Analysis of the kinetics of the thermal decomposition of poly(1,6-bis-*N*-carbazolyl-2,4-hexadiyne) obtained using thermogravimetric analysis

Friedrich P. Bradner and Jacob S. Shapiro*
School of Chemistry, Macquarie University, North Ryde, NSW 2109, Australia
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The thermal decomposition of crystalline poly(1,6-bis-*N*-carbazolyl-2,4-hexadiyne) was examined by thermogravimetric analysis (t.g.a.) using both isothermal and temperature-programmed methods over a temperature range of 400–600°C. Extents of decomposition *versus* time data were fitted to an Avrami–Erofeyev equation with the exponent equal to three. Two consecutive processes were observed, each with its own Arrhenius parameters. An independent study, reported by us elsewhere, involving a flow system, leads to results consistent with the parameters obtained by t.g.a. reported in this investigation. Differences in reactivity between polymer crystals prepared by heating and by γ-radiation have been noted and discussed. Levels of imperfection of the crystals, determined by the choice of polymerization method, appear to correlate with the observed pre-exponential factors. The numerical value of the activation energy found for the second kinetic regime, which is attributed to the chemical process itself, is consistent with a process of bond breaking at the methylene–carbazole bond being the rate-determining step of the decomposition.

(Keywords: t.g.a.; poly(1,6-bis-*N*-carbazolyl-2,4-hexadiyne); kinetics; thermal decomposition)

INTRODUCTION

Thermogravimetric analysis (t.g.a.) can serve as a useful tool for studying the thermal decomposition of polymers, and indeed its application can be extended to the determination of kinetic parameters. Various t.g.a. methods employed to determine kinetic data have been proposed, and their relative merits have been extensively reviewed in the literature[1–3]. Both isothermal and non-isothermal techniques can be employed, leading to similar results under some favourable circumstances[4]. Advantages of using the temperature-programming approach over the isothermal method include: (1) sufficient data may be obtained from a single experiment to determine the kinetic parameters (depending on the method employed)[5]; (2) kinetics may be probed over a temperature range in a continuous manner; (3) pre-reaction occurring during the heat-up period in isothermal experiments is eliminated. However, isothermal techniques have been often favoured due to their mathematical simplicity. Both methods are, however, limited to kinetically simple processes with respect to only a single process occurring at any one time, and if sequential steps occur, then these must be well defined.

In this study, both isothermal and the temperature-programmed method of Ozawa[6–8] will be employed to determine the kinetics of decomposition of the polymer, poly(1,6-bis-*N*-carbazolyl-2,4-hexadiyne) or polyDCH, which is a specific derivative of the general class of polymer known as polydiacetylenes. The chemical formula of the polymer is $=(CR\text{–}C\text{–}CR=)_n$, where $R=CH_2C_{12}H_9N$. This particular polydiacetylene was chosen because of its known thermal stability[9], as well as its high resistance to radiation damage[10], thus representing one of the most stable derivatives of this class of polymer. Its decmposition products are stable, hence the possibility of consecutive reactions is eliminated and the t.g.a. study remains uncomplicated. Additional interest arises in establishing the influence of a completely crystalline environment on the kinetics of thermal decomposition of such polymers, of which so little is known.

EXPERIMENTAL

The monomer was synthesized by the method described by Yee and Chance[9] and was recrystallized from deoxygenated acetone under a nitrogen atmosphere. Large crystals of monomer were transformed into a polymer with a golden metallic appearance by irradiation (^{60}Co source, 0.1–1.1 MGy) or on heating (150°C, 110 h) in a sealed evacuated tube. T.g.a. was performed on a Perkin Elmer DSC-4 t.g.a. unit with a dedicated data station, using pure nitrogen to sweep away volatile products.

RESULTS

Temperature-programmed t.g.a.

It has been established using independent experiments

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* To whom correspondence should be addressed

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that the decomposition of polyDCH occurs almost exclusively via side group cleavage[11], with the major product, carbazole, comprising >97% of the product by mass (the minor product being 9-methylcarbazole, whose contribution was neglected in the following kinetic treatment). Complete loss of carbazole moieties should result in a theoretical weight loss of 81% of the total initial mass. In actual fact, a limiting weight loss of ~70% was generally observed, reaching the theoretical value only after prolonged heating. The degree of conversion at any time, α, may be calculated from the t.g.a. weight loss curve by:

$$\alpha=(W_0-W_t)/W_{\max}$$

where W_0 and W_t represent the sample weight initially and at time t, respectively. $W_{\max}$ represents the maximal weight loss for the process, in this case $0.81W_0$.

In general, the thermal decomposition of solids is a very complex process even in the simple case of the reaction expressed by the stoichiometric equation

$$A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}}$$

The rate of reaction, r, can be described in terms of two functions: $k(T)$ and $f(\alpha)$, thus:

$$\frac{d\alpha}{dt}=k(T)f(\alpha) \tag{1}$$

By substitution of the Arrhenius equation and rearrangement, the following equation results:

$$\frac{d\alpha}{f(\alpha)}=\frac{A}{\beta}\exp^{(-E_a/RT)}dT \tag{2}$$

where α is the conversion and β is the heating rate used in t.g.a. experiments, i.e. dT/dt, and A and E_a are Arrhenius parameters. Equation (2) must be integrated if kinetic parameters are to be obtained from t.g.a. data. Ozawa[6–8] has shown that the activation energy for the process can be obtained from equation (3) by following gravimetrically the decomposition of reactant at several different heating rates:

$$\log F(\alpha)=\log\left(\frac{AE_a}{R}\right)-\log\beta-2.315-0.4567\left(\frac{E_a}{RT}\right) \tag{3}$$

The terms on the right-hand side of equation (3) were derived from the empirical relationships developed by Doyle[12,13] and were found to be applicable to this kind of process. Equation (3) generates a straight line when $\log\beta$ is plotted against $1/T$ for isoconversional fractions, the slope of the line being equal to $0.4567E_a/R$. The kinetic parameters A and n (the traditional reaction order) can be determined by comparing theoretical conversion functions, i.e. first- or second-order equations or more complex solid state equations, with the experimental master curve which is obtained by plotting $\log[(E_a/\beta R)p(E_a/RT)]$ [where p is equal to $(-\log\beta - 2.315 - 0.4567)$ and is obtained from equation (3) shown above[13]] against α using the determined values of E_a for each conversion at a single heating rate. This master curve must be shifted along the abscissa by a factor of $\log A$ for this curve to become superimposible on the theoretical master curve. Thus A is determined from the shift along the abscissa and n or the conversion function is found by comparison of the experimental master curve with theoretical curves, the best fitted being the desired conversion function or kinetic equation.

