline and amorphous content of each polymer for a given blend composition. This is accomplished by means of figure 36. At a given blend composition one can find the crystalline fraction of each component by going up to the diagonal line and drawing a line parallel to the composition axis. The crystalline fraction of each polymer corresponds to the intersections of this line with the full curves.

TABLE XXIX

Enthalpies of fusion in joules g.⁻¹ of iPS-PP0 (1) and aPS-PP0 (2) blends resulting from annealing of the prior solvent-treated blend films, at 140°C for 24 hours.

<u>Composition</u>	<u>Enthalpy of fusion joules g.⁻¹</u>		
Weight fraction of PS	(1)	(2)	(3) ^a
1.00	25.58	0	25.58
0.90	24.00	0	24.00
0.80	-	9.46	-
0.75	29.45	11.28	18.17
0.50	19.28	15.65	3.63
0.25	16.68	17.43	0
0.10	18.34	17.52	0
PP0	19.16	19.16	0

a) Calculated as the differences between the data in columns 1 and 2.

TABLE XXX

Enthalpies of fusion in joules g.⁻¹ of iPS-PP0 (1) and aPS-PP0 (2) blends resulting from annealing of the prior solvent-treated blend films, at 170°C for 24 hours.

<u>Composition</u>	<u>Enthalpy of fusion, joules g.⁻¹</u>		
Weight fraction of PS	(1)	(2)	(3) ^a
1.00	28.78	0	28.78
0.90	26.81	0	26.81

TABLE XXX (Cont.)

<u>Composition</u>	Enthalpy of fusion, joules g. ⁻¹		
Weight fraction of PS	(1)	(2)	(3) ^a
0.75	34.84	13.74	21.10
0.50	22.30	14.88	7.42
0.25	15.32	16.06	0
0.10	15.40	15.78	0
PPO	16.57	16.57	0

a) Calculated as the differences between the data in columns 1 and 2.

TABLE XXXI

Values of specific heat increase, ΔC_{pA} , in joules g.⁻¹ deg⁻¹ for iPS-PPO (1) and aPS-PPO (2) amorphous blends of composition shown

<u>Composition</u>	(1)	(2)
Weight fraction PS	C_{pA}	C_{pA}
1.00	0.298	0.296
0.90	0.292	0.289
0.75	0.287	0.282
0.50	0.281	0.260
0.25	0.265	0.252
0.10	0.256	0.253
0	0.242	0.242

TABLE XXXII

Values of specific heat increase, ΔC_p , in joules g.⁻¹ deg⁻¹ for iPS-PPO and aPS-PPO blends crystallized by thermal treatment at 140 (1) and 170 °C (2) of the previously solvent treated films.

<u>Composition</u>	C_p (iPS-PPO)		C_p (aPS-PPO)	
Weight fraction of PS	(1)	(2)	(1)	(2)
1.00	0.201	0.179	-	-
0.90	0.162	0.158	-	-
0.75	0.140	0.133	0.166	0.168
0.50	0.145	0.115	0.150	0.142
0.25	0.106	0.090	0.124	0.114

TABLE XXXII (Cont.)

<u>Composition</u>	ΔC_p (iPS-PP0)		ΔC_p (aPS-PP0)	
weight fraction of PS	(1)	(2)	(1)	(2)
0.10	0,069	0.072	0.081	0.082
0	0	0	0	0

The fractional crystallinities can be evaluated in the two ways just described, using the data of the tables XXIX to XXXII. These values are recorded in tables XXXIII and XXXIV and plotted against blend composition for each particular treatment in figures 27 to 30.

TABLE XXXIII

Degree of crystallinity (fractional of iPS-PP0 and aPS-PP0 blends crystallized by annealing of the solvent pre-treated films at 140°C for 24 hours.

x_f : Calculated from ΔQ_f data

x_c : Calculated from ΔC_p data

Composition	iPS-PP0		aPS-PP0	
Weight fraction of PS	x_f	x_c	x_f	x_c
1.00	0.306	0.326	-	-
0.90	0.287	0.445	-	-
0.75	0.486	0.512	0.269	0.400
0.50	0.417	0.488	0.374	0.464
0.25	0.396	0.604	0.421	0.528

TABLE XXXIII (Cont.)

<u>Composition</u>	iPS-PP0		aPS-PP0	
Weight fraction of PS	x_f	x_c	x_f	x_c
0.10	0.439	0.730	0.420	0.727
0	0.458	1.0	0.458	1.0

TABLE XXXIV

Degree of crystallinity (fractional) of iPS-PP0 and aPS-PP0 blends crystallized by annealing of the solvent pre-treated films at 170°C for 24 hours.

x_f : Calculated from Q_f data

x_c : Calculated from C_p data

<u>Composition</u>	iPS-PP0		aPS-PP0	
weight fraction of PS	x_f	x_c	x_f	x_c
1.00	0.347	0.394	-	-
0.90	0.320	0.459	-	-
0.75	0.580	0.537	0.328	0.404
0.50	0.445	0.591	0.355	0.450
0.25	0.362	0.657	0.385	0.563
0.10	0.368	0.718	0.377	0.676
0	0.396	1.000	0.396	1.000

TABLE XXXV

Melting temperatures of PPO in blends with iPS (1) and aPS (2), and of iPS (3)

Blend Composition Weight fraction iPS	Melting Temperature °C		
	1 (PPO)	2	3 (iPS)
1.00	-	-	231
0.90	-	-	228
0.75	233	232	222
0.50	238	235	219
0.25	243	240	-
0.10	249	247	-
0.00	261	261	-

DISCUSSION OF THE RESULTS

Development of considerable crystallinity has been achieved in iPS-PP0 blends by the action of MEK or acetone vapor. At relatively low temperatures (lower than 75°C) only iPS is able to crystallize, either pure or in blends containing more than 50 weight percent iPS.

The degree of crystallinity has been found to depend on the crystallization conditions. Crystallinity increases with increasing crystallization time and temperature in the interval 25-75°C. Plots of enthalpy of fusion versus temperature of crystallization result in sigmoidal-shaped curves. These curves appear to be approaching a maximum level of crystallinity near 75°C. These curves resemble a half section of those obtained for isothermal annealing of the same blends, which is suggestive of the existence of similarities in the crystallization processes. It is well known that for thermal induced crystallization, a spherulitic morphology is commonly obtained whether one crystallizes from the melt or from the glass. By solvent induced crystallization a similar morphology has been revealed in a number of polymers through small angle light scattering ⁵⁴⁻⁵⁶, wide angle x-ray scattering ^{57,58,34} and scanning electron microscopy ^{53,59}. Although small angle light scattering studies of solvent induced crystalline

polyethylene terephthalate indicated a diffusion controlled crystallization ^{55,56}, the crystallization of polystyrene does not appear to be diffusion controlled. This is concluded from the fact that the sample films exhibit a steadily growing crystallinity after attaining the maximum weight uptake of solvent, which is expected due to the well known low rate of crystallization of iPS. The preceding discussion is brought forward in order to establish the effective role of the solvent. Thus, the solvent does not seem to exert any significant effect on the final morphology or on the crystallization kinetics. Therefore, the major effect is to cause a reduction in both T_g and T_m so that nucleation and crystal growth can occur. For the case of iPS, acetone and MEK cause a decrease in its melting point of 64 and 51°C respectively, when the solvent concentration in the polymer is taken as that at equilibrium. The equations and the values of the parameters used in these calculations are discussed later. Attempts to measure the T_g of iPS containing solvent concentrations near the equilibrium value, failed because of interferences owing to the desorption of the solvent while scanning the sample in the DSC. By making certain assumptions one can estimate an approximate value of T_g . Thus, if one assumes, on the basis of our results, that

maximum crystallinity for a given time occurs at $T_c = 80^\circ\text{C}$, which is approximately equal to $\frac{1}{2}(T_g + T_m)$, by calculating the depression in T_m , a T_g value may be evaluated. When the solvent is MEK, the value of T_g found is approximately -21°C . This means that the solvent lowers both T_g and T_m , but T_g is lowered more drastically. As a result, the interval $T_g - T_m$ is expanded considerably.

In order to obtain a good polymer-solvent interaction and consequently maximum T_g and T_m depression, solvents with a solubility parameter close to that of the polymer have been used.

The interaction parameter for the system PS-MEK has been reported to be 0.66⁶⁰. Other values have been calculated using an equation developed by Bueche:

$$\chi = b + \frac{V_1}{RT} (\delta_1 - \delta_2)^2$$

where V_1 is the molar volume of the solvent and b is a constant which has been evaluated by using the experimental value of χ for the PS-MEK system. These interaction parameters were used to determine melting point depressions due to diluents by means of the known Flory's equation mentioned earlier (Eq. 7 Chapter 1). Even under these favorable circumstances PPO does not exhibit detectable crystallinity following just acetone and/or MEK vapor exposure. Concentrations as high as 10% by weight of

acetone in PPO cause a decrease in T_m of 79°C whereas the experimental T_g measured at that concentration (fig. 21) is 100°C . Therefore, a weight fraction of 0.1 makes the T_m - to T_g interval double. The weight fractions of acetone used in our experiments were actually higher than 0.10 but not so high as to produce depressions in T_g below 75°C . As a result, under our experimental conditions, probably only incipient nucleation occurs in pure PPO or PPO-rich blends, during the solvent exposure.

Other investigators ³⁴ have reported that wet films of PPO exposed to various solvents, display crystallinity, but the crystallinity disappears after drying. Since drying involves additional thermal treatment, presumably the melting point of the polymer was so drastically reduced, that at the drying temperature, melting of the crystallites occurred. Accordingly, this fact was taken into account by us, and a range of temperatures was chosen in accord with the calculated melting point depressions.

Annealing of the blends at temperatures of 90°C or higher, develops crystallinity because the crystallization temperature is now further from T_g and the usual compromise between nucleation and crystal growth is achieved. However, unlike the crystallization of iPS, which is carried out into the vapor phase of the solvent, PPO crystal-

lization is governed by kinetic factors. This is illustrated with the aid of figures 21 and 22. Thus, referring to figures 21 and 22, if a crystallization process were to be initiated at 140°C in PPO samples containing 10% by weight of acetone, after three hours the acetone has been reduced to 4% and the corresponding T_g becomes 145°C . This implies that after three hours no crystallization is possible. In addition, the rate of crystallization is changing due to the displacement of the glass transition temperature, decreasing as T_g approaches the crystallization temperature. In brief, at higher temperatures, the rate of crystallization is higher, but the effective times of crystallization are shorter.

The combined effect of the variations in the rate of crystallization and the effective times of crystallization can be discussed on the basis of the data plotted in figure 23. At low temperatures one can observe an increasing enthalpy of fusion with increasing temperature until a maximum is passed, followed by a sudden, almost linear decrease with increasing temperature. In the region where crystallinity increases, there appears to be no limiting action by time, but after the maximum heat of fusion is reached, the monotonic decrease in the

level of crystallinity is very likely to be due to the reduction of the effective time of crystallization. Therefore, the location of a maximum level of crystallinity might lie at higher temperatures if time was not the limiting factor.

On the other hand, as far as morphology is concerned, the DSC thermograms showed relatively broad melting peaks for PPO and its blends. Sharper melting peaks were obtained for pure PPO when thermally treated at 140°C . These broad melting peaks are suggestive of small and/or poorly formed crystalline regions. Two more experimental facts seem to support the previous statement. First, most of the crystallization process is carried out in a range of temperatures which, with the passage of time, is closer to the T_g of the material, until eventually T_g surpass T_c . Polymers crystallized at temperatures near T_g , where spontaneous nucleation is rapid, and crystal growth rate is low, have crystalline regions consisting of numerous tiny spherulites. Second, blends displayed consistently even broader melting peaks than that of the pure polymers. Also, PPO-rich blends showed relatively high degrees of crystallinity as compared to pure PPO (figs. 25 and 26). An interpretation of these facts can be made based on the expected high levels of miscibility of the polymers. At temperatures close to T_g , where the mobility of the

molecules becomes restricted and the growth of a developing center is controlled by a diffusional process, most of the available energy becomes consumed in activating nuclei rather than supplying the demand of energy to increase the crystal surface. The blends, in the case of good compatibility, may be considered as an aggregate of very small clusters, or domains of segments of each polymer. During spontaneous nucleation, those clusters are the sites where the nuclei start to form and give rise to spherulites, which since nucleation is favored over crystal growth, their size can become reasonably smaller than that of the clusters. Thus, the physical boundaries of the cluster are not completely responsible for preventing the crystal growth. This fact explains why PPO crystallizes in the blends at compositions as low as 20%. This does not exclude the existence of a high degree of crystallinity, indeed fractional crystallinity of ca. 0.6 has been obtained in iPS-PPO blends (fig. 26). Moreover, the mutual impingement of growing spherulites upon one another cannot be discarded.

The presence of crystalline PPO in the blends confers to the crystalline region a certain degree of heterogeneity which is reflected in the large departures from the two-phase behavior.

