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ISOTHERMAL CRYSTALLIZATION OF POLYPHOSPHAZENES BY DSC
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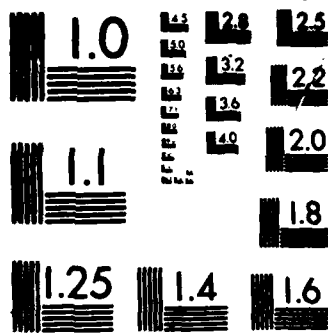
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ISOTHERMAL CRYSTALLIZATION OF POLYPHOSPHAZENES BY DSC:

PART I POLY-[BIS(TRIFLUOROETHOXY)PHOSPHAZENE], PBFP

Manuscript Prepared for 16th NATAS Conference, Sept. 27-30, 1987

by

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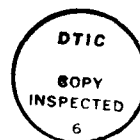
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Work has been conducted on the isothermal crystallization kinetics of poly-[bis(trifluoroethoxy)phosphazene], PBFP, and poly-[bis(phenoxy)phosphazene], PBPP, in both the T(1) and melting transition regions. This paper presents preliminary DSC results for PBFP's kinetics in the T(1) transition region. Avrami analysis of these data supports a two dimensional mechanism (n=2). An explanation of this morphology is presented.					
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Isothermal Crystallization of Polyphosphazenes by DSC:

Part I Poly-[bis(trifluoroethoxy)phosphazene], PBFP

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INTRODUCTION

Differential scanning calorimetry is well known as a technique for measuring the transition and transformation kinetics of homopolymers from the melt¹. Its application to thermotropic polymers is somewhat novel, there being very few examples in the literature. So far as we know this study represents the first measurements on the rate of isothermal crystallization of polyphosphazenes by DSC. Recently however, other techniques^{2,3} have been employed to study these materials, which exhibit several phase transitions^{4,5,6} upon heating and cooling in the DSC. Poly-[bis(trifluoroethoxy)phosphazene], PBFP, exhibits three thermal transitions, a glass transition, T_g , and two first order transitions. Upon reheating after melting, the first transition at $T(1)$ consists of a change from a three dimensional orthorhombic γ -form to a two dimensional hexagonal δ -form, followed by a melting transition, T_m , above which an isotropic phase exists. Extensive work has been done to determine the morphological texture and structure of PBFP and the changes that occur on heat treatment^{4,5,6}. However, we are not aware of any published work on the kinetics of isothermal crystallization by DSC in either of the $T(1)$ or T_m regions. This paper provides preliminary results on this issue in the $T(1)$ region.

Since the mechanism of isothermal crystallization seems to be invariant during most of the phase transformation, we have assumed that the familiar Avrami equation is an acceptable measure of the crystallization kinetics. The equation is:

$$1 - X(t) = \exp[-kt^n] \quad (1)$$

where k is a temperature dependent rate constant, n is the mode of nucleation and subsequent crystal growth, and $X(t)$ is the fraction of transformed material after some

time t . Since the transformation isotherms were constructed from enthalpy-time curves obtained under isothermal conditions, the $X(t)$ value at any time was defined as:

$$X(t) = \int_0^t (dH_t/dt) dt / \int_0^{\infty} (dH_t/dt) dt \quad (2)$$

where dH_t/dt represents the rate of evolution of heat at time t . The extent of the transformation at time t could therefore be simply reduced to:

$$X(t) = \Delta H_t / \Delta H_{\infty} \quad (3)$$

where ΔH_t is the total heat of the 2D to 3D transformation at time t , and ΔH_{∞} is the total heat for the 2D to 3D transformation.

Besides the kinetic aspects of crystallization, we also considered the general melting behavior of PBFP. For example, the nature and enthalpy of the T(1) transition for this polymer (i) solution crystallized and (ii) subsequently preconditioned in the thermotropic state is examined. Significant changes have been observed under heat treatment specified in this paper.

EXPERIMENTAL

Material: The Poly-[bis(trifluoroethoxy)phosphazene]⁷ used in this study was characterized by GPC and had a polydispersity index of less than 3.

Heat Treatment of Samples: In the kinetic studies, the samples were fused above T_m to eliminate or to control sample histories and then quenched at 40 K min^{-1} to room temperature. The samples were then heat treated as given in Cases 1 and 2 below.

