# Crystallization Kinetics of Polyaryl Ether Ketones*

J. P. JOG and V. M. NADKARNI†, *Polymer Science and Engineerng Group, Chemical Engineering Division, National Chemical Laboratory, Pune 411 008, India*

## Synopsis

The crystallization kinetics of a grade of polyaryl ether ketone has been investigated over a temperature range of 295–315°C by differential scanning calorimetry. The results of the present investigation are compared with other members of the polyaryl ether ketone family in the context of the effect of chemical structure on the crystallizability of the polymers. It is concluded that the crystallizability is reduced with increasing amount of ketone linkages in the chain, and therefore the optimum molding conditions for different grades of polyaryl ether ketones will be different.

## INTRODUCTION

The polymers containing paraphenylene units linked by ether and ketone linkages are termed polyaryl ether ketones, and they represent a family of engineering plastics with exceptional thermal, chemical, and mechanical properties. The synthesis and thermal properties of these polymers are reported in the literature.[1,2] They are crystalline thermoplastics with high melting points between 320° and 365°C. The thermal properties of the polymers can be manipulated by varying the sequence and relative amounts of the ether and ketone linkages in the polymer chain,[2] as illustrated in Table I. Because of their thermal stability and excellent mechanical properties, polyaryl ether ketones are prime candidates for use in high-performance composites reinforced with carbon fibers.

Injection molding is the most common process used for manufacturing engineering components of polymeric materials. The mechanical properties and the dimensional stability of the molded part depend on the morphology of the polymer formed during the molding cycle. Therefore, a prior knowledge of the crystallization behavior of the polymer is necessary for optimizing the molding parameters such as the mold temperature and cycle time.

The rate of crystallization of polyaryl ether ketones would be expected to be different for various members of the family, because the sequence and relative amounts of the ether and ketone linkages would affect the chain flexibility and therefore, the molecular mobility. As the ratio of the ketone to ether linkages increases, the chain flexibility and mobility would be reduced.

The present work reports the isothermal crystallization kinetics of one member of the polyaryl ether ketone family studied by differential scanning

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* NCL Communication No. 3432.
† To whom correspondence should be addressed.

TABLE I
Effect of Chemical Structure on the Thermal Properties of Polyaryl Ether Ketones

| Structure no. | Polymer repeat unit | Melting point, $T_m$ (°C) | Glass transition temp. $T_g$ (°C) | Ratio of ketone to ether linkages |
|---|---|---|---|---|
| 1 | —O—$\phi$O—$\phi$CO—$\phi$(PEEK)[a] | 335 | 144 | 0.50 |
| 2 | —O—$\phi$O—$\phi$CO—$\phi$ + —O—$\phi$—CO—$\phi$— | 345 | 154 | 0.66 |
| 3 | —O—$\phi$O—$\phi$CO—$\phi$CO—$\phi$ | 358 | 154 | 1.00 |
| 4 | —O—$\phi$—CO—$\phi$ (PEK)[a] | 367 | 154 | 1.00 |
| 5 | —O—$\phi$—CO—$\phi$—CO—$\phi$—O—$\phi$—CO—$\phi$ | 383 | — | 1.50 |
| 6 | —O—$\phi$—O—$\phi$—$\phi$—CO—$\phi$— | 416 | 167 | 0.50 |

[a] PEEK, polyether ether ketone; PEK, polyether ketone.

calorimetry (DSC). The observed thermal and crystallization characteristics of the polymer are compared to those of another member of the family with a different sequence of ketone to ether linkages, reported by Blundell and Osborn.[3]

## EXPERIMENTAL

The polymer pellets used for the present study were obtained from Imperial Chemical Industries Ltd. (UK) under the trade name Victrex PEEK. The polymer sample was first characterized by DSC (Fig. 1). The melting temperature and the glass transition temperature were found to be 355°C and 150°C, respectively, at a heating rate of 10°C/min. The heat of fusion of the polymer was found to be 7.87 cal/g.

