DAA/ LANGLEY

17P.

IN - 31459

# THE CRYSTALLIZATION OF TOUGH THERMOPLASTIC RESINS IN THE PRESENCE OF CARBON FIBERS

Grant number - NAG-1-525 S-1

Semi-Annual Progress Report
November 1,1985 to May 1, 1986

submitted by

Dr. Michael H. Theil, Principal Investigator
School of Textiles
Box 8302, North Carolina State University
Raleigh, NC 27695-8302

submitted to

Dr. Noel T. Wakelyn
Technical Officer
MD M/S 226B
National Aeronautics and Space Administration
Langley Research Center
Hampton, VA 23665

(NASA-CR-179810) THE CRYSTALLIZATION OF TOUGH THERMOPLASTIC RESINS IN THE PRESENCE OF CARBON FIBERS Semiannual Progress Report, 1 Nov. 1985 - 1 May 1986 (North Carolina State Univ.) 17 p CSCL 11G G3/27
N87-11006
Unclas
43790

## I. Introduction

Efforts in the past half year were devoted to studying the crystallization kinetics of the thermoplastic resins poly(phenylene sulfide) (PPS) and poly(aryl-ether-ether-ketone) (PEEK) in the presence and in the absence of carbon fibers. Our objectives have included the determination of how carbon fiber surfaces in composites affect the crystallization of tough thermoplastic polymers that may serve as matrix resins. The crystallization kinetics of such substances can provide useful information about the crystallization mechanisms (1) and, thus, indicate if the presence of carbon fibers cause any changes in such mechanisms.

## II. Crystallization Kinetics

### A. Isothermal crystallization studies of PPS

### 1. Experimental

### a. Materials

The neat PPS used was Phillips Petroleum's Ryton MR03 molding grade resin. The composite samples used were cut from a panel prepared at the Polymeric Materials Branch at NASA's Langley Research Center. It was designated GD441.

### b. Procedures

Crystallizations of the neat resin and of the of the composite samples were each conducted in two different temperature ranges. The low temperature range, in the vincinity of 395 K, was below that temperature at which PPS crystallizes the fastest ($T_{max}$).

The high temperature range, in the vicinity of 495 K, is above $T_{max}$.

Prior to each low temperature isothermal crystallization of the neat resin, a fresh sample was prepared by heating the powdered polymer as received in a furnace for two minutes at 343 °C. The polymer so heated was then quenched to the nearly amorphous state by quickly plunging it into ice water. At this point the fused, quenched polymer was clear, but of uneven shades of amber. The less discolored regions of the polymer were selected for differential scanning calorimetry (DSC) crystallization experiments.

The composite samples crystallized at low temperatures were cut from the GD441 sample with a razor blade and a coping saw. These samples were preheated for 5 minutes at 343 °C before quenching. Otherwise they were treated in the same manner as the neat polymer.

The quenched samples were encapsulated in DSC sample pans and placed in the sample head of a DSC-2C differential scanning calorimeter. They were heated to a predetermined isothermal crystallization temperature at 320 °C/min. The power required to maintain the sample pan holder at the same temperature as the reference pan holder was recorded by the DSC-2C system as a function of time. Data thus acquired was analyzed for extent of the phase transformation as a function of time.

High temperature crystallizations were conducted in much the same way as the low temperature crystallizations with the following differences: 1) Samples were conditioned in their aluminum sample pans at 327 °C and then cooled to the isothermal crystallization temperature ($T_c$) at 320 °C/min 2) Samples crystallized at high temperatures could be reused. The high temperature crystallizations of fresh samples reproduced well the crystallizations of samples that had been crystallized several times previously.

## 2. Results

Our isothermal crystallization studies of Ryton MR03 as a neat resin and as a component of composites, *i.e.*, in the presence of carbon fibers, have been conducted at a number of isothermal crystallization temperatures. We herewith report some preliminary findings.

