

Kinetic and Property Parameters of Poly(ethylene naphthalate) Synthesized by Solid-State Polycondensation

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ABSTRACT: A low molecular weight prepolymer with reactive end groups was annealed at temperatures between 200 and 245°C to obtain kinetic parameters for solid-state polymerization of poly(ethylene naphthalate) (PEN). An equation was developed to describe the relationships among time, temperature, and final molecular weight for PEN. The intrinsic viscosity and melting point during polymerization were used to monitor the molecular weight and the thermal stability of the resulting resins. The effect of moisture concentration on solid-state polymerization was also investigated. Hydrolytic degradation caused initial reductions of the molecular weight if prepolymers were solid-stated without being dried. With increased exposure to solid-state conditions, however, the hydrolytically degraded resin dried and repolymerized at rates similar to those samples that had undergone hydrolysis. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2055–2061, 2001

Key words: poly(ethylene naphthalate); solid-state polycondensation; kinetic

INTRODUCTION

Engineering plastics have found wide applications in automobiles, precision instruments, and electronic, electrical, and communication industries. However, the requirements of superior performance in heat and chemical resistance, flame retardance, and electrical, optical, and mechanical properties are getting severe. The high-performance poly(ethylene naphthalate) (PEN), with its superior physical and mechanical properties and processability, has claimed a niche in specialty films,^{1–3} fiber applications,^{4,5} and stretch-blow-molded containers.⁶

PEN is commonly synthesized either by transesterification of dimethylnaphthalate with ethylene glycol or by the direct esterification of naphthalene dicarboxylic acid with ethylene glycol. In both cases, side reactions occur during the condensation reaction, owing to the high temperature needed for the processes. The major side reaction observed is the formation of diethylene glycol which is included as di(oxyethylene)oxy units (DE) in the polyester chain.⁷ The inclusion of the DE unit strongly influences the degree of whiteness as well as the melting temperature of the product.

Solid-state polymerization is a commonly practiced technique to obtain polyesters with high molecular weight and melting points⁸ as well as low diethylene glycol and residual acetaldehyde content. This technique involves heating the prepolymer slightly below the T_m , resulting in chain extension by the reaction of end groups of the polymer in the solid state. The technique has

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practical significance as polymers of such high molecular weight cannot, generally, be produced in a stirred reactor, under a melt polycondensation condition, due to their prohibitively high melt viscosity.

Our previously reported investigations^{9,10} followed the effects of the catalyst, reaction temperature, and time upon polymerization and degradation of PEN. Activation energies were calculated for transesterification with various catalysts. This work concerns the polymerization and degradation behavior of PEN at solid-state conditions and the effect of environments on the resin molecular weight, purity, and thermal stability. Equations have been developed to describe the relationships among time, temperature, and final molecular weight for PEN with specified catalyst and monomer systems. From the reaction engineering viewpoint, the major task in the kinetic study of solid-state polymerization is to determine the optimum operating conditions and to establish a kinetic model useful for reactor design.

EXPERIMENTAL

Material and Sample Preparation

2,6-Dimethylnaphthalate (Amoco, Naperville, Illinois) is a commercial product and was used without further purification. Ethylene glycol (Ferah, Berlin, Germany) was reagent grade and used without further purification. *o*-Chlorophenol, used for intrinsic viscosity measurements of the polymers, was also used without purification.

The prepolymer of poly(ethylene naphthalate) used in this study was prepared from 2,6-dimethylnaphthalate and ethylene glycol using a melt-interchange reaction as described previously.¹⁰ Before solid-state polymerization, prepolymers were vacuum-dried overnight at 120°C in a shallow tray. Moisture concentrations were reduced to less than 0.01% in order to minimize hydrolytic degradation during the initial stages of polymerization. Samples specifically solid-stated with a high initial moisture concentration are designated as "wet" and were used to study the effect of moisture upon the solid-state polymerization. In addition to moisture reduction, the amorphous prepolymer was crystallized to 30–40% by annealing in a vacuum oven to prevent agglomeration of prepolymer particles at subsequent solid-state polymerization temperatures. A density-

gradient column was used to determine the crystallinity of the polymers.

