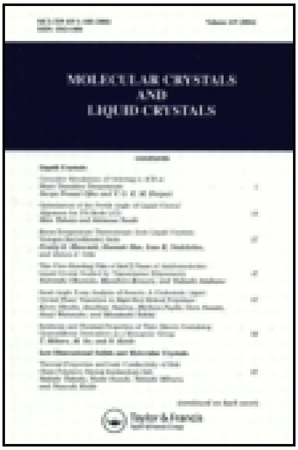

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Solid State Polymerization of a Diacetylene: 2,4-Hexadiyne-1,6-Diol bis (p-Toluenesulfonate) (PTS)

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Solid State Polymerization of a Diacetylene:

2,4-Hexadiyne-1,6-Diol *bis* (*p*-Toluenesulfonate) (PTS)

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Thermal polymerization of 2,4-hexadiyne-1,6-diol *bis* (*p*-toluene-sulfonate) in the solid state has been studied by differential scanning calorimetry. Slow polymerization during an induction period is followed by a fast polymerization regime which appears to obey first order kinetics. The induction period is almost sample independent whereas the fast polymerization is very sample dependent. The heat of polymerization is constant for single crystal samples, $\Delta H_p = -31.2$ kcal/mole, but increases for polycrystalline samples and for single crystals which have undergone some slow polymerization ($< 5\%$).

1. INTRODUCTION

The phenomenon of topotactic or lattice controlled chemical reactions in organic molecular crystals has been known for many years, and much of the definitive work in this area was done by Schmidt, Cohen and co-workers[1] on photodimerization reactions. More recently, Wegner[2] has reexamined some older solid state polymerization reactions of diacetylenes. He identified the mechanism as a 1,4 addition reaction that yields a linear polymer which is fully conjugated according to the reaction in Figure 1. The final polymer can exist in either the acetylene or butatriene forms both of which have been identified by x-ray structural analysis.

Solid state polymerization of diacetylenes is dependent both on the substituent group R and the occurrence of a suitable polymorphic crystalline form. Only a few systems are known which undergo a homogeneous single phase reaction to complete conversion, and one example is 2,4 hexadiyne-1,6-diol-*bis* (*p*-toluenesulfonate) (PTS).[3] This material polymerizes thermally, photochemically and with ionizing radiation (x- or γ-ray). The kinetics of polymerization have been studied by extraction techniques;[3,4,5] that is, after

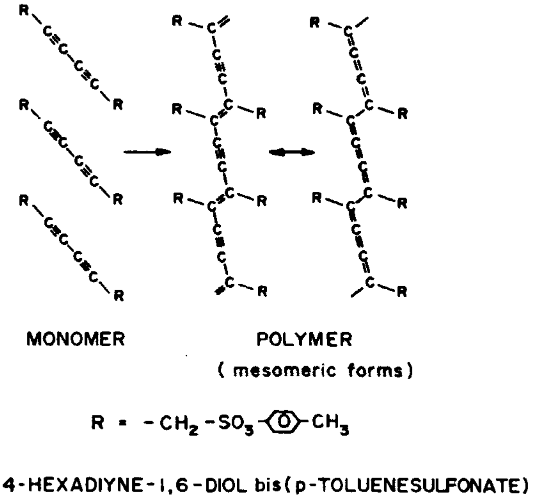

FIGURE 1 Polymerization of 1,3 diacetylenes.

partial polymerization the residual monomer was removed by solvent extraction and the remaining insoluble polymer weighed. This technique is time consuming, requires relatively large quantities of material and is subject to errors at both low and high conversion. More suitable, higher precision methods for studying the kinetics of polymerization, while additionally obtaining the thermodynamic value of the heat of reaction, are provided by direct thermal measurements such as differential scanning calorimetry (DSC).

A known characteristic of PTS is that a pronounced induction period, of the order of hours near the melting point, occurs during which polymerization is very slow up to approximately 10 % polymer formation whereupon a rapid "autocatalytic" increase in reaction rate ensues. DSC techniques are ideally suited to studying such solid state transformations and reactions, and the present work, together with the recent independent measurements of Barrall *et al.*[6] and Patel *et al.*[7] represent the first such studies on the polymerization of diacetylenes.