DSC Measurements: Thermal measurements were made using a calibrated Perkin-Elmer DSC-2 interfaced with an IBM-PC for data acquisition. All runs were made under nitrogen using a dry-ice/ethanol bath as a coolant.

RESULTS AND DISCUSSION

Figure 1(a) shows the enthalpy change at the T(1) transition for a solution cast sample of PBFP. Whenever PBFP was preconditioned at 380 K (ie. 30 K above T(1)) and subsequently cooled at 20 K min^{-1} to selected crystallization temperatures, T_c 's, indicated in Figure 1(b), it was found that there were considerable differences in the magnitude of the enthalpy change at T(1) measured upon reheating the specimen. However, the position of the T(1) peak at 351 K is invariant. This behavior indicates that the nucleation from the thermotropic phase at 380 K is the same for each T_c studied, but the extent of crystallization decreases substantially as T_c is increased. Note that at T_c 's greater than 340 K, no detectable enthalpy change is observed on reheating (after crystallizing for 15 minutes). This does not exclude nucleation/crystallization at much longer times. This behavior strongly contrasts with isothermal crystallization in

homopolymers.

In the kinetic studies described here, two aspects of 2D to 3D isothermal crystallization of melt crystallized PBFP were involved. In Case 1 the sample was heated to 545 K (ie. 30 K above the melt temperature of the solution cast polymer) and annealed for 5 minutes. Afterwards the specimen was cooled at 40 K min^{-1} to the selected T_c , and the change in enthalpy, measured isothermally, was recorded. Two resulting curves are shown in Figure 2(a). Avrami plots of this data are shown in Figure 2(b). The Avrami parameters, the rate constant, k , and the nucleation parameter, n , are tabulated (see Table 1).

In Case 2 a previously melted sample was heated to 393 K and annealed for 5 minutes. Afterwards it was cooled at 40 K min^{-1} to a selected T_c and isothermal crystallization was carried out. Figure 3(a) illustrates several isothermal plots made under these conditions. Avrami plots are shown in Figure 3(b), and the parameters are again listed in Table 1. The k and n values were generated using linear least square regression. For all results correlation coefficients of greater than .99 were obtained.

The n values in Table 1 suggest that a two dimensional mechanism of transformation is associated with the crystallization from the 2D thermotropic state to the 3D state. A transitional map of the overall physical changes in PBFP, verified by DSC and X-ray and electron diffraction, are shown in Figure 4 for reference purposes.^{8,9} Since the 2D state is considered to be a chain extended $\sqrt{3}$ -hexagonal phase, the transformation to the 3D, $\sqrt{3}$ -orthorhombic form, may be explained by growth in two directions transverse to the chain direction, with minor translation along the chain itself as the 2D to 3D transformation occurs. The high levels of crystallinity attained under such conditions via this route supports this mechanism.^{2,4}

Figure 5 is a clear example of the increase in crystallization enthalpy associated with the different heat treatment conditions described in Cases 1 and 2. Higher $T(1)$'s and $\Delta H[T(1)]$'s are noted on heating for Case 1 compared to Case 2. Therefore similar thermal histories prior to crystallization in the 2D to 3D region give rise to the same $T(1)$ peak position in line with the extent of crystallization. However changing the thermal history prior to 2D to 3D crystallization can substantially effect the $T(1)$ peak position and the extent of crystallization.

Of course, more convincing results on the mode of nucleation/growth should come from work on fractionated specimens now being prepared. Uncertainties arising from the inherent distribution of chain lengths in bulk materials may be minimized or even eliminated in this way. Other crystallization paths will also be explored kinetically.