Solid-state Polymerization

A gas–solid reactor (composed of a glassware column of 1-in. diameter and a porous filter for supporting the sample and distributing gas), with a 40-g sample capacity, was used to polymerize the solid prepolymer at various times, temperatures, and atmospheric conditions. The reactor was heated in a constant temperature bath. A temperature-controlled electric heater was used to heat inlet gas. The purge gas flow rate was chosen such that no polymer molecular weight gradient existed in the bed and the by-product concentration in the gas phase was essentially zero. Thermocouples at three individual locations within the reaction chamber were used to monitor the pellet bed temperature during polymerization. It was determined that ~50 min was required to achieve the desired reaction temperature.

Reaction times were measured only after the temperature had been attained. The following polymerization steps were followed for various time and temperature conditions during this study: Samples designated as "wet" were not predried before polymerization, and precautions for removing oxygen from the reaction chamber were omitted for samples solid-stated in air. During each run, the samples were taken from the reactor at certain time intervals and cooled with an external airflow. The experiment was then restored and the total time for each sampling was no more than 30 s. The reactor was still under a nitrogen purge and maintained at a constant temperature. These samples were then removed for further analysis.

Molecular Weight Determination

Intrinsic viscosities (IVs) of the samples were measured by an Ubbelohde viscometer (Schott-AVS310). The solvent used was *o*-chlorophenol. A sample concentration of 0.25 g/100 mL was used. All samples were dried in a vacuum oven at 160°C prior to viscosity measurements. The viscosity-average molecular weight was calculated according to ref. 11.

Determination of Moisture in PEN Pellets

A DuPont solids moisture analyzer was used to measure the moisture content of PEN pellets used in these experiments. Samples were heated at

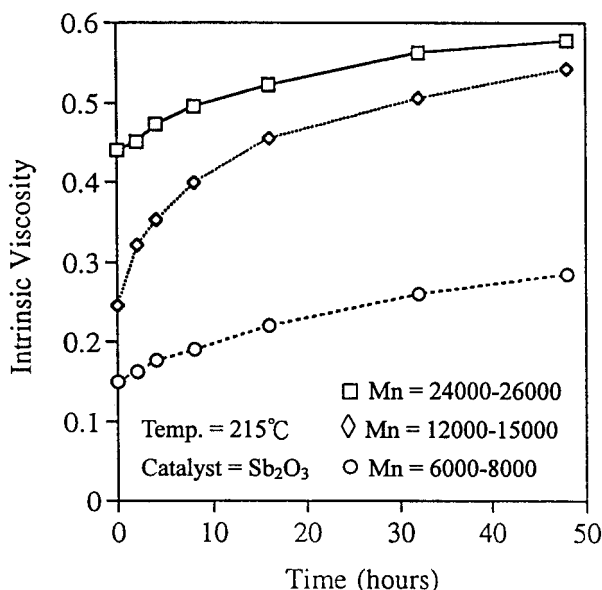


Figure 1 Intrinsic viscosity changes as a function of time for PEN solid-stated at various initial viscosities.

130°C until all moisture had been expelled. The moisture was calculated as

$$\text{Percent moisture} = (C_s - C_b)/W_s \times 100.$$

where C_s is the counts obtained for samples (μg); C_b , the counts obtained for blanks (μg); and W_s , the weight of the sample (μg). The above procedure yields an accuracy of $\pm 0.001\%$.