2. GENERAL DSC CHARACTERISTICS OF PTS

Initially a batch of monomer crystals was annealed isothermally in a temperature controlled bath and the batch sampled with time. Each sample, ~5 mg, was temperature scanned on a DuPont 990 DSC in an hermetically

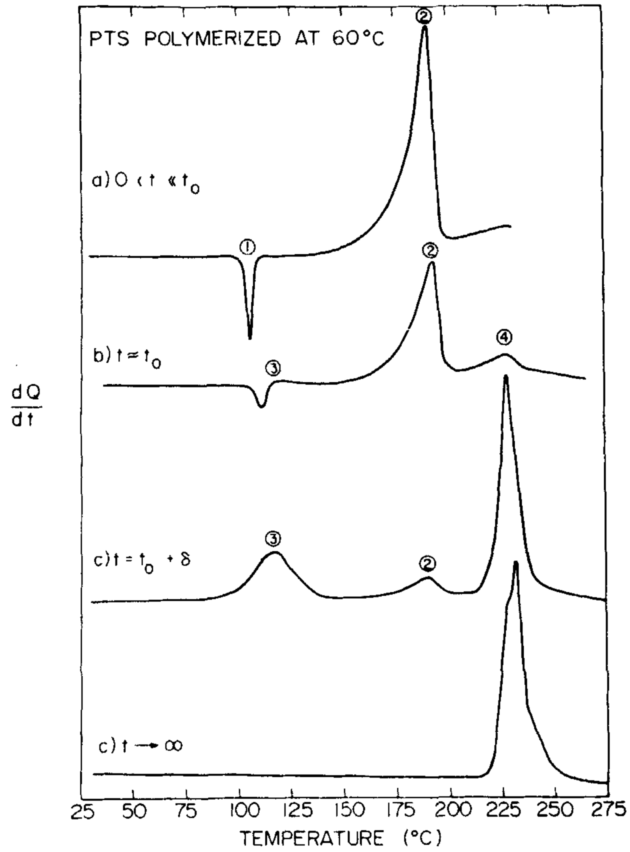

FIGURE 2 DSC scans of PTS after isothermal annealing in the solid state.

sealed aluminium pan from room temperature to 275°C at 5°C/min. Figure 2 shows some representative thermograms with the following features.

a) Peak ① represents the melting endotherm of the pure monomer and ② is an exothermic reaction in the liquid phase. This peak has not been studied in detail but is probably a combination of decomposition and liquid phase polymerization. The magnitude of this peak varies with the remaining monomer concentration.

b) As $t \rightarrow t_0$, the induction period, several new phenomena appear. The apparent melting point of the monomer increases; this is exactly what would be expected from a system which forms a solid solution in which the distribution coefficient of the second component (polymer) is greater than unity. ③ represents the continued growth of solid state initiated polymer chains in the melt which eventually terminate and are followed by ②. The exothermic peak, ④, is due to decomposition of solid state formed polymer.

c) Here peak ③ represents a combination of fast solid state polymerization and continued polymerization in the melt. The small peak ② shows that some melt still remains and ④ shows that the amount of crystalline polymer has grown.

d) After a long anneal time the only feature observable is the very narrow decomposition peak of the crystalline polymer.

It is possible, in principle, to follow the kinetics of polymerization by measuring the areas of peaks ② and ④, which are proportional to the concentration of monomer and crystalline polymer respectively, with time. Figure 3 shows a plot of the heat of liquid phase reactions, ②, as a function of time for two samples of PTS annealed at 60.0 ± 0.5°C. The scatter in the data is due to the choice of baseline used for calibration. This figure shows that initially during the induction period the heat of reaction has approximately the same constant value for both samples 116 ± 8 kcal/mole and then rapidly falls to zero but at a rate which is sample dependent. This method is useful but not sufficiently accurate for precise measurement of the poly-