Figure 1 compares the crystallization rates of the neat resin with those of the composite over a range of crystallization temperatures. They are given as time required for a given isothermal crystallization to reach its maximum rate, which is the time at which an isothermal DSC scan becomes most highly exothermic. Our results show that the composite always crytallizes faster than the neat resin. We currently have the greatest amount of data for crystallizations performed above $T_{max}$. It is seen that crystallizations of PPS in the composite occur at about the same rate as in the neat resin when the composite's temperature is 15° above that of the neat resin. Thus, the neat resin must be supercooled by that much more than the composite in order for the polymer to crystallize at an equivalent rate. This is a highly significant difference. Our more limited low temperature data indicate that the composite's PPS crystallizes more readily below $T_{max}$ as well. In this case, where the melt viscosity makes an important contribution to the crystallization rate, we see the composite crystallizing as fast as the neat resin when it is at a lower temperature than the neat resin.

Johnson and Mehl (2), Avrami (3), and Evans (4) developed a phenomenological treatment for the kinetics of a nucleation governed phase change. An equation which bears Avrami's name

$$X = \exp\{-k't^{n}\}$$

describes such a transformation. Here $X$ is the mass fraction of a phase that is untransformed at time $t$. The modified rate constant $k'$ is related to a rate constant $k$ by a proportionality constant that allows for the fact that total crystallinity is not usually attained in synthetic polymers. Also, $k'$ contains parameters that are concerned with nucleation frequency, the relative densities of the phases involved, the geometry of the growing center, and the growth vectors in the directions of growth. The value of the exponent of time $n$ is a function of the types of nucleation and growth as well as the growth habit of the developing phase. A value of three, for example, could be indicative of a non-diffusion controlled nucleation mechanism in which the embryonic crystallites all begin to grow at the beginning of the crystallization process (1).

Rate data that we obtained from DSC in terms of the fractional extent of the total transformation experienced as a function of time has been analyzed as indicated by the Avrami equation. The equation as writtten above was plotted in double logarithmic form yielding linear plots. Figures 2 and 3 are, respectively, Avrami plots for isothermal crystallizations of the composite conducted at 390 K and at 500 K. The symbol $C$ in thse plots is equivalent to $1 - X/X_o$, the overall fraction of crystallizable polymer that has crystallized at time $t$. The temperatures chosen (given here as uncorrected values) were close to, but not identical to the crystallization temperatures previously given in Avrami plots for the neat resins. From the slope of these plots it can been seen that $n$ has a value of 3.0 for the neat resin's crystallization, and 2.6 for the composite sample's crystallization. The results for the composite and the neat resin are summarized in Table I.

Table I

The $n$ Parameter for Isothermal Crystallizations

| | $n$ | |
|---|---|---|
| $T_c$, K* | Neat Resin | Composite |
| 390 | – | 3.7 |
| 395 | 3.2 | – |
| 405 | 3.6 | – |
| 475 | 3.0 | – |
| 485 | 3.0 | – |
| 490 | 3.0 | – |
| 495 | 3.1 | – |
| 500 | 3.0 | 2.6 |
| 505 | 3.8 | 2.9 |
| 510 | – | 2.8 |

* The horizontal line below 405 K is a divsion between low temperature crystallizations and high temperature ones. See text.

These preliminary results indicate that carbon fibers alter the mechanism of crystallization in the high temperature crystallization region but not at low temperatures. Previous results have indicated that the presence of carbon fibers can orient adhering amorphous PEEK. Kim and Mandelkern reported that the value of *n* decreased with increasing extension ratio in natural rubber networks (5). Perhaps we are seeing this kind of influence on the crystallization of PPS selectively at the higher temperature region, thus lowering *n*. Another possibility is that the nucleation of PPS in the composites is enhanced by carbon fiber surfaces that come in contact with crystallizable PPS segments. The carbon fiber surfaces would be more influential in facilitating nucleation at the high temperatures where rates are sensitive to surface free energies rather than at low temperatures where crystallization rates are diffusion controlled. Such a hypothesis is supported by the fact that the composite crystallization rates are enhanced more in the high temperature range than in the low temperature range. The fact that *n* for the composite changes to a lower value when $T_c$ is shifted to the high temperature range could either mean that diffusion is becoming a rate limiting step in transporting crystallizing chains to the carbon fiber surfaces where they can crystallize rapidly or that the growth habit of the transformed phase is other than isotropically three-dimensional. Further experimental work and thought is needed to verify and perhaps to explain these findings. The rate constants $k'$ can be determined from the intercepts of the Avrami plots, but intercomparison of them is meaningful only when *n* does not change from case to case When sufficient data is obtained the $k'$ values will be intercompared and temperature coefficient analyses will be conducted where it is meaningful.