Melting Behavior

Melting behaviors of samples solid-stated at various conditions were monitored using a Perkin-Elmer DSC-7. Endotherms of samples were recorded at heating rates of $10^\circ\text{C}/\text{min}$ in a dry nitrogen atmosphere with an empty aluminum pan as a reference. Standards used for enthalpy and temperature calibration were indium (28.5 J/g , 156.6°C), tin (60.5 J/g , 231.9°C), and lead (23.05 J/g , 327.5°C). The experimental error was found to be ($\pm 0.5^\circ\text{C}$ in temperature determination).

RESULTS AND DISCUSSION

Optimum Prepolymer for Solid-state Polymerization

First, the relationship between final intrinsic viscosity and reaction time for different molecular weight prepolymers is shown in Figure 1. It is

found that if the molecular weight of the prepolymers is too large, the variation of viscosity with reaction time is small; however, low molecular weight prepolymers need more time to reach the equilibrium viscosity. So, the optimum molecular weight of the prepolymers was selected to be between 12,000 and 15,000 for solid-state polymerization.

Second, to determine the relationship between the particle size of the prepolymer and the reaction time of the solid-state polymerization, the prepolymer was synthesized by an alcoholysis reaction and was crushed. After selection and sizing, uniform particle-size prepolymers were obtained for experiments. The relationship between viscosity and reaction time for different particle sizes is shown in Figure 2. It is found that the viscosity of a polymer increases with a decrease in the particle diameter. The result indicated that, as the surface/volume (S/V) ratio increases, the solid-state polymerization rate increases.

From the results of above two preliminary studies, prepolymers with molecular weight between 12,000 and 1,5000 and a particle diameter between 35 and 60 mesh were chosen for this study. Before solid-state polymerization, precursor samples were vacuum-dried overnight at 120°C in a shallow tray. Moisture concentrations were reduced to less than 0.01% in order to minimize hydrolytic degradation during the initial stages of polymerization. In addition to moisture reduction, the amorphous precursor sample was

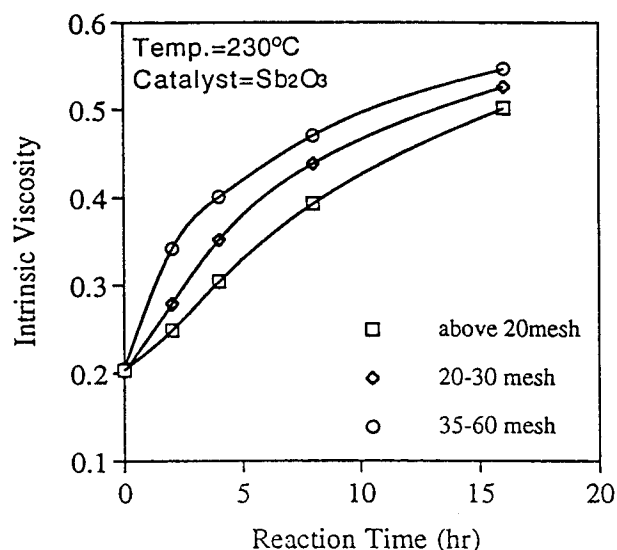


Figure 2 Intrinsic viscosity as a function of time at various sample sizes.

crystallized to 30–40% by annealing in a vacuum oven. From these processes, we can promise the same conditions of the reaction at the beginning of polymerization and eliminate the influence of other variations in the kinetic study of solid-state polymerization.

Kinetics of Polymerization in the Solid State

IV changes were used to monitor the molecular weight increases of PEN at various solid-state conditions. Vacuum-dried samples were polymerized under a 1000-cc/min nitrogen purge for times from 2 to 32 h, at a temperature from 200 to 245°C. Figure 3 shows viscosity as a function of the reaction time at a variety of temperature conditions.