When solely iPS crystallized, this departure is relatively small, although the amorphous phase is appreciably rich in PPO. Such behavior can be further indication of morphological differences between iPS and PPO crystallites. The absence of a detectable change in specific heat at the T_g of pure crystalline PPO might be adduced in favor of showing the crystalline structure of the polymer as a mass of numerous tiny spherulites (50% crystallinity) whose uniform distribution in the amorphous region, inhibits the amorphous phase from responding to the thermal events associated with T_g . Thus, the independence of phases assumed in the two-phase model is no longer valid.

Completely amorphous iPS-PPO blends exhibit monotonic variation of the changes of specific heat at T_g with composition as long as the presence of PPO in the crystalline phase is small. Therefore, deviations of the two phase behavior seem to be produced solely by reason of the nature of the crystalline structure of PPO, i.e. the contribution of PPO crystallites to the crystalline phase of the system.

The existence of a binary polymer mixture characterized by a high degree of miscibility and the ability of its constituents to crystallize at various compositions has prompted us to consider the feasibility of constructing a polymer phase diagram.

We are aware that a phase diagram is an equilibrium diagram and that courses of crystallization predicted from it presuppose the absence of such nonequilibrium conditions arising in polymer systems.

A reasonable approach to the problem requires that similarities and differences between the behavior of multiphase systems of high and low molecular weight compounds be stated.

Our system presents some similarities to those of low molecular weight, as long as a state of equilibrium is assumed.

Thus, a high degree of homogeneity is revealed through a number of test performed in this and other previous works 8, 15, 22.

The two components present a relatively high degree of crystallinity and show depression in their melting points with increasing content of the diluent.

On the other hand, there exist great differences between the behavior of the two systems:

- 1) Crystal polymers, as a rule, also contain an amorphous phase.
- 2) Even highly crystalline polymers do not possess a sharp melting point but a broad melting band.
- 3) Crystallinities, and hence, melting points of the polymers depend upon the treatment employed in the

development of these crystallinities.

4) Polymer system have a glass transition temperature which adds further complications to a phase diagram since it represents the separation line between two inexistent phases, rubbery and glassy, in low molecular weight systems. On top of it all, polymer crystals contain a larger number of defects and may vary in size and in degree of crystallinity, depending on a variety of parameters such as the molecular weight distribution, tacticity, inherent impurities, etc.

Some of these differences might be circumvented by defining the conditions under which accuracy and reproducibility of critical properties can be obtained. In our case, for example, the conditions to be defined must ensure a high and constant degree of crystallinity, so that, an invariant melting point can be measured reproducibly.

Furthermore, the mathematical treatment of the problem adds some difficulties. Equations derived to examine the reduction in chemical potential that occurs on mixing a polymer in a low molecular weight diluent, are not completely applicable in the case of mixing two polymers. The inapplicability lies in the statistical mechanics considerations implied in the model used in the derivation of such a treatment.

However, in face of the lack of appropriate treatment.

However, in face of the lack of appropriate treatment of polymer-polymer mixtures, an analysis of our experimental data can be made using the equation derived by Flory³¹, which relates the depression of the melting point caused by addition of diluent to the volume fraction of diluent, v_1

$$(1/T_m) - (1/T_m^0) = (R/\Delta H_u)(V_u/V_1)(v_1 - \chi v_1^2) \quad (7)$$

Where all the terms of this equation are explained in chapter one.

When dT_m/dv_1 , i.e. the derivative of the melting point with respect to molar volume of the diluent, is evaluated, one finds that for all values there is a depression in the melting point of the polymer with increasing v_1 . The second derivative turns out to be negative at least for values of χ in the range of interest. this means that the curve representing the melting points of the polymer at the various values of v_1 must be convex, if they are to be described by this equation. However, our experimental results produced a curve which appears to be concave, i.e. the second derivative is positive. Therefore, one might think of the experimental curve as being affected by factors other than those causing melting point depression of the polymer under equilibrium conditions. Of course, this presupposes

the validity of equation 7. Depressions in the melting points of polymers in compatible blends have been found to be brought about by morphological defects and differences in molecular weight of the diluent. However, the effective size of the molecule acting as a diluent cannot be pictured as the entire molecule of the polymer, but instead as a relatively small part of it. The better the level of mixing, the smaller the size of the effective diluent molecule.

Therefore, the experimental melting point depressions must be considered as the sum of the contributions due to two effects. These two effects cannot be considered independently. When the changes in the chemical potentials of the components allow a very intimate degree of mixing (at level of a few polymer segments) the development of crystallinity becomes restrained. Accordingly, smaller and more defective crystallites should form. On the other hand, if thermodynamic equilibrium is assumed, a reduction in the melting point must occur as a result of the changes in chemical potential owing to the presence of a diluent, which although a high polymer, interacts with its partner at level of a few monomer units.

If the contributions due to the changes in the morphology of the polymer upon mixing could be subtracted from the total melting point depressions, the shape of

the experimental curve might shift to the convex curve predicted by eq. 7.

In view of the above, additional theoretical and experimental work is required to formulate an acceptable solution to the problem.

SUGGESTIONS FOR FUTURE RESEARCH

We feel that there is need of studying more extensively the melting behavior of isotactic polystyrene. Although many investigations have been made to explain the presence of multiple melting peaks, it is by no means clear. Heating rates lower than $10^{\circ}\text{K}/\text{min.}$ should be used in DSC techniques, to determine if recrystallization is complete at a given heating rate. In addition samples with the highest tacticity should be used. To do that samples must be purified by dissolving them, repeatedly, in MEK in order to eliminate as much atactic content as possible. The material should be crystallized from both the melt and the glassy state to check for expected differences in the melting behavior and crystalline structure.

Another feature concerning PS, is its adherence to two phase model. We have found that the product of the specific heat increase by the heat of fusion remains constant. For the case of polystyrene, when both ΔC_p and ΔH_f are given in joules g.^{-1} (deg^{-1}) this value is around 4.5. Polymers showing close adherence to two phase behavior are thought of having similar constant products. It is felt that such a characterization would be of some interest.

The systems composed of amorphous and semicrystalline polymers appear to be of great interest not only for examining the properties of the mixtures, but also for obtaining information on the behavior of individual polymers.

A further research must be conducted to elucidate how and at what extent the presence of a polymer diluent affects the crystalline structure of the polymer.

Studies of the morphology of the crystalline component must be performed by using the adequate technique, x-ray, electron microscopy, etc. The morphology of the pure polymer should be contrasted to that of the polymer in the compatible blend at different compositions. By applying known equations relating temperatures of fusion with the size of crystallites, the effect of defective morphology may be estimated.

This study can be extended to incompatible blends. By choosing appropriate polymer pairs the differences in the crystalline structure and in the melting behavior between compatible and incompatible blends may be determined.

Furthermore, polarizing microscopy can be used to measure radial increase in size of the spherulites in the pure polymer and its blends, whether compatible or not. By using a wide range of compositions and different molecular weights of the diluent one should be able to

observe the effect of the compatibility alone.

Crystallization induced by solvent also offers an auspicious subject for future research. A variety of solvents in conjunction with different experimental conditions, temperature, pressure etc, can be employed to examine the role of the solvent in the process. On particular, we believe that higher degrees of crystallinity and/or larger crystallites can be obtained for PPO either pure or in its blends if the thermal treatment could be carried out in a high pressure chamber containing the solvent.

X-ray studies of the morphology of PPO and iPS-PPO blends is also important to confirm the observations made on the basis of thermal results.

Kinetic studies of the combined thermal plus solvent crystallization would be very useful in order to improve the experimental conditions to achieve higher levels of crystallinity. This, in turn will be helpful for formulating the set of necessary conditions to obtain reproducible data. As it was said earlier the achievement of optimum properties with a high degree of reproducibility are essential requirements in any attempt to construct a polymer phase diagram.

Finally, the search of new compatible blends of semicrystalline polymers is very important if the results obtained for PS-PPO blends are to be generalized.

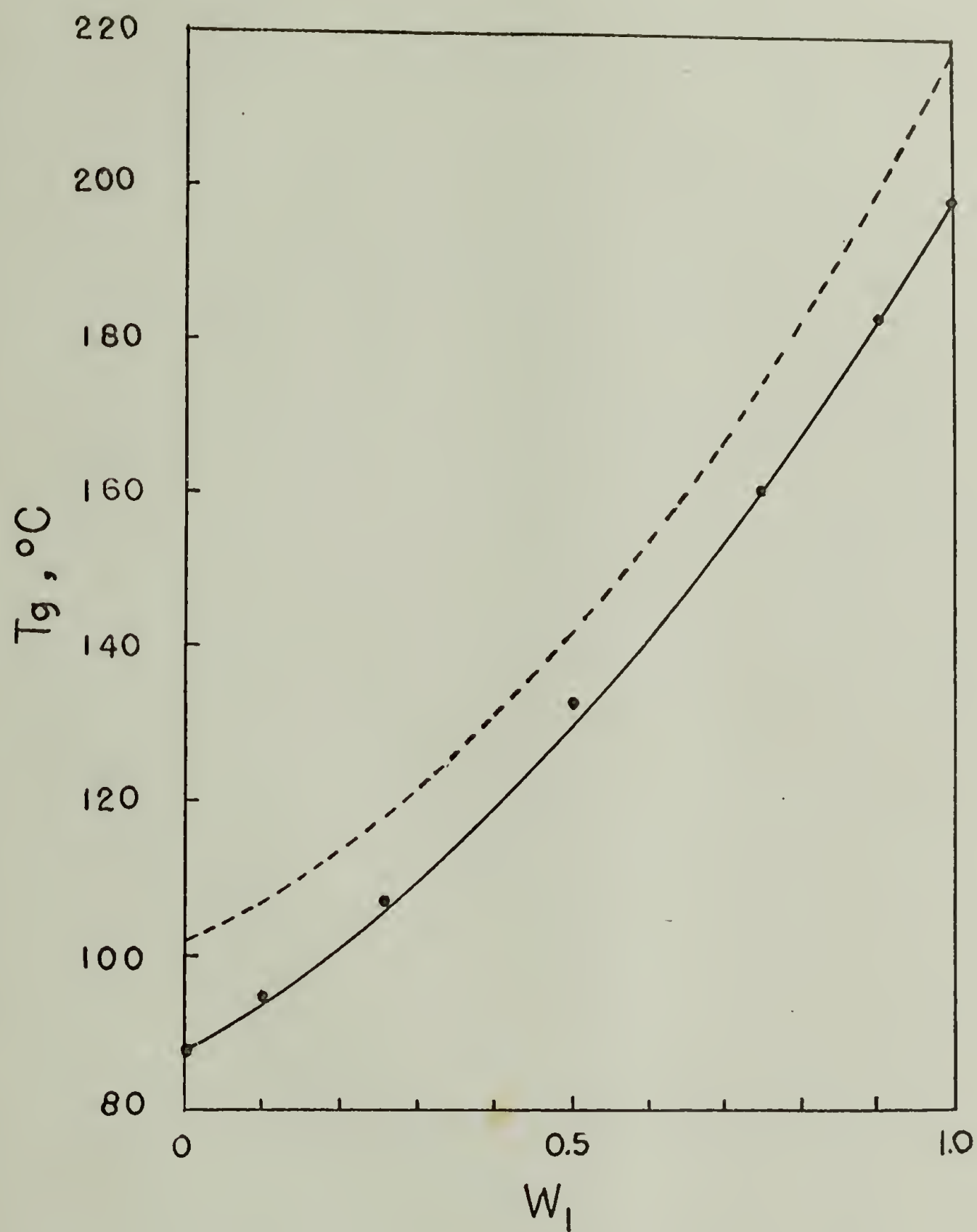
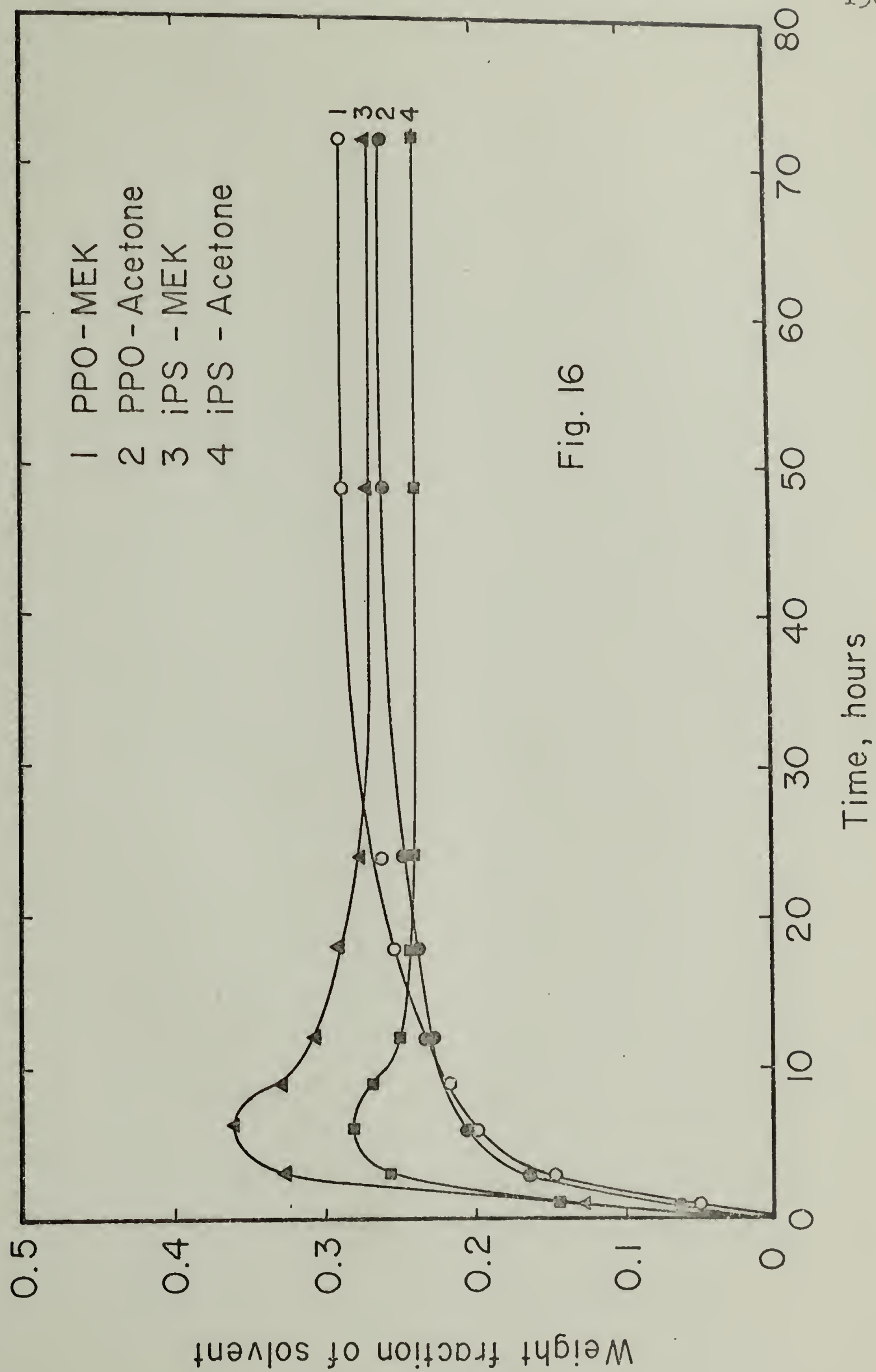