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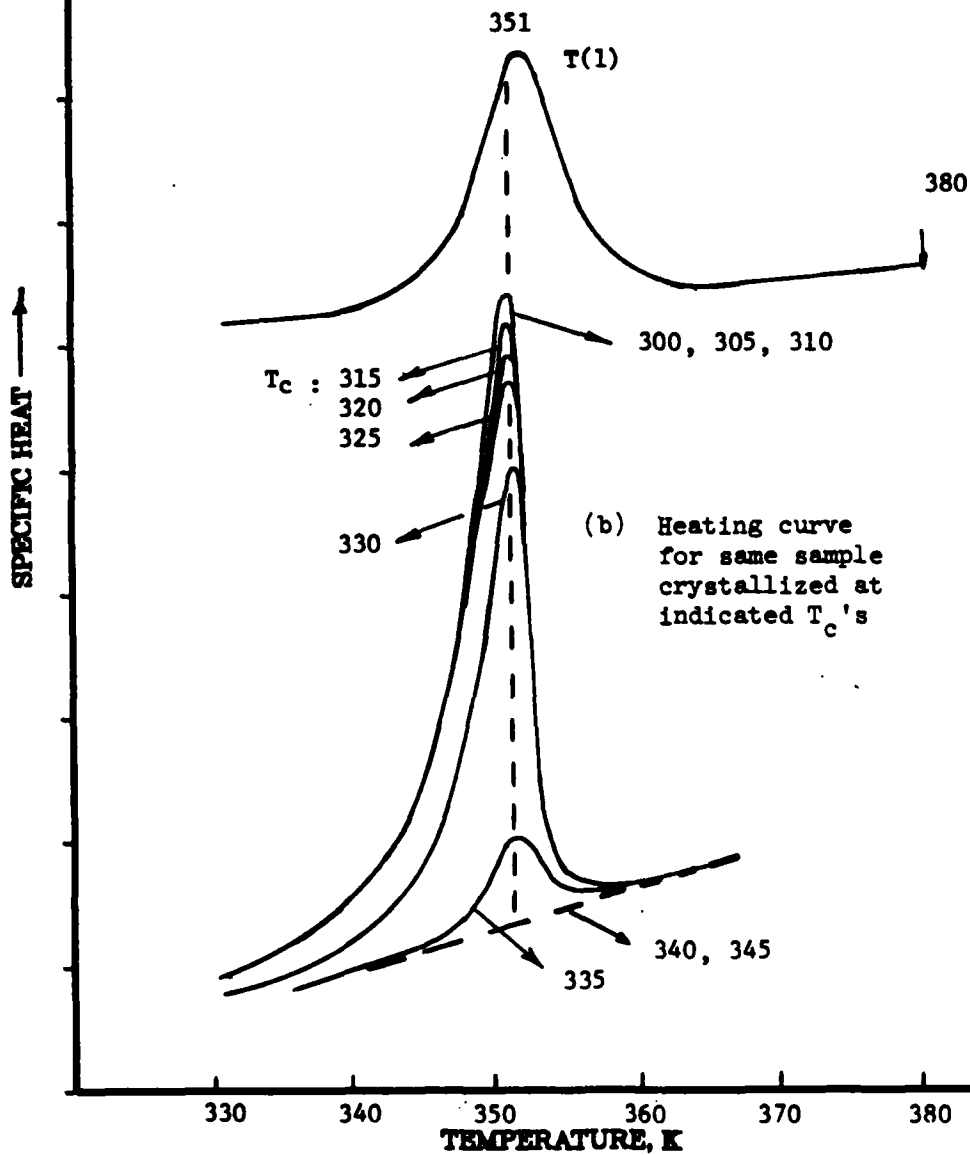
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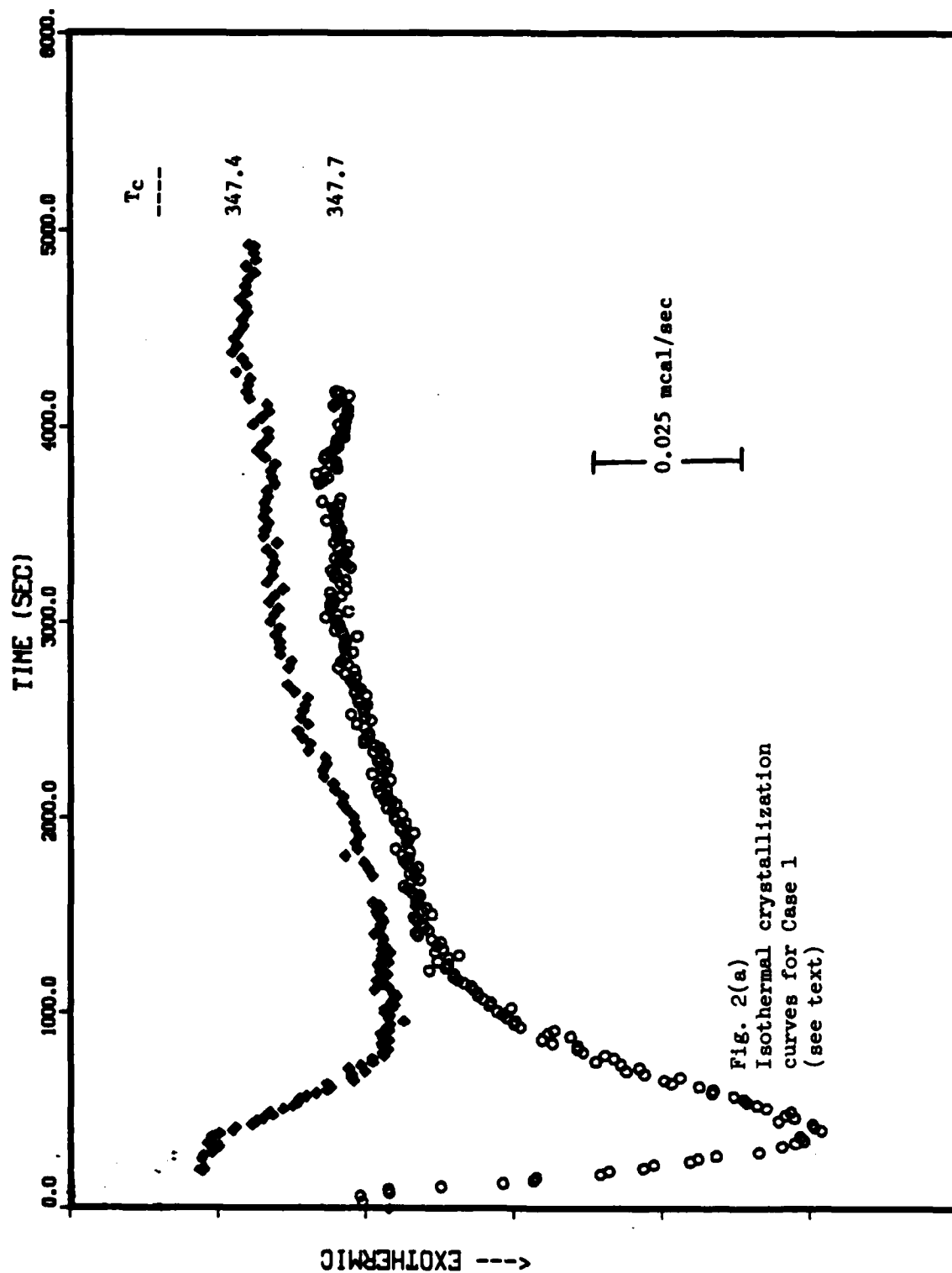
1. B. Wunderlich, "Macromolecular Physics", vol. 2, Academic Press, New York, 1976.
2. T. Masuko, R. L. Simeone, J. H. Magill and D. J. Plazek, *Macromolecules*, 17, 2857(1984).
3. J. H. Magill and C. Rieckel, *Makromol. Chem. Rapid Comm.*, 7, 287(1986).
4. D. C. Sun and J. H. Magill, *Polymer* (to be published 1987).
5. M. Kojima and J. H. Magill, *Makromol. Chem.*, 186, 649(1985).
6. M. Kojima, H. Satake, T. Masuko, and J. H. Magill, *J. Materials Sci.*, 6, 775(1987)
7. T. Masuko, private communication.
8. J. H. Magill, J. Petermann, and U. Rieck, *Colloid and Polymer Sci.*, 264, 570(1986).
9. M. Kojima and J. H. Magill in "Morphology of Polymers" (ed. B. Sedláček), p.435, Walter de Gruyter and Co., Berlin and N. York, 1986.