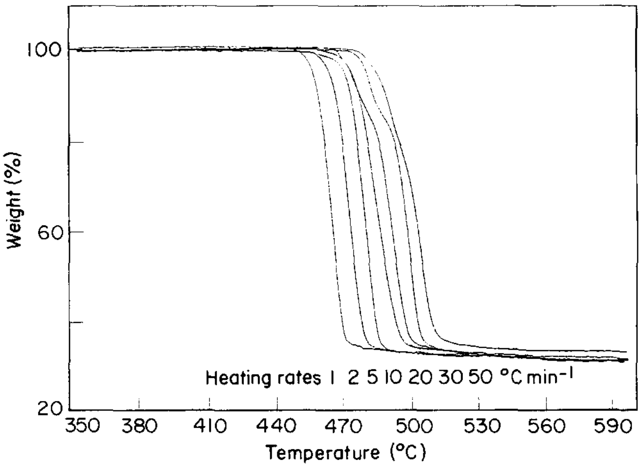

Figure 1 Temperature-programmed t.g.a. analysis of R-polyDCH at the heating rates shown

Figure 1 shows thermograms for the decomposition of radiation polymerized polyDCH (R-polyDCH) using a range of heating rates from 1 to 50°C min^{-1}. At heating rates above 10°C min^{-1} a small bump was observed. This was attributed to strain, believed to have developed during the polymerization process. This bump is absent in t.g.a. experiments conducted at slower heating rates, where annealing, relieving this strain, can occur. Other evidence supporting such a hypothesis is reported elsewhere[11]. The thermograms displayed in *Figure 1* were used to determine the kinetics of decomposition using the method of Ozawa[6–8]. *Figure 2* displays the plot of $\log\beta$ *versus* $1/T$ for isoconversional fractions. Clearly evident is the break in slope, which was found to occur throughout the entire conversion range. The activation energies obtained from the Ozawa plots are listed in *Table 1*. Two sets of activation energies are obtained: their average values being 227 ± 10 and 337 ± 22 kJ mol^{-1} for low and high heating rates, respectively.

The experimental master curve obtained using the Ozawa method, i.e. plotting $\log[(E_a/\beta R)p(E_a/RT)]$ against the fractional conversion, is shown in *Figure 3* for the low heating rate experiments. While various theoretical master curves are shown in *Figure 4*, comparison of the experimental master curve with the various theoretical master curves in *Figure 4* indicates that none are of similar shape. However, as seen from *Figure 5*, when the experimental master curve is compared to the theoretical master curve of the form $-[\ln(1-\alpha)]^{1/3}$, which is known as the Avrami–Erofeyev equation[14–17] with an exponent $n=3$, a clear superimposition can be achieved by shifting the experimental curve along the abscissa, by a factor equal to $\log A$. A similar treatment applied to data obtained at high heating rates yields the corresponding A factors.

Thermograms obtained for thermally polymerized polyDCH (T-polyDCH) are shown in *Figure 6*. These thermograms did not exhibit the bumps found in the radiation polymerized crystals. Ozawa plots were similarly obtained (not shown). The same theoretical master curve, the Avrami–Erofeyev equation, with $n=3$, was found to provide the closest fit to the experimental data. A summary of the kinetic parameters obtained using the Ozawa temperature-programming method is given in *Table 2* for both R-polyDCH and T-polyDCH samples.

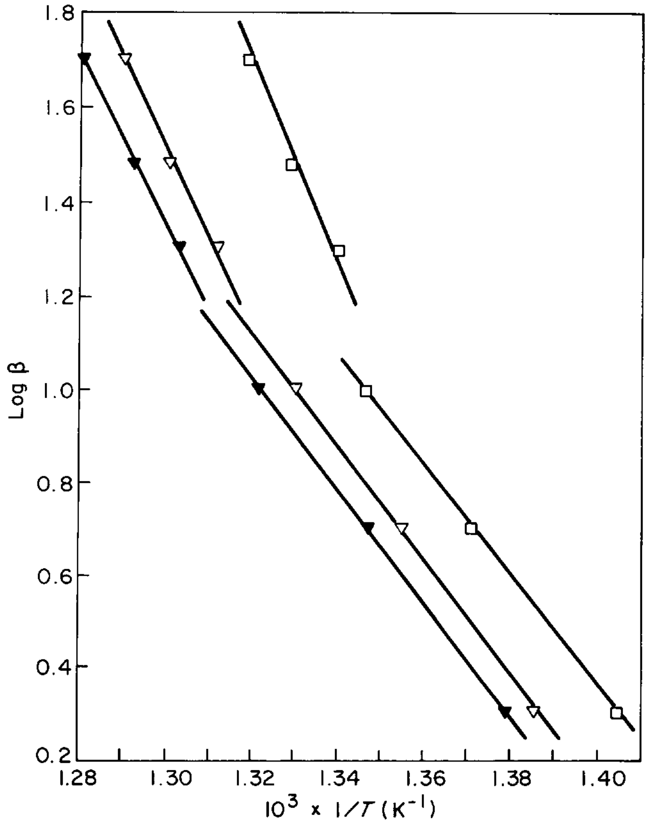

Figure 2 Ozawa plot of log β *versus* $1/T$ for isoconversional fractions. For the sake of clarity, only the isoconversional fractions (□) 0.05, (▽) 0.4 and (▼) 0.7 are shown

Table 1 Activation energies (kJ mol^{-1}) obtained from Ozawa plots of temperature-programmed decomposition of R-polyDCH