## B. Isothermal crystallization studies of PEEK

### 1. Experimental

#### a. Materials

The neat resin used was obtained from the Polymeric Materials Branch of NASA's Langley Research Center. It had been manufactured by ICI and was designated Grade 450G, Batch # SPG 9-30G. It was used as received.

Composite samples had been cut from APC-2 composite panels manufactured by ICI at the request of NASA's Langley Research Center.

#### b. Procedures

Preliminary studies of the rate of isothermal crystallization of PEEK have been done by DSC at $T_c < T_{max}$. PEEK samples were heated to 390 K, maintained at that temperature for several minutes, and then quench cooled in liquid nitrogen. They were then heated rapidly in the DSC-2C to a preselected $T_c$ that was below the temperature of maximum crystallization rate for the polymer.

### 2. Results

The shallow exothermic peaks obtained show some promise of quantitative interpretation. However, results to date are in their very early stages. Encouraged by our productive efforts with PPS, we intend to resume quantitative isothermal crystallization kinetic studies on PEEK and its composites in the near future.

## C. Non-isothermal Crystallization Studies

We have recognized that although most polymer crystallization kinetics studies have been carried out isothermally, industrial practices that lead to polymer crystallization generally proceed under non-isothermal conditions. While the analysis of a non-isothermal crystallization is more complicated than that for a isothermal one, the non-isothermal experiment is actually easier to perform on the DSC-2C.

### 1. Experimental

The PEEK samples and pellets of composites made with PEEK that were used in these experiments were described above in II.B. The samples were prepared for their non-isothermal crystallizations in much the same way that the preliminary treatments were performed prior to the iosthermal crystallizations. The samples were then cooled in the high temperature range or heated in the low temperature range at a constant rate that was precribed for each experiment.

### 2. Results

In some non-isothermal crystallizations, neat PEEK's crystallization behavior was compared qualitatively to that of APC-2, ICI's designation for a composite made with AS-4 carbon fibers and PEEK. Preliminary results indicate that the onset of crystallization of APC-2 occurred sooner, i.e., at higher temperatures than did the PEEK. While the temperature coefficients for the two appeared to be similar, the earlier crystallization of the APC-2 is suggestive that carbon fibers may be facilitating the crystallization of PEEK in the composite.

We have conducted a series of non-isothermal crystallizations of PEEK over a wide range of controlled cooling rates that are available on the DSC-2C. Ziabicki has presented a quite general phenomenological analysis of the effects of non-equilibrium conditions on a polymer crystallization process (6), but we feel that our experimental conditions allow for analysis by the less general but more structured method of Ozawa (7). We have analyzed and plotted our data according to Ozawa; at this stage the results obtained with PEEK have not yielded the expected linear plots. The curved plots may be indicative that the crystallization mechanism of our PEEK samples is changing with temperature.

As mentioned above, we have good indication from isothermal experiments that the mechanism for the crystallization of PPS does not change over a 100° temperature range. Thus, we are optimistic that we may obtain meaningful, linear Ozawa plots for PPS. Work in this area is about to proceed.

## III. Summary

This progress report cites the following accomplishments:

1) We have developed the capability for measuring the crystallization kinetics of PPS and its composites in a meaningful

and consistent way at temperatures both below and above $T_{max}$.

2) We find that the crystallization of PPS in composite samples occurs more readily than it does as a neat polymer at given temperatures.