The relationship¹¹ between the IV and the weight-average molecular weight (MW) is given by

$$IV = 5.4 \times 10^{-5} \times (M_w)^{0.83} \quad (1)$$

in *o*-chlorophenol at 25°C. For PEN,

$$M_w = 2 \times M_n$$

Therefore,

$$M_n = 7.31 \times 10^4 (IV)^{1.21} \quad (2)$$

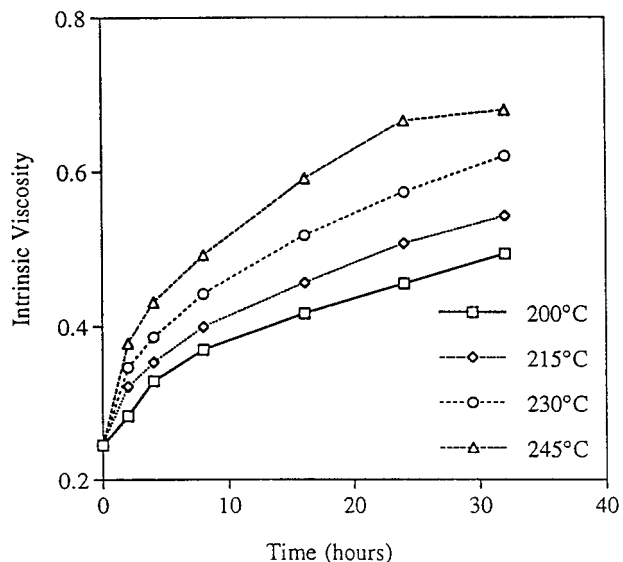


Figure 3 Intrinsic viscosity as a function of time at various solid-state temperatures. Nitrogen purge is at 1000 cc/min.

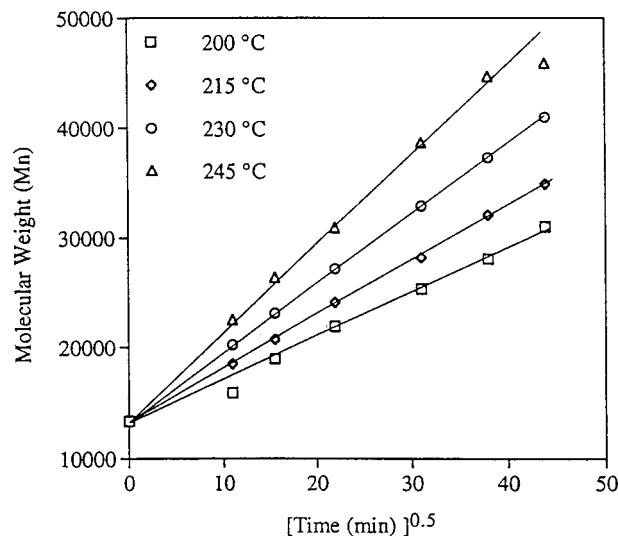


Figure 4 Molecular weight as a function of the square root of time at various solid-state temperatures. Nitrogen purge is at 1000 mL/min.

Molecular weights were calculated from IV values using the relationship shown in eq. (2).

Flory¹² showed the degree of polymerization to be approximately proportional to the square root of time for third-order condensation reactions, except during early stages of the reaction. The relationship of molecular weight to the square root of the solid-state reaction time is shown graphically in Figure 4.

These data represent the reaction of the PEN precursor at various temperatures and a linear relationship between the molecular weight and the square root of reaction time is obtained. These data also show an increased slope at higher solid-state temperatures. We found these relationships to hold for times up to 32 h from 200 to 230°C. At very long times, degradation effects produce deviations from linearity of the relationships at 245°C.

As can be seen in Figure 4, lines extended from initial precursor molecular weight, through values obtained after solid stating for various times at each temperature, are described by the following empirical equations:

$$M_n = M_{n0} + k \sqrt{t} \quad (3)$$

which can be solved to give the equilibrium rate constant (k) for solid-state polymerization at each condition:

$$k = \frac{M_n - M_{n0}}{\sqrt{t}} \quad (4)$$

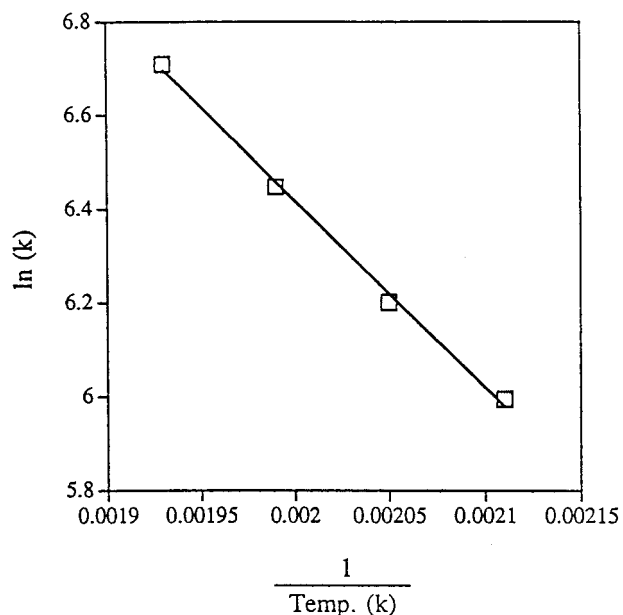


Figure 5 Arrhenius plot of rate constants for molecular weight increases at various solid-state temperatures.

where M_n is the number-average molecular weight at time t ; M_{n0} , the initial number-average molecular weight of the precursor; and t , the time (min) of the solid-state reaction at each time.

At each solid-state temperature, an average value for k is obtained. The natural logs of this value $[\ln(k)]$ can be plotted versus $1/T$ (K) to obtain an Arrhenius plot as shown in Figure 5. Values for the activation energy (Ea) and the frequency factor (A) may be calculated from this plot or using an exponential regression program:

$$k = Ae^{-Ea/RT} \quad (5)$$

where A is the collision frequency factor for propagation; Ea , the energy of activation for propagation cal/mol; R , the gas constant, 1.987 cal/mol K; and T , the temperature (K).

Combining eqs. (4) and (5), one obtains

$$\frac{M_n - M_{n0}}{\sqrt{t}} = A \times e^{-Ea/RT} \quad (6)$$

which can be rearranged to give

$$M_n = M_{n0} + (Ae^{-Ea/RT})(\sqrt{t}) \quad (7)$$

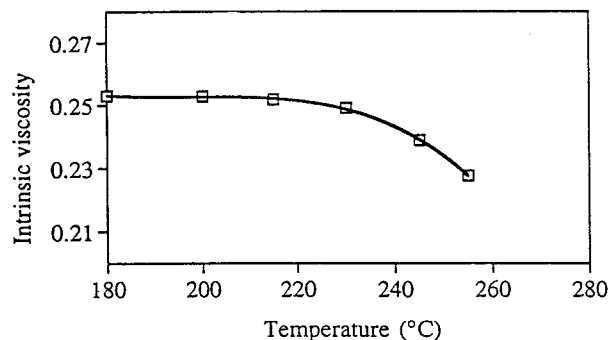


Figure 6 Intrinsic viscosity changes as a function of temperature for PEN samples solid-stated "wet" without drying.

This kinetic rate equation describes the empirical relationship of solid-state time, temperature, and polymer molecular weight. With values for Ea and A substituted, the following equation was obtained for precursors evaluated in this study:

$$\text{PEN: } M_n = 1.33 \times 10^4 + 1.78 \times 10^6 \times e^{-7922.83/RT} \times \sqrt{t} \quad (8)$$

These results are very similar to the work reported by Jabarín and Lofgrin¹³ for PET prepared with an antimony catalyst system:

$$\text{PET: } M_n = 1.99 \times 10^4 + 624 \times 10^{10} \times e^{-22800/RT} \times \sqrt{t} \quad (9)$$

Effect of Moisture

The effects of solid-stating the undried PEN precursor were investigated in terms of IV changes