Conversion level	Heating rates (2, 5 and 10°C min^{-1})	Heating rates (20, 30 and 50°C min^{-1})
0.05	221.8	344.0
0.1	222.4	316.2
0.2	217.7	351.1
0.3	233.9	356.2
0.4	233.9	340.4
0.5	233.1	330.2
0.6	233.1	333.4
0.7	223.3	323.9
0.8	223.2	–
Average	226.9 ± 10	336.9 ± 22

Isothermal data

When isothermal t.g.a. of R-polyDCH was performed, conversion *versus* time data obtained from these experiments were found once again to fit closely an Avrami–Erofeyev equation with $n=3$. *Figures 7a–d* show the results for the data fitted to such an equation at four decomposition temperatures (675, 693.5, 703 and 711K). While only the data at 675K fitted into a single linear plot, data obtained at higher temperatures displayed a break, followed again by a change in slope, dividing the results into two regions: A (low slope) and B (high slope). The position of the break was noted to occur at increasingly higher levels of conversion with increasing isothermal decomposition temperatures. Arrhenius plots for the two regions are shown in *Figures 8a* and *b*, and the Arrhenius parameters are summarized in *Table 3*. Isothermal t.g.a. was also performed on T-polyDCH samples, with data also best fitting the Avrami–Erofeyev equation with $n=3$. However, these results failed to display a break with a change in slope, as is shown in *Figure 9a*. An Arrhenius plot (*Figure 9b*) of the decomposition experiments performed at 643, 653, 663 and

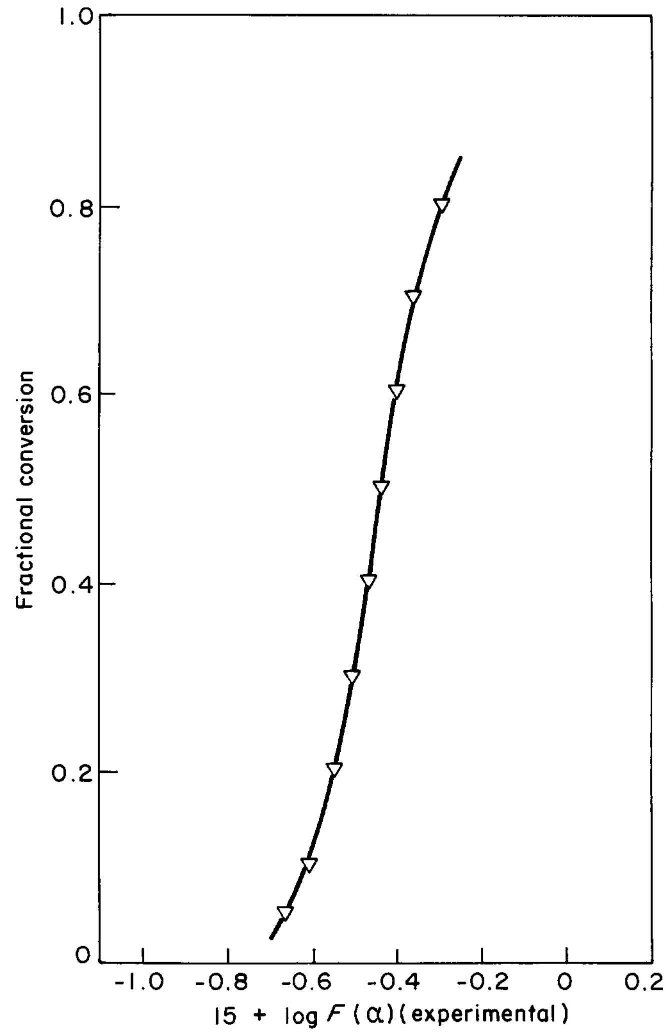

Figure 3 Experimental master curve obtained by employing the Ozawa method. Note that this curve has been shifted along the abscissa by a factor of 15

Table 2 Summary of the kinetic parameters obtained using temperature-programmed t.g.a. of R-polyDCH and T-polyDCH

	Low heating rates (2, 5 and 10°C min^{-1})	High heating rates (20, 30 and 50°C min^{-1})
R-polyDCH		
E_a (average) (kJ mol^{-1})	227 ± 10	337 ± 22
A (graphical) (s^{-1})	$3.2 \times 10^{13} \pm 15\%$	$1.6 \times 10^{22} \pm 15\%$
A (algebraic) (s^{-1})	$3.2 \times 10^{13} \pm 11\%$	$3.3 \times 10^{22} \pm 18\%$
T-polyDCH		
E_a (average) (kJ mol^{-1})	233.4 ± 21	581.4 ± 76
A (graphical) (s^{-1})	$1.83 \times 10^{15} \pm 15\%$	$2.83 \times 10^{41} \pm 15\%$
A (algebraic) (s^{-1})	$5.73 \times 10^{14} \pm 7.5\%$	$2.52 \times 10^{40} \pm 11.1\%$

All errors, except the graphical determination of A, were determined as two standard deviations of the slope and intercept of the Ozawa plot with the largest error

The pre-exponential factor listed in this and all subsequent tables is given in units of s^{-1} (ref. 3). As theoretical decomposition of the type $A \rightarrow B + C$ should be first order in reactant, this was deemed justified. However, it is recognised that in reality this may not be the case, due to diffusion and other complicating factors