FIGURE 15



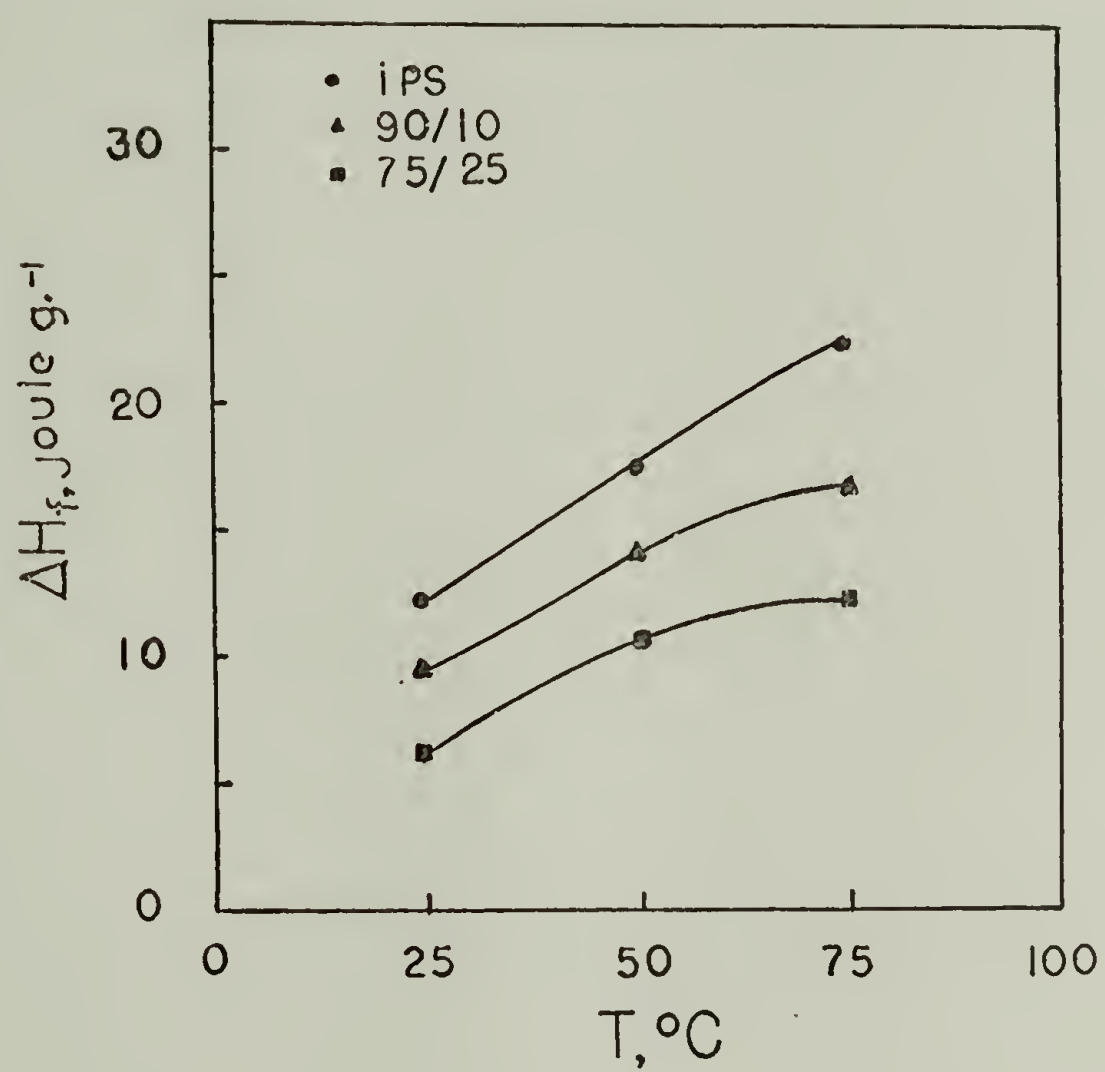


FIGURE 17

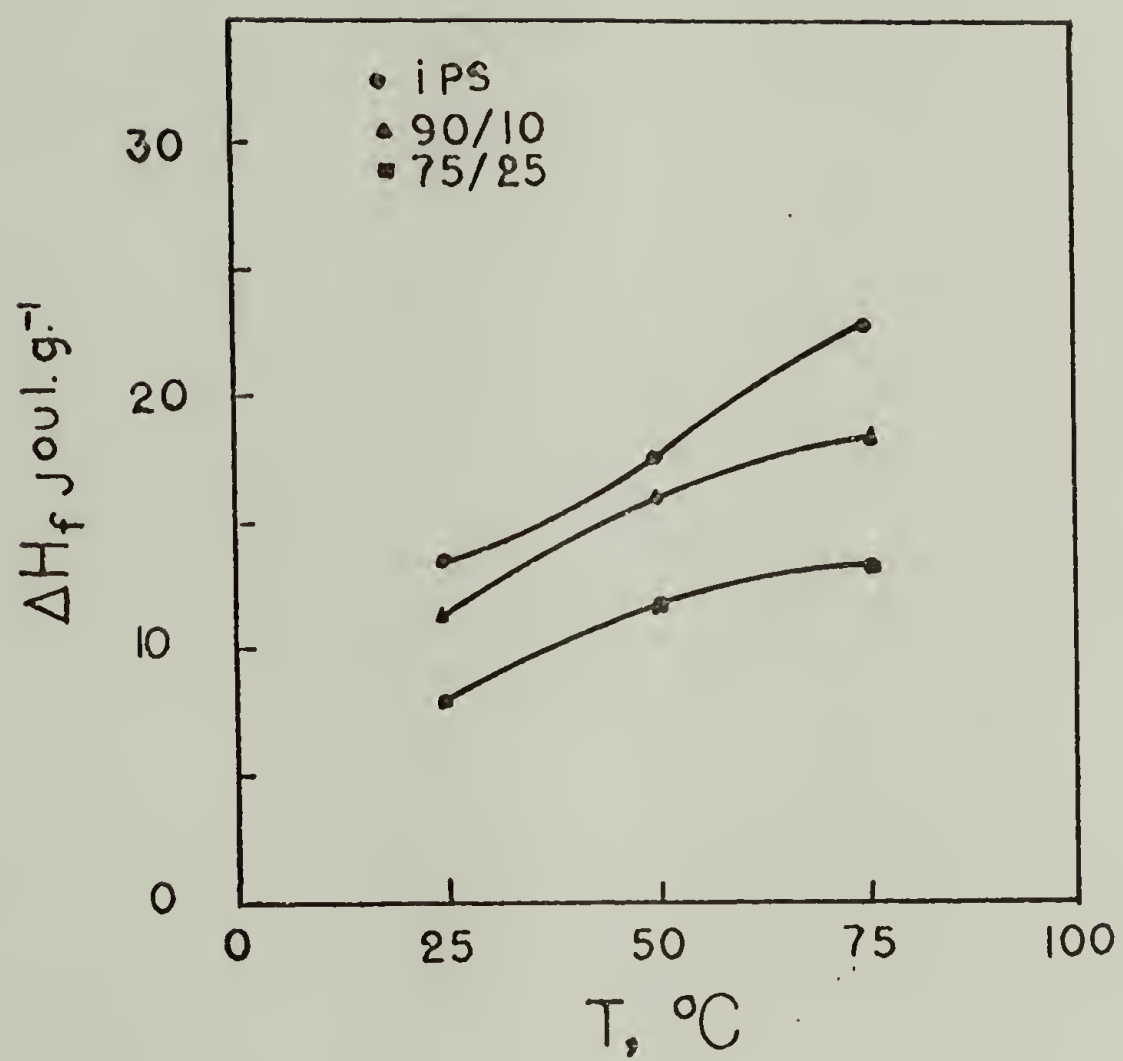


FIGURE 18

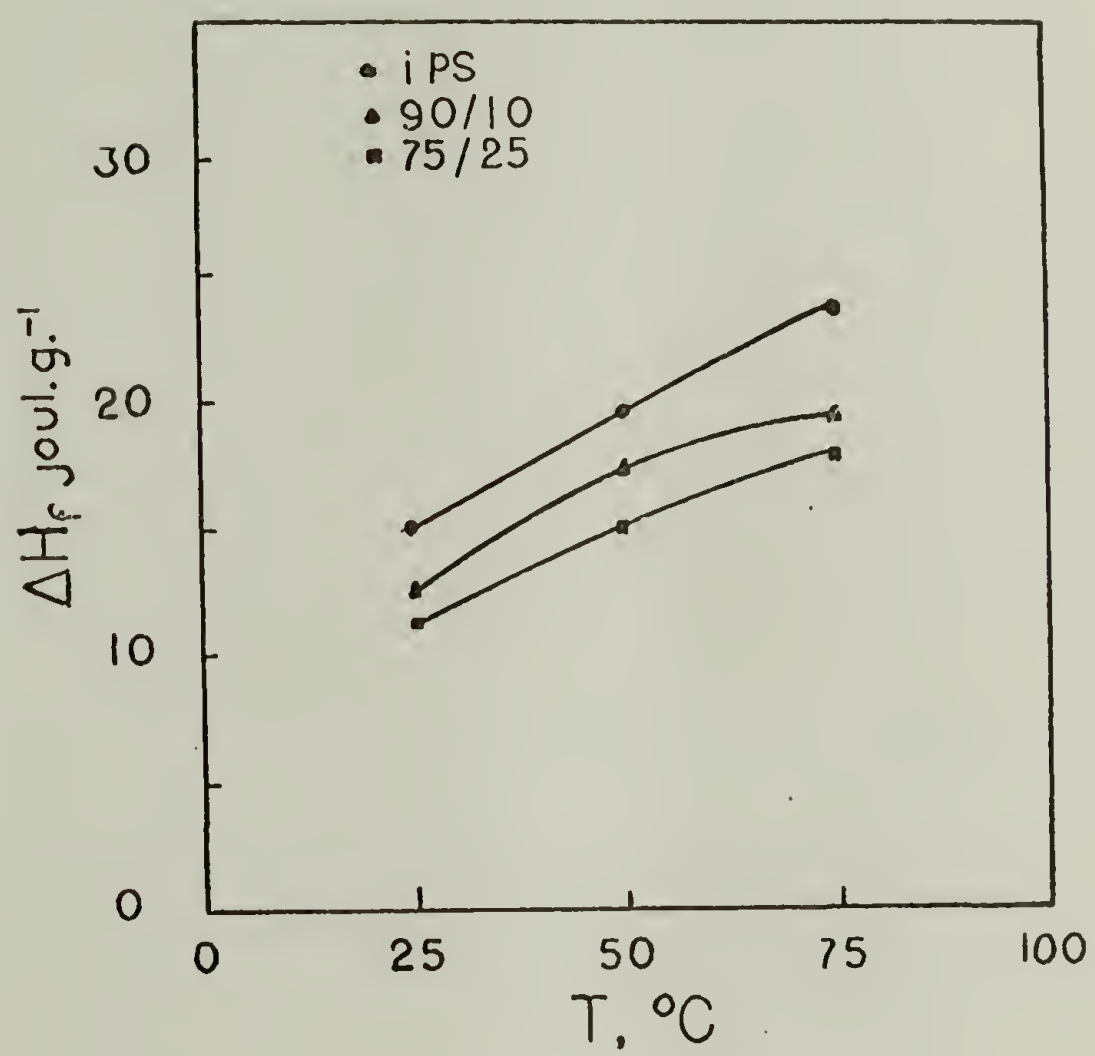


FIGURE 19