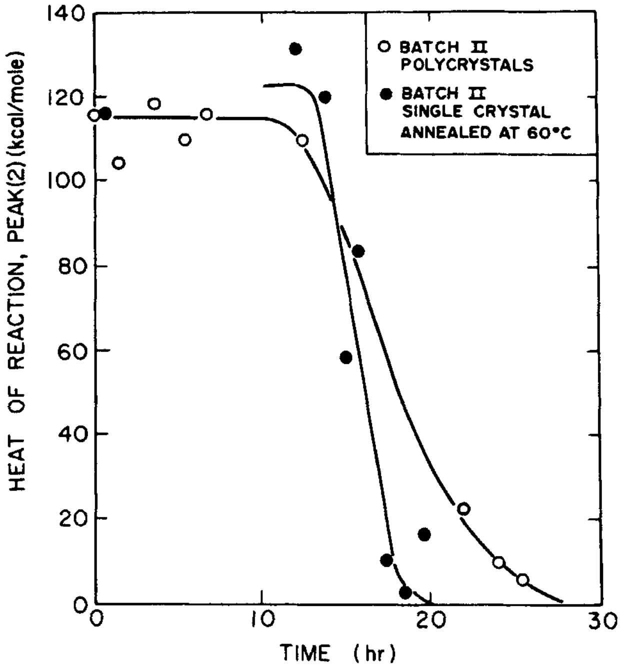

FIGURE 3 Variation of the heat of liquid phase reaction with time for PTS.

merization kinetics; hence we proceeded to the more reliable technique of isothermally annealing the sample in the DSC cell at temperatures below the melting point. All subsequent measurements used this technique.

3. ISOTHERMAL DSC STUDIES ON PTS

Two batches of PTS were used in this study and prepared according to Wegner,[3] the only difference being that in batch II the starting material 2,4-hexadiyne-1,6-diol was used as received, and in batch I it was recrystallized twice from toluene. Single crystals were grown from both batches by slow evaporation of dry acetone solution using high purity argon as carrier gas. The four preparations of PTS, two in the form of polycrystalline samples and two as batches of relatively large single crystals, had identical elemental chemical analyses.

The preliminary results for batch I single crystals have been reported recently.[8] Briefly, samples, 5–15 mg, were run isothermally in hermetically sealed aluminum pans in the temperature range 60–92°C. A schematic of a typical thermogram is given in Figure 4. A major feature of this curve is that it can be viewed as two polymerization regimes; a slow polymerization during an induction period followed by fast polymerization which appears to follow

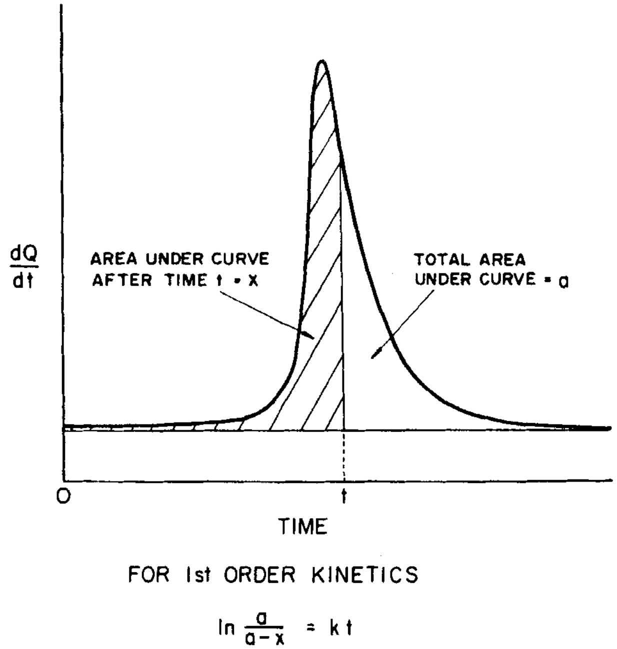

FIGURE 4 Schematic of a typical isothermal DSC polymerization run.

first order kinetics over the range $\approx$20–95 % polymerization. Our previous paper[8] shows plots of log $a/(a - x)$ vs. t, where a = total area under the curve and x = partial area up to time t, in which the initial slow polymerization is followed by the linear dependence of the fast polymerization regime. Extrapolation of this line back to log $a/(a - x) = 0$ yields the induction period, t_0. The slope of this line yields the first order rate constant, k. It was previously shown that Arrhenius plots of log k vs. $1/T$ and log $(1/t_0)$ vs. $1/T$ both give the same activation energy, $E_A = 22.3 \pm 0.9$ kcal/mole for batch I single crystals.[8] This indicated that the same mechanism, that of chain initiation, was controlling in both regimes. Further measurements show that different batches of crystals give different, but internally consistent, values of k which give the same activation energy. These are shown in Figure 5 along with the plots of log $(1/t_0)$ vs. $1/T$ for the four batches of crystals. It is apparent from this plot that the induction period is almost independent of crystal form and purity.