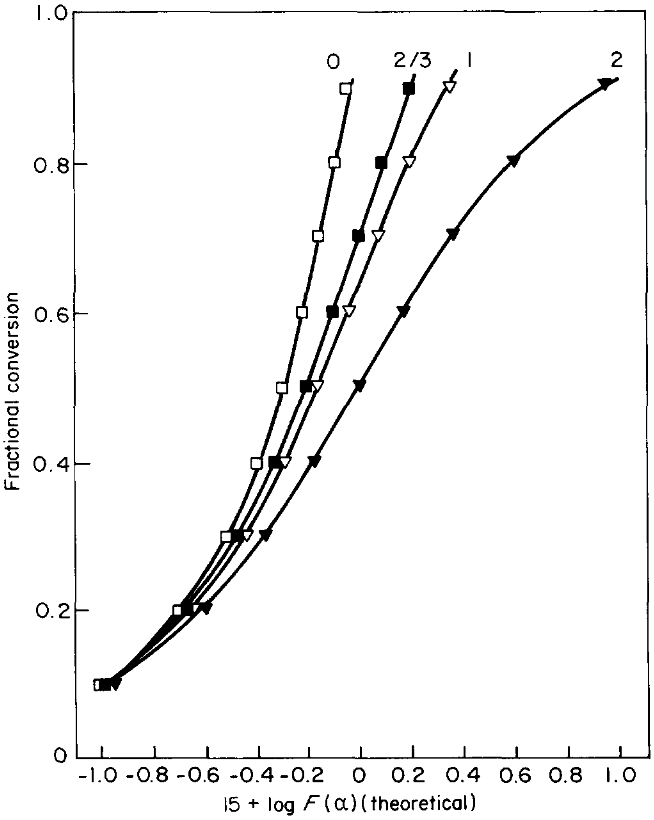

Figure 4 Theoretical master curves obtained for reactions of the various orders indicated. Comparison of these with the experimental master curve show no similarity

673K yielded the parameters that are summarized in *Table 4*.

DISCUSSION

Arrhenius parameters obtained by the present t.g.a. study indicate a similarity between the two heating rate regions observed in the temperature-programmed results (*Table 2*) and those obtained in the regions of differing slope in the isothermal work (*Tables 3* and *4*). Such agreement was found to be better in the case of R-polyDCH than in the case of T-polyDCH. Thus the kinetic parameters obtained indicate that there is a relationship between the low heating rate data obtained from temperature-programmed studies and region B in isothermal studies. Similarly, a relationship is also observed between the high heating rate data and region A. For example, low heating rate temperature-programmed t.g.a. yielded an activation energy of 227 kJ mol^{-1} compared to 206 kJ mol^{-1} obtained for region B in isothermal experiments. High heating rate t.g.a. resulted in an activation energy of 337 kJ mol^{-1} whereas region A from isothermal experiments resulted in an activation energy of 364 kJ mol^{-1}. The pre-exponential factors are also in reasonable accord for the two types of experiments, although in the case of the T-polyDCH the agreement between the two methods is less satisfactory. Since only one region of slope was observed during isothermal t.g.a. analysis of T-polyDCH, the data could not be compared to the low heating rate results obtained from temperature-programmed t.g.a. The pre-exponential factor obtained for the temperature-programmed t.g.a. of such samples at higher heating rates seems unusually high, and may well be in error.

Comparison of the kinetic data obtained for the thermal decomposition of R-polyDCH and T-polyDCH indicates that the latter is more reactive, with samples decomposing 40°C lower than the former. Such a difference in reactivity can only be attributed to the higher pre-exponential factor found in the case of T-polyDCH,

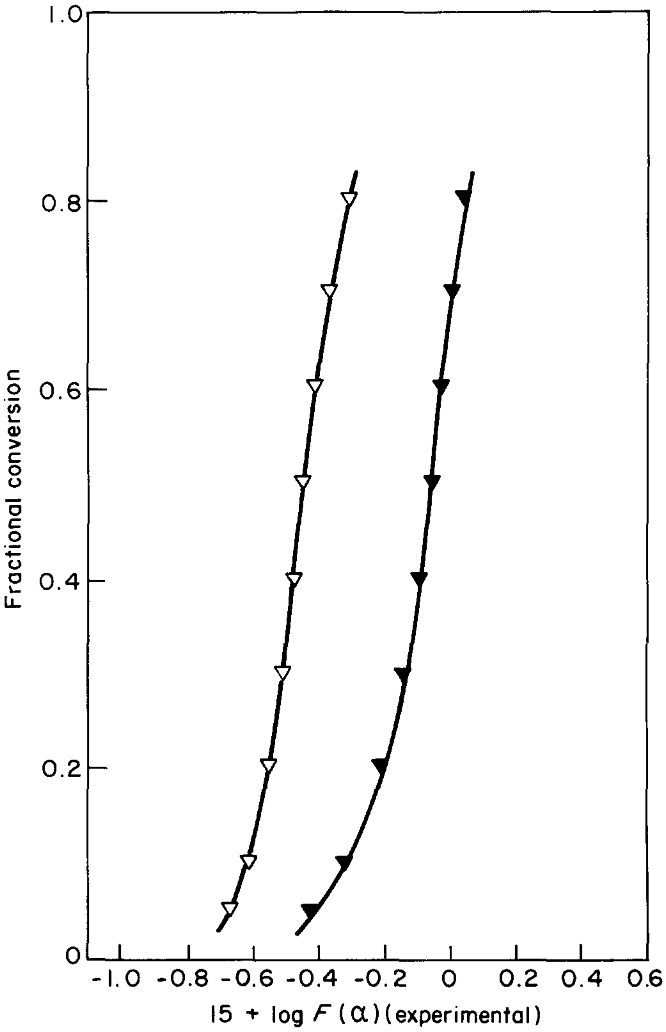

Figure 5 Experimental master curve (▽) and the theoretical master curve (▼) generated by the Avrami–Erofeyev equation with $n=3$. The experimental master curve has been shifted along the abscissa by a factor of 15