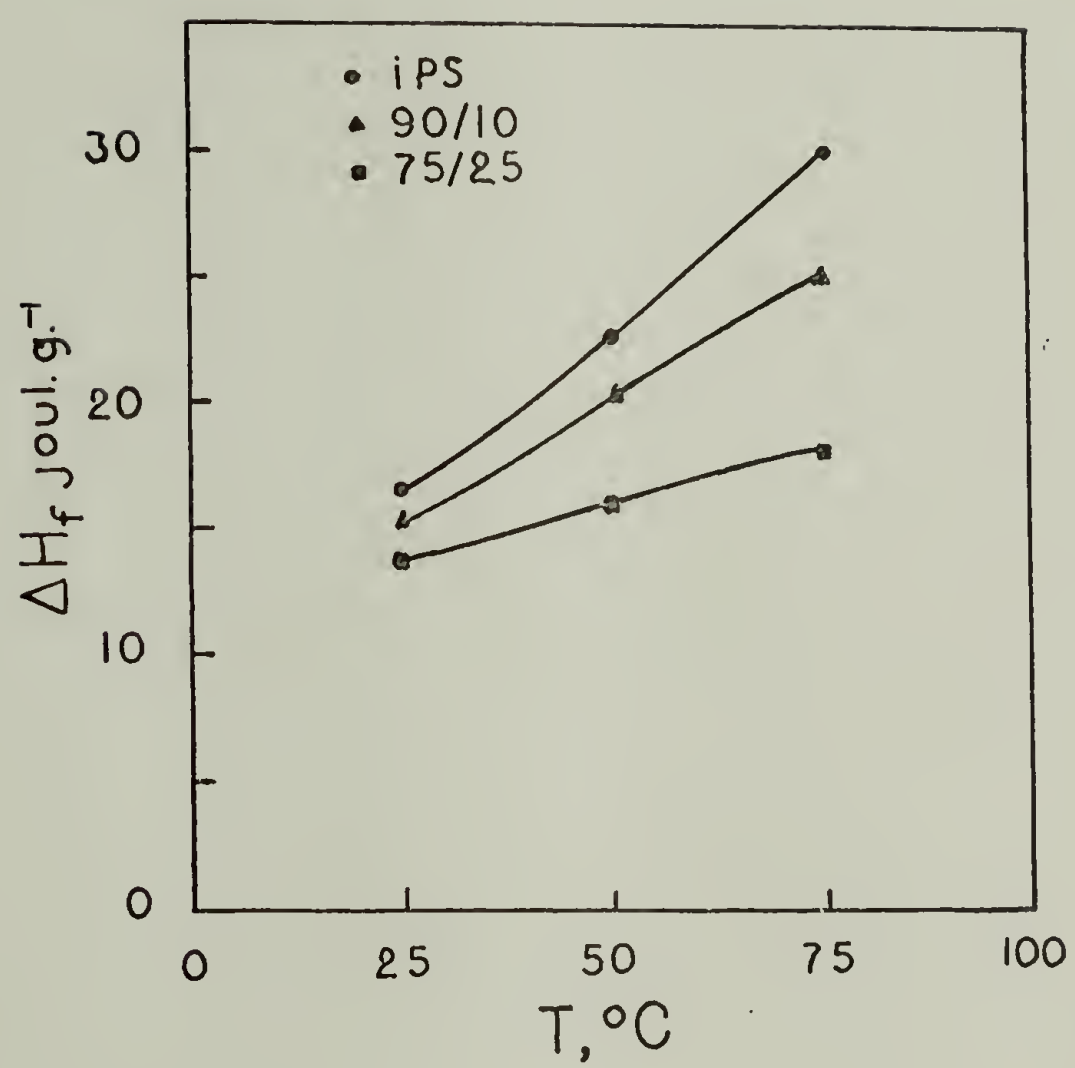


FIGURE 20

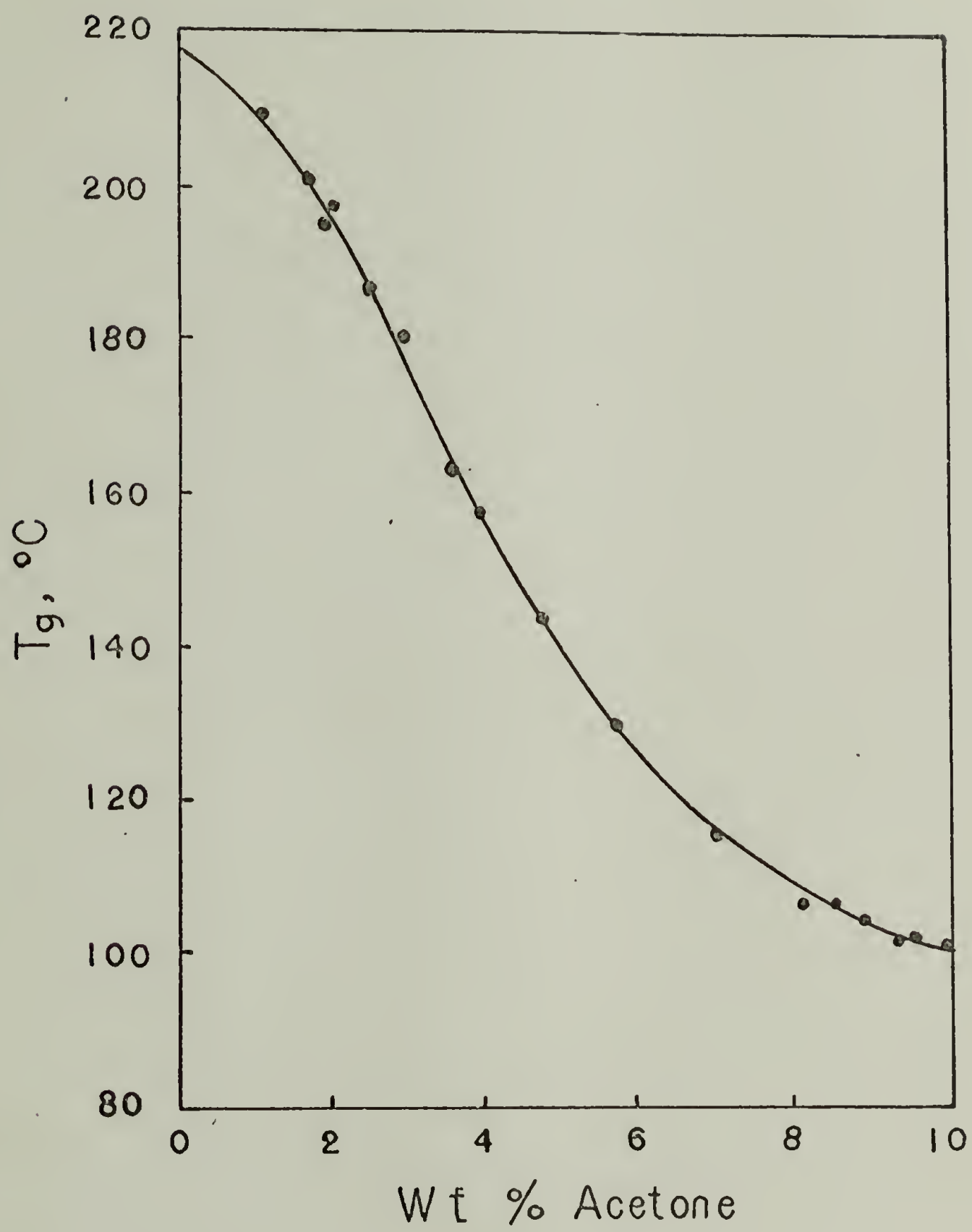


FIGURE 21

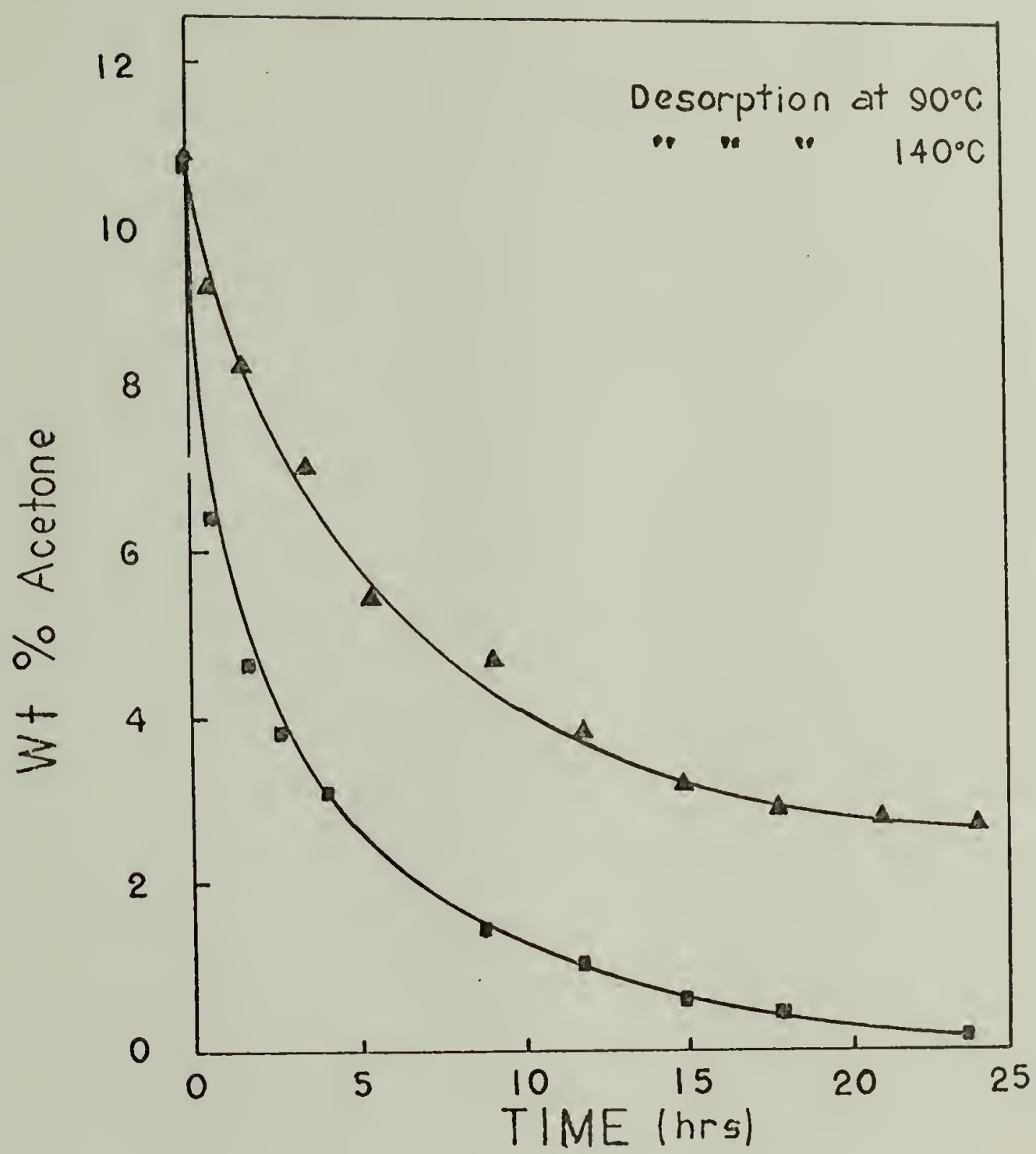


FIGURE 22

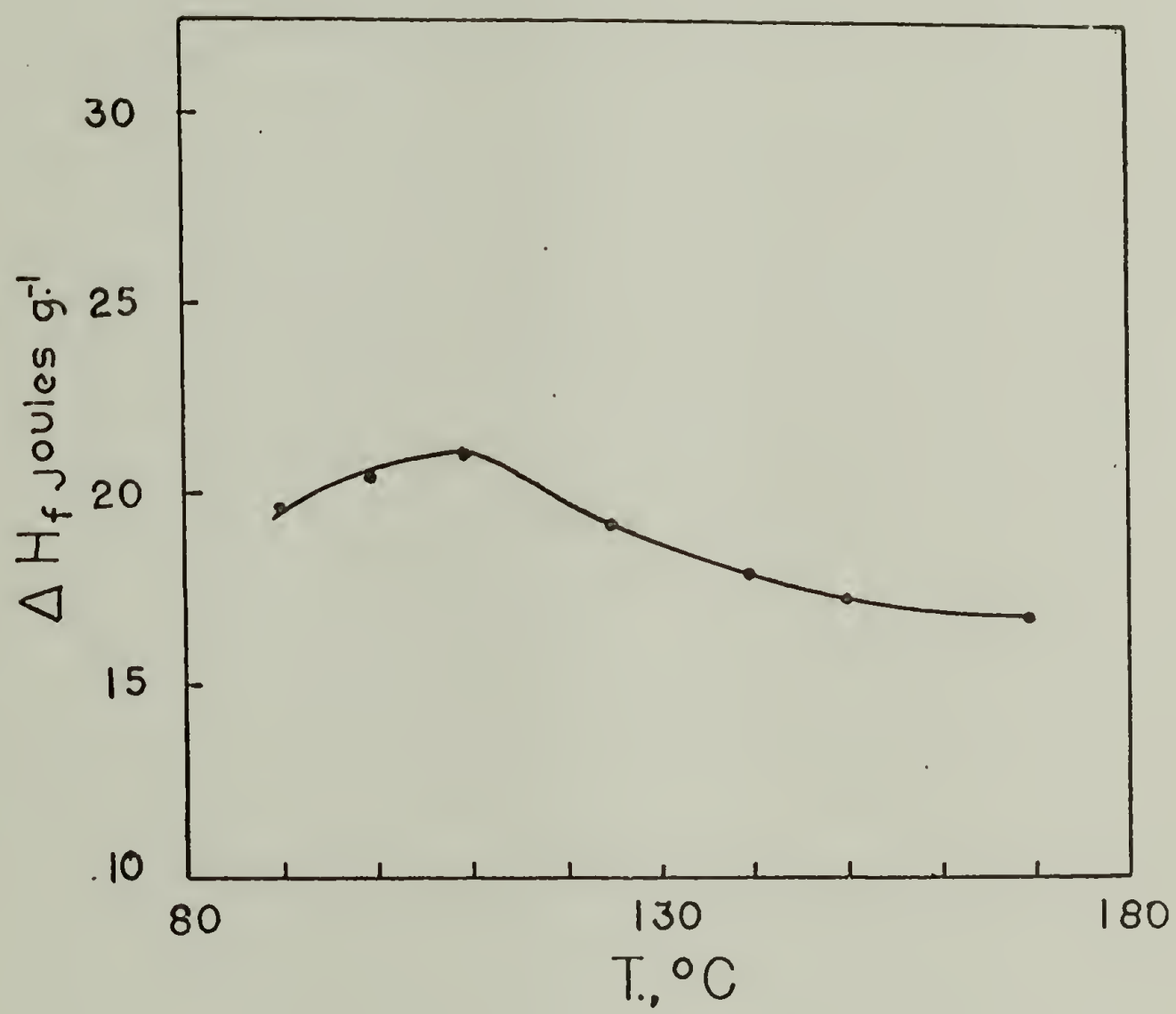