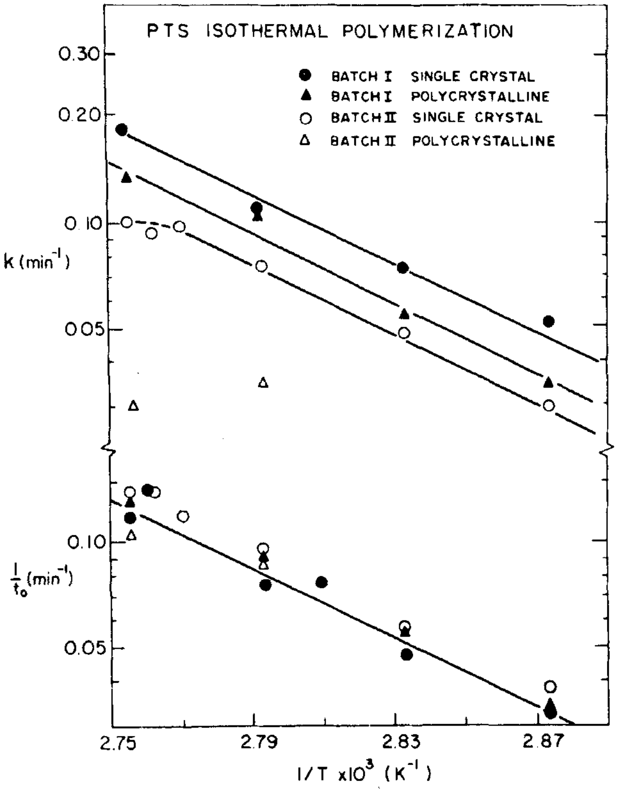

FIGURE 5 Arrhenius plots of log k and log $(1/t_0)$ vs. $1/T$ for four different samples of PTS.

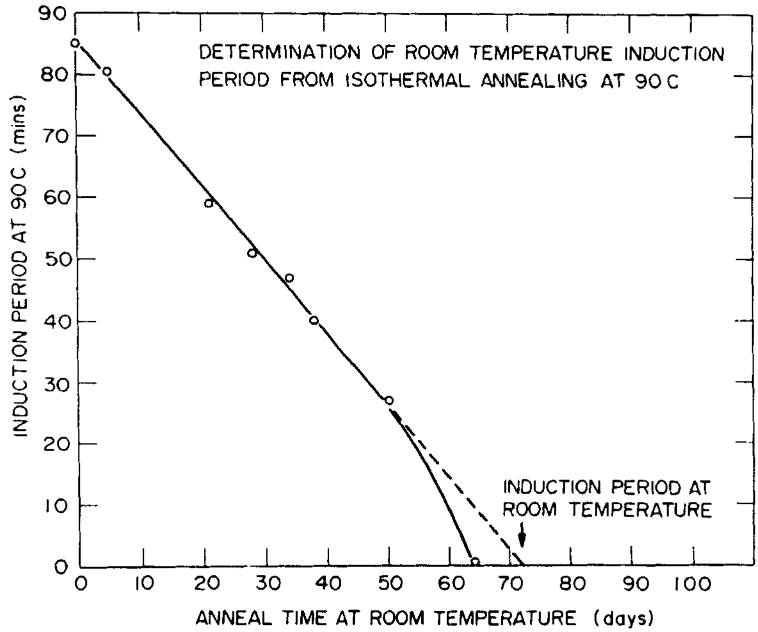

FIGURE 6 Dependence of induction period at 90°C on room temperature anneal time for batch I single crystals.