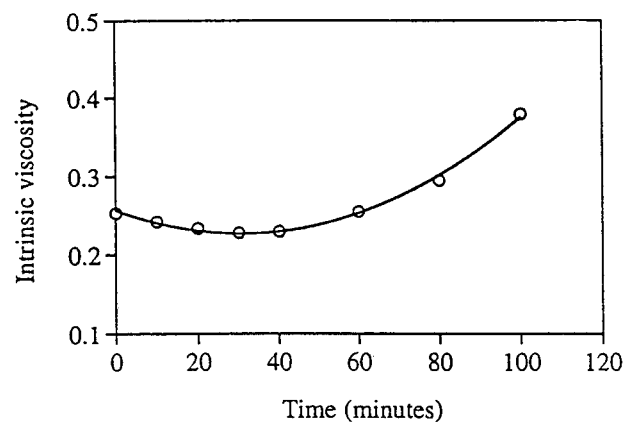


Figure 7 Intrinsic viscosity changes as a function of time for PEN samples solid-stated "wet" without drying.

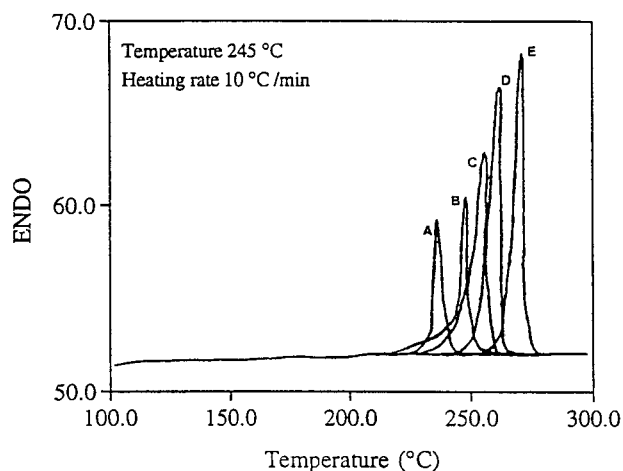


Figure 8 DSC diagrams of solid-state condensed PEN for different times of annealing: (A) 2 h; (B) 8 h; (C) 16 h; (D) 24 h; (E) 32 h.

resulting from various exposure conditions. Samples (~ 0.8 g) with moisture concentrations of 0.24% prior to solid-stating were heated in a Perkin-Elmer thermogravimetric analyzer (TGA-7) oven for times up to 100 min. The TGA system was chosen for this portion of the study because it provided better short-time temperature control than did the bench-scale reactor. Dry nitrogen (~ 40 cc/min) was used to prevent oxidative degradation and to remove volatile reaction products.

Figure 6 shows the IVs plotted as a function of the reaction temperature, after 30 min of exposure. As can be seen at temperatures up to 230°C , no IV loss was measured. Losses increased at temperatures above 230°C . Figure 7 illustrates

the effects of increased exposure time at 255°C . At this temperature, the material begins to degrade immediately upon thermal exposure, reaching its lowest value after ~ 30 min. With longer exposure time, the IV increases, indicating that polymerization is occurring more rapidly than is hydrolytic degradation, as drying at solid-state conditions reduces their moisture contents.

Melting Behavior

Figure 8 shows DSC traces of samples reacted at 245°C for various times. The melting endotherms shift to higher temperature with increasing reaction times and they are very sharp. The half-widths of these peaks are approximately $2\text{--}4^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$.

Other differential scanning calorimetry endotherms obtained at heating rates of $10^\circ\text{C}/\text{min}$ for samples solid-stated at various temperatures are shown in Figure 9. Similar multiple-peak behavior was observed by others¹⁴⁻¹⁶ and interpreted on the basis of distributions of crystallite sizes or perfection induced by thermal treatments. As can be seen, at higher solid-state temperatures, less temperature difference occurs between the first melting peak (T_{p1}) and the second melting peak (T_{p2}). Figure 10 shows graphically the relationship $\Delta T (T_{p2} - T_{p1}) = T$ as a function of the solid-state temperature. It can also be noted that, as the solid-state polymerization temperature is increased, smaller temperature differences occur between the reaction temperature and the first melting temperature.