FIGURE 23

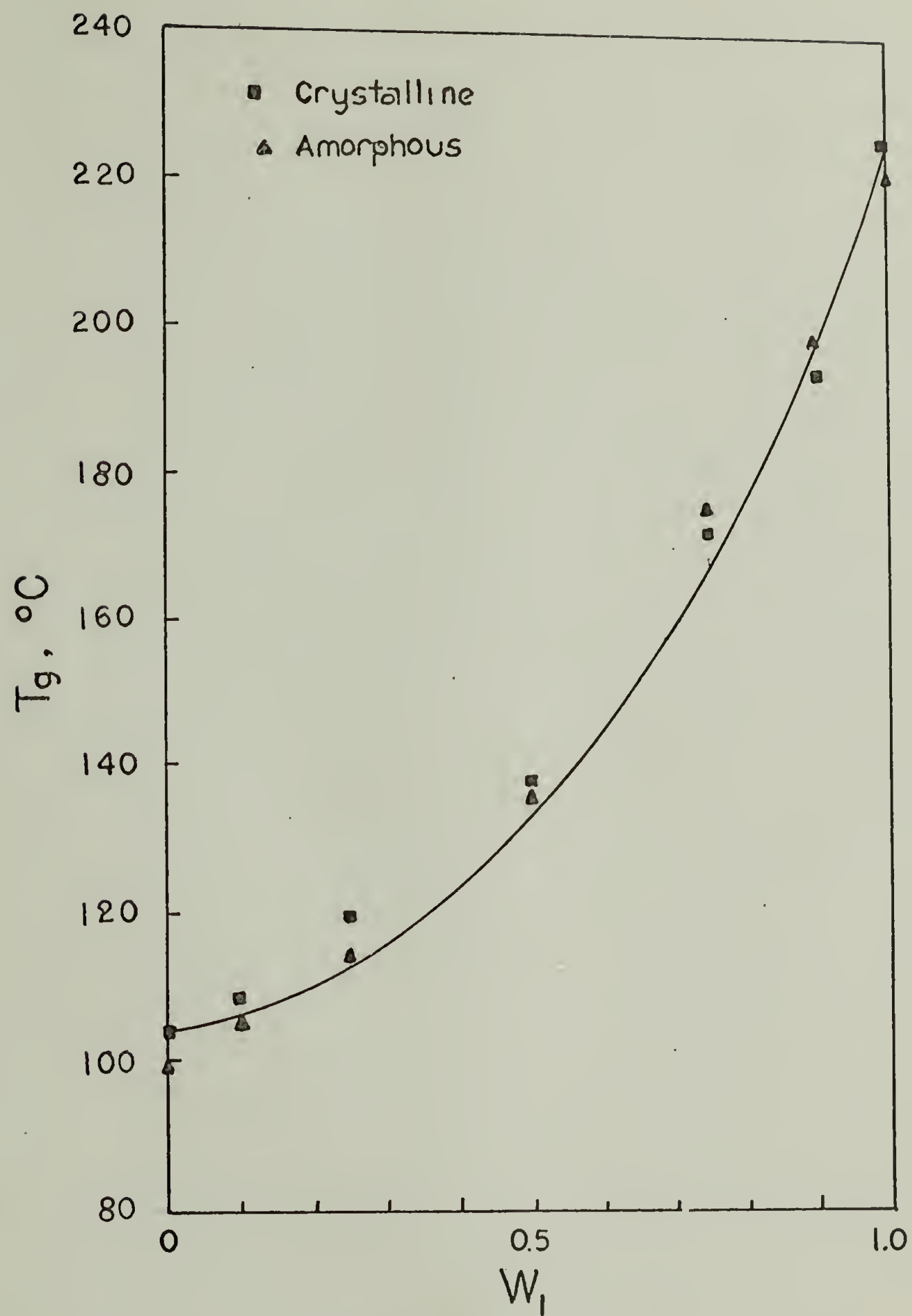
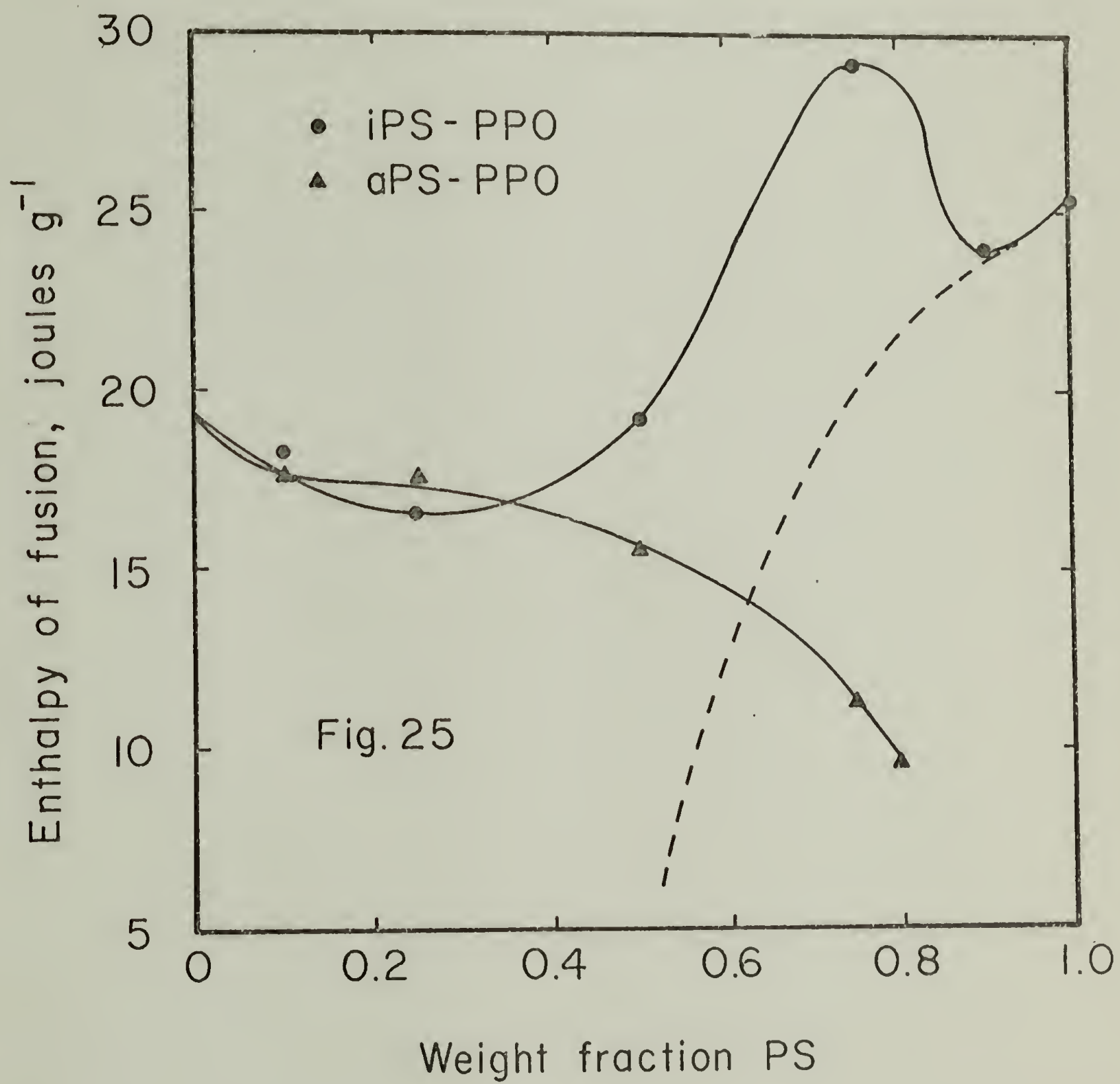
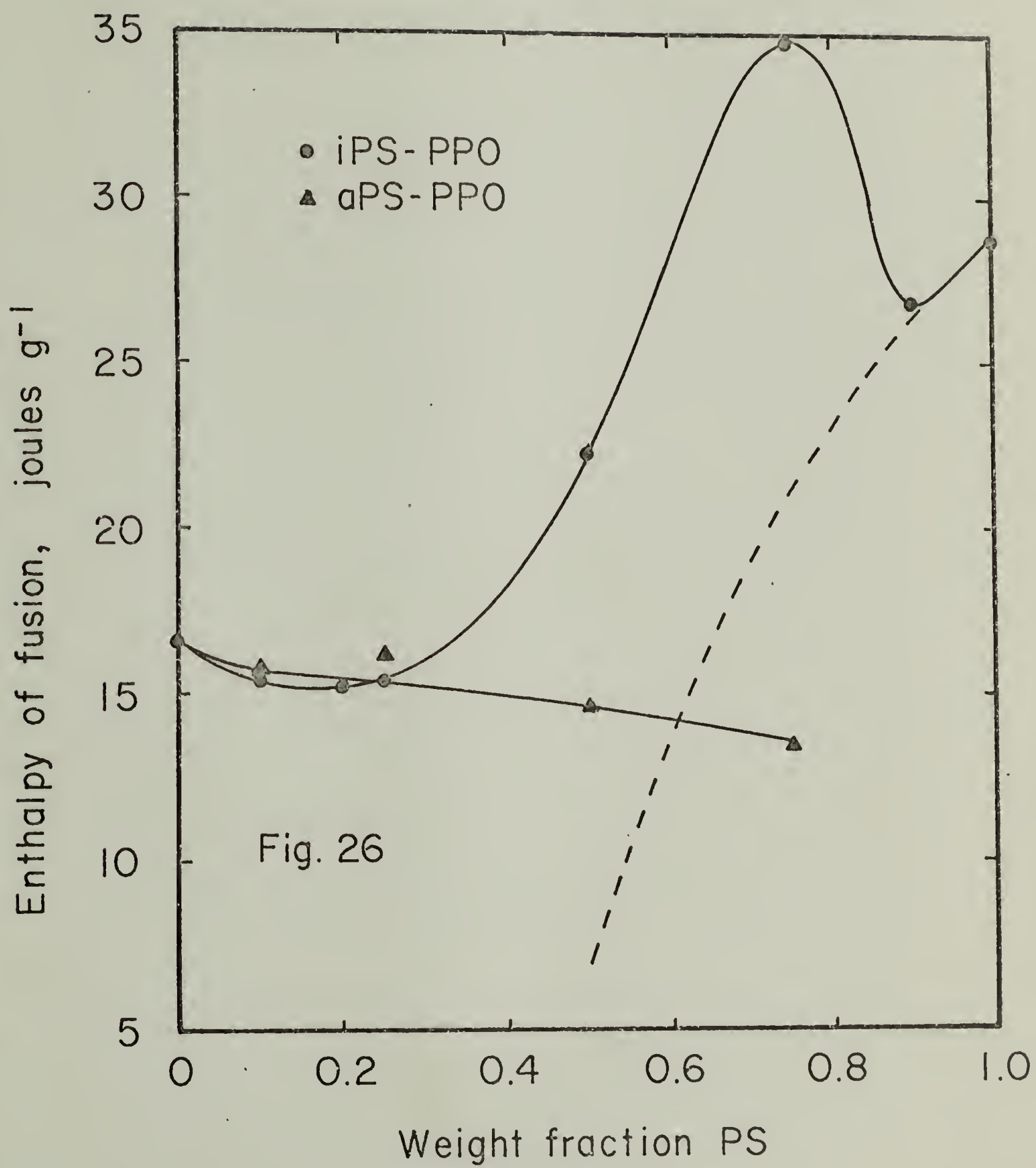
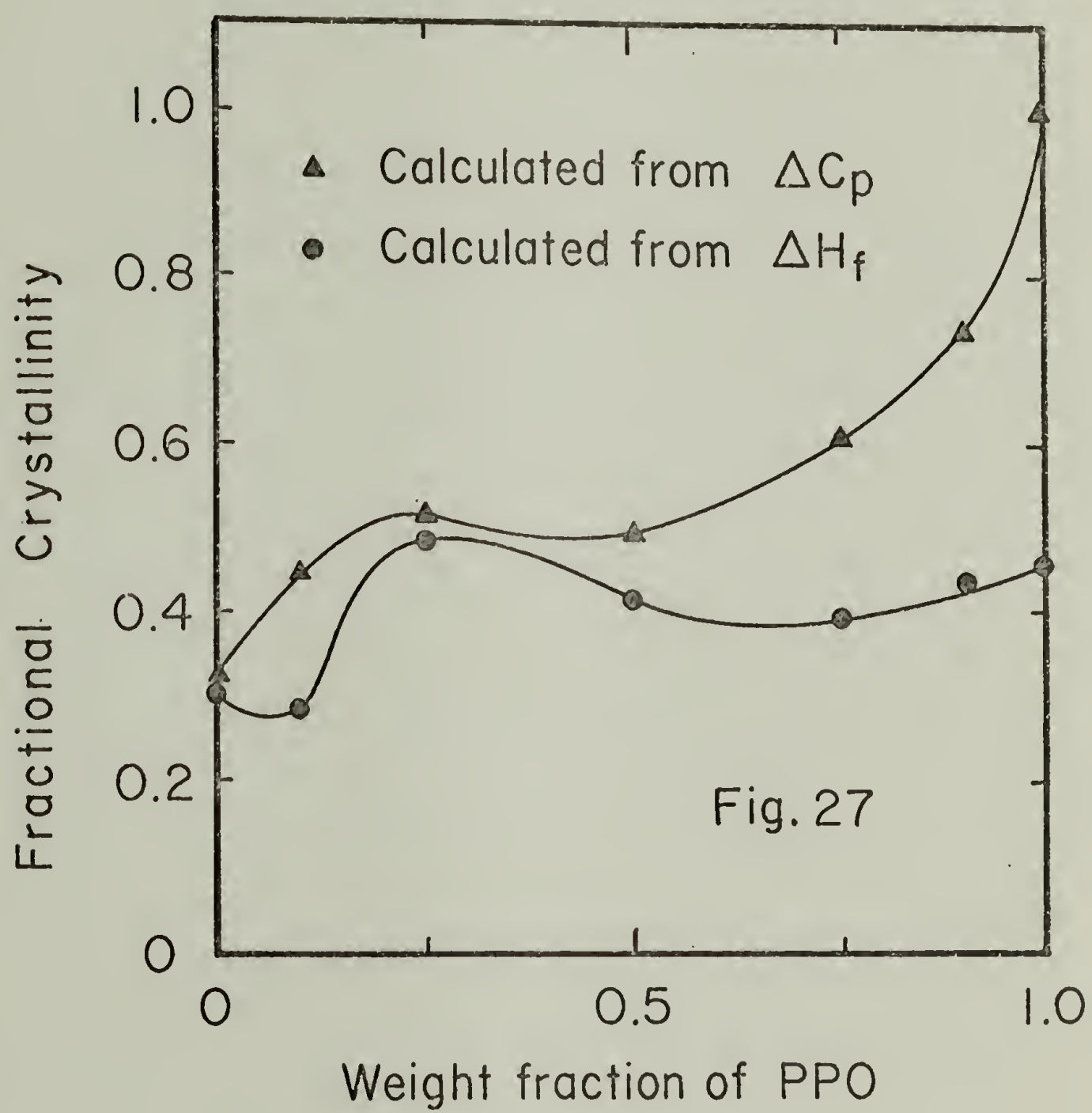