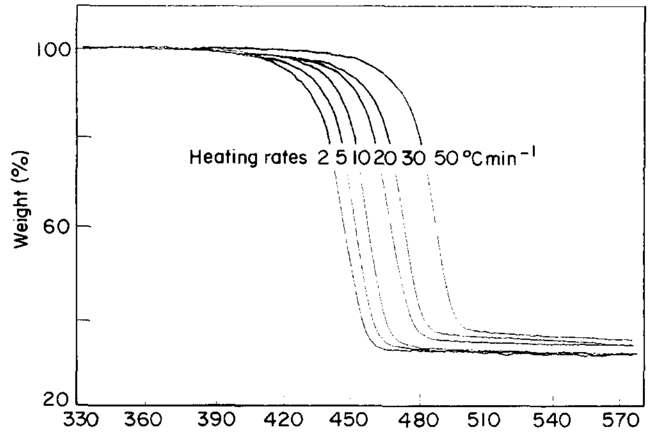

Figure 6 Temperature-programmed t.g.a. of T-polyDCH at the heating rates shown

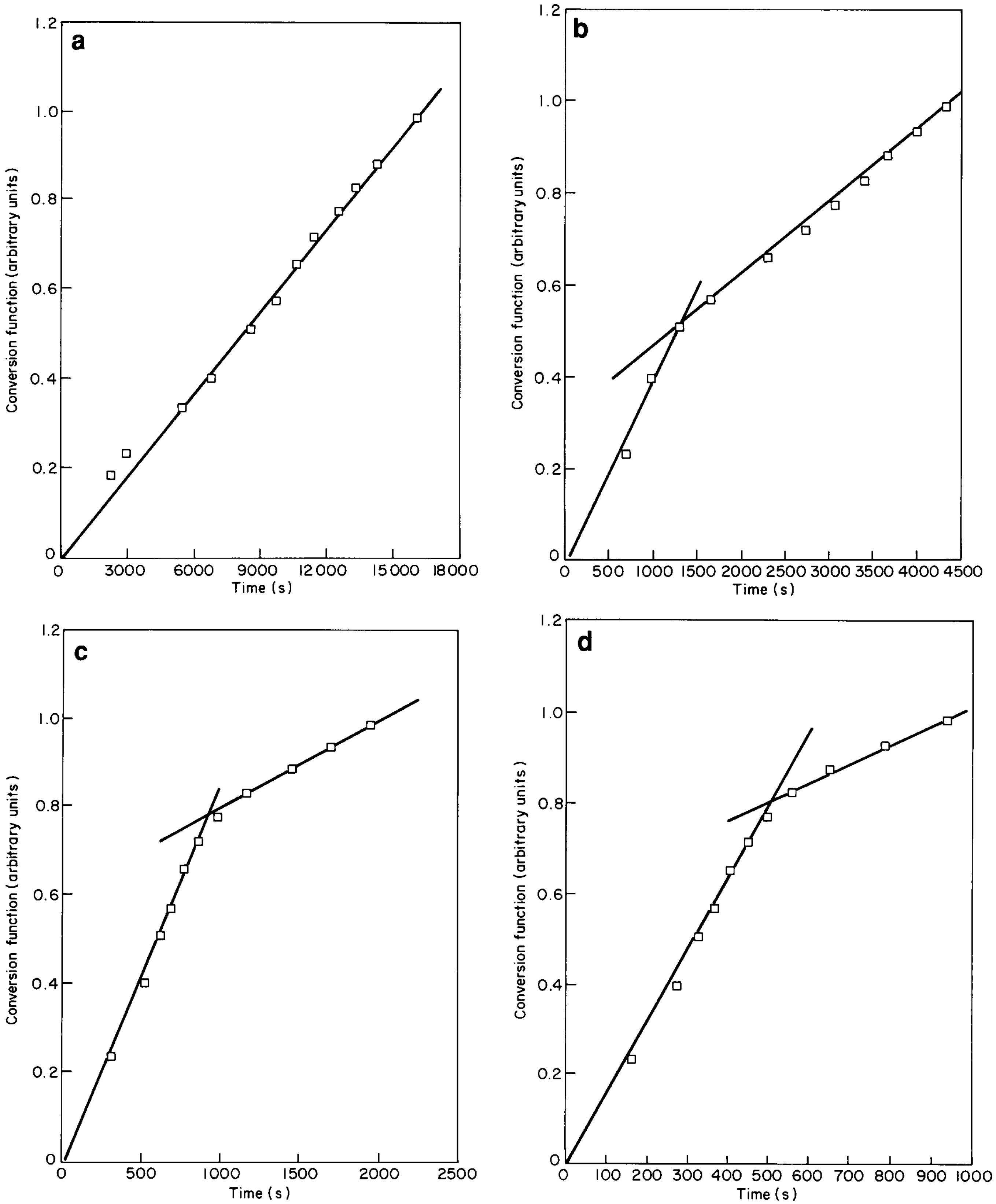

Figure 7 Plots of conversion data obtained from isothermal t.g.a. of R-polyDCH that were fitted to the Avrami–Erofeyev equation. Decompositions performed at: (a) 675 K; (b) 693.5 K; (c) 703 K; (d) 711 K

since the activation energies obtained for both materials are similar (with the exception of the set of results obtained for region B using temperature-programmed t.g.a. of T-polyDCH).

In a parallel study, the thermal decomposition of polyDCH was examined by means of a flow type apparatus, whereby the rate of reaction was followed by monitoring the evolution of the major and minor products, carbazole and 9-methylcarbazole, respectively, using gas chromatography[11,18]. This investigation revealed that there are indeed two distinct kinetic regimes, as the t.g.a. data suggest, each associated with its own

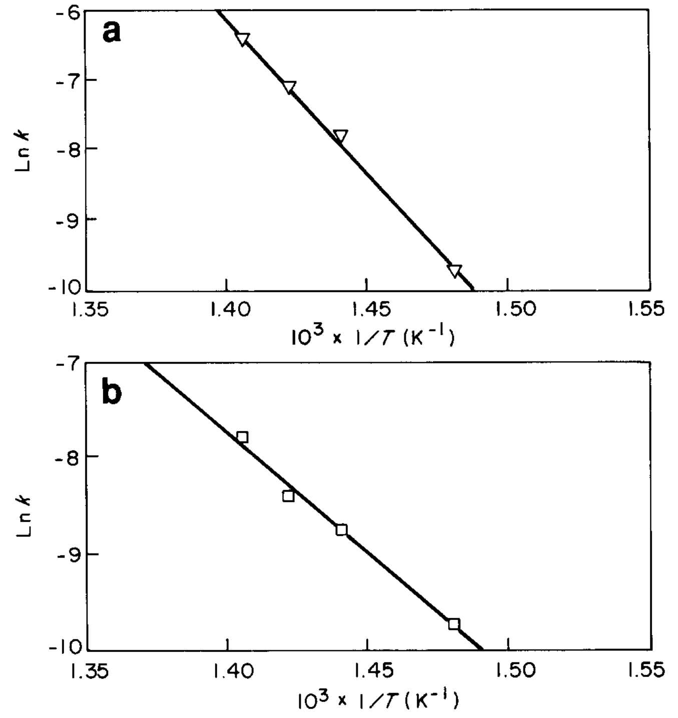

Figure 8 Arrhenius plots obtained from isothermal t.g.a. analysis of R-polyDCH: (a) high slope region; (b) low slope region

Table 3 Summary of kinetic parameters obtained for R-polyDCH using isothermal t.g.a.