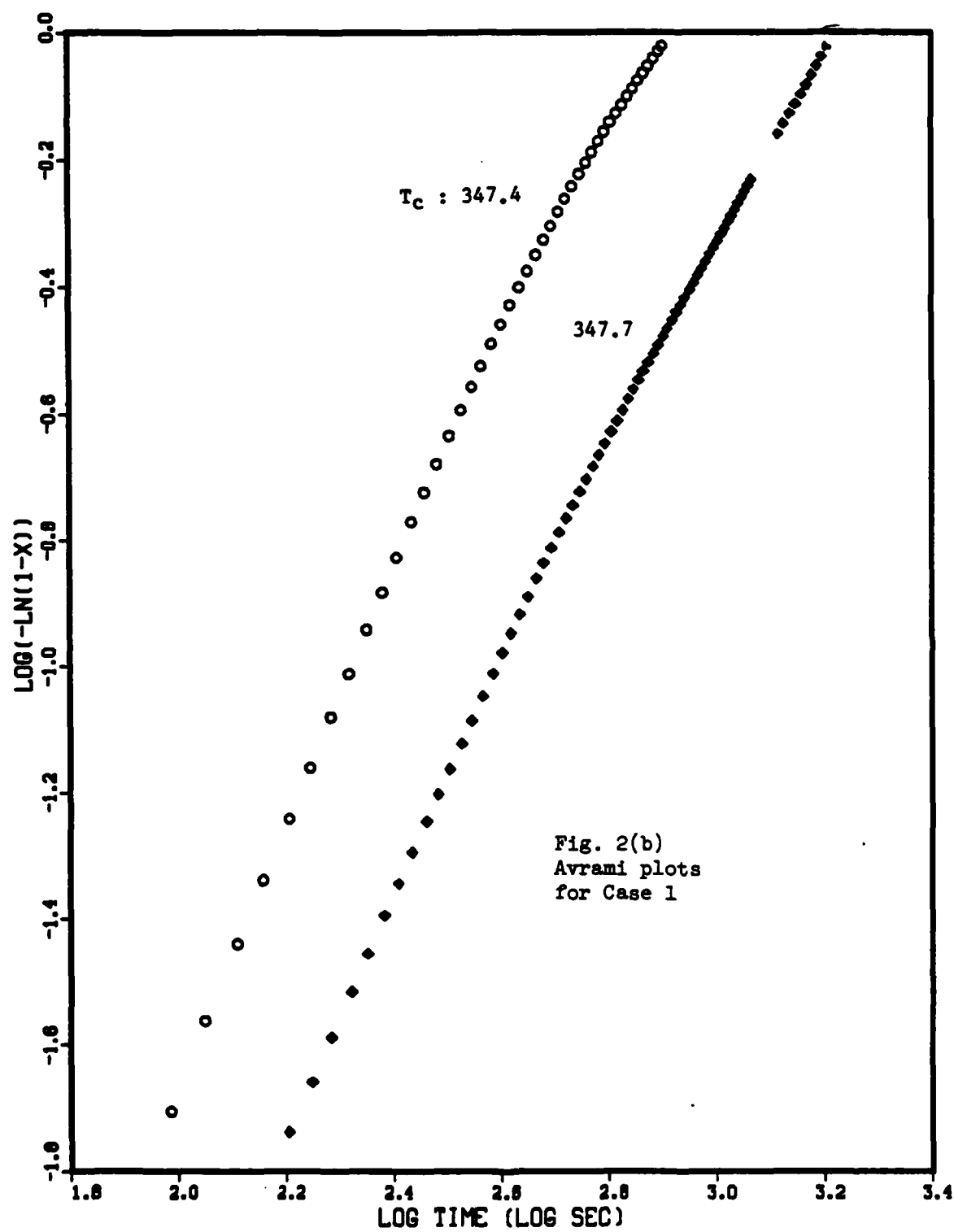
PBFP 6.02 mg
(soln. poly.)