FIGURE 24







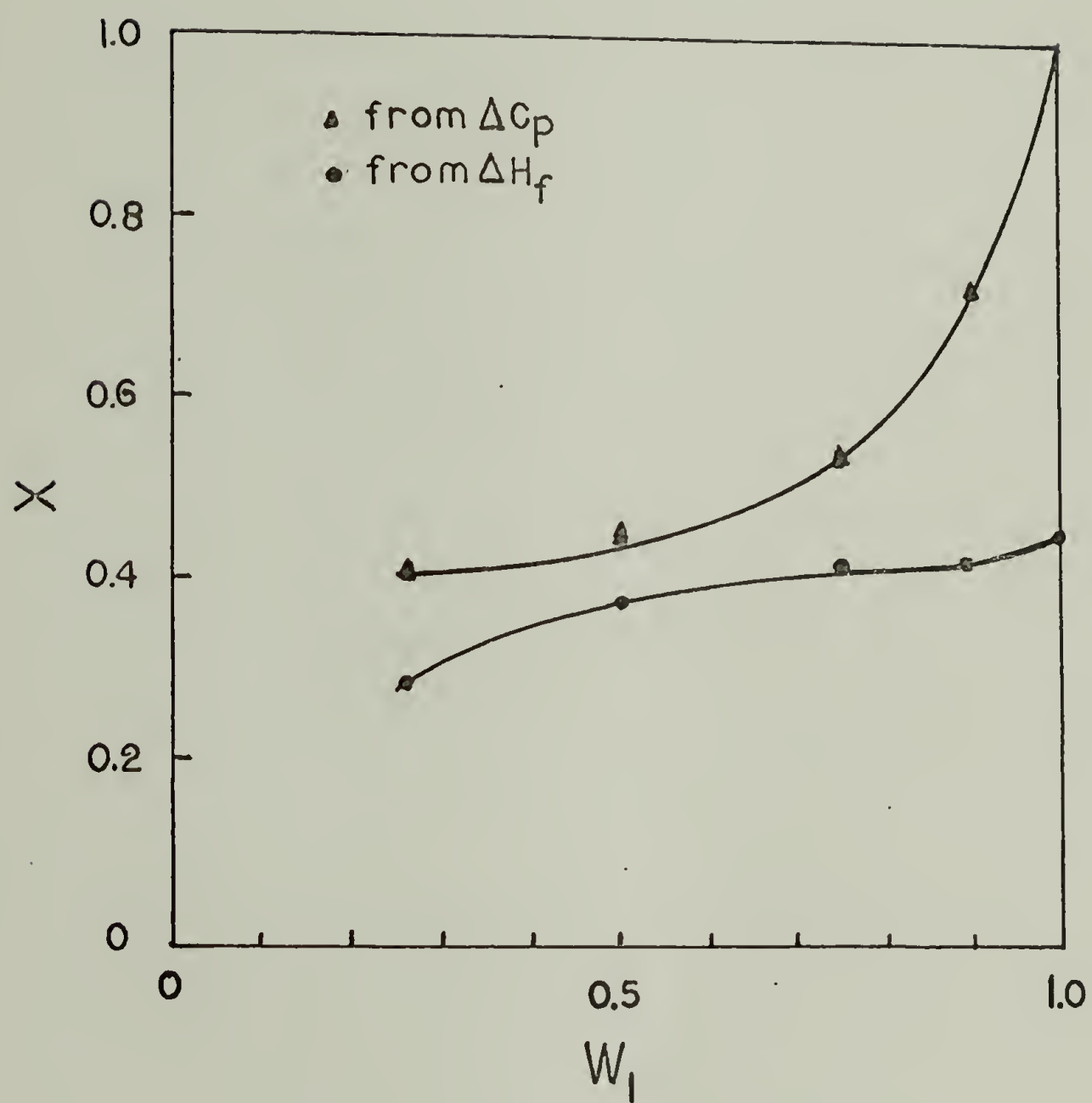
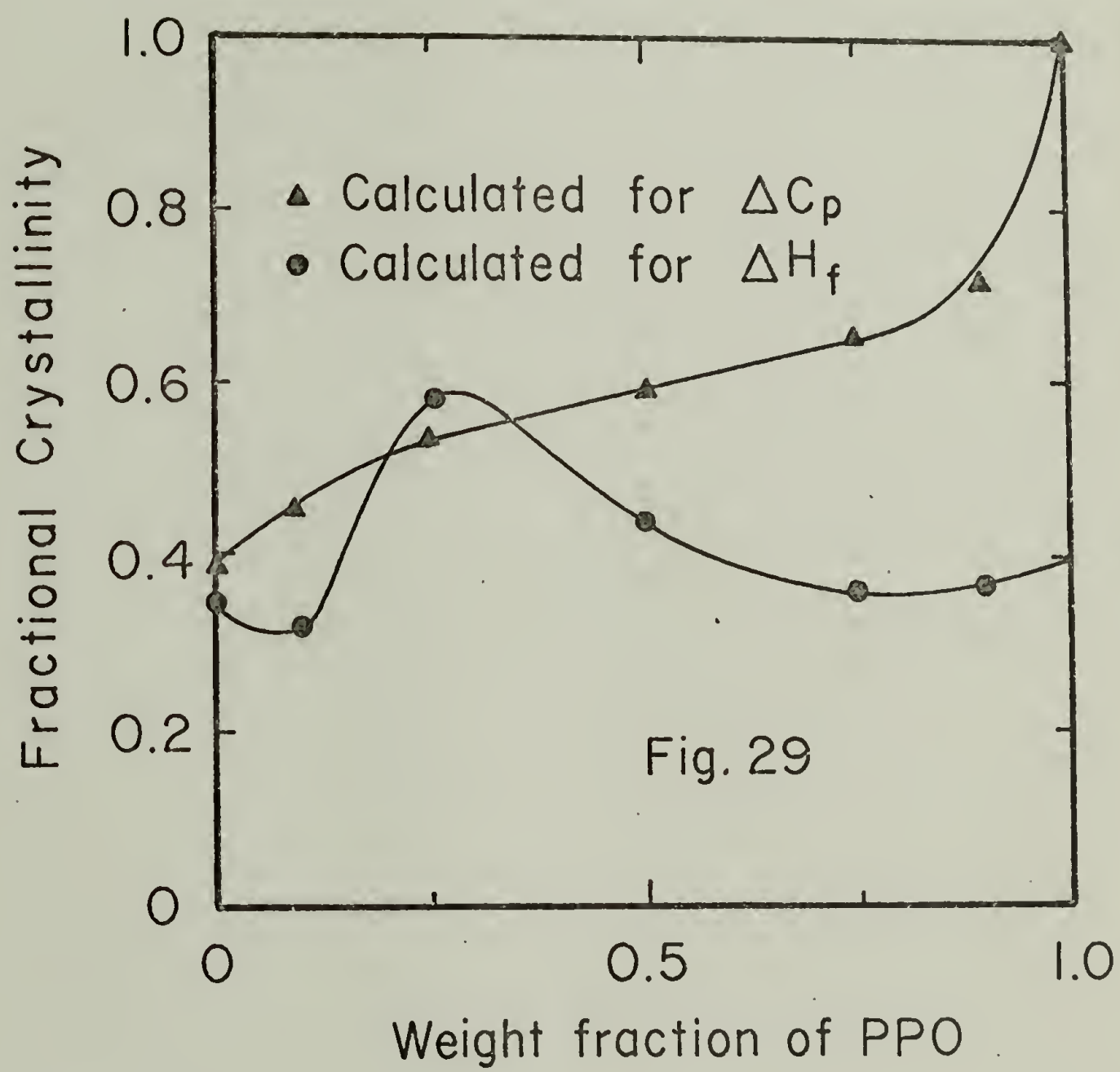