The crystallization isotherms were obtained over a temperature range of 295–315°C with DSC scans in the cooling mode. The polymer sample (5–7 mg) was heated to 375°C and held at that temperature for 5 min to destroy any residual nuclei. Then it was cooled at a rate of 160°C/min to the predetermined crystallization temperature, $T_c$ at which the exothermic crystallization peak was recorded. The details of the experimental procedure are reported by the authors elsewhere.[4]

## RESULTS AND DISCUSSION

The isothermal crystallization curves were analyzed by the Avrami equation:[5]

$$(1 - X_t) = \exp(-kt^n) \tag{1}$$

where $X_t$ is the weight fraction of the material crystallized at time $t$, $k$ is the rate constant, and $n$ is the Avrami exponent.

The extent of crystallization completed at a fixed time was determined from point-by-point area measurements of the crystallization peak, with the assumption that the fractionial crystallization at a given time is proportional to the ratio of the crystallization peak area (up to that time), to the total peak area. The crystallization half-time, $t_{0.5}$, and the Avrami
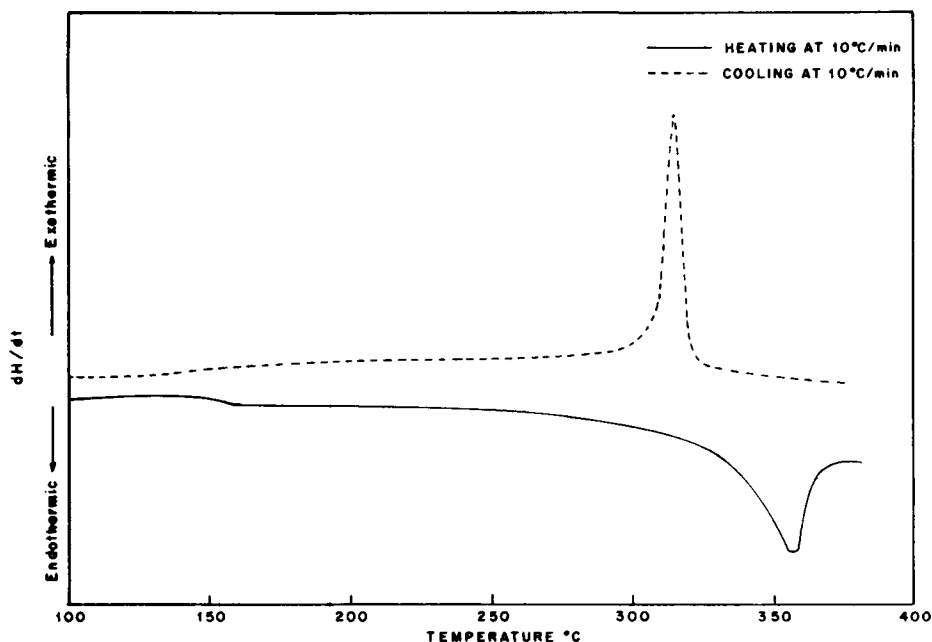
Fig. 1. DSC scan for polyaryl ether ketone (polymer I).

exponent, $n$, were determined from the Avrami plots. The rate constant $k$ was then calculated using the following equation

$$k = \frac{\ln 2}{(t_{0.5})^n} \tag{2}$$

where $t_{0.5}$ = crystallization half-time and $n$ = Avrami exponent.

The results are presented in Table II, and the crystallization half-time data are reported in Figure 2. The average value of the Avrami exponent, $n$, was found to be 2.23 for polyaryl ether ketone which is equal to the value of $n$ reported for polyphenylene sulfide.[4] Therefore, the nucleation mechanism and the crystal growth geometry appear to be similar for these two polymers. The crystal lattice of polyaryl ether ketones has been reported to be orthorhombic,[6] similar to other aromatic polymers with hinge atom

TABLE II
Isothermal Crystallization Data for Victrex PEEK (Melting Temperature, 355°C)

