METHOD TO REDUCE EXPERIMENTATION DURING CRYSTALLIZATION STUDIES DONE BY THERMOANALYTICAL TECHNIQUES

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ABSTRACT

An easy method has been suggested to estimate the temperature at which crystallization rate is maximal using differential scanning calorimetry. The technique is found useful in curtailing the extensive experimental exercise for poly(phenylene sulfide), poly(vinylidene fluoride), poly(ethylene terephthalate) and a copolymer of ethylene terephthalate/sebacate.

INTRODUCTION

Knowledge of the crystallization behaviour of semi-crystalline polymers is important to achieve process economics, increased production rates and product quality. In the processing of semi-crystalline polymers the penalty of requiring additional heat to melt the crystallites to bring the plastics material to processing conditions applies also to the cooling stage, for the latent heat of crystallization is liberated and retards the cooling process, increasing cycle time and reducing the economy of the process. Since cooling is usually the rate-determining part of a molding cycle, as the only mechanism of heat loss is conduction to the cooled surfaces of the mold, liberation of the latent heat of crystallization is a phenomenon of considerable importance. Moreover, low temperature and low thermal energy favour the tendency to pack and retain heat and stable crystalline structures; high temperature and high thermal energy produce the mobility which permits the polymer molecules to find their way initially into position to form such structures. Slow cooling results in large spherulites; quick cooling in small ones, which in turn considerably affect the mechanical, electrical and

fracture performance of the molded components. The extended time of cooling also has some compensation in allowing a long time for relaxation of the orientation induced during mold filling, thereby giving strain free, precision molded products. Therefore, it is desirable to look for a procedure for obtaining the crystallization temperature. One of the most rapid techniques for determination of the kinetics of crystallization is by differential scanning calorimetry. The crystallization exotherm as a function of time was followed to estimate the kinetics of crystallization. The dependence of the extent of crystallization X_c on time is generally followed by the Avrami equation [1]

$$-\ln(1 - X_t) = Zt^n \tag{1}$$

relating the volume fraction degree of crystallinity to a composite rate constant Z and time t. Both Z and n are diagnostic of the crystallization mechanism. During crystallization kinetic studies, importance is also given to the determination of the temperature relating to minimum crystallization
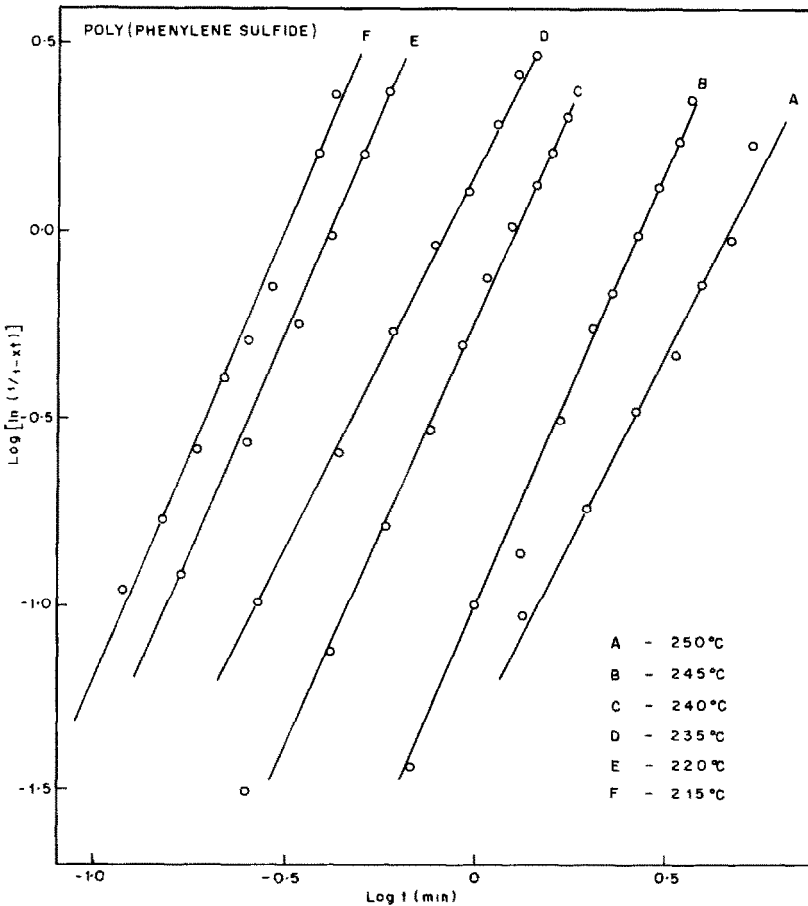