The induction period at room temperature was obtained by annealing samples of batch I single crystals at room temperature and then measuring their induction period at 90°C as a function of room temperature anneal time. Figure 6 shows that these are linearly related and extrapolation of the curve yields a room temperature induction period of 72 days which is consistent with the data in Figure 5.

These results are interpreted as indicating that the slow polymerization process is due to the lattice strain generated when polymer chains are incorporated in the monomer lattice at low conversion, due to the ~5% contraction of polymer in the chain direction in the crystal.[13] This strain prevents the polymer chains from growing, and it is believed that these short chains are still active and can continue to grow when the strain field is reduced.

Evidence for the existence of short, unterminated chains during the induction period includes the following observations:

1. Heating crystals of PTS, which had been standing for several weeks at room temperature, resulted in a distinct initial maximum in the polymerization rate upon reaching the isothermal temperature which then decreased to a steady state value before the fast polymerization process began.

TABLE I

Batch I single crystals isothermally annealed at 90°C as a function of room temperature anneal time

Sample No.	Room temperature anneal time, days	90°C Induction period, mins.	$\gamma = \frac{h_m M}{w \cdot \Delta H_p} \times 10^{-3}\ \mathrm{sec}^{-1}$
1	0	85	2.04 ± 0.05
2	5	81	1.87
3	28	51	2.67
4	38	40	2.68
5	50	27	2.37

2. Samples of batch I single crystals, which had been annealed at room temperature, showed an increase in the maximum polymerization rate,[9] γ, compared with a fresh sample as shown in Table I.

It is believed that this ~30% increase in γ is due to short chains generated and trapped at room temperature which become free to grow at higher temperature.

The fast polymerization regime occurs when lattice strain is relieved at approximately 10% conversion, and polymerization proceeds at a rate which is still thermally controlled by chain initiation but whose chain length, n, is determined by the concentration of chain terminating sites in the crystal. There is almost an order of magnitude difference in rate constant, k, between our best single crystals from batch I and the polycrystalline samples of batch II. It was observed in the batch II polycrystalline samples, after isothermal solid state polymerization appeared to have gone to completion, that subsequent temperature programmed DSC from room temperature to 275°C showed the presence of significant amount of monomer, i.e. peak ② in Figure 2. This was not observed in the other samples and is believed due to premelting effects in this impure batch.

The analysis for first order kinetics allows a unique value to be assigned to the induction period, t_0. It is the point at which the first order process appears to start. Other workers[4,5] have shown by extraction measurements that the shape of the polymerization curve is independent of temperature; hence, it is reasonable to assume that the fast polymerization process is initiated at a particular fraction of polymer. If this is the case, this fraction is approximately 10%, and thus as the slow polymerization process has been shown to obey first order kinetics by diffuse reflectance spectroscopy,[10] we can estimate the first order rate constant at the start of polymerization to be $k_0 = 0.0015\ \mathrm{min}^{-1}$ at 90°C.

In addition this rate constant can be calculated by measuring the heat of polymerization during the initial part of the induction period. With the assumption that the heat of polymerization is approximately constant throughout the range of polymerization studied, the calculated value of k_0 is 0.0012 min^{-1} at 90°C for batch I single crystals which agrees well with the value obtained from the extraction results. The value of the first order rate constant in the fast polymerization regime is $k = 0.019\ \text{min}^{-1}$ at 90°C for batch I single crystals yielding the ratio $k/k_0 = 153 \pm 15$. If the major effect of the autocatalytic reaction is to increase the chain length of the polymer, then the chain length increases by a factor of 150 during polymerization. Yee and Chance,[11] have estimated the chain length in the induction period at $n > 24$, and Wegner[12] has determined a value of $n \sim 5$–10. These results indicate a final polymer with $n \approx 1500$ corresponding to chain lengths of the order of microns.

Our measurements further provide strong evidence that particle size has considerable influence on the polymerization kinetics especially in the on-set region between slow and fast polymerization. Of the four batches of crystalline material studied, three had crystals of significant dimensions, the two single crystal samples, of course, plus batch II polycrystals (our least pure sample) whose crystallites had dimensions of $\approx 500\ \mu$. Batch I polycrystals, on the other hand, had very small crystallite sizes ranging $\geq 10\ \mu$. That the crystallite size had a dramatic effect on the polymerization curves is shown in Figure 7 for batch I single crystals and polycrystals. It can be observed that a significant fraction of polymerization occurs before the maximum is reached.