3) Data obtained for crystallizations conducted at optimal conditions have been plotted and analyzed according to the Avrami equation. The analyses suggested that the nucleation for the crystallization of the neat resin obeys the same mechanism at both low and high crystallization temperatures. The value of approximately 3 is suggestive of a process in which the embryo nuclei are already present at the beginning of a three-dimensional process. The disparate values of $n > 3$ for crystallizations of the composite at low temperatures and $n < 3$ for low temperature crystallizations of the composite suggests a change in mechanism with temperature. The alternative possibilities of orientation effects by the carbon fibers upon the polymer prior to crystallization or nucleation effects by the carbon fiber surfaces merit consideration and further investigation.

4) Qualitative findings concerning the crystallization kinetics of PEEK resins and of PEEK in composites are showing that the presence of carbon fibers enhances the rate of crystallization of that polymer.

## IV. Future Work

We still need to learn more about the stability of crystalline PEEK. Not only is it important to learn how crystallization conditions affect the melting point and the morphology of PEEK, but we must address ourselves to the potentially troublesome problem suggested by the dual endotherms that this polymer can exhibit (8-10). We have observed behavior in PEEK that strongly suggests that heating the polymer at temperatures more than 75 °C below its practical melting temperature for brief periods of time can detectably alter its crystalline phase. We will study this phenomenon in neat polymer in some detail and try to learn its basis. From knowledge so gained we may be able to deduce how to control the crystallization to best advantage by modifying processing conditions.

Another phenomenon that could cause instability of the crystalline phase below its melting point could be an order-disorder transition associated with the creation or disappearance of what some investigators call a superlattice (see above). Such a phenomenon, if it exists in this system, could be associated with the dual endotherm. However, it is not likely that this kind of order-disorder transition would be a necessary condition for a dual endotherm to exist. Poly(ethylene terephthalate) has never been considered to be likely to undergo the isomorphous substitution that must be a prerequisite for the order-disorder transition we have been discussing, yet it can display a dual endotherm.

We will continue to develop the theory of the order-disorder transition in $(AAB)_n$ type polymers. If theoretical predictions show promise, we will look for such an order-disorder transition experimentally.

A knowledge of crystallization kinetics is essential to the understanding of how to properly fabricate composite structures using these crystallizable matrix resins. To this end we are developing a high temperature dilatometry system that will be able to monitor the crystallization kinetics of PEEK at tmeperatures close to its melting point. Our dilatometers will employ gallium as the the confining liquid rather than the more volatile mercury. Problems encountered in handling this easily oxidizable metal are being addressed and should soon be overcome. A fluidized bed, thermostatted bath is being purchased and assembled for the purpose of conducteing these high temperature crystallizations. Combined with DSC we should have the capability of conducting crystallization kinetics studies over a broad temperature range, thus leading to meaningful practical and fundamental information about the crystallization of these tough thermoplastic resins both in the presence and in the absence of carbon fibers.

Fiber breakage tests are planned in order to learn how the nature and the extent of crystallinity of the matrix resin affects resin to fiber adhesion.