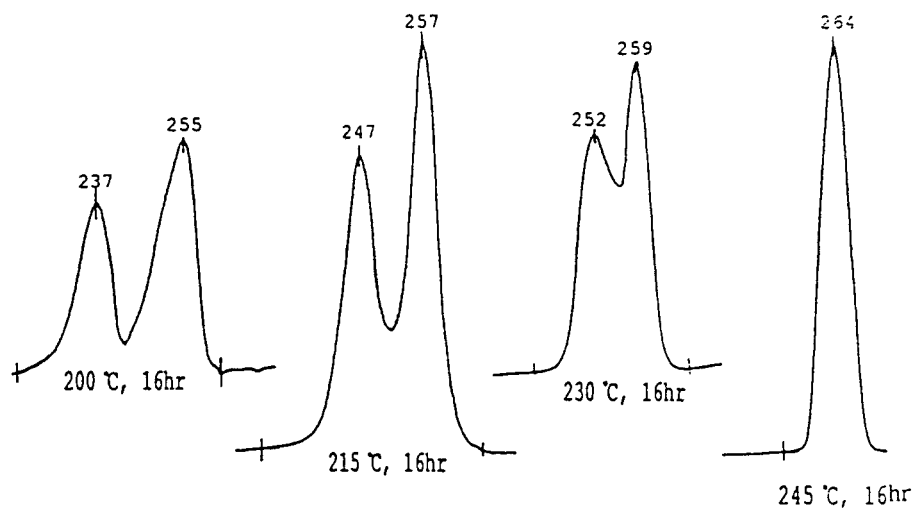


Figure 9 DSC endotherms for samples solid-stated at various temperatures.

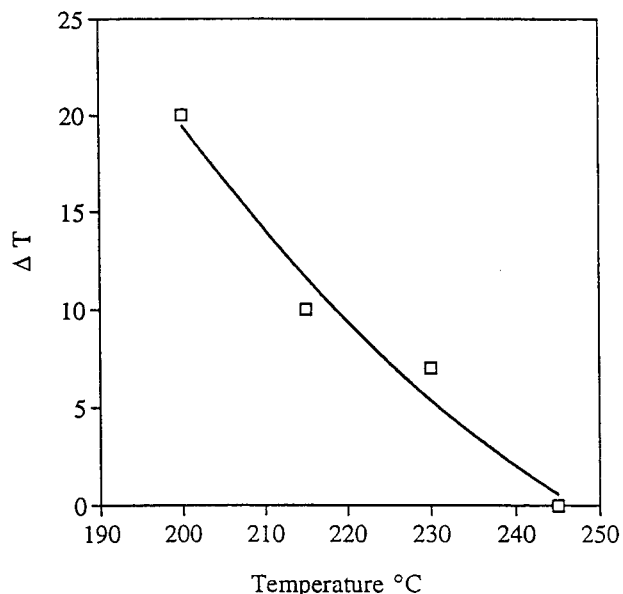


Figure 10 Relationship of endothermic peak temperature changes to solid-state temperatures.

CONCLUSIONS

1. The following equation was developed to describe the relationships of time, temperature, and final molecular weight during solid-state polymerization of PEN:

$$M_n = M_{n0} + (Ae^{-E_a/RT})(\sqrt{k})$$

2. Hydrolytic degradation causes initial reductions of the molecular weight if precursors are solid-stated without being dried. With increased exposure to solid-state conditions, however, the hydrolytically degraded resin dries and repolymerizes at rates similar to those observed for resins that have not undergone hydrolysis.
3. At higher solid-state temperatures, the temperature difference between the first and second melting peak is reduced, as is

the difference between these peak temperatures and the solid-state temperature.

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