Fig. 1

(a) Heating curve
of solution
cast. Sample







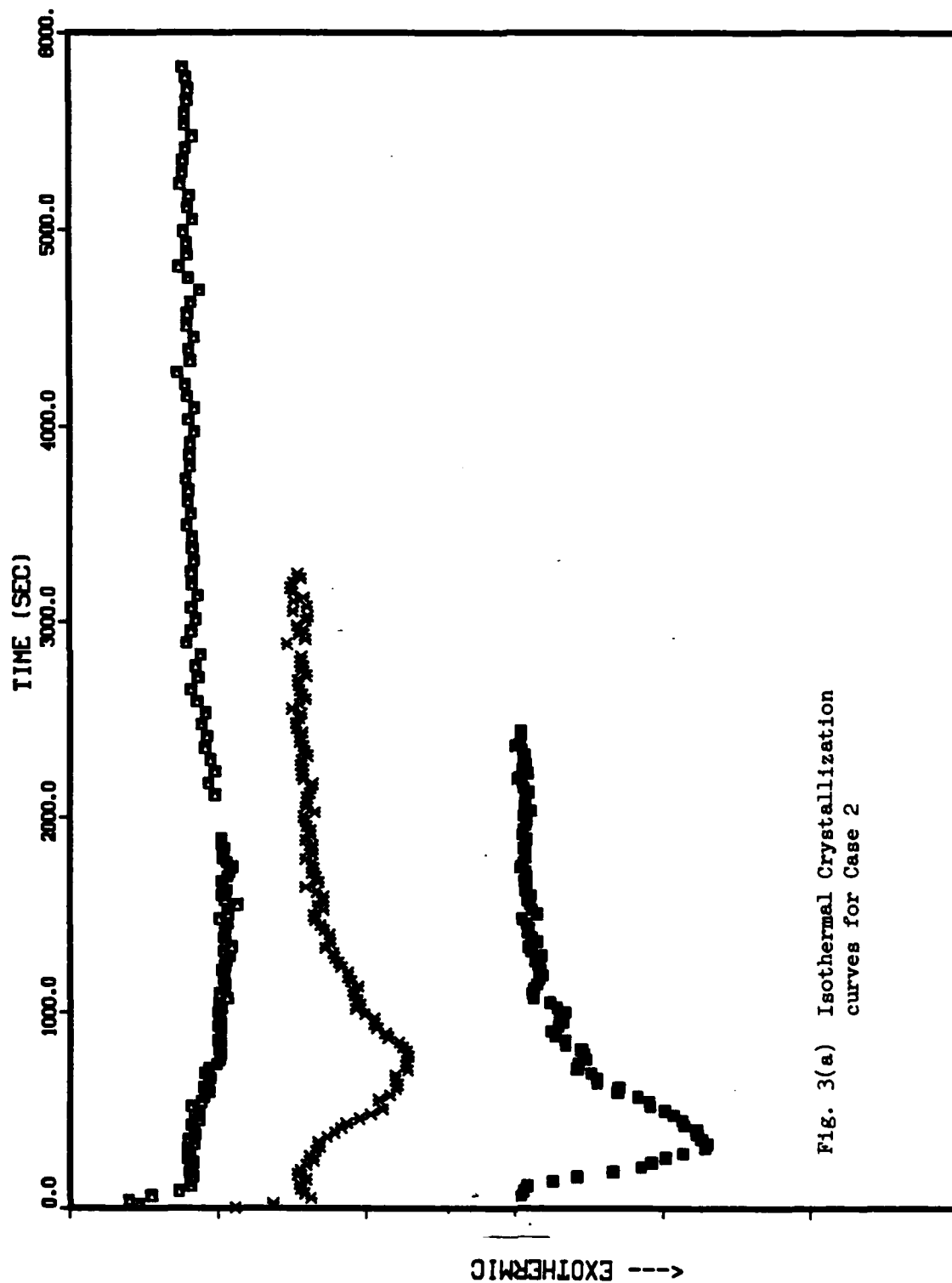


Fig. 3(a) Isothermal Crystallization curves for Case 2

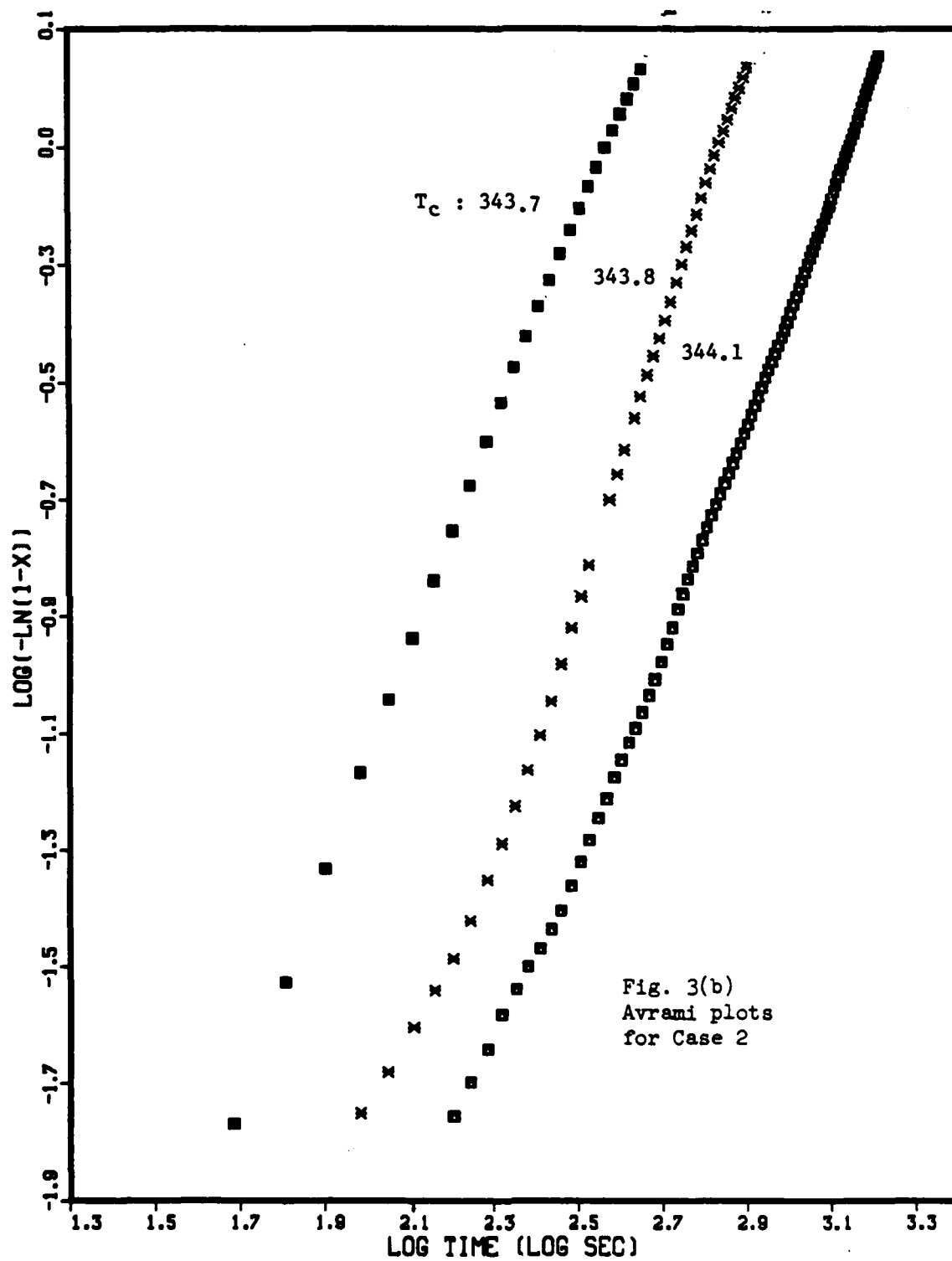


Fig. 3(b)
Avrami plots
for Case 2