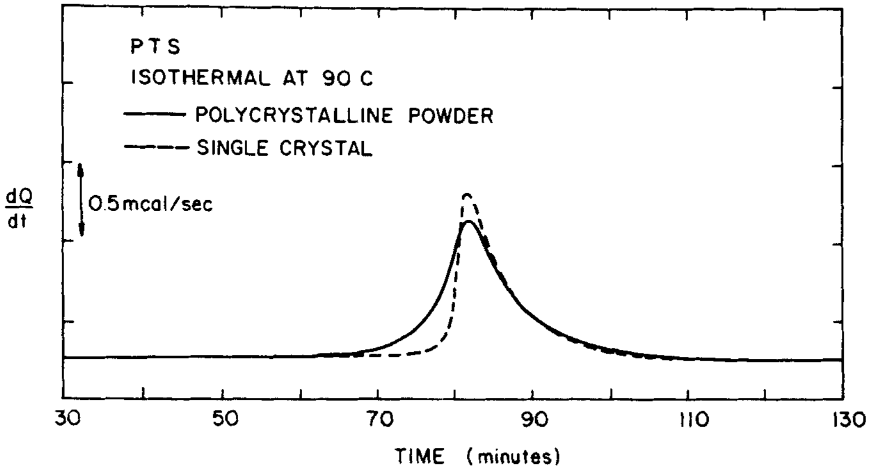

FIGURE 7 Comparison of isothermal DSC polymerization for batch I single crystals and batch I polycrystalline powder.

The fraction polymerized up to the peak maximum, calculated as the ratio of the area under the exotherm up to the peak to the total area of the exotherm, was 0.4–0.45 for batch II polycrystals in good agreement with the polycrystalline value obtained by Patel *et al.*[7] of 0.42. For batch I single crystals, however, the value was 0.19–0.25, and this corresponds to a very sharp on-set to the fast polymerization regime.

The other important quantity obtained from these studies is a measure of the heat of polymerization, ΔH_p. This is determined by integrating the total area under the exotherm during the isothermal anneal using the standard relation $\Delta H_p = m/A(\Delta q_s \cdot E \cdot TB)$ mcal/mg where m = sample weight in mg, A = area under curve in sq. inches, TB = time base of recorder in seconds/inch, Δq_s = calorimeter sensitivity in mcal/sec/inch and E = calibration factor for DSC cell which was obtained by calibration with ultra high purity organic standards; naphthalene (m.p.t. 80.2°C), durene (m.p.t. 79°C) and benzoic acid (m.p.t. 122.4°C). These materials are preferred over the indium standard normally used because they more closely represent the actual organic material being studied in melting point, thermal conductivity and specific heat.

The area under the isothermal exotherm was initially determined by planimetry and subsequently by digitizing the data using a computer controlled *x-y* plotter. In both methods, the true baseline was not known precisely, and it has been our practice to use the final baseline after polymerization as the baseline throughout polymerization; see Figure 4. It is difficult to determine the heat of polymerization during the induction period because the rate of evolution of heat is so low. We know from extraction experiments, however, that the fraction polymerized up to the start of fast polymerization is ~10%; hence, we would estimate that our measured values for ΔH_p are no more than ~5% low.

We have found that the values obtained for ΔH_p are very dependent on the crystalline form of the PTS and on sample history. These results are summarized in Table II. They were all obtained by isothermal annealing in the temperature range 60–90°C. Consistent results were obtained for single crystals from batches I and II, giving $\Delta H_p = -31.7$ and -30.6 kcal/mole respectively. Consistently higher values were obtained for batch I single crystals which had been annealed at room temperature for 1–2 months, giving an average $\Delta H_p = -38.0$ kcal/mole and also for batch I polycrystalline samples which gave $\Delta H_p = -38.7$ kcal/mole. This latter result is higher than the value obtained by Patel *et al.*,[7] and, in fact, their polycrystal results fall between our single crystal and polycrystal values. The unexpectedly high values of the room temperature annealed samples, which are identical to the polycrystalline values, suggest that both highly strained lattice and large surface area samples can undergo further exothermic reaction which may involve the thermal decomposition in the solid state as reported by Bloor.[4] We