FIGURE 28



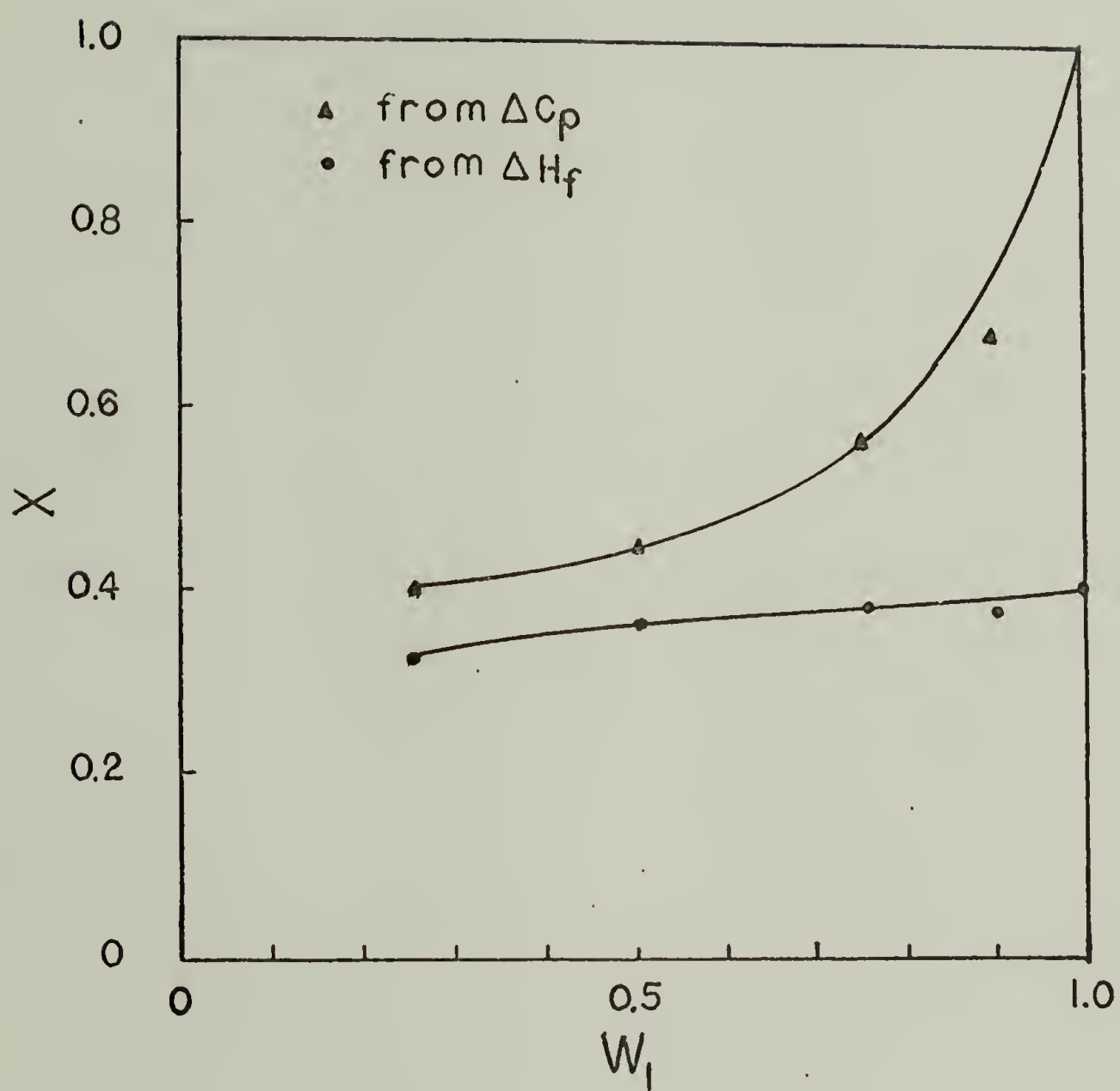


FIGURE 30

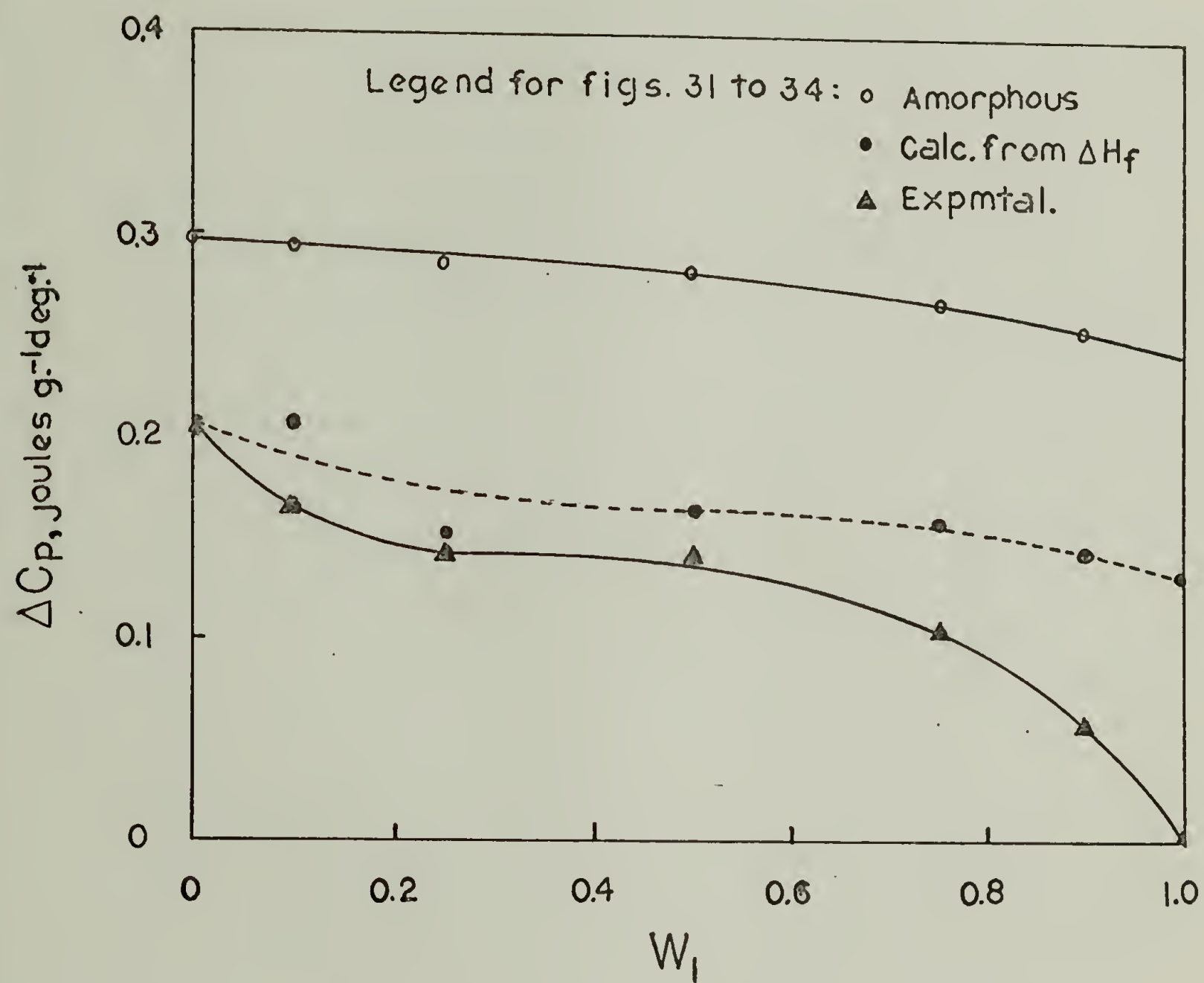


FIGURE 31

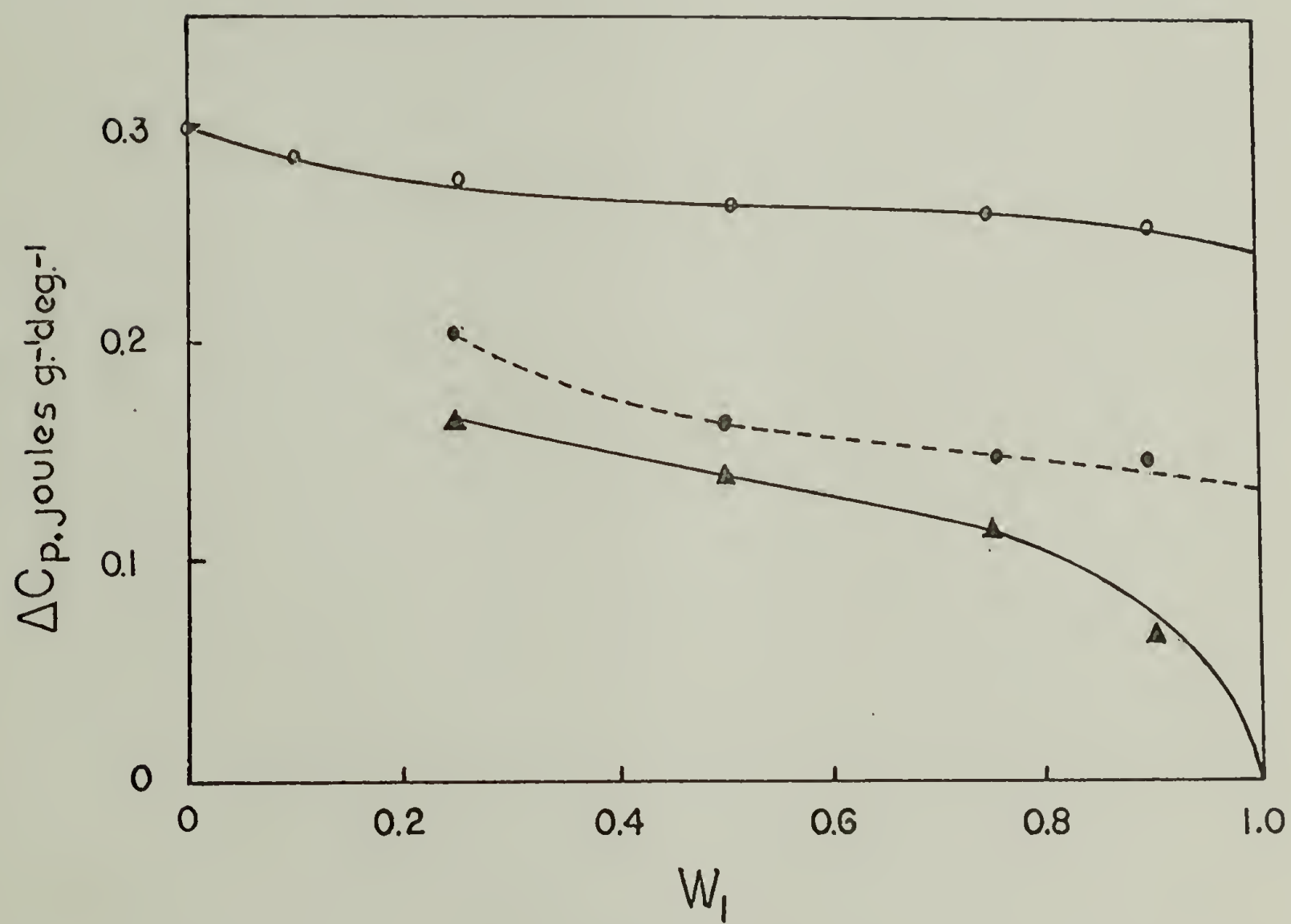


FIGURE 32

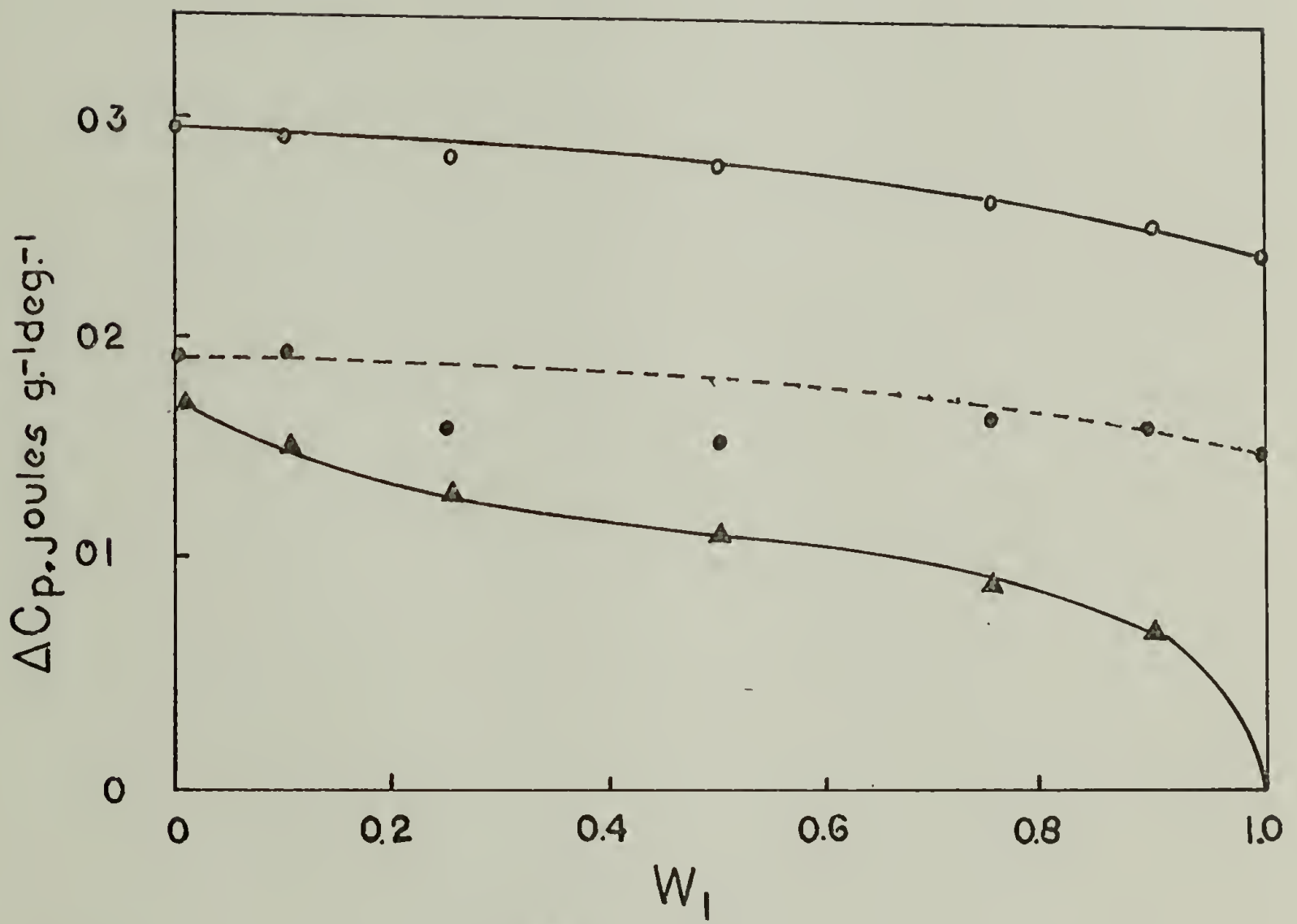