Kinetic parameter	Region A	Region B
E_a (kJ mol^{-1})	364 ± 25	206 ± 35
A (s^{-1})	$9 \times 10^{23} \pm 8\%$	$5 \times 10^{11} \pm 21\%$

Errors determined as two standard deviations of the slope and intercept from Arrhenius plots

Table 4 Summary of kinetic parameters obtained for T-polyDCH using isothermal kinetics

Kinetic parameter	Value
E_a (kJ mol^{-1})	201.8 ± 22
A (s^{-1})	$9.1 \times 10^{11} \pm 11\%$

Errors determined as two standard deviations of the slope and intercept from Arrhenius plots

Arrhenius parameters, and these were found to be in good agreement with the present study. As was mentioned earlier, observation of two distinct regimes suggested that some type of annealing process is operative. When the samples are heated slowly to the decomposition temperature, only one maximum rate of decomposition is observed, however, if the samples are heated rapidly to the decomposition temperature, two rate maxima are observed. These results based on the flow reactor decomposition studies are described elsewhere[18].

Thus, during temperature programming experiments, when the polymer crystals are heated slowly, crystals have ample time to anneal slowly, prior to undergoing any appreciable decomposition. At higher heating rates however, the temperature increases so rapidly that annealing cannot occur slowly, and when rearrangement of the crystal lattice takes place, it occurs suddenly and with concurrent decomposition. Similarly, in the isothermal experiments, the annealing discussed above must also take place at lower temperatures. This accounts for the observation of a single slope, corresponding to the lower activation energy process, for the sample decomposed isothermally at 675K. However, when decomposition is examined isothermally at higher temperatures, two regions are observed. These are region A, where the higher activation energy process occurs due to the rapid annealing or lattice rearrangement leading to decomposition, whereas in region B decomposition occurs independently of the rate of annealing.

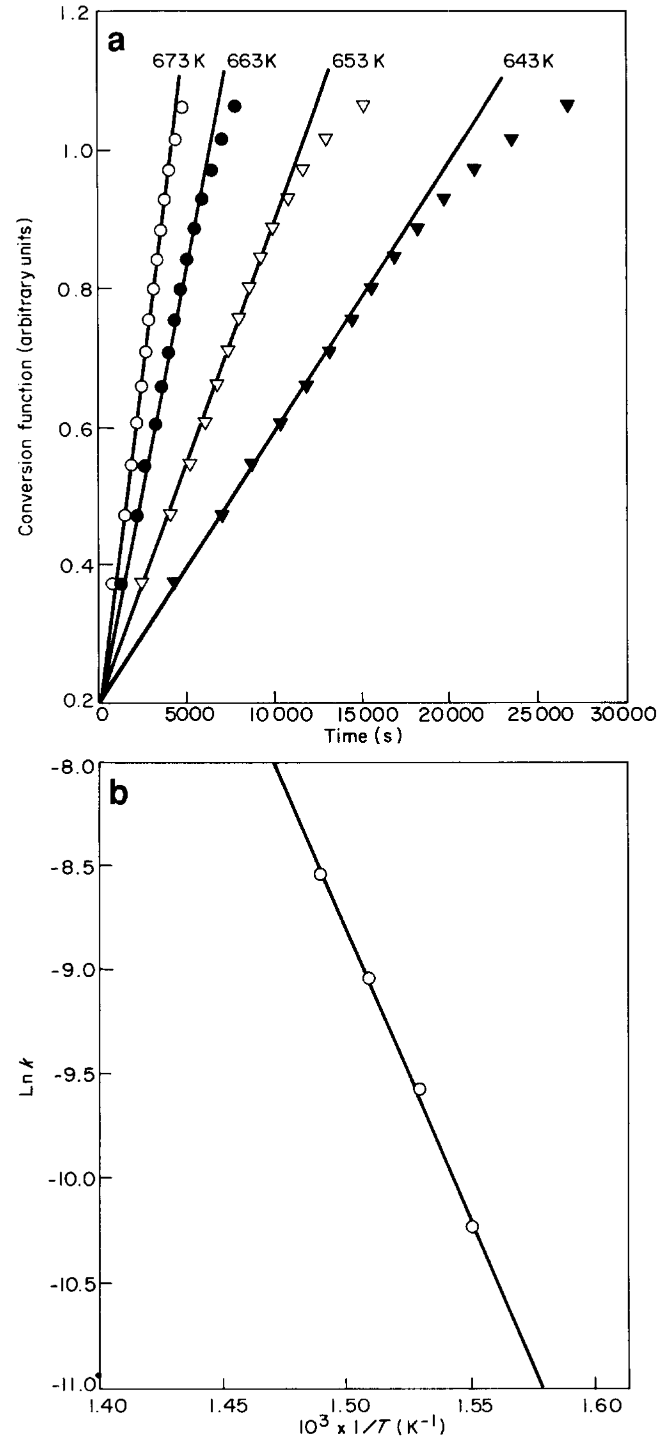

Figure 9 (a) Plot of conversion function *versus* time at various temperatures for samples that were thermally polymerized. Data fitted to the Avrami–Erofeyev equation with $n=3$. (b) Arrhenius plot obtained by decomposing thermally polymerized polyDCH using the isothermal t.g.a. method

One might then question why the isothermal decomposition of T-polyDCH crystals does not exhibit the same type of decomposition found in the case of R-polyDCH, and why do the T-polyDCH crystals decompose at a temperature ~40°C lower than for R-polyDCH. The polymerization methods are suspected of being responsible for the observed differences in reactivities. Radiation-polymerized crystals undergo polymerization homogeneously, resulting in nearly defect-free large single crystals[9], whereas thermally polymerized crystals, undergo a heterogeneous type polymerization with associated phase separation, and resulting in a less perfect polycrystalline material[9]. Since solid state decomposition reactions are often initiated at crystal defect sites[19], one might expect that the imperfect crystals would decompose at lower temperatures, as observed. Since the highest isothermal experiment was performed on T-polyDCH at a temperature lower than the lowest one used in the decomposition of R-polyDCH, one might expect that slow annealing is an important factor at all temperatures over which T-polyDCH was examined, explaining the absence of any break in slope that could have been expected in the isothermal decomposition of T-polyDCH.