TRANSITIONS IN PBFP

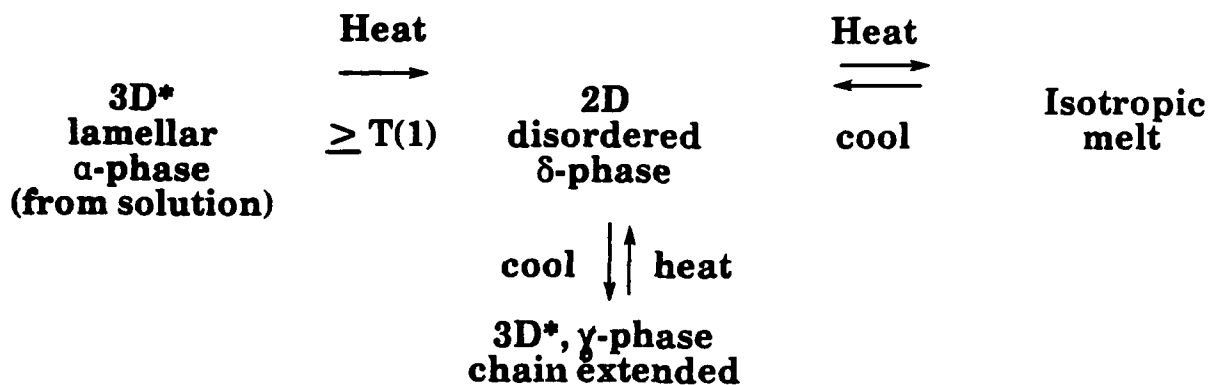


Figure 4

*Crystallographically 3D (γ -phase) is equivalent to chain extended α -phase although subtle morphological difference exist because of thermodynamic paths involved.