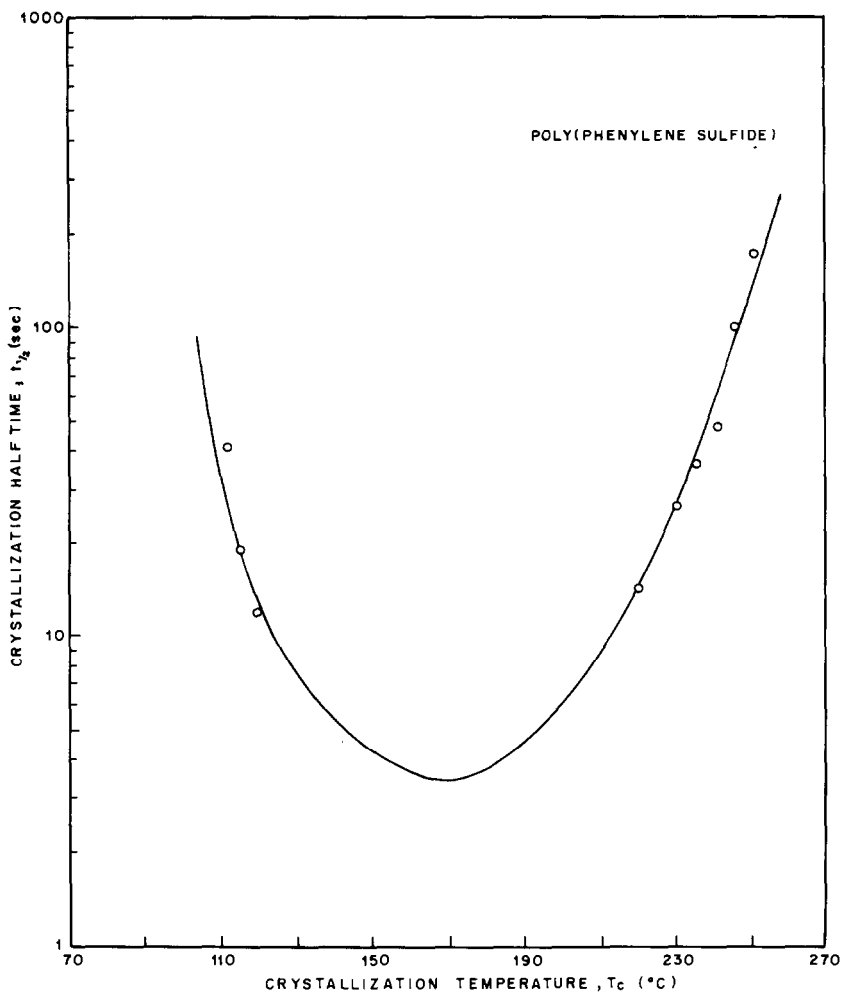Fig. 1. Avrami plots for poly(phenylene sulfide).

Fig. 2. Variation of crystallization half time $t_{1/2}$ (s) with crystallization temperature T_c (°C) for poly(phenylene sulfide).

time. It is general practice to conduct a series of experiments and generate plots like those shown in Figs. 1 and 2 taken from ref. 2. This entire data generation programme is certainly time consuming. It is undoubtedly beneficial to seek methods of curtailing this extensive experimental exercise. In the present paper we present a method for obtaining the same information quickly within reasonable limits of accuracy, but with less than half the number of experiments.

Quick estimation technique

It can be seen [1] from Fig. 1 that the Avrami exponent *n* takes values from 2.04 to 2.48 at different crystallization temperatures as shown in Table

TABLE 1

Crystallization temperature, T_c (°C)	250	245	240	235	220	215
Avrami exponent, n	2.04	2.43	2.16	2.06	2.48	2.19

1. There appears to be no discernable trend or relationship between the crystallization temperature and the Avrami exponent. It has generally been understood that the Avrami exponent is characteristic of the crystallization mechanism [1], but more often than not it has been found to be misleading [3]. There are several limiting factors in the Avrami analysis and these have been discussed in detail by Grenier and Prud'homme [3]. The Avrami model depends upon a large number of assumptions such as constancy in shape of crystal growth, uniqueness of nucleation mode, lack of induction time, etc. Obviously all the assumptions are not met simultaneously and some of them can hardly be met at all for certain polymers. Consequently, it has often been found that, contrary to the theoretical predictions, non-integral meaningless values of n are obtained [4–18]. When such is the case, it would not be improper to look for average Avrami exponent values rather than specific values at each crystallization temperature. If an average value would suffice, then the experiments could be curtailed by realizing that the plots in Fig. 1 can be coalesced into one by normalizing the X-axis with $t_{1/2}$ which is the half crystallization time. The slope of this line would give the average Avrami exponent which is equal to 2.3 in the present case. One need not take measurements at different crystallization temperatures as the data for two temperatures alone would suffice.