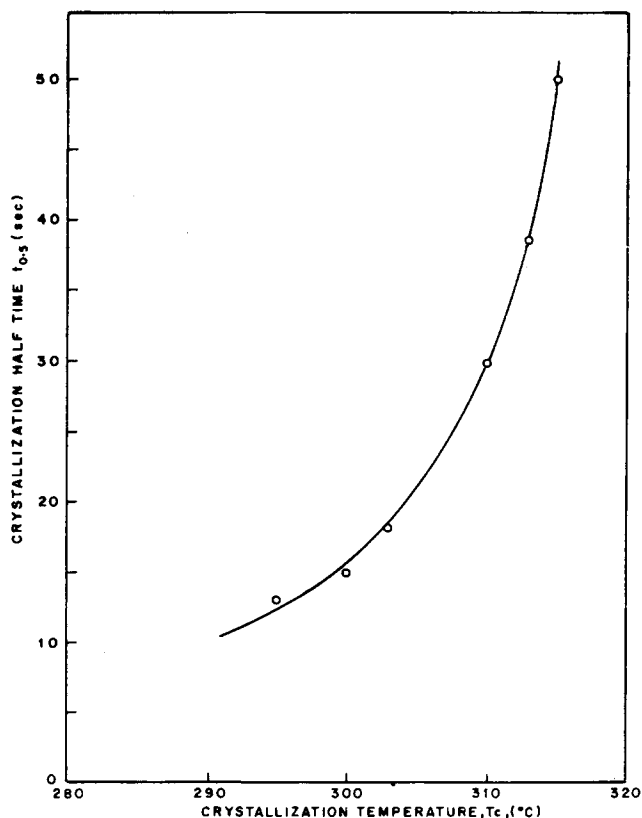| $T_c$ (°C) | $t_c$ (s) | $t_{0.5}$ (s) | $n$ | $k$ (s$^{-n}$) |
|---|---|---|---|---|
| 315 | 125 | 50 | 2.4 | $5.79 \times 10^{-5}$ |
| 313 | 110 | 36 | 2.4 | $1.27 \times 10^{-4}$ |
| 310 | 95 | 30 | 2.0 | $7.70 \times 10^{-4}$ |
| 305 | 70 | 26 | 2.2 | $5.34 \times 10^{-4}$ |
| 303 | 56 | 18 | 2.2 | $1.20 \times 10^{-3}$ |
| 300 | 50 | 15 | 2.2 | $1.79 \times 10^{-3}$ |
| 295 | 45 | 13 | 2.2 | $2.45 \times 10^{-3}$ |

Fig. 2.  Variation of crystallization half-time with crystallization temperature for polyaryl ether ketone (polymerI).

linkages between rigid ring segments, such as polyphenylene sulfide (PPS) and polyphenylene oxide (PPO).

The thermal properties of a few members of the family of polyaryl ether ketones, as reported by Attwood et al.,[2] are summarized in Table I. The reported melting and glass transition temperatures were measured by DSC at a heating rate of 16°C/min. The ratios of ketone to ether linkages reported in the table were calculated by us from the structure of the polyaryl ether ketones shown in the table. The ratio for structure no. 2 has been calculated by assuming a 50/50 composition of the two monomer units. It is clear from the Table I that the melting point and the glass transition temperatures of the polymers increase with increasing ratio of ketone to ether linkages.

The melting point and the glass transition temperature of the polymer under present study (polymer I) are 355°C and 150°C, respectively, whereas the melting point and glass transition temperature of the polymer studied by Blundell and Osborn[3] (polymer II) are 335°C and 144°C, respectively. The higher thermal properties of the polymer under present study indicate a higher ratio of ketone to ether linkages relative to that of the polymer investigated by Blundell and Osborn. In view of the increased rigidity of the polymer chain at the higher amount of ketone linkages, the crystalli-

zation behavior of the polymers would be expected to be affected by the
ratio of the ketone to ether linkages.