In gas phase and in solution kinetic studies where concentrations are physically definable, the experimentally determined parameters such as the pre-exponential factor and the reaction order may contribute information regarding the reaction mechanism. In contrast, the term concentration in solid state decompositions cannot apply (with respect to reactant), hence interpretation of A and n (the reaction order) loses its traditional meaning. However, many kinetic equations describing the behaviour of solid state reactions incorporate variables that provide some information concerning the mechanism of decomposition. The Avrami–Erofeyev treatment with its resultant equation is based on the concept of nucleation and subsequent growth of these nuclei[20,21]. This equation has previously been used extensively to describe the thermal decomposition of inorganic crystals[22–25]. In the case of polyDCH, it seems reasonable to assume that nucleation occurs at crystal defect sites. Differences in the density of the crystal defects, known to exist between the two types of crystals, can thus account for the difference in reactivity. The polycrystalline T-polyDCH contains a greater density of crystal imperfection, hence is more reactive. In support of this hypothesis, when crystals of R-polyDCH are ground up their decomposition commences at lower temperatures and induction periods are eliminated. In addition, the size of the pre-exponential factor A, appears to correlate with the density of crystal defects in the crystals.

The Avrami exponent n (unrelated to conventional reaction order) can be used to predict the type of growth that the nuclei may follow. The term n is equal to the sum of two variables such that $n=\beta+\gamma$, where β relates to whether initiation occurs homogeneously or heterogeneously, one or zero, respectively, while γ relates to the dimensionality of nuclei growth, and is equal to one (one-dimensional or rod-like), two (two-dimensional or disc-like) or three (three-dimensional or spherical). Since the best fit to the t.g.a. data in the present study was found using $n=3$ for both types of crystals, one must conclude that since in the case of R-polyDCH $\beta=1$, $\gamma=2$, and therefore disc-like or two-dimensional nuclei growth occurs. In the case of T-polyDCH, one might expect heterogenous nucleation, associated with a high defect density, which would thus require $\gamma=3$ since $\beta=0$. So, in this case three-dimensional growth is envisaged. Care should be taken in placing too much importance on the value determined for n, because the flow system study (described elsewhere[18]) indicated that although the Avrami–Erofeyev equation was again found to provide the most applicable mathematical description of the decomposition kinetics, the value of n was found there to be equal to two. The difference observed between the two methods of analysis probably stems from the different sample geometry used. In the flow system study, the sample is present in the form of a tightly packed plug, whereas in the case of t.g.a. the sample lies loosely packed in an open pan. For the kinetics, determined from flow system experiments to be meaningful, the system is required to be well displaced from equilibrium. This condition reduces the likelihood of back addition of the product to the polymer backbone. In the case of the t.g.a. experiments, this criterion is not fully met, due to the lack of carrier gas flow through the entire bulk of the decomposing sample. Thus if any back reaction were to occur, this would have the effect of reducing the conversion. Consequently, this would have the effect of increasing the exponent n in the Avrami–Erofeyev equation, which is determined from the slope of $\ln[\ln(1-\alpha)]$ *versus* $\ln t$. It can be readily demonstrated that if α is reduced this would lead to an increase in the slope. In the physical terms defined by the Avrami–Erofeyev equation, n may be raised due to either a change in initiation due to back reaction (i.e. change in β) or due to a change in the dimensionality of nuclei growth because of the possibility of products diffusing away from the region of polymer they were formed, and then re-reacting (change in γ). Since n consists of two components (β and γ), it is not possible to determine which of the two variables or indeed if both, are responsible for the change in n.

Perhaps a better way of rationalizing the value of γ and therefore n is to consider the structure of the undecomposed starting material. PolyDCH exists as a highly aligned fibre, i.e. one-dimensional material. Therefore one might anticipate propagation of nuclei to proceed readily in one dimension. Decomposition of R-polyDCH observed under a microscope fitted with a hot stage indicated that at low conversions, striations were observed in the crystal, propagating in the fibre axis direction[18]. This supports the concept of one-dimensional growth.

It is relevant to discuss the significance of the conversion *versus* time data being best represented by the Avrami–Erofeyev equation. The general shapes of the t.g.a. traces are sigmoidal, typically quite characteristic of an autocatalytic or chain branching process. Flow system and e.s.r. studies[11] indicate that free radicals are not responsible for the observed chain branching process, therefore it follows that there must exist another kind of chain branching process—most likely a physical one. The Avrami–Erofeyev equation has in the past been applied to the decomposition of inorganic crystalline material where sigmoidal conversion *versus* time curves were commonly observed. Since both the polymer examined in this study and the inorganic materials referred to above are highly crystalline, one can conclude that it is the crystalline structure that controls the decomposition process, with a physical process providing the driving force for the decomposition reaction. In this case it is assumed to be the crystal strain. The complex bimodal decomposition exhibited by t.g.a. experiments can be explained if strain within the crystal is indeed the driving force governing decomposition. To account for the first region found in t.g.a. experiments one must consider the latent strain, stored up initially within the intact crystal. Such a strain most probably arises from the lattice mismatch, developed during polymerization, between monomer to polymer, known to be of the order of 6%[9]. As the crystals are heated, fibre bundles begin moving relative to one another. Sudden heating causes rapid readjustment, resulting in concurrent decomposition due to the shearing of carbazole side groups past one another. However, once such strain is relieved, the rate of decomposition begins to slow down. This explains why low heating rate temperature-programmed and isothermal experiments at lower temperatures exhibit plots of a lesser slope. At these lower temperatures or with slower heating rates crystals have a longer time to anneal, resulting in very little concurrent decomposition. This process is believed to be operative up to ~20% mass loss.