FIGURE 33

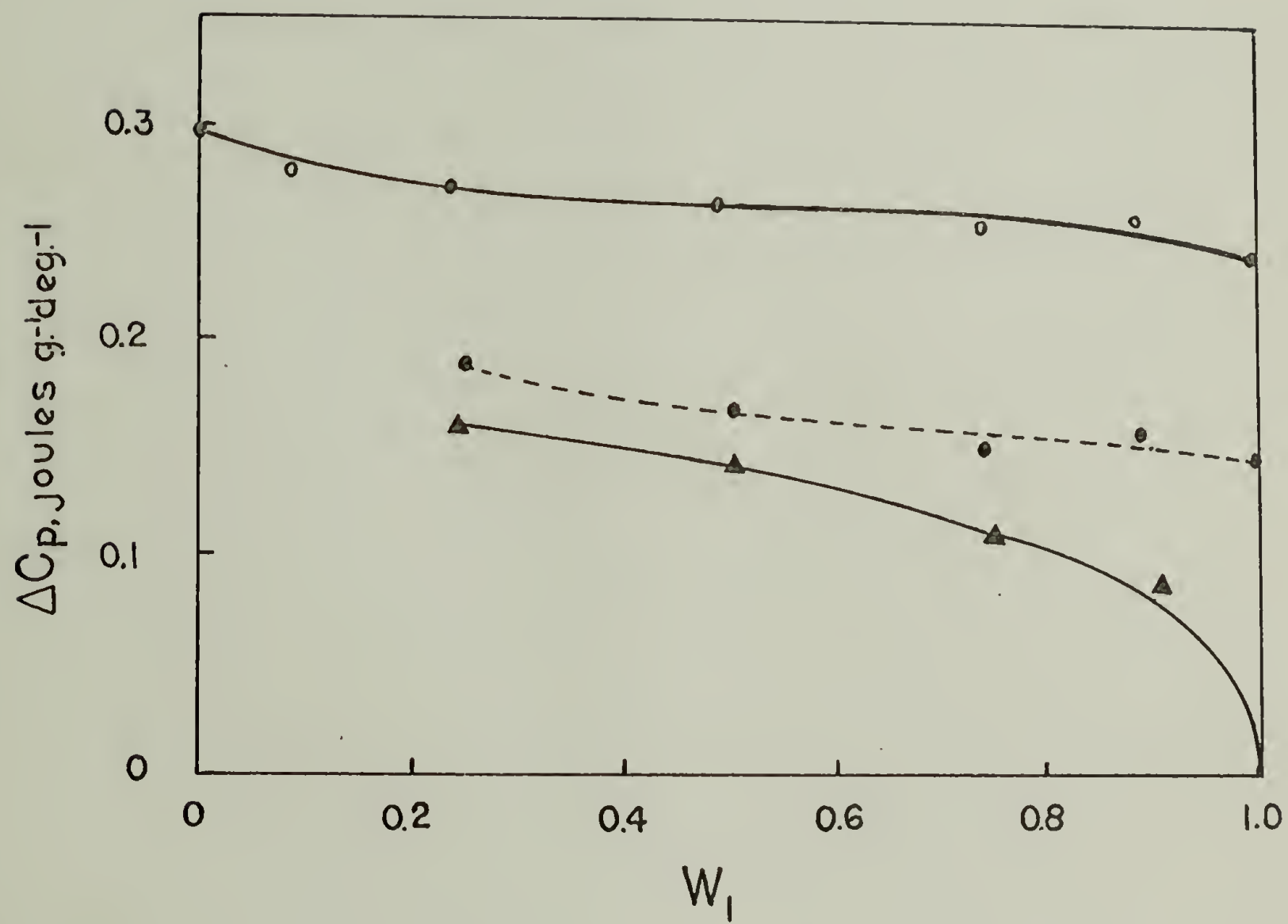


FIGURE 34

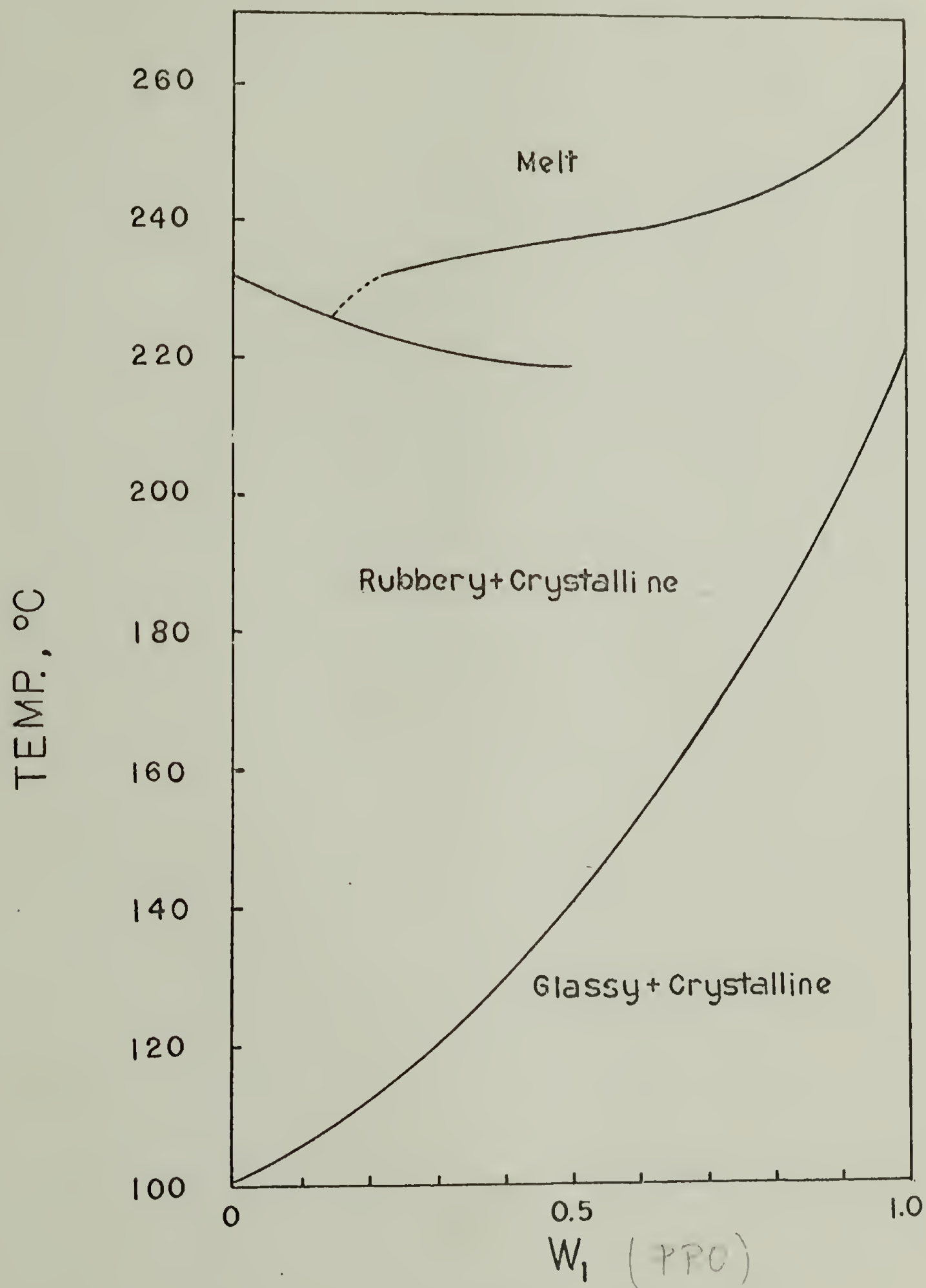


FIGURE 35

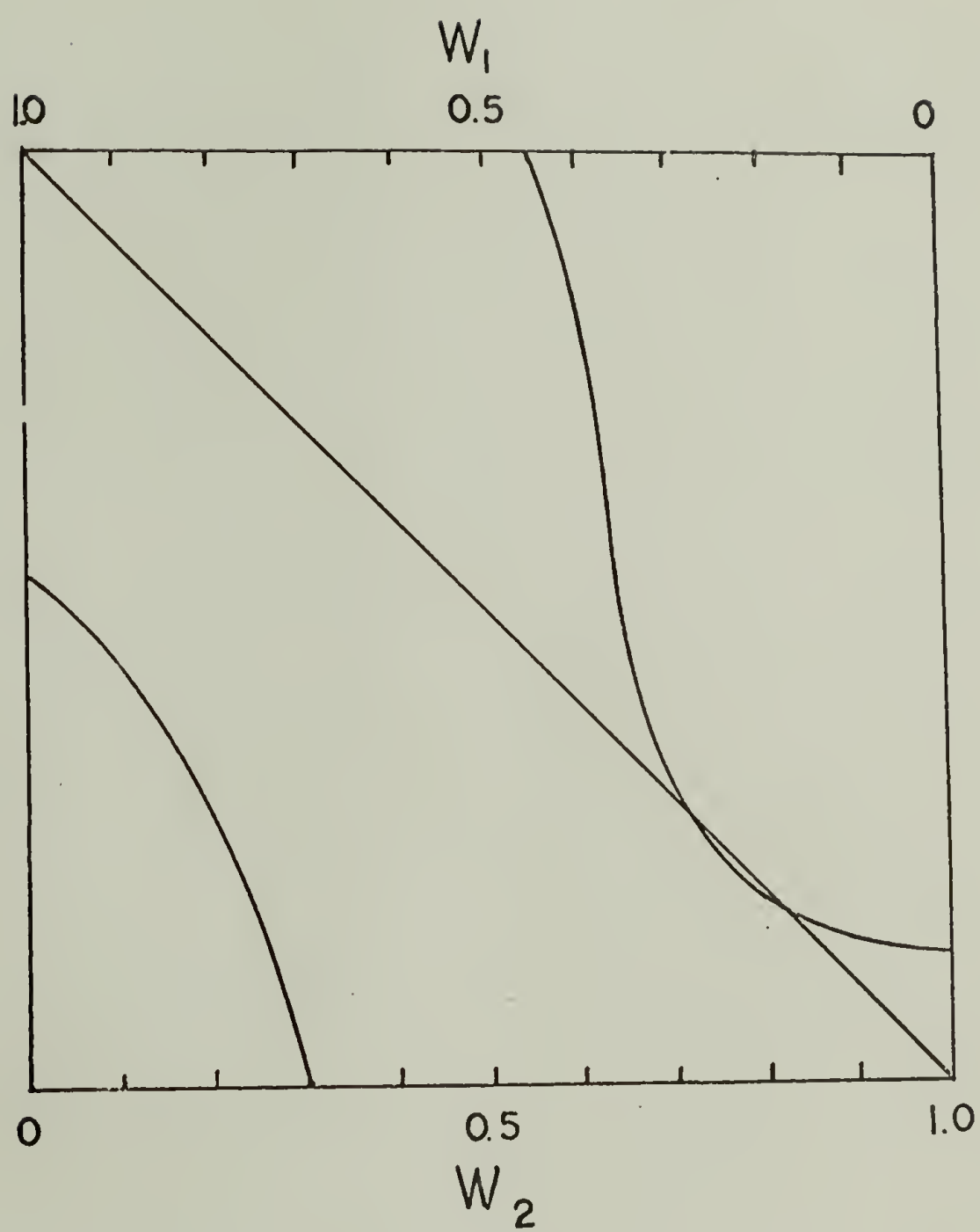


FIGURE 36

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