TABLE II

Heat of polymerization of PTS

Sample	Temperature °C	Heat of polymerization[a] ΔH_p, kcal/mole	
Batch I single crystal	90	−32.8	
	90	−31.9	
	85	−32.5	*AVE* = −31.7 ± 0.7
	80	−31.1	
	75	−30.5	
	60	−31.2	
Batch I single crystals annealed at *RT*			
28 days	90	−38.3	
38 days	90	−35.5	*AVE* = −38.0
50 days	90	−40.1	
Batch I polycrystals	85	−39.1	
	80	−39.5	*AVE* = −38.7
	75	−37.6	
Batch II single crystals	90	−28.4	
	88	−32.9	
	85	−30.8	*AVE* = −30.6
	80	−31.0	
	75	−29.7	

[a] These values include an estimated 5% undetected during the induction period.

conclude that the best value for the heat of polymerization of PTS single crystals is $\Delta H_p = -31.2 \pm 0.9$ kcal/mole.

4. CONCLUSIONS

From our DSC measurements of the kinetics of the solid state polymerization of PTS, we have shown that two distinct regions can be identified. Slow polymerization takes place during an induction period followed by a rapid transition to a fast polymerization regime which appears to obey first order kinetics over the range ~20–95% polymer formation. Both regimes have been shown to have the same rate controlling step, namely, that of chain initiation, having an activation energy $E_A = 22.3 \pm 0.9$ kcal/mole. This value is independent of sample purity and crystalline form, either single crystal or polycrystalline samples. At a constant temperature all samples had approximately the same induction period but the first order rate constants varied by almost an order of magnitude. We interpret this in terms of crystal strain effects in which the polymer chains initially formed in the monomer lattice are prevented from growing by the crystal strain field set up due to the ~5% contraction of the polymer in the chain direction.[13] This results in many short chains in the monomer matrix. As their concentration rises strain is relieved and the system attains the polymer crystal structure. Polymer chains are then free to polymerize until a chain terminating site is reached. The concentration of these sites will vary from batch to batch so that the rate of conversion will vary and this is observed as a difference in first order rate constant.

In addition, it was observed that the polymerization of polycrystalline powder differed significantly from that of single crystals with considerably more conversion taking place before the maximum polymerization rate was reached. The results for our polycrystalline material are similar to those reported by Patel *et al.*[7] Single crystal data, however, show much sharper transitions, with the maximum occurring at 20% conversion, and faster conversion rates.

The ratio of polymerization rate in the fast polymerization regime to that in the induction period, $k/k_0 \approx 150$. This effect is primarily due to an increase in chain length and predicts final chain lengths of the order $1\text{–}3 \times 10^3$ monomer units long.

The heat of polymerization, ΔH_p, shows considerable variation depending on the crystalline form and sample history. The average value for two batches of single crystals is $\Delta H_p = -31.2 \pm 0.9$ kcal/mole. Polycrystalline samples from batch I gave $\Delta H_p = -38.8 \pm 1.5$ kcal/mole and aged single crystals $\Delta H_p = -38.0 \pm 1.5$ kcal/mole. These values include an estimated 5% contributed from the heat of polymerization undetected during the induction period. The single crystal value of -31.2 kcal/mole is in good agreement with calculated value, -31.5 kcal/mole,[7] using the bond energy/bond length relations of Dewar.

The significantly higher ΔH_p values for polycrystalline and aged single crystals may be a consequence of greater thermal degradation of the monomer due to increased surface area or internal strain.

Note added in proof

Barrall, *et al.*[6] have just recently reported DSC results on PTS that are qualitatively similar to ours. However, an activation energy, $E_A = 18.97$ kcal/mole was obtained which is considerably lower than our value and that of Patel, *et al.*[7] The thermal polymerization process is described in terms of a random homogeneous nucleation following a phase transition which differs from both our interpretation and those of Patel, *et al.*[7] and Bloor, *et al.*[4]

Acknowledgment

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