The newly decomposed material, generated from strain induced during the early decomposition stage (as mentioned above) now suffers from further strain occurring within the already partially decomposed crystal. Therefore the rate of reaction again begins to increase, and decomposition proceeding via the shearing of side groups resumes. Finally, the rate of decomposition begins to slow down, as the fraction of decomposed phase exceeds that of the intact polymer, leading eventually to the complete destruction of the crystalline structure of the polymer. The final rate becomes extremely slow at ~65–70% conversion.

Finally, it should be stressed that when the t.g.a. method is used to follow the decomposition kinetics of solids, the resultant Arrhenius parameters are in a strict sense only the *apparent* activation energy and pre-exponential factor, since the data are not derived from changes in concentrations of reactants and products. In the case of the isothermal t.g.a. and flow system, α, the fraction of polymer decomposed was first determined directly without requiring any assumptions to be made. Fitting of α into an Avrami–Erofeyev expression led to values of n and k. The pseudo rate constant (more correctly growth rate constant) was then fitted into an Arrhenius equation leading to estimates of the activation energy and pre-exponential constant. For the temperature-programmed t.g.a., arriving at estimates of Arrhenius parameters is less direct and depends on curve fitting as outlined above.

In general t.g.a. does not provide information on the chemical nature of the decomposition except in very simple, uncomplicated reactions. Even then it is essential to verify this information by independent studies employing techniques that allow direct estimation of specific products (e.g. gas and high performance liquid chromatography, mass spectrometry). While the present t.g.a. study on its own is insufficient, the parallel study with a flow system, where the volatile products were monitored quantitatively by gas chromatography[18,26], leads to similar conclusions. In both studies evidence emerges of the existence of two kinetic regimes, each with its own set of apparent Arrhenius parameters. Table 1 in reference 18 displays these parameters for the decomposition obtained by the three methods discussed above. Only those for the second kinetic regime (second autoacceleratory region in the flow system, low heating rate results in the temperature-programmed t.g.a. experiments and high slope results in isothermal t.g.a.) are comparable and the respective activation energies (in $\mathrm{kJ\,mol^{-1}}$) and pre-exponential factors (expressed as if the process were of first order, in $\mathrm{s^{-1}}$) reported are as follows: temperature-programmed t.g.a., 227 and 3.2×10^{13}; isothermal t.g.a., 206 and 5.0×10^{11}; flow system, 223 and 6.4×10^{13}. Of the two kinetic regimes the first one is believed to be a complex, composite one involving stress release due to initial polymerization conditions, superimposed on the actual chemical reaction. It has been shown to be dependent not only on the polymerization method but also on the thermal history and crystal size[26]. The second kinetic regime is attributed to represent the decomposition itself and therefore it leads to comparable parameters in the three cases cited above. It is significant that the same products are observed in the two regimes, indicating that the actual chemical process and more importantly the true rate-determining step is the same in both regimes.

What is the exact nature of the chemical transformation and the rate-determining step cannot be deduced from the information accumulated thus far. We have considered possible chemical models, described elsewhere[18,26]. It appears tht whatever its nature the decomposition is likely to consist of several steps, with the most important one, i.e. the rate-determining one, being the initial breaking of a weak bond following mechanical rather than chemical activation, followed by a step or steps leading to the final products. Thus, the actual numerical value of the activation energy (206–227 $\mathrm{kJ\,mol^{-1}}$) is not inconsistent with the bond breaking of a carbazole group from the methylene group attached to the polymer backbone. We have established that 9-methylcarbazole is not a precursor to the carbazole and is formed independently, though at a much slower rate than carbazole itself during the entire course of decomposition. If the relative rates of formation of the two products are related to the respective bond dissociation energies, then it is not unreasonable to speculate that the methylene–carbazole bond is weaker than the methylene–backbone bond. Both carbazole and methylcarbazole were found to be thermally stable over the temperature range studied. Using known hydrocarbon bond dissociation energies and the extent by which such bonds are weakened by the presence of allylic structures[27], it is possible to make a rough estimate of the strength of the methylene–carbazole bond in the side chain. While this bond dissociation energy is unreported, the closest model compound is $C_6H_5NH–CH_3$, which has a bond strength[27] of 297 $\mathrm{kJ\,mol^{-1}}$. The allylic stabilization energy in hydrocarbons is ~75 $\mathrm{kJ\,mol^{-1}}$, i.e. the C–C bond in $C–CH_2CHCH_2$ is lowered by that amount relative to a hydrocarbon. Thus the methylene–carbazole bond must be to a first approximation equal to 297–75 or ~220 $\mathrm{kJ\,mol^{-1}}$, in good agreement with the observed activation energy for the second kinetic regime. We can only surmise, on the basis of the observed product distribution, that the methylene–backbone bond is likely to be somewhat stronger than the methylene–carbazole bond, assuming the difference in reactivity is due entirely to bond strength rather to configuration of transition states.

In summary, since this type of physical chain branching mechanism has been successfully applied to the decomposition of inorganic crystals in the past, we propose that this mechanism also operates in the case of the crystalline polymer polyDCH and may possibly extend to other polydiacetylenes. Since the direct synthesis of extended chain crystals is only a relatively new development and decomposition studies like the present one are just beginning to appear, no one has yet attempted to demonstrate this type of behaviour among conventional crystalline polymers (with typically chain-folded crystals), the only types previously known and studied. It would have been interesting to determine whether the thermal decomposition of chain-folded crystalline polymers such as isotactic polypropylene and polystyrene and linear polyethylene or even the crystalline fraction in poly(vinyl chloride) is also controlled wholly or partly in a similar way by their crystalline nature and is initiated by mechanical energy transfer. Unfortunately, in practical terms this question cannot be answered because such polymers melt before reaching decomposition temperatures.

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