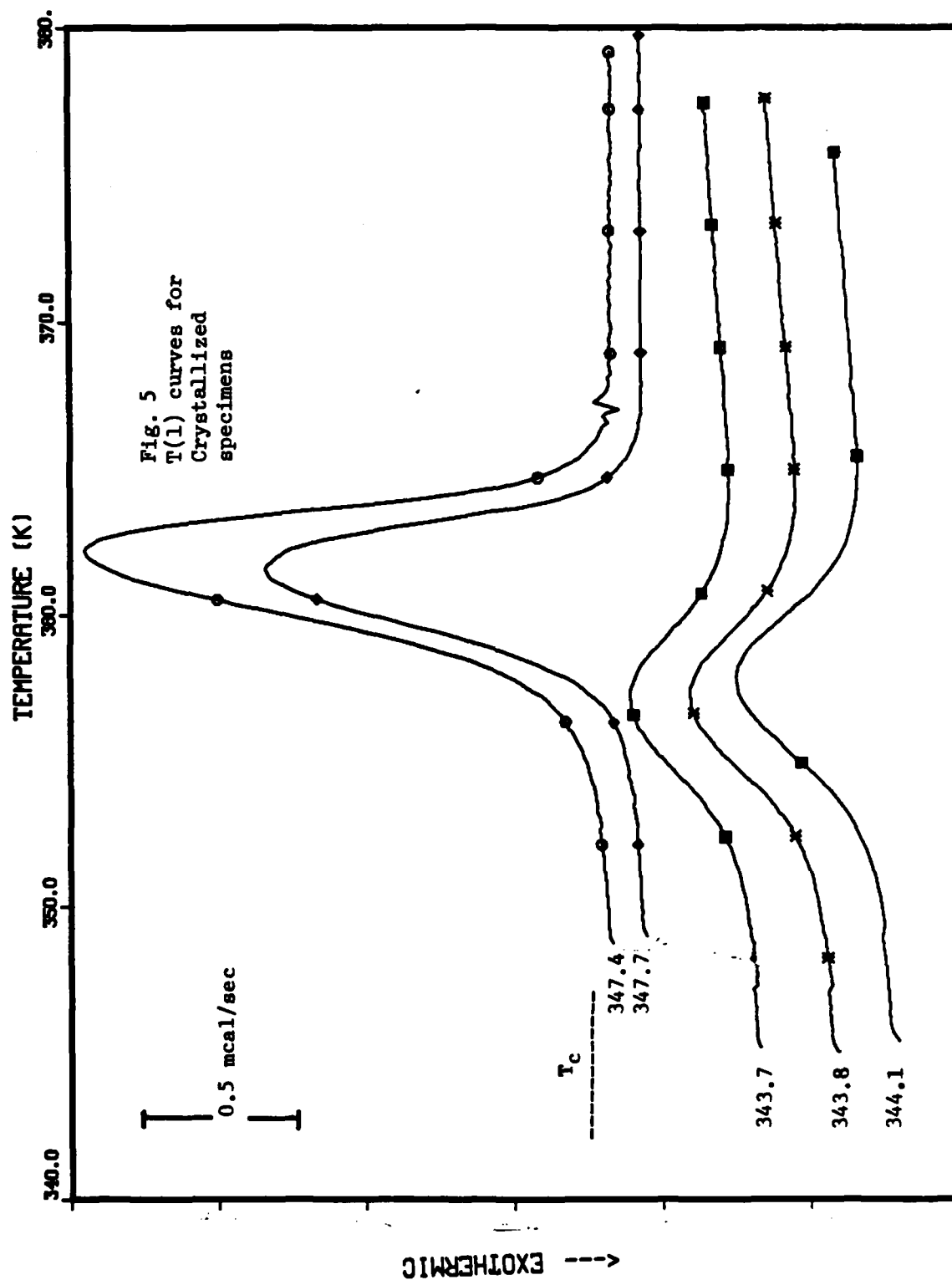


Table 1 Avrami Parameters

Case 1

T_c, K	$k, \text{sec}^{-n} \times 10^6$	n	$T(1), K$
347.4	3.04	1.9	363.1
347.7	3.26	1.9	363.4

Case 2

343.7	13.9	1.9	357.3
343.8	0.51	2.2	357.5
344.1	0.97	1.9	358.0

T_c denotes the transformation temperature

k the rate constant for the isothermal transformation

n the mode of nucleation

$T(1)$ the thermotropic transition temperature

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