In the case of Fig. 2, the shape of this curve is known to be a parabola and hence it is a futile exercise to do a dozen experiments in order to determine its exact details, especially because the experiments in certain ranges of temperatures are difficult to perform. We therefore suggest a mathematical approach for this.

As it has been already established in the literature that the curve is a parabola on a semilogarithmic plot, the following equation can be used to define it

$$\log t_{1/2} = a + bT_c + cT_c^2 \tag{2}$$

In order to determine the values of the unknowns, it is essential to have at least three sets of values of $t_{1/2}$ and T_c. If the choice of T_c values are made with good discretion, then eqn. (2) would predict the relationship between $t_{1/2}$ and T_c quite accurately. In making such a choice, one value of T_c should be nearer to T_m and the other nearer to T_g. The third value could be arbitrarily chosen between T_g and T_m. With these values of $t_{1/2}$ and T_c, the coefficients a, b and c may be calculated.

In order to determine the value of T_c for minimum $t_{1/2}$ a simple mathematical calculation can be performed as follows

$$\frac{d}{dT_c}\left(\log t_{1/2}\right) = b + 2cT_c \tag{3}$$

Thus T_c at minimum $t_{1/2}$ will be

$$T_{c_{max}} = -\frac{b}{2c} \tag{4}$$

$T_{c_{max}}$ then gives the temperature at which the rate of crystallization is maximal.

RESULTS AND DISCUSSION

The idea of generating a coalesced curve and determining the average Avrami exponent can be seen from Figs. 3 and 4, each for a different
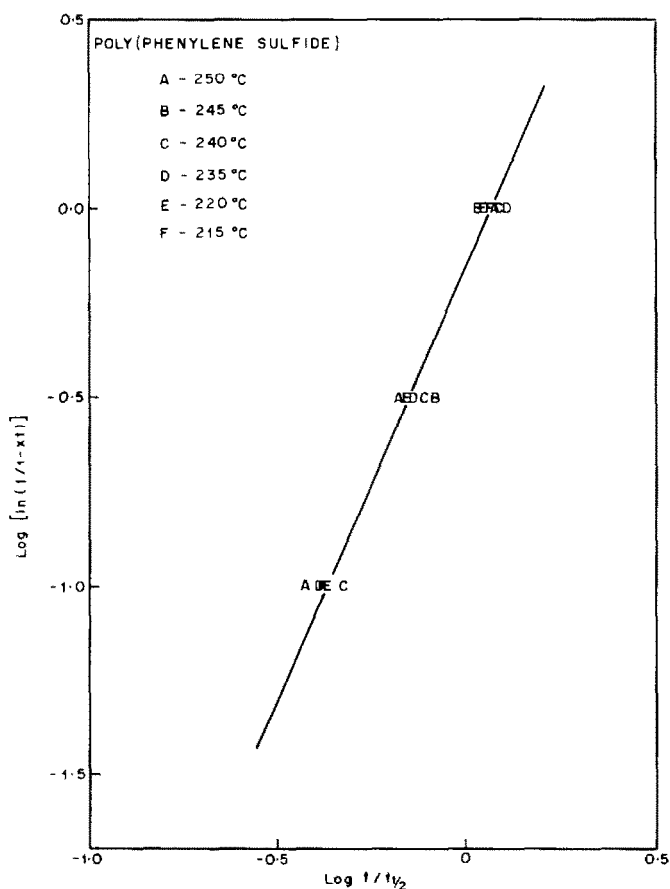
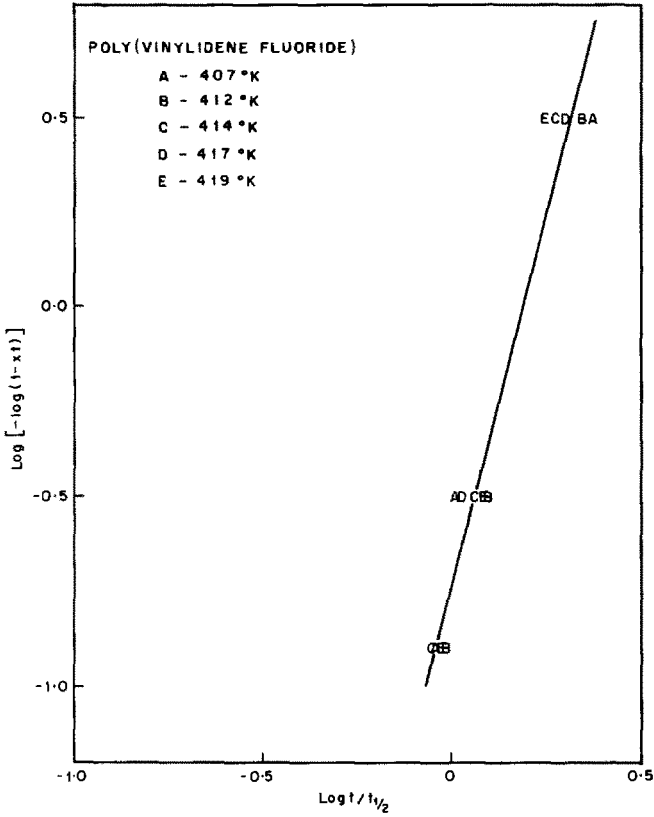
Fig. 3. Coalesced curve for poly(phenylene sulfide).