In Figure 3, the experimental data are compared with the data reported
by Blundell and Osborn by plotting the crystallization time versus the
degree of supercooling, defined as:

$$\Delta T = T_m - T_c \tag{3}$$

where $T_m$ is the melting point and $T_c$ is the crystallization temperature.

Referring to Figure 3, at an equivalent degree of supercooling, polymer
II with a lower value of the ketone to ether ratio exhibits a lower crystal-
lization time relative to polymer I. The chain flexibility of the polymer is
expected to decrease with an increasing ratio of ketone to ether linkages.
That is, polymer II with a greater chain flexibility is more readily crys-
tallizable than polymer I. This observation is consistent with the crystal-
lization behavior of other polymers, notably thermoplastic polyesters; thus
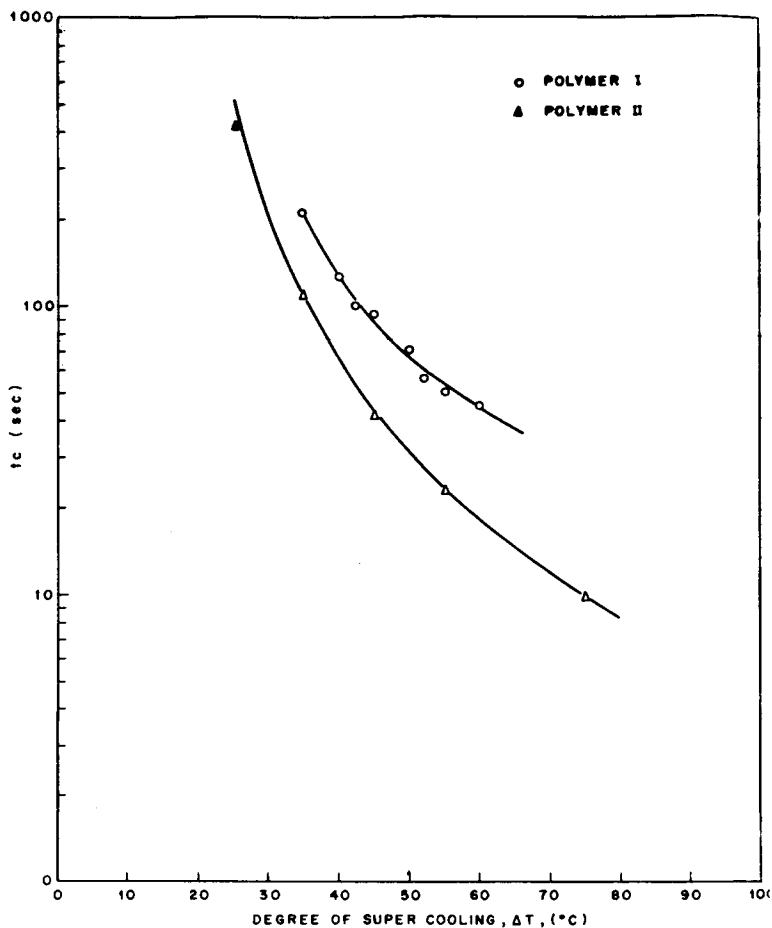polybutylene terephthalate (PBTP) exhibits greater crystallizability than



Fig. 3.   Isothermal crystallization time versus degree of supercooling for polymer I (present
study) and polymer II (Blundell and Osborn[3]).

polyethylene terephthalate (PETP), due to its higher chain flexibility.

The difference in the crystallizability of the two polymers becomes increasingly more noticeable at higher degrees of supercooling. Polymer II would exhibit greater molecular mobility due to its flexible structure, thereby leading to faster crystal growth relative to polymer I.

Thus it is concluded that the crystallizability of polyaryl ether ketone polymers is reduced with an increasing amount of the ketone linkage, although a higher ratio of ketone to ether linkages is preferred for improving the thermal and mechanical performance levels of the polymer. Because the minimum crystallization time is expected to increase with a higher amount of ketone linkages, the molding conditions will also be different for different polymers. Accordingly, a longer cycle time and higher mold temperature may be required for polymer I as compared to polymer II.

## References

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