## V. References

1. L. Mandelkern, "Crystallization of Polymers", McGraw-Hill, New York, 1964, Chap. 8.

2. W. A. Johnson and R. F. Mehl, Trans. Amer. Inst. Mining Met. Engrs., 135, 416 (1939).

3. M. Avrami, J. Chem. Phys., 7, 1103 (1939); 8, 212 (1940); 9, 177 (1941).

4. R. U. Evans, Trans. Farady Soc., 41, 365 (1945).

5. H. Kim and L. Mandelkern, J. Polym. Sci. A-2, 6, 181 (1968).

6. A. Ziabicki, Colloid & Polym. Sci., 252, 207 (1974); A. Ziabicki, ibid., 433 (1974).

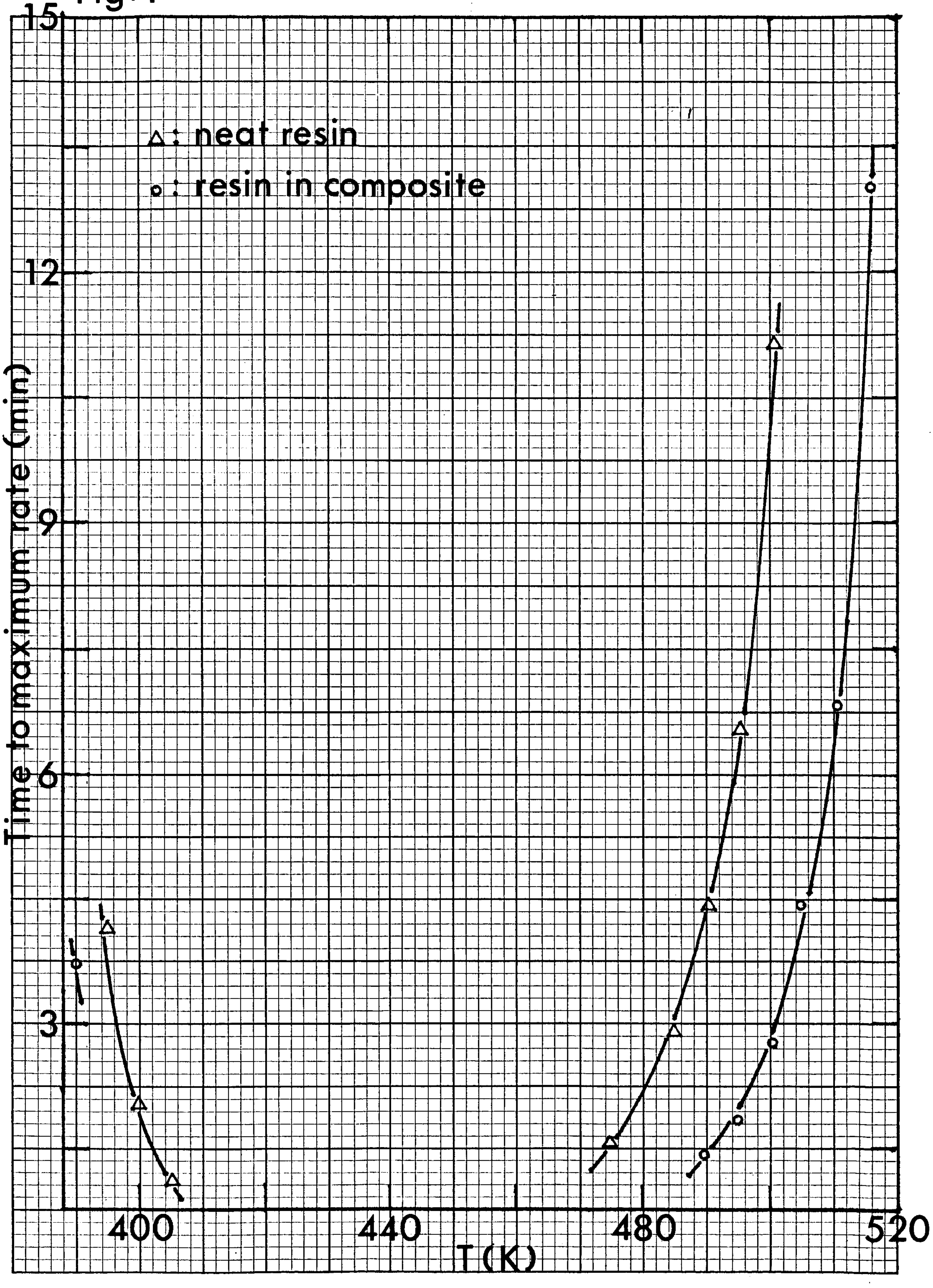
7. T. Ozawa, Polymer, 12, 150 (1971).

8. D. J. Blundell and B. N. Osborn, Polymer, 24, 953 (1983).

9. M. H. Theil and T. Towell, North Carolina State University, report, Thermal Analysis of Composite Samples Made with PEEK Thermoplastic Resin, submitted to N. J. Johnston, NASA, Langley Research Center, July 1985.

10. M. H. Theil, North Carolina State University, Semi-Annual Report of Work Done on NAG-1-525, The Crystallization of Tough Thermoplastic Resins in the Presence of Carbon Fibers, submitted to NASA, June 1985.

Fig. 1



△ : neat resin
○ : resin in composite
Time to maximum rate (min)
15
12
9
6
3
400
440
480
520
T(K)

Fig. 2

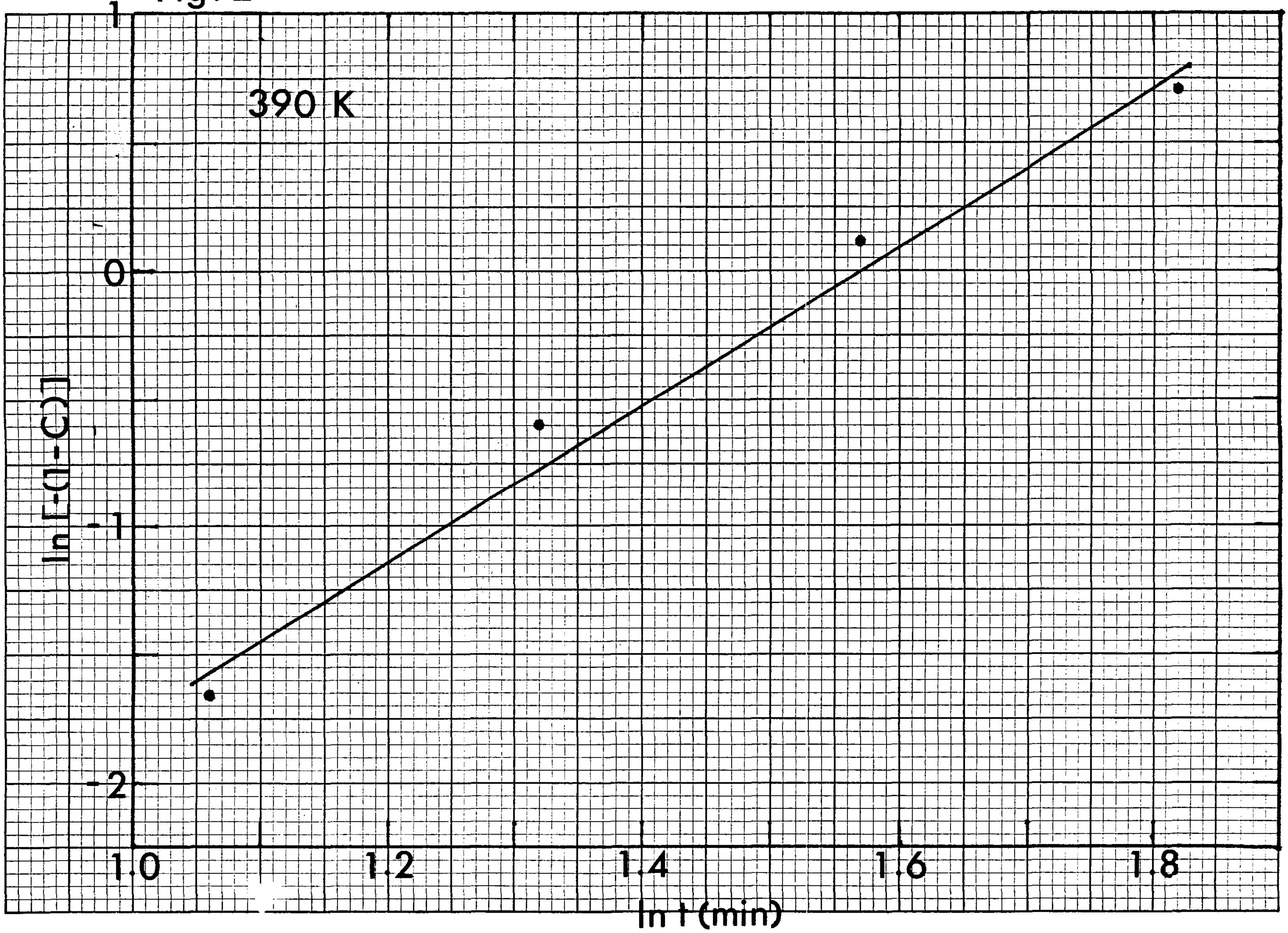


Fig. 3