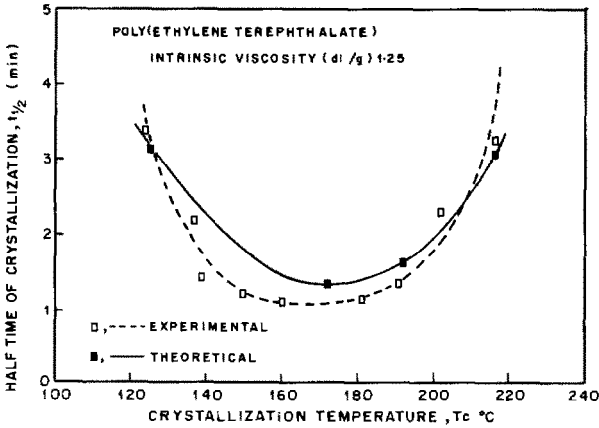Fig. 4. Coalesced curve for poly(vinylidene fluoride).

Fig. 5. Variation of crystallization half time $t_{1/2}$ (min) with crystallization temperature T_c (°C) for poly(ethylene terephthalate) IV 1.25.
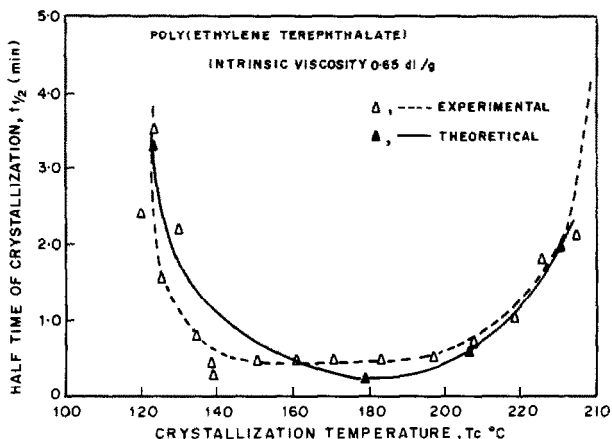
Fig. 6. Variation of crystallization half time $t_{1/2}$ (min) with crystallization temperature T_c (°C) for poly(ethylene terephthalate) IV 0.65.

polymer.

The technique would, undoubtedly, be applicable to a wide variety of cases wherein the Avrami model is used for analysis.

In order to assess the validity of the mathematical technique to determine the temperature for fastest crystallization, several cases have been tried and the curves are given in Figs. 5–7. The three cases are chosen in such a way that different shaped parabola could be considered. The method is seen to
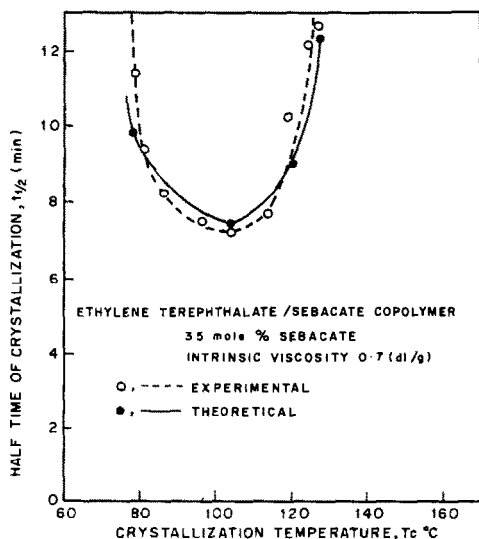

Fig. 7. Variation of crystallization half time $t_{1/2}$ (min) with crystallization temperature T_c (°C) for ethylene terephthalate/sebacate copolymer IV 0.7.

work rather well in all cases. This is thus an easy method to determine the temperature at which the crystallization rate